

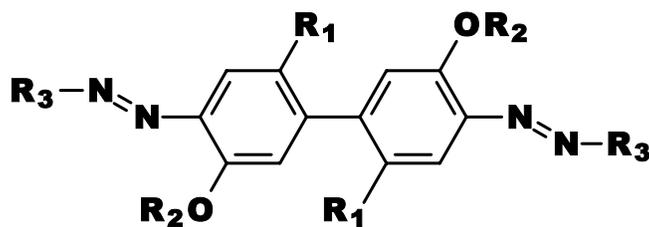
ABSTRACT

SUWANRUJI, POTJANART. The Design, Synthesis and Application of Easy Wash Off Reactive Dyes. (Under the direction of Harold S. Freeman)

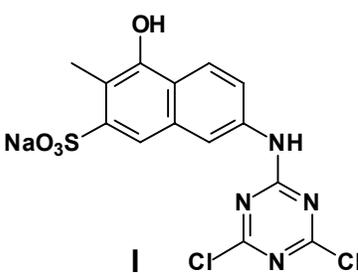
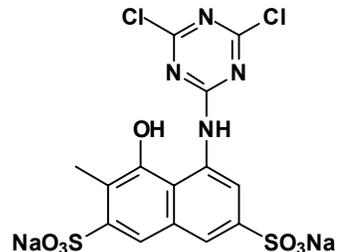
Reactive dyes are colorants used mainly on cotton to achieve high washfastness on leisurewear. The basis for their good washfastness is the formation of a covalent bond to cellulose chains during the fixation step. Unfortunately, fiber fixation is always accompanied by alkali-induced dye hydrolysis, 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. 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 the coplanarity that is usually required between dyes and cellulose for high substantivity. In this regard, type (i) reactive dyes were synthesized. Specifically, bis-dichlorotriazine (bis-DCT) bifunctional and bis-monochlorotriazine/bis-sulphatoethylsulphone (bis-(MCT/SES)) tetrafunctional

reactive dyes were made (cf. dyes **1-20**). The dyes were applied to cotton fabric using pad-batch, pad-dry-cure, and exhaust dyeing methods. Bis-DCT bifunctional reactive dyes were applied to cotton by a pad-batch method, since the dichlorotriazine reactive groups are highly reactive and can be applied at room temperature. Bis-(MCT/SES) tetrafunctional reactive dyes were applied to cotton by pad-dry-cure since monochlorotriazine reactive groups require higher temperatures for fixation. The exhaust dyeing method was not suitable for these reactive dyes because of their low water solubility. Evaluation of colorfastness on dyed cotton showed that the fabrics had moderate to good colorfastness to rubbing and laundering, and had low colorfastness to light.



(i)

<u>Group</u>	<u>Dye</u>	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>
a	1	Me	Pr	 I
	2	H	Pr	I
	3	Me	Me	I
	4	H	Me	I
	5	Me	Et	I
<hr/>				
b	6	Me	Pr	 II
	7	H	Pr	II
	8	Me	Me	II
	9	H	Me	II
	10	Me	Et	II

<u>Group</u>	<u>Dye</u>	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>
c	11	Me	Pr	<p style="text-align: center;">III</p>
	12	H	Pr	III
	13	Me	Me	III
	14	H	Me	III
	15	Me	Et	III

d	16	Me	Pr	<p style="text-align: center;">IV</p>
	17	H	Pr	IV
	18	Me	Me	IV
	19	H	Me	IV
	20	Me	Et	IV

**THE DESIGN, SYNTHESIS AND APPLICATION
OF EASY WASH OFF REACTIVE DYES**

By

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I. INTRODUCTION

1. DEFINITION

Fiber reactive dyes are colored organic compounds that are capable of forming a covalent bond between reactive groups of the dye molecule and nucleophilic groups on the polymer chains within the fiber [1-4]. Consequently, the dyes become chemically part of the fiber by producing dye-polymer linkages [5, 6]. In this regard, covalent dye-polymer bonds are formed, for instance, with the hydroxyl groups of cellulose, the amino, hydroxyl and mercapto groups of proteins, and the amino groups of polyamides [2, 3, 7, 8].

The possibility of forming a covalent bond between dyes and fibers had long been attractive to dye chemists, since attachment by physical adsorption and by mechanical retention had the disadvantage of either low washfastness or high cost [9, 10]. It was anticipated that the covalent attachment of the dye molecules to the fiber would produce very high washfastness because covalent bonds were the strongest known binding forces between molecules [11, 12]. The energy required to break this bond would be of the same order as that required to break covalent bonds in the fiber itself [13].

Reactive dyes were initially introduced commercially for application to cellulosic fibers, and this is still their most important use [14, 15]. The growth rate of reactive dyes for cellulosic fibers is expected to continue increasing, as shown in Table 1, because reactive dyes continue to gain market share at the expense of other dye types such as azoic dyes [16]. Reactive dyes have also been developed for application on protein and polyamide fibers. In addition,

investigations into the development of reactive dyes for polyester and polypropylene fibers have been demonstrated to the level of technical possibility but such dyes are not yet of commercial interest [14, 15].

Table 1. Estimated annual consumption of dyes for cellulosic fibers.

Dye	Usage per Annum (tons)		
	1988 ^a	1992	2004 ^b
Sulphur	90000	70000	70000
Direct	74000	60000	68000
Vat	36000	21000	22000
Indigo	12000	12000	12000
Azoic	28000	18000	13000
Reactive	60000	109000	178000
Total	300000	290000	354000

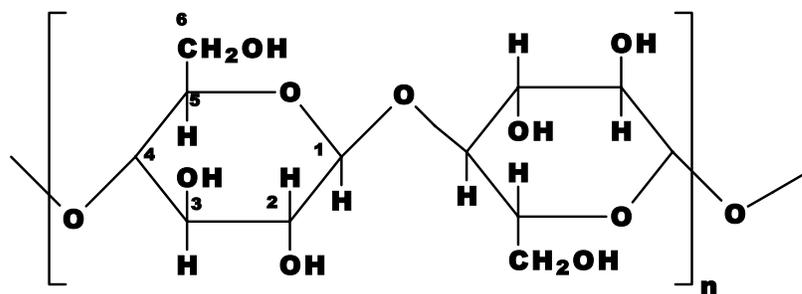
a: Does not include India, China and Eastern Europe

b: Projected figures from Business Research Service Ltd. [16]

2. HISTORICAL DEVELOPMENT

2.1 Reactive Dyes for Cellulosic Fibers

Cellulosic fibers are significantly dominated by cotton. Other cellulose-based fibers include viscose rayon, linen, cupraammonium rayon, jute and lyocell, and these can be dyed with dyes used on cotton [1]. The structure of cellulosic fibers is characterized by the poly-(1,4)- β -D-glucopyranose molecule (1), and consequently may be considered as a polyhydric alcohol. Each glucopyranose ring on the cellulose chain contains three hydroxyl groups, a primary hydroxyl group in the 6 position and secondary hydroxyl groups in the 2 and 3 positions.



$n = 600-1500$

(1)

A polyhydric alcohol such as cellulose is more acidic than a simple alcohol and, in fact is comparable with water as shown by the dissociation constants (K) listed below.

Water	$K = 2.09 \times 10^{-14}$
Methanol	$K = 8.1 \times 10^{-15}$
Manitol	$K = 7.5 \times 10^{-14}$
Cellulose	$K = 1.84 \times 10^{-14}$

The dissociation constant for cellulose refers to the ionization of the hydroxyl group in the 6 position of the glucopyranose ring. The hydroxyl groups in positions 2 and 3 of the ring are less acidic. Therefore, cellulose is ionized under alkaline conditions and can behave as a nucleophile towards compounds containing electron-deficient carbon atoms (e.g. reactive dyes) [11, 16].

A variety of attempts have been made to bring about the formation of a covalent bond between a dye and a fiber. In this respect, there are two general approaches: producing a dye within the fiber, and producing a dye that is reactive towards the fiber [10]. A covalent dye-cellulose combination

was achieved in 1895 by Cross and Bevan. These workers showed that cellulose (Cell-OH) treated with strong alkali was changed into "soda cellulose" which could be treated with benzoyl chloride to form benzoyl cellulose. The resultant benzoyl cellulose was nitrated, the nitro group was reduced, and the amino group was diazotized. The diazo group was coupled with *N,N*-dimethylaniline to give "dyed" fibers. The reactions used to produce this red cellulose are shown in Figure 1 [17, 18].

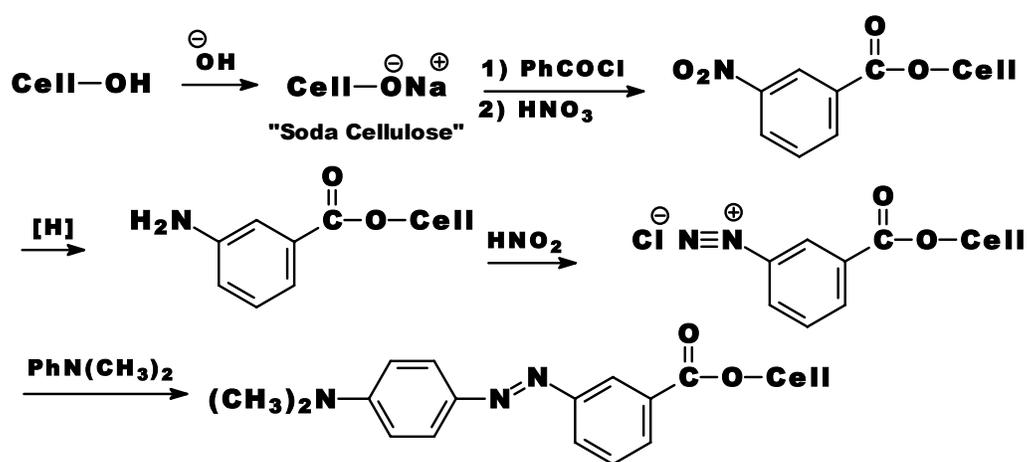
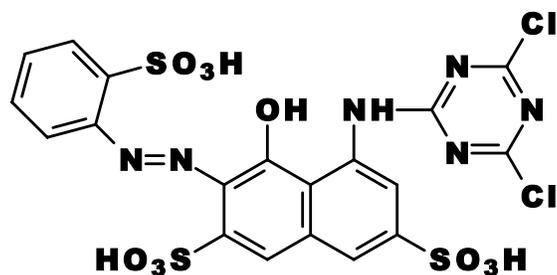


Figure 1. Preparation of red cellulose.

The first commercial reactive dyes for cellulose were developed by Rattee and Stephen and marketed by ICI in 1956 under the trade name Procion M [19-24]. These dyes were introduced for the production of fast bright shades on cellulosic fibers using continuous dyeing methods [15]. Procion Brilliant Red M-2B in (2) is one of the early members of this family [10]. Procion M dyes contained the highly reactive dichlorotriazine group, and reacted with cellulose under alkaline conditions at room temperature [18, 20, 25].



(2)

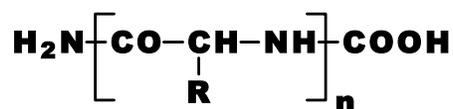
The major factor contributing to the long delay in producing the first reactive dye for cellulose was the belief that cellulose was a relatively inert substrate and that conditions required to effect a chemical reaction would cause serious fiber degradation [2, 5, 9, 10]. Therefore, in early studies dyestuff chemists were led astray in thinking that they needed to convert cellulose to the more reactive soda cellulose to make fiber reactivity possible [16, 26, 27]. No one expected that any reactive group would prefer to react with a hydroxyl group of cellulose when cotton was placed in an aqueous dyebath containing numerous competitive hydroxyl groups from water [14, 25]. However, a large number of reactive dyes with varieties of reactive groups have been developed. A summary of the industrial history of reactive dyes for cellulosic fibers is shown in Table 2 [10, 28].

Table 2. Summary of industrial history of reactive dyes for cellulosic fibers.

Year	Commercial name	Company
1956	Procion M	ICI
1957	Procion H	ICI
1957	Cibacron	Ciba
1958	Remazol	Hoechst
1959	Levafix	Bayer
1959	Reactone	Geigy
1959	Drimarene	Sandoz
1961	Levafix E	Bayer
1963	Elisiane	Francolor
1964	Primazin P	BASF
1964	Solidazol	Cassella
1966	Levafix EA, Levafix P	ICI
1968	Reactofil	Geigy
1970	Procion HE, Procion Supra	ICI
1977	Procion T	ICI
1978	Cibacron F	Ciba
1979	Sumifix Supra	Sumitomo
1984	Kayacelon	Nippon Kayaku
1988	Cibacron C	Ciba

2.2 Reactive Dyes for Protein Fibers

Protein fibers are natural polyamides, which have a variety of amino acids as building blocks. Amino groups or carboxylic groups exist either as terminal groups on the polymer chain or in side chains. Hence, the chemical structure of a protein fiber can be written as (3). Protein fibers include all animal fibers such as wool, silk, mohair and cashmere. Wool and silk are dominant in this class of fibers [2].



(3)

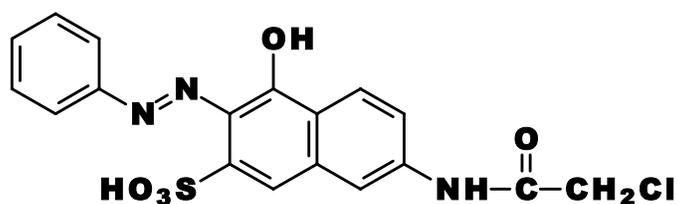
The name of the protein in wool is keratin. Keratin contains a variety of groups that are able to combine with reactive dyes [29]. The most important sites on keratin that are available for reactions with reactive dyes are shown in Table 3 [30]. There is plenty of evidence that reactive dyes react with the various side-chains of wool [31]. Remazol Brilliant Blue R reacts with the lysine, histidine, cysteine and the N-terminal amino acids of wool. About two thirds of the bonds formed involve the lysine and histidine groups [21].

Interestingly, wool was assumed to be more chemically reactive than cotton, and attracted more attention in the initial stages of reactive dyes research [5]. Although fiber-reactive dyes were first introduced commercially for cellulosic fibers, it is generally acknowledged that the first examples occurred among the acid dyes and were applied to wool [32].

Table 3. The sites within wool for reaction with reactive dyes.

Amino acid	Reactive side chain (R)
Lysine	$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$ $\varepsilon\text{-amino}$
Cysteine	$\text{-CH}_2\text{-CH}_2\text{-SH}$ $\beta\text{-thiol}$
Histidine	$\begin{array}{c} \text{---CH---CH}_2 \\ \quad \diagdown \quad \diagup \\ \quad \text{N} \quad \text{NH} \\ \quad \diagup \quad \diagdown \\ \quad \text{CH} \end{array}$ Imidazole imino
Threonine	$\begin{array}{c} \text{---CH---CH---CH}_3 \\ \quad \quad \\ \quad \quad \text{OH} \end{array}$ $\text{Secondary aliphatic hydroxyl}$
Serine	$\text{-CH}_2\text{OH}$ $\text{Primary aliphatic hydroxyl}$
Tyrosine	$\text{-C}_6\text{H}_5\text{-OH}$ Phenolic hydroxyl
Methionine	$\text{-CH}_2\text{-S-CH}_3$ Mercapto-ether
N-terminal	-CO-CHR-NH_2 $\alpha\text{-amino}$

Supramine Orange R (C.I. Acid Orange 30) (4) was the first recorded reactive dye for wool, and was introduced by I.G. Farben in 1932. Supramine Orange R is an acid dye containing a chloroacetamido group. However, the high washfastness of this dye compared with that of the acetamido analogue was not attributed at that time to the reactivity of the ω -chlorine atom. Thus, these dyes were not clearly recognized as reactive dyes when they were first introduced [8, 33, 34].



(4)

Later, a number of reactive dyes for wool were produced, as shown in Table 4 [8, 19, 33, 35]. It is also known that Sumifix Supra dyes can be applied to wool with a high degree of fixation and high fastness. The highest fixation on wool with Sumifix Supra dyes is obtained in the pH 4-5 region. The fastness is greatly influenced by the dyeing temperature and dyeing time. Dyeing at 95-100°C for 40-60 minutes produces high washfastness. A leveling agent is also used to prevent skitteriness on wool because Sumifix Supra dyes are highly hydrophilic and have high affinity for wool [36].

Table 4. Summary of industrial history of reactive dyes for wool.

Year	Commercial Name	Reactive System	Company
1932	Supramine Orange R	ω -Chloroacetamido	Bayer
1952	Remalan	Vinylsulphone	Hoechst
1961	Cibacrolan	Monochlorotriazine	Ciba
1962	Lanasyn	α -Chloroacrylamide	Sandoz
1962	Drimalan	ω -Chloroacetamido	Sandoz
1963	Remazolan	β -Sulphatoethylsulphone	Hoechst
1964	Procilan	Acrylamido, ω -chloroacetamido	ICI
1966	Lanasol	α -Bromoacrylamido	Ciba
1967	Lanafix	Sulphatoethylsulphoneacrylamide	Sumitomo
1970	Verofix	Difluorochloropyrimidine	Bayer
1970	Drimarene F	Difluorochloropyrimidine	Sandoz
1970	Reactolan	Difluorochloropyrimidine	Geigy
1970	Hostalan	2-Chloro-4-methoxytriazine	Hoechst

In the case of silk, the chemistry of silk parallels that of wool in some respects. However, reactive dye application is easier with wool than silk since there is a higher percentage of basic groups on wool [37]. The protein fibroin comprising silk has the same general formula as keratin of wool, but silk contains no sulfur [2]. The reaction between fibroin and reactive dyes takes place mainly at the ϵ -amino group of lysine, the imino group of histidine and

the terminal α -amino groups in the peptide chain. In an alkaline medium, the hydroxyl groups of tyrosine and serine can also react. The most important sites of silk for reaction with reactive dyes are shown in Table 5 [38].

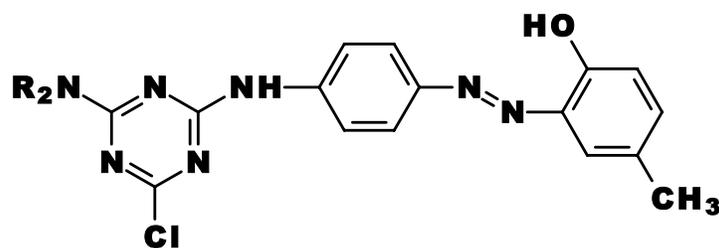
Table 5. The sites within silk for reaction with reactive dyes.

Amino acid	Reactive side chain (R)
Lysine	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ϵ -amino
Histidine	$ \begin{array}{c} \text{---CH---CH}_2 \\ \quad \\ \text{N} \quad \text{NH} \\ \backslash \quad / \\ \text{CH} \end{array} $ Imidazole imino
N-terminal	$-\text{CO}-\text{CHR}-\text{NH}_2$ α -amino
Tyrosine	$-\text{C}_6\text{H}_5-\text{OH}$ hydroxyl
Serine	$-\text{CH}_2-\text{OH}$ hydroxyl

Very little work on the application of reactive dyes to silk has been carried out. In fact, ranges of reactive dyes have not been developed specifically for silk. However, all reactive dyes can theoretically be used for dyeing this fiber [37, 39].

2.3 Reactive Dyes for Synthetic Fibers

Many studies involving reactive dyes for synthetic fibers have been investigated. Scott and Vickerstaff have summarized the application of Procynyl dyes (**5**) to synthetic fibers [40]. These dyes may be applied to nylon in the same level manner as achieved with disperse dyes. When exhaustion has been achieved, the dyebath is made alkaline, causing a reaction to occur between the dye and fiber. Level dyeings of attractive shades with high fastness to heat sublimation have been achieved. Procynyl dyes may also be applied to secondary cellulose acetate and cellulose triacetate in the same way as disperse dyes. Although there is no evidence of chemical reaction with these fibers, washfastness is generally higher than with normal disperse dyes. While the Procynyl dyes are of limited interest for dyeing these fibers, they are of interest for printing on secondary cellulose acetate. They offer advantages over conventional disperse dyes that include reduced steaming time and superior washfastness. On polyacrylonitrile fibers such as Orlon and Courtelle, the build-up of Procynyl dyes is limited. Procynyl dyes are generally not useful for dyeing Terylene and other polyester fibers, because of poor lightfastness and uptake.

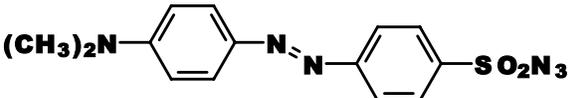
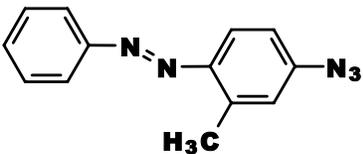
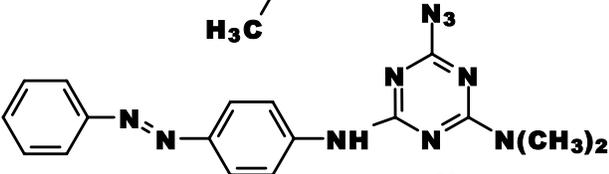
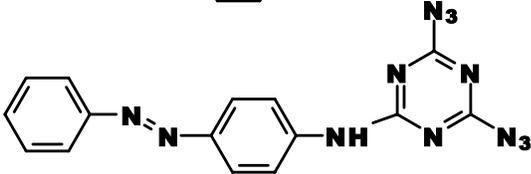


(5)

Studies pertaining to dyeing nylon with reactive dyes designed for use on wool have been undertaken by Burkinshaw and co-workers [41-43]. In this regard, the build-up and washfastness characteristics of commercial chlorodifluoropyrimidinyl (Drimarene) dyes [41], α -bromoacrylamido (Lanasol) dyes [42], vinylsulphone (Remazol) dyes and chlorotriazine (Procion HE) dyes [43] were examined on nylon. It was found that weakly acidic conditions (pH 4) gave good color strength.

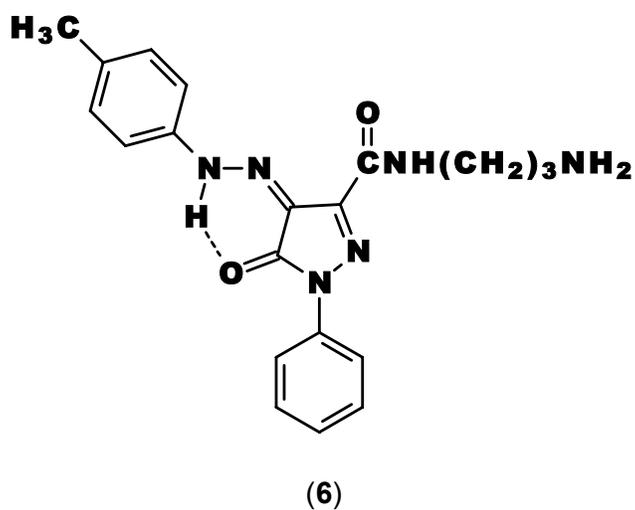
The study of reactive disperse dyes for polypropylene fibers was also investigated by using a nitrene group as a reactive system [44]. Polypropylene fibers were used as a model for testing the advantages of these dyes. Four typical dyes are shown in Table 6.

Table 6. Percentage of fixation of azide dyes on polypropylene fibers.

Dye	% Fixation
 <chem>CN(C)c1ccc(cc1)/N=N/c2ccc(cc2)S(=O)(=O)N</chem>	47
 <chem>Cc1ccc(cc1)/N=N/c2cc(N=[N+]=[N-])cc2C</chem>	43
 <chem>CN(C)c1nc(NC(=O)c2ccc(cc2)/N=N/c3ccccc3)n1</chem>	26
 <chem>Cc1nc(NC(=O)c2ccc(cc2)/N=N/c3ccccc3)n1[N+]=[N-]</chem>	58

The results showed that although the fixation efficiencies were not particularly high, it was evident that percent fixation increased with the number of azide groups in the dye molecule. These dyes gave a significant increase in washfastness.

A number of 3-[N-(3'-aminopropyl) carboxamido]-4-arylazopyrazolone dyes (**6**) were studied as reactive dyes for polyester. It was anticipated that the reaction with the polyester fiber would be one of transamidation which probably occurred mainly at an end group ester moiety. Bonding generally occurred under thermosol dyeing conditions [45].



3. CONSTITUTIONAL CHARACTERISTICS OF REACTIVE DYES

The four characteristic features of a typical reactive dye molecule are a reactive group, a chromophoric group, a bridging group and a solubilizing group [10, 18, 46]. The sections that follow provide details on each feature.

3.1 Reactive Groups

Reactive dyes owe their covalent bond forming ability to the presence of the reactive groups in their structure [11]. The important reactive groups including monofunctional and bifunctional reactive systems are listed in Table 7.

3.1.1 Monofunctional Reactive Systems

These systems can react only once with the nucleophilic groups in the fiber. Examples are halotriazine and vinylsulphone systems. Regarding the dichlorotriazine, difluoropyrimidine and dichloroquinoxaline heterocyclic ring systems, there are two equivalent replaceable halogeno substituents. However, when one of these halogen atoms is displaced by reaction with functional groups in the fiber or with alkali in the dyebath, the reactivity of the remaining halogeno substituent is greatly decreased [46].

Table 7. Important reactive systems.

System	Commercial Name
<u>Monofunctional</u>	
Dichlorotriazine	Procion MX
Monochlorotriazine	Procion H
Monofluorotriazine	Cibacron F
Trichloropyrimidine	Drimarene X
Difluorochloropyrimidine	Drimarene K
Dichloroquinoxaline	Levafix E
Sulphatoethylsulphone	Remazol
Sulphatoethylsulphonamide	Remazol D
<u>Bifunctional</u>	
Bis(monochlorotriazine)	Procion HE
Bis(monocotinotriazine)	Kayacelon React
Monochlorotriazine-sulphatoethylsulphone	Sumifix Supra
Monofluorotriazine-sulphatoethylsulphone	Cibacron C

3.1.2 Bifunctional Reactive Systems

Bifunctional reactive dyes contain two separate reactive centers for reaction with suitable groups in the fiber. They also have the potential to combine with more than one group in the fiber chain molecule. Such reactions may lead to covalent bond formation either within the same polymer chain or between two adjacent chains. Analytical techniques, viz. electron microscopy, surface area determination, and swelling in cadoxen solvent,

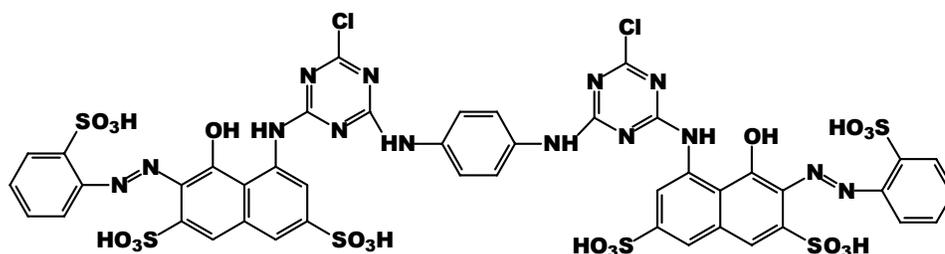
have been used to obtain results which provide evidence for the formation of crosslinks between adjacent cellulose chains in cotton dyed with different types of bifunctional reactive dyes [47]. Bifunctional reactive dyes can be divided into two types [16]:

3.1.2.1 Homobifunctional Reactive Dyes

These dyes consist of two similar reactive groups, examples of which are shown in sections A and B below.

A. Bis-monochlorotriazine dyes

C.I. Reactive Red 120 (7) is an example of Procion HE dyes that contain two monochlorotriazine groups in a dye molecule [25]. Their high substantivity allows them to produce high exhaustion levels at 80°C in batchwise dyeings, leading to fixation values of 70-80%. Unfortunately, the wash off process is slow because of the high substantivity of these dyes [46].

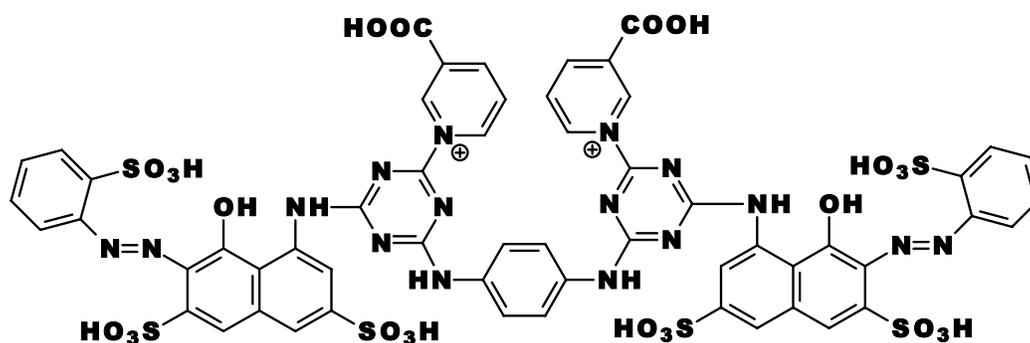


(7)

B. Bis-monocotinotriazine dyes.

A full range of bis-monocotinotriazine dyes was introduced in 1984 by Nippon Kayaku. An example of this range is C.I. Reactive Red 221 (Kayacelon React Red CN-3B) (8). Exhaust dyeing requires a neutral dyebath at a temperature above the boil. Operating the temperature in the region of 130°C minimizes the diffusion problems expected with such a large

molecule. These dyes are suitable for the one-bath dyeing of polyester/cotton blends [46].



(8)

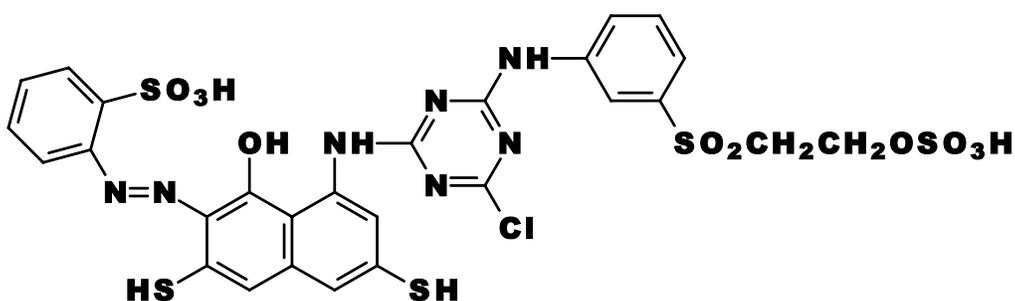
3.1.2.2 Heterobifunctional Reactive Dyes

These dyes consist of two different types of reactive groups. Examples are the following.

A. Monochlorotriazine/sulphatoethylsulphone dyes

The presence of monochlorotriazine and sulphatoethylsulphone groups within the same dye molecule leads to higher fixation values [4, 16, 48, 49]. At low dyeing temperatures, the reaction between the vinylsulphone group and fiber is preferred and at higher temperatures fixation via chlorotriazine group is preferred [46]. Both reactive groups can contribute to the fixation process but the relatively higher reactivity of the vinylsulphone group ensures that most of the fixation occurs through this functional group [36, 50]. Further benefits of this system are attributed to the triazine ring that is capable of linking with a wide range of chromophores. Although these dyes give a high degree of exhaustion, they also have good wash off properties. A typical

example of these dyes is C.I. Reactive Red 194 (Sumifix Supra Brilliant Red 2BF) (9).



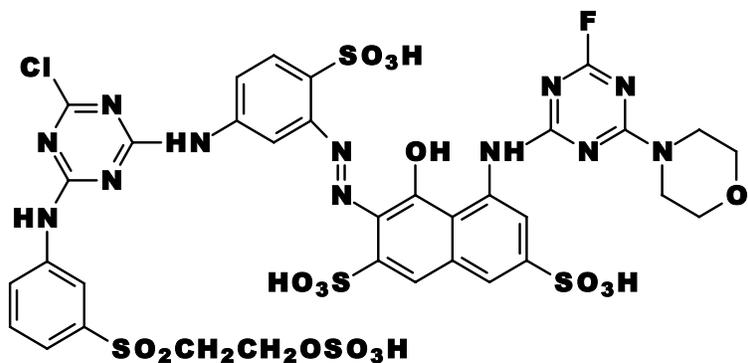
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B. Monofluorotriazine/sulphatoethylsulphone dyes

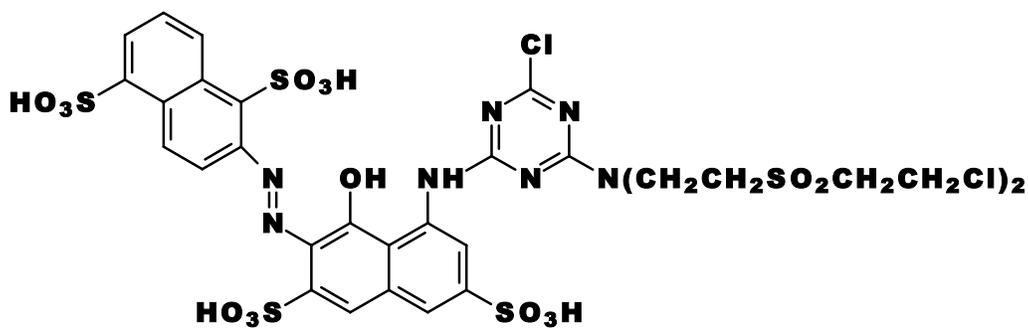
With the combination of monofluorotriazine and vinylsulphone systems, e.g. Cibacron C dyes, both groups contribute to effective fixation under virtually the same conditions. The reactivity of the fluorotriazine group matches more closely that of the vinylsulphone group and makes a larger contribution to fixation than the less reactive chloro analogues [51]. The fluorotriazine-fiber bonds are stable to an alkaline medium while the vinylsulphone-fiber bonds are stable to an acidic medium [25, 52]. These dyes also provide an environmental advantage since they give very high fixation, minimizing effluent color [53]. They are generally designed for pad application. Their excellent bath stability, high fixation and easy wash off properties make them especially suitable for pad-batch dyeing [46].

3.1.3 Polyfunctional Reactive Systems

Theoretically, it should be possible to increase fixation efficiency by incorporating additional reactive groups into the dye molecule. In practice, these additional reactive groups can have an impact on important physical properties such as solubility, aggregation, substantivity, and migration. Reactive groups increase the molecular weight of a dye but do not improve color strength. The additional reactive groups sometimes can lead to lower fixation, especially at heavy depths, and poor build-up. However, several patents pertaining to polyfunctional reactive dyes have been issued [51, 54]. In this regard, the structure of trifunctional reactive dyes such as a monochlorotriazine, monofluorotriazine and vinylsulphone combinations (**10**), have been disclosed by Bayer [54]. Other combinations of trifunctional reactive dyes include a bis-vinylsulphone/difluorochloropyrimidine [55], bis-monofluorotriazine/ vinylsulphone [56], chloroethylsulphone, sulphatoethylsulphone and monochlorotriazine [57], three halotriazine [58] and monochlorotriazine, sulphatoethylsulphone and difluorochloropyrimidine groups [59]. Relatively few trifunctional reactive dyes have been marketed, an example of which is C.I. Reactive Red 181 (**11**) [54].



(10)



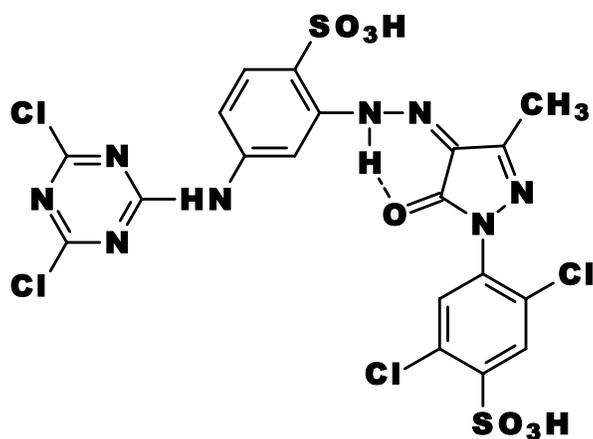
(11)

3.2 Chromophoric Groups

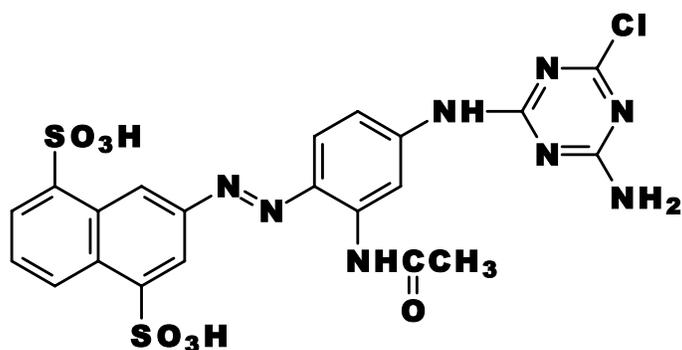
Chromophoric groups contribute color to textile fibers [46]. The proper selection of chromophores for commercial reactive dyes is essential to achieving a given shade area [60]. Market data also show that reactive dyes are increasingly selected on the basis of shade [61]. In practice, monoazo, disazo, metallized monoazo, metallized disazo, formazan, anthraquinone, triphenodioxazine, and phthalocyanine chromophores have been used for the preparation of reactive dyes [1, 10, 62].

3.2.1 Azo Reactive Dyes

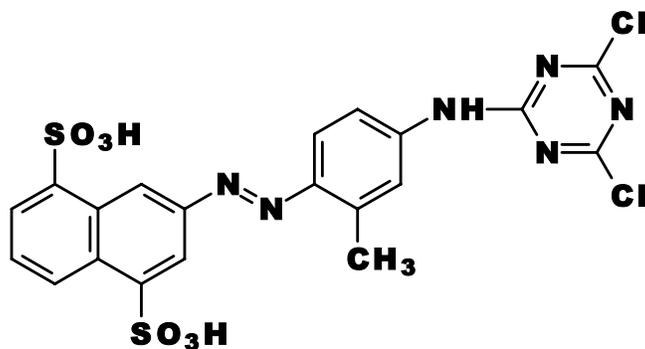
From the azo chromophore, many dyes can be obtained by varying different couplers, diazo components and reactive systems. Greenish yellow reactive dyes, such as C.I. Reactive Yellow 1 (**12**), are usually monoazo dyes based on heterocyclic couplers, whereas reddish yellow reactive dyes usually have monoazo structures from aniline or naphthylamine couplers (e.g. C.I. Reactive Yellow 3 (**13**) and C.I. Reactive Yellow 4 (**14**)) [1, 10, 46, 63].



(12)

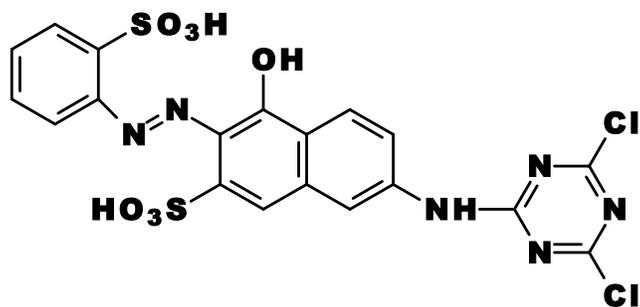


(13)

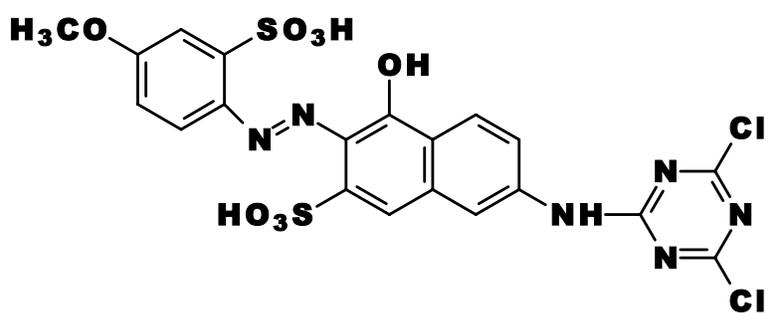


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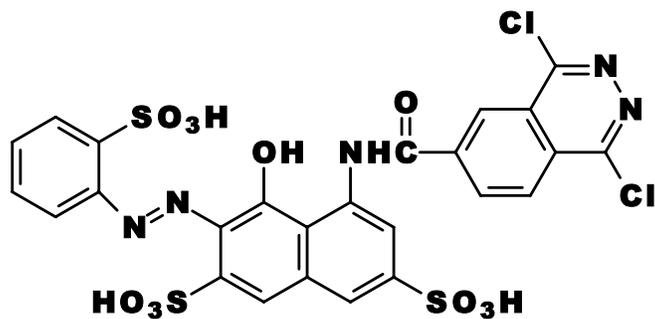
The coupling components employed for dyes of this type are mainly aminonaphthols, and are used to produce orange to black hues. J-acid is usually used in the production of orange dyes such as C.I. Reactive Orange 1 (15). 4-Methoxyanilinosulphonic acids give scarlet dyes such as C.I. Reactive Red 8 (16). A bright bluish-red dye such as C.I. Reactive Red 96 (17) can be produced by the replacement of J-acid with H-acid. Rubine, violet and blue shades are produced generally by using copper complexes which are planar and provide enhanced substantivity. Copper complexes of 2-aminophenolsulphonic acids, diazotized and coupled with J-acid give rubine dyes such as C.I. Reactive Red 6 (18) and with H-acid give violet dyes such as C.I. Reactive Violet 1 (19). The use of copper complexes of aminonaphtholsulphonic acid with H acid, leads to blue dyes such as C.I. Reactive Blue 13 (20). An example of a navy blue dye is C.I. Reactive Blue 40 (21) [1, 63].



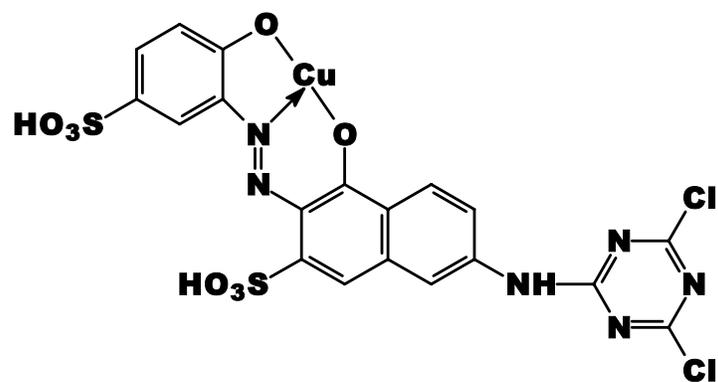
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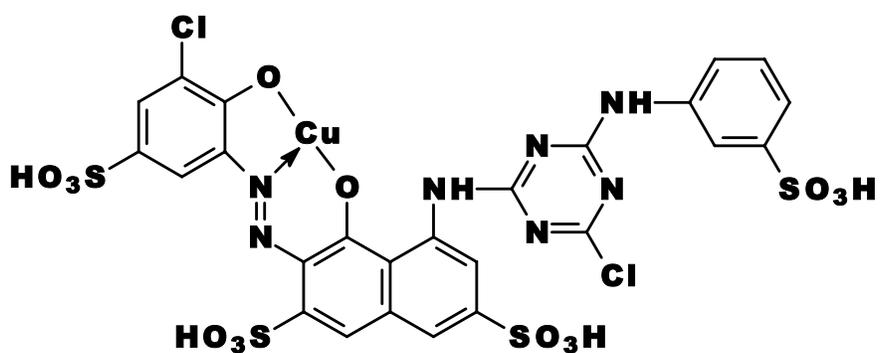
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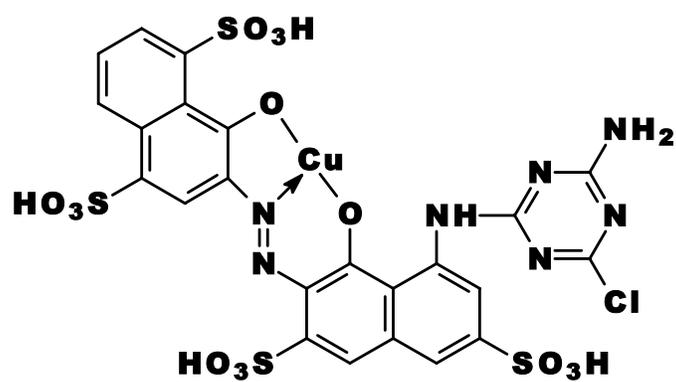
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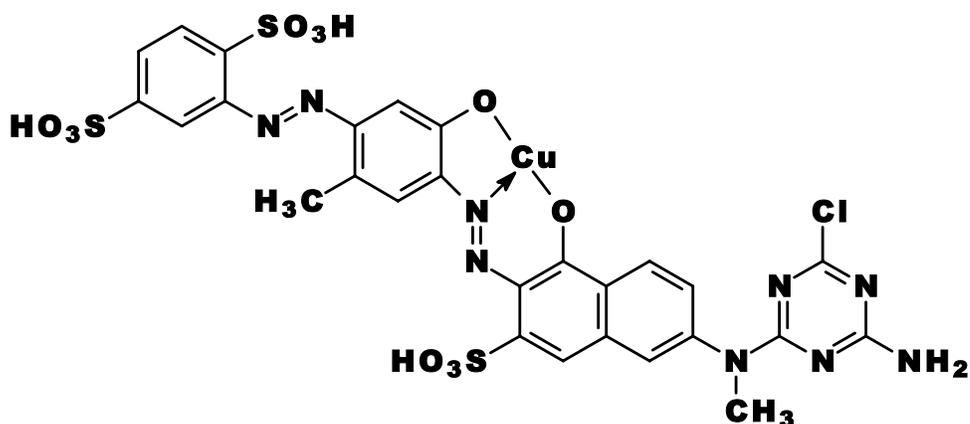
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(19)

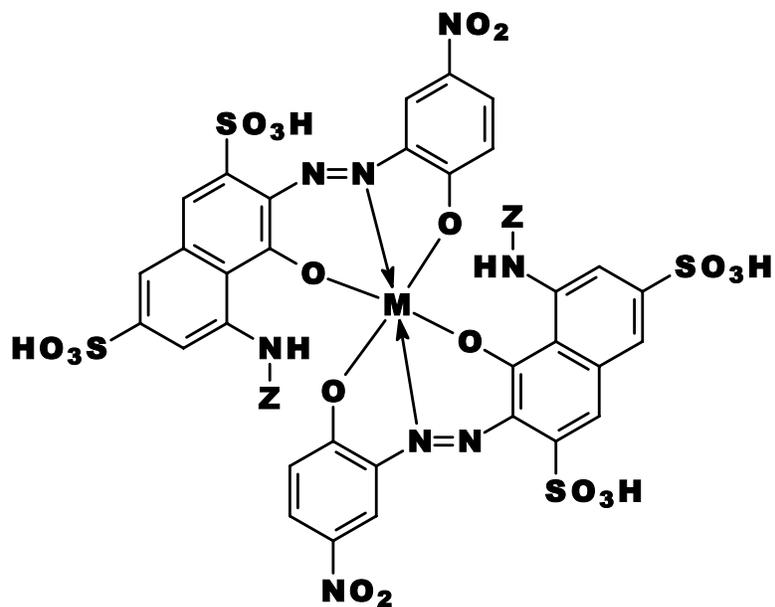


(20)



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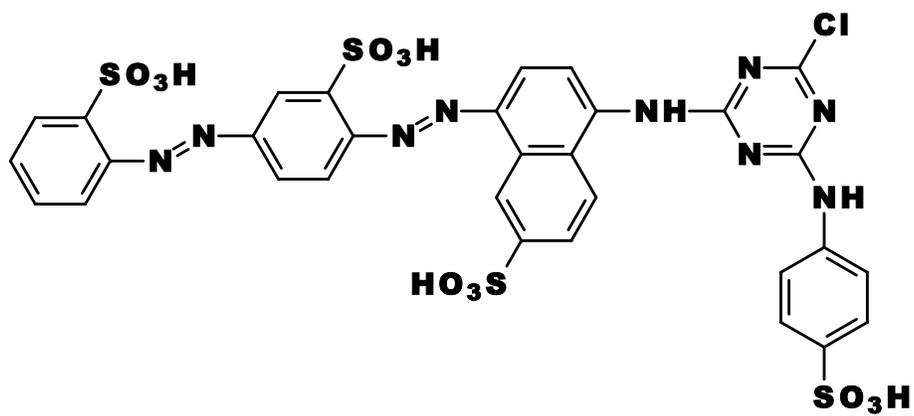
Cobalt and chromium complexes are used to produce gray and black dyes such as C.I. Reactive Black 4 (**22**). These dyes are large molecules and have nonplanar structures and low substantivity on cotton. They are mainly restricted to printing applications. Reactive brown dyes having disazo structures, e.g. C.I. Reactive Brown 1 (**23**), can be produced by using one, two and often three naphthylamine molecules. Reactive green dyes can be prepared by combining a blue chromophore with a yellow chromophore via a triazine moiety [1, 10]. Twice coupled H-acid structure can give dull green if the diazo components are properly selected, as in the case of C.I. Reactive Green 19 (**24**). Only a limited number of green azo reactive dyes have been marketed [63, 64].



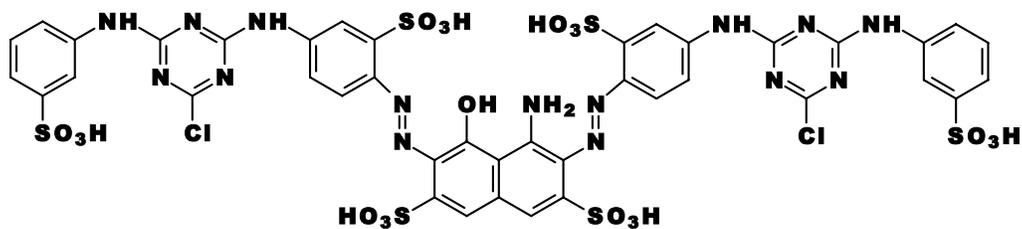
$M = Cr$ or Co

$Z =$ a halogeno heterocyclic reactive group

(22)



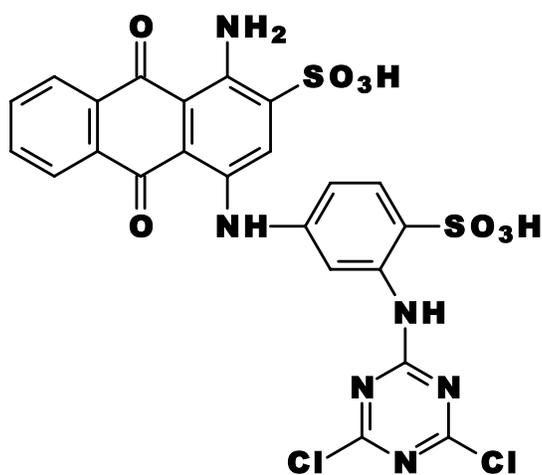
(23)



(24)

3.2.2 Anthraquinone Reactive Dyes

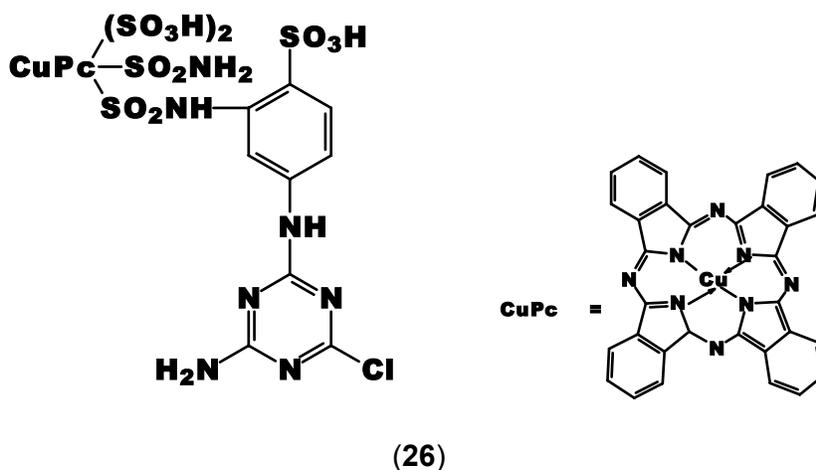
Until the end of the 1970s, anthraquinone reactive dyes dominated the market for brilliant blue dyes, despite their relatively low color strength and high cost. Their molar extinction coefficient (E_{max}) is in the ranges of 12,000-18,000 $Lmol^{-1}cm^{-1}$ which is approximately half that of an azo dye. However, anthraquinone dyes have good fastness properties [60, 65]. The most commonly used anthraquinone reactive dyes are derived from bromaminic acid and by variation of ring substituents give bluish-violet to bluish green hues. The bright reddish to mid-blue hues are the most important [1, 10]. C.I. Reactive Blue 5 (25) is an example of anthraquinone reactive dyes [14].



(25)

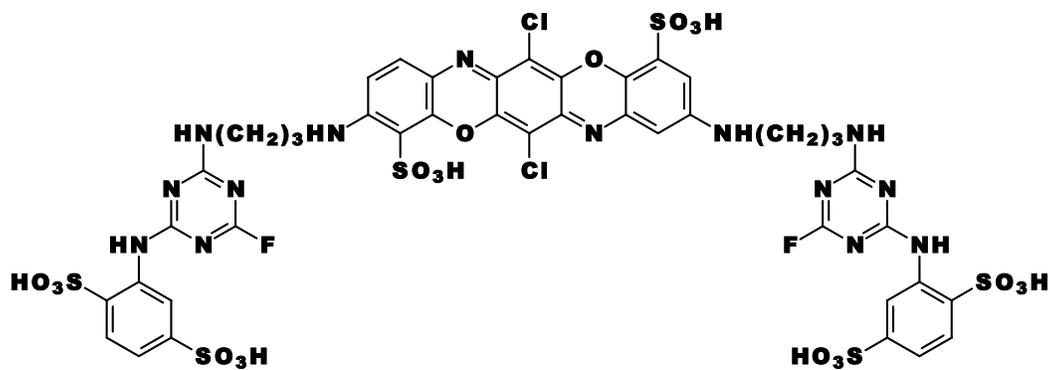
3.2.3 Phthalocyanine Reactive Dyes

Phthalocyanine reactive dyes are used for turquoise hues that cannot be produced by using either azo or anthraquinone dyes [1, 10]. In fact, turquoise blue dyes remain dominated by copper and nickel phthalocyanine derivatives [63]. Copper phthalocyanine is normally the most often used chromophore and it produces dyes such as C.I. Reactive Blue 7 (**26**) [1, 10].



3.2.4 Triphenodioxazine Reactive Dyes

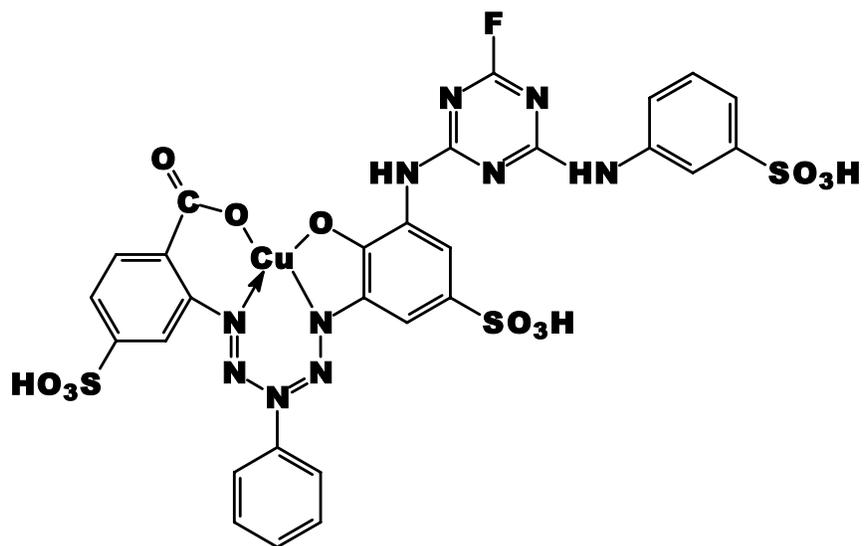
Triphenodioxazine dyes can be used to produce deep, bright blue shades on cotton. The first triphenodioxazine reactive dye was marketed by ICI in the mid-1970s [60, 66]. The gradual replacement of the anthraquinone chromophore by the triphenodioxazine chromophore is now a well-established trend [51]. Triphenodioxazine dyes have gained an important share of the blue shade area because of their very high color strength ($E_{\max} = 70,000\text{--}85,000 \text{ Lmol}^{-1}\text{cm}^{-1}$) and low production cost. C.I. Reactive Blue 204 (**27**) developed by ICI is an example of this dye type [65].



(27)

3.2.5 Formazan Reactive Dyes

Copper complexes of formazan dyes are capable of producing red to greenish blue shades. Research activity in the formazan reactive dye area has increased, since these dyes exhibit high color strength. An example of a formazan reactive dye is (28) [10, 65].



(28)

3.3 Bridging Groups

A bridging group is the group that links the reactive system to the chromophore [2, 11, 46, 47]. While these groups are necessary for synthetic reasons, they also influence the reactivity, degree of fixation, stability of the reactive dyeing and other dyeing characteristics, such as substantivity and migration, significantly [62, 67]. The typical bridging group is an imino (-NH-) group. Ether or mercapto bridging groups have been examined but generally the bonds do not have acceptable stability. They are also less easy to form than imino bridging groups. Carboxamide and sulphonamide groups are stable and can be used as bridging groups to a limited extent [18].

3.4 Solubilizing Groups

Solubilizing groups provide characteristics such as water solubility, substantivity, migration and wash off [18, 68]. The dominant solubilizing group in reactive dyes is the sulphonic substituent [46].

4. REACTIVE DYE-FIBER FIXATION

The common steps for reactive dyeings from a dyebath involve [2, 52]:

1. The exhaustion of dye from the dyebath to the fiber surface
2. The adsorption of dye at the fiber surface
3. The diffusion of dye from the fiber surface into the pore of the fiber
4. The migration of dye to give dye uniformity. Migration occurs when an equilibrium is reached between the dye in the solution and the dye in the fiber

5. The fixation of dye via covalent bond formation between the dye and fiber. Fixation to cellulose occurs mainly under alkaline conditions whereas fixation to polyamide can be achieved under weakly acidic conditions.

During the fixation stage, competitive hydrolysis of reactive dye also occurs, when the dye reacts with hydroxide ions in the dyebath [4, 9, 48, 69-71]. Since the hydrolyzed dye is usually very similar to the original reactive dye in diffusion and adsorption properties, it exhausts along with the reactive form onto the fiber surface. In some cases, the hydrolyzed dye is held tenaciously on the fiber surface through physical forces characteristic of a direct dye on cotton [48, 71, 72]. The hydrolysis of reactive dyes results in a degree of fixation less than 100% [14, 70, 73]. After dyeing, the unfixed, hydrolyzed dye must be removed from the fiber via a wash off process, to enhance crockfastness and washfastness [9, 70].

In practice, fixation predominates over hydrolysis due to important factors. Firstly, cellulose has a lower dissociation constant than water, resulting in approximately a 25-fold excess of cellulosate ions over hydroxyl ions. Secondly, the affinity of the dye for the fiber reduces the amount of dye available for hydrolysis in the dyebath [20]. Thirdly, the pH within the fiber is primarily maintained by cellulosate ions and the charge on the fiber surface expels hydroxide ions from the fiber interior [63].

4.1 Chemical Reactions between Reactive Dyes and Fibers

4.1.1 Nucleophilic Substitution

Nucleophilic substitution characterizes dye-fiber fixation that occurs when a leaving group in the reactive system is displaced as a result of an interaction with a nucleophilic group on the polymer chain. The reaction of a monochlorotriazine reactive dye with a hydroxy group of cellulose and/or an amino group of keratin is typical of this process (cf. Figures 2 and 3) [11, 28, 44, 48, 74]. The same process accounts for the competitive hydrolysis reaction between the dyes and water during dye application (Figure 4) [75]. A summary of the reactive systems that undergo this type of reaction is provided in Table 8 [19].

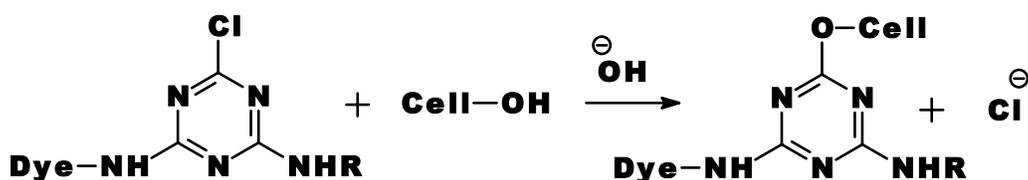


Figure 2. Reaction of a monochlorotriazine dye with cellulose.

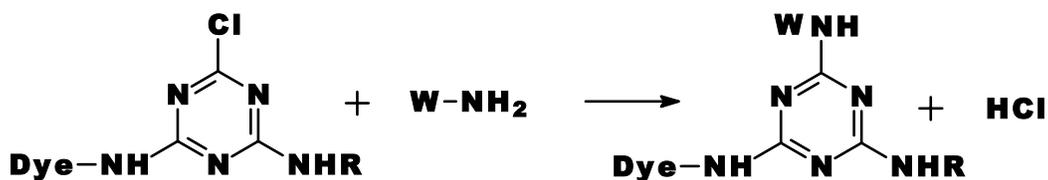


Figure 3. Reaction of a monochlorotriazine dye with wool.

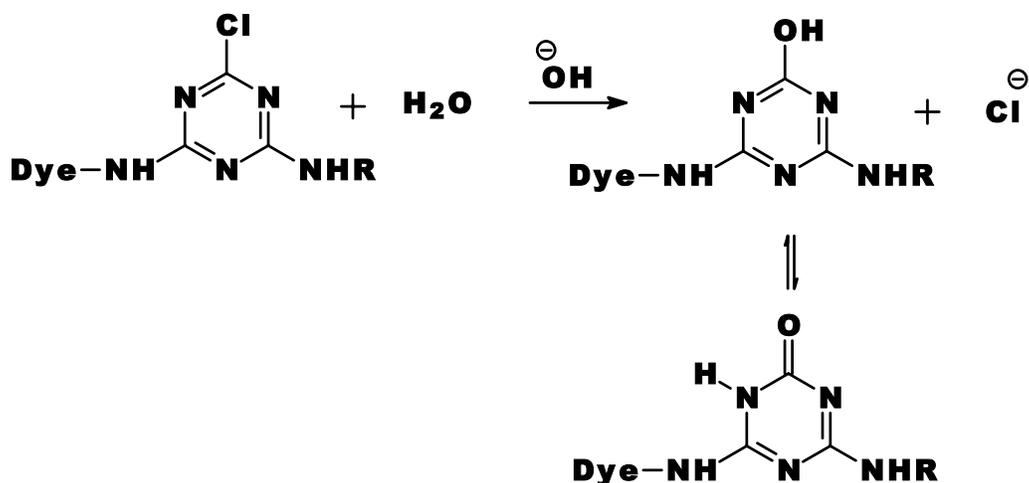
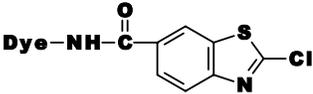
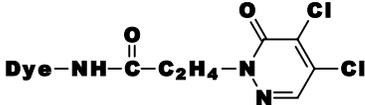
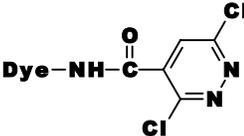
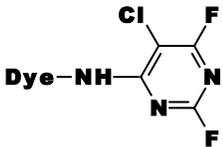
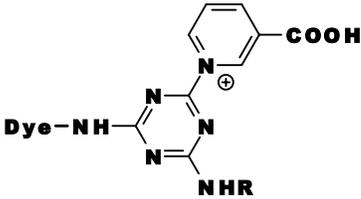


Figure 4. Hydrolysis of a monochlorotriazine dye.

Table 8. Examples of reactive groups reacting by nucleophilic substitution.

Reactive Group	Chemical Structure
Dichlorotriazine	
Monochlorotriazine	
Trichloropyrimidine	
2,3-Dichloroquinoxaline-6-carbonyl	
Dichlorophthalazine	

Table 8 (continued)

Reactive Group	Chemical Structure
Benzchlorothiazole	
Dichloropyridazone	
Dichloropyridazine	
Difluorochloropyrimidine	
Mononicotinotriazine dyes	

4.1.2 Nucleophilic Addition

Nucleophilic addition characterizes the dye-fiber reaction in which a nucleophilic group in the fiber adds across an activated carbon-carbon double bond in the reactive group. Most of reactive systems used contain a vinylsulphone moiety. The vinylsulphone reactive group itself is usually not present in commercial form of the dyes employed. Instead, more stable precursor such as the β -sulphatoethylsulphone group is used. The two-stage process associated with fiber fixation is shown in Figure 5 [36, 44, 48, 74].

Structurally related dyes containing a β -sulphatoethylsulphamoyl group probably form a cyclic compound capable of reacting with cellulose to give a cellulose ether (Figure 6) [9, 63, 75]. Systems based on activated double bonds also undergo a competitive hydrolysis reaction (Figure 7) [75]. The reactive systems in this category are given in Table 9 [19].

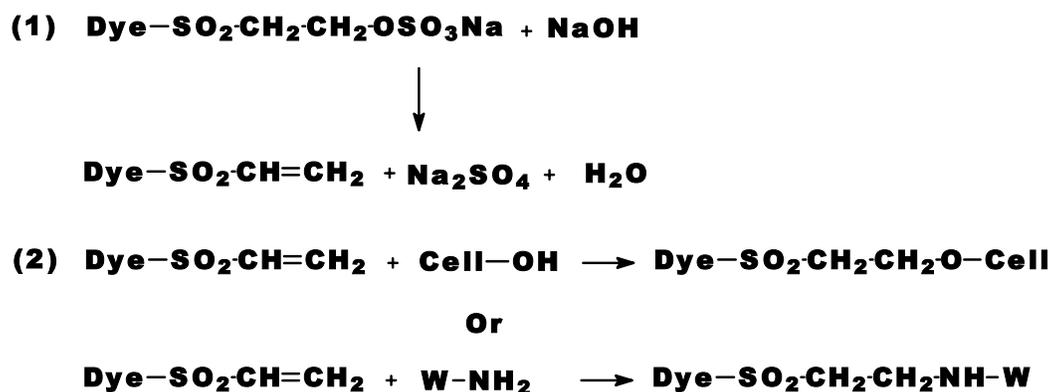


Figure 5. Fixation via nucleophilic addition to a vinylsulphone dye.

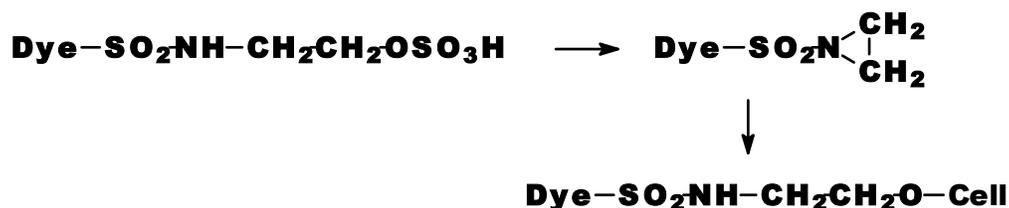


Figure 6. Nucleophilic addition involving a β -sulphatoethylsulphamoyl dye.



Figure 7. Reaction of water with a vinylsulphone dye.

Table 9. Reactive groups reacting by nucleophilic addition.

Reactive Group	Chemical Structure
β -Sulphatoethylsulphone	Dye—SO₂·CH₂·CH₂·OSO₃H
β -Sulphatoethylsulphamoyl	Dye—SO₂·NH·CH₂·CH₂·OSO₃H
Chloropropylamido	$\text{Dye—NH—}\overset{\text{O}}{\parallel}\text{C—CH}_2\text{·CH}_2\text{·Cl}$
Sulphatopropylamido	$\text{Dye—NH—}\overset{\text{O}}{\parallel}\text{C—CH}_2\text{·CH}_2\text{·OSO}_3\text{H}$
Acrylamido	$\text{Dye—NH—}\overset{\text{O}}{\parallel}\text{C—CH=CH}_2$
α -Chloroacrylamido	$\text{Dye—NH—}\overset{\text{O}}{\parallel}\text{C—}\underset{\text{Cl}}{\text{C}}=\text{CH}_2$
α,β -Dibromoacrylamido	$\text{Dye—NH—}\overset{\text{O}}{\parallel}\text{C—}\underset{\text{Br}}{\text{C}}=\underset{\text{Br}}{\text{CH}}$
Methyl-aurine-ethylsulphone	$\text{Dye—SO}_2\text{·CH}_2\text{·CH}_2\text{·}\underset{\text{CH}_3}{\text{N}}\text{·CH}_2\text{·CH}_2\text{·OSO}_3\text{H}$

4.1.3 Fixation involving a phosphonic acid group

The fixation of a phosphonic acid reactive dye to cellulose takes place under acidic conditions in the presence of cyanamide or a carbodiimide at temperature around 200°C. The reaction occurs via the esterification process shown in Figure 8 [76]. In this case, a competitive hydrolysis reaction does not occur. While carbodiimide has the unfavorable competition side reaction

resulting in an unsatisfactory degree of fixation, high fixation values can be achieved by using cyanamide at 160°C [6, 62, 77].

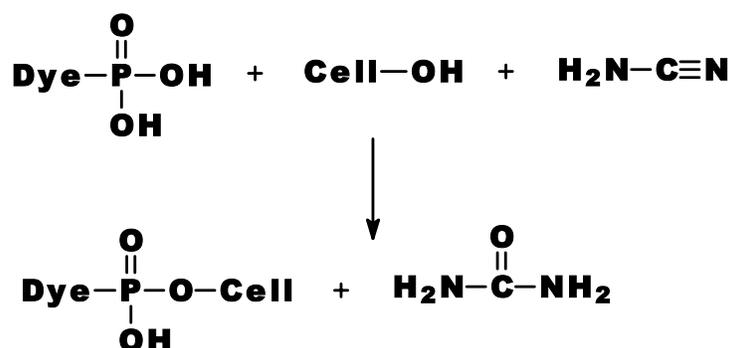


Figure 8. Reaction of a phosphonic acid reactive dye with cellulose.

4.2 Fixation of Bifunctional Reactive Dyes

One of the important characteristics of bifunctional reactive dyes is their ability to provide a high percent fixation. Figure 9 demonstrates why a typical bifunctional reactive dye gives higher percent fixation than conventional monofunctional reactive dyes. In the pad-batch method, monofunctional reactive dyes achieve an average of 75% fixation. The remaining 25% of the dye is hydrolyzed and finds its way into the wastewater. In the case of a bifunctional reactive dye, one reactive group (R_1) could react with the fiber to the same degree (75%) as a monofunctional reactive dye, with 25% unreacted. However, the partially hydrolyzed but still reactive dye can react further, via the second reactive group (R_2). Therefore, about 94% of the amount of dye applied bonds to the fiber and only 6% is wasted. The same principle can apply in exhaust dyeing. The degree of fixation in exhaust dyeing is lower than that of pad dyeing because the dye does not entirely exhaust onto the fiber. When a bifunctional reactive dye exhausts to 85%, a

fixation of 80% can be reached. For the same degree of exhaustion, the fixation of a monofunctional dye on average only to 60-65% and much more dye has to be removed during the wash off process [2, 52]. The reaction of a bifunctional reactive dye such as Sumifix Supra dye with cellulose [25] proceeds by the pathways shown in Figure 10.

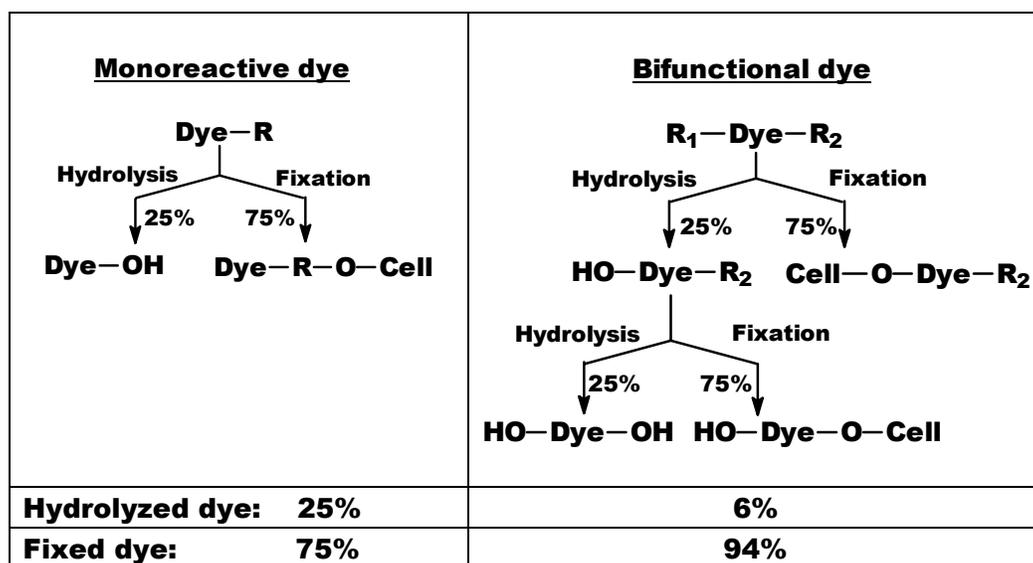


Figure 9. Fixation values for monofunctional and bifunctional reactive dyes having 75% fixation per reactive group.

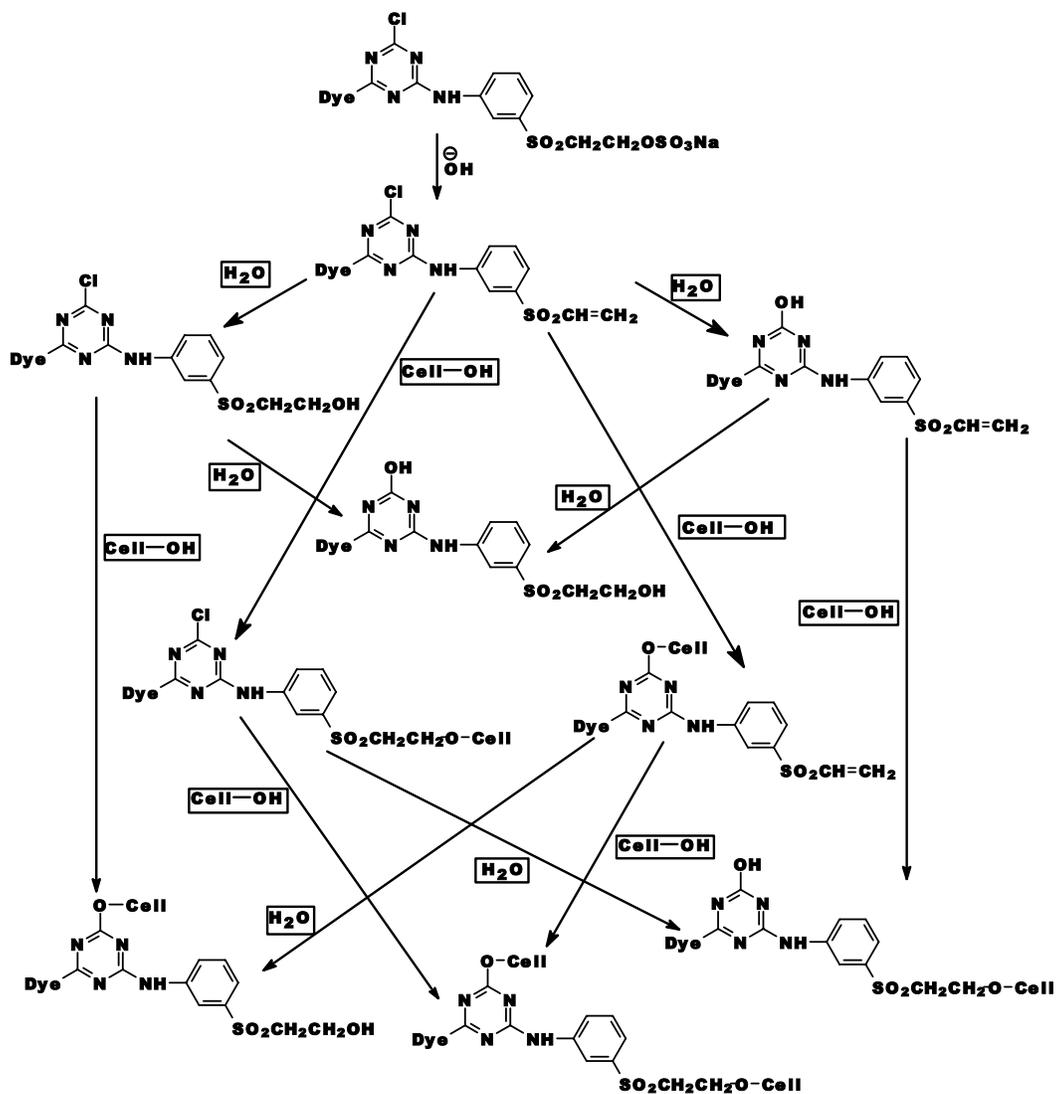


Figure 10. Reaction combinations for a heterobifunctional Sumifix Supra dye with cellulose in alkaline media.

5. DYE APPLICATION

There are four main methods used for applying reactive dyes to cellulosic fibers: batchwise, semi-continuous, continuous dyeing processes and printing [52, 72].

5.1 Batchwise or Exhaust Dyeing Processes

The basic principle in the batchwise dyeing process is to exhaust as much of the dye as possible onto the fiber using neutral or weakly acidic conditions, prior to initiating the fixation step. The initial dyebath contains a dye dissolved completely in water, a solubilizing agent such as urea, and an electrolyte such as common salt or Glauber's salt. Under these conditions, the dye does not react or reacts very slowly and leveling takes place. The pH of the dyebath is then increased by the addition of alkali so that the dye-fiber fixation takes place [5, 78]. The particular type of reactive dye being used usually governs the choice of temperature. The last step is the wash off process, which removes unfixed dye, alkali and electrolyte [1, 5, 9].

These dyeing processes are often divided into four different categories. Three of these are characterized by the nature of the exhaustion and fixation phases and the fourth is an All-In method.

5.1.1 The Traditional or Conventional Method

This method involves adding the dyestuff and electrolyte to the bath below the fixation temperature and then heating the bath to the fixation temperature prior to alkali addition. This method is used when rapid exhaustion is undesirable or if the dyeing equipment has efficient heating control. If the rate of salt addition and temperature increase are not well controlled, unlevel dyeings may occur.

5.1.2 The Constant Temperature Dyeing Method

In this method, the temperature is set at the start of the cycle and remains constant throughout the dyeing process. Dye is also added at the beginning of the cycle. Electrolyte may be added at the beginning or in portions and then alkali is added after a proper time interval to achieve dye-fiber fixation. This procedure is widely used and simple to run. The problem of improper temperature control during the heating phase is completely eliminated.

5.1.3 The High Temperature Dyeing Method

This method involves starting the dyeing process at an elevated temperature and then allowing the temperature to drop to the fixation temperature before the addition of alkali. Starting at an elevated temperature promotes more rapid diffusion and better leveling and migration of the dye. The exhaustion is also much lower for dyes with high substantivity. The principal use of this method is in dyeing fabrics from high twist yarns, tightly woven goods, or for viscose rayon fabrics [2, 68].

5.1.4 One Step or All-In Method

This method involves the addition of dye, salt and alkali at the beginning of the cycle. Because alkali is added at the beginning, the starting temperature must be low in order to minimize hydrolysis. The advantages of this method are simplicity and reduction of cycle time, since dye and chemicals are added at the beginning of the cycle. However, this method is

less suitable for goods that are difficult to penetrate and level. Maintaining the starting temperature is critical for repeatability, and controlling the rate of heating is essential for levelness since exhaustion and fixation occur simultaneously from the beginning. Moreover, there is a possibility of lower color yield due to hydrolysis [2, 16, 68].

Batchwise dyeing may be done on a jig machine for woven cotton or a winch and jet machine for knitted or lightweight woven fabrics. Developments in the automation of reactive dyeing have been made that reduce the need for manual intervention in batchwise dyeing process. Isothermal process cycles based on automatic controls have been devised. The dye, electrolyte and alkali may be added according to predetermined profiles over a given time period and additions are controlled by dyeing programs. The automatic control contributes to the high level of reproducibility between repeat batches [46]. This process also approaches the market demand of "Right first time" production that ensures timely delivery and minimizes the cost of production [16, 79].

The lower limit of the liquor ratio in a batchwise dyeing process is about 10:1 to 5:1, or in specially designed ULLR (Ultra-low liquor ratio) equipment, possibly 3:1 [80]. Padding methods enhance this further to the range 1:1 to 0.5:1. Thus, the advantages of improved exhaustion and fixation characteristics of short liquor exhaust dyeing can be markedly enhanced by using semi-continuous or continuous dyeing processes [46].

5.2 Semi-Continuous or Pad-Batch Dyeing Processes

This is an exhaust method conducted at extremely low liquor ratios and ambient temperature. The goal of this process is to pad on a solution of dye and alkali and to batch the goods as uniformly as possible. After padding, the goods are then wrapped with plastic to prevent water evaporation and the reaction of alkali with the carbon dioxide in the air. The beams are rotated to prevent preferential drainage, and the goods stored in a temperature-controlled area to help ensure a high degree of reproducibility. The dye will react slowly but evenly throughout the batching time. Batching time can be 2-4 hours for highly reactive dyes and 6-24 hours for less reactive dyes. The goods can then be efficiently washed off on perforated beams with a slow flow of hot or cold water [2, 5, 24, 78].

The advantages of pad-batch over exhaust dyeing are low initial cost, reduced consumption of water, energy and chemicals, reduced effluent control and labor costs, a significant increase in productivity, and improvement in quality of the dyed goods such as shade consistency and reproducibility [81]. Another benefit associated with processing woven fabrics is the tendency for pad-batch methods to be smaller, which is a disadvantage in continuous processing where the minimum economical lot size is considered to be about 5,000 meters [82].

5.3 Continuous Dyeing Processes

From the viewpoint of organization and management, continuous dyeing methods offer economic advantages when long runs are required in a

limited range of colors. Excellent reproducibility is possible with saving in handling and labor costs [46]. The basic procedure is to impregnate the fabric in open width form with a dyebath, by means of a padding unit. This step can be carried out either by a one-bath process or by two-bath process. In a one-bath process, alkali is incorporated in the lone pad bath whereas in the two-bath process, the alkali is padded from the second bath [78]. Then the impregnated goods are subjected to the fixation process, which is generally done using dry heat, i.e. thermofixation, or using moist heat, i.e. steam fixation, followed by the wash off step [78, 83].

5.3.1 The Conventional Dyeing Process (Pad-Dry-Pad-Steam)

The dye is applied from the first padder and then the fabric is dried. Since many of the dyes could easily undergo migration on drying, salt and an antimigration may be necessary in the first pad bath to achieve uniformly colored fabrics. After drying, the goods are passed through a second pad bath containing salt and alkali, and bleeding into the pad bath should be minimal. Then the goods are steamed and washed off [2, 48, 83]. This method is suitable for polyester/cotton blend dyeing when a thermosol step is introduced between the drying and the second padding steps [5].

5.3.2 Pad-Steam Dyeing Process

The dye, alkali and salt are introduced together to the pad bath. Dye hydrolysis should not pose a problem if the dye and alkali are continuously fed into the pad from separate feed tanks. However, the salt concentration may

cause dye solubility problems [2]. This process was developed so that the intermediate costly drying step could be eliminated. The main application of this system is for fabrics that experience migration problems during the intermediate drying step [81]. This method is used for towels and pile fabrics where the cost and difficulty of drying dyed goods is prohibitive. Dyes of high reactivity are preferred [5].

5.3.3 Wet-On-Wet Method (Pad-Pad-Steam)

The fabric is padded with a dye solution and then with a dilute solution of alkali and salt before steaming to achieve dye-fiber fixation. This wet-on-wet sequence can lead to a serious problem of dye bleeding into the alkali bath even at high salt concentration [46]. This method is used for towels and pile fabrics, giving higher levels of fixation in full shades than when the pad-steam sequence is used for many dyes applied under these conditions [5].

5.3.4 Pad-Dry-Cure Method

Some reactive dyes are padded onto cotton in the presence of sodium bicarbonate and urea. The urea acts as a humectant, providing moisture to the fiber that aids fixation of the reactive dye [2, 19, 84]. However, the limitation in this process has been the use of urea which causes fume generation during curing [48].

A recent development in the continuous reactive dye application is the E-control process produced from a joint project involving Monforts and BASF. In this process dichlorotriazine dyes are applied using only sodium

bicarbonate, as no urea, salt, sodium silicate or other chemicals are required. The chemicals normally used are eliminated in the E-control process by maintaining the relative humidity content at 25% in the dryer. The E-control process consists padding dye and alkali, drying for two minutes at 120°C and then washing off unfixed dye [48, 83, 85]. Color yields by this process are higher than in other continuous methods. The challenges associated with this process are the accurate measurement of the humidity in the dryer and the ability to maintain the required level consistently [48]. .

The dyeing of cotton by impregnation of the fabric with an alkaline solution of a reactive dye followed by infrared heating has been investigated. Infrared dye fixation yields were higher and achieved in much shorter times than dyeings produced by heating the impregnated fabric in air, particularly in cases involving dyes of lower reactivity. Continuous dyeing trials showed that the infrared fixation process provided high fixation yields with no visible color variation. Infrared fixation of reactive dyes on cotton could be valuable for reducing the environmental impact of unfixed dyes and dyeing assistants in the dyehouse effluent [70].

5.4 Printing

Textile printing is a very important area of application for reactive dyes. There is no fundamental difference in principle between reactive dye applications by dyeing versus printing techniques. During printing, a reactive dye is applied from a print-paste containing a thickening agent and auxiliaries such as urea, alkali, oxidizing agents, instead of being applied from an

aqueous solution. Two main methods for the fixation of reactive dye prints are atmospheric steaming using saturated steam and dry-heat fixation. To be suitable for this application, the reactive dyes must possess good water solubility. However, the preferred dyes have less substantivity towards cellulose than have those intended for dyeing. The reactivity of these dyes should be such that the print may be fixed using the temperature and processing times normally employed. At the same time, alkali-containing print pastes must remain stable for a long time. Washing out hydrolyzed dyes should also be easy. Ease of wash off minimizes staining of adjacent white areas, making the lower substantive dyes preferred. The fixation of reactive dyes on the cotton after printing is not high. Whereas in dyeing a degree of fixation exceeding 90% can be achieved, the reactive dyes used in printing often have a fixation level of only 60% [9, 86, 87].

6. ADVANTAGES AND DISADVANTAGES OF REACTIVE DYES

Reactive dyes have already caused far-reaching and fundamental changes in the dyestuff manufacturing and dyeing industries because of their ability to undergo stable covalent bond formation. Reactive dyes offer the following advantages to the dyers:

1. They provide bright shades unattainable with other classes of dyes. The brilliance of reactive dyeings is due to the ability to use low molecular weight acid dye molecules [49, 75, 88-90].
2. A full spectrum of shades is possible, as reactive groups can be easily introduced into a large number of chromophores [5, 24, 25, 49].

3. Reactive dyes provide good overall fastness properties. They give good to excellent washfastness with minimal color loss and excellent ratings for the staining of adjacent white goods, and moderate to good lightfastness [2, 68, 90-92]. Their good washfastness is the result of the stable covalent bond between the dye and fiber.

4. Ease and versatility of dyeing and printing applications are observed. Excellent leveling allows simple, reproducible dyeing procedures. High solubility allows easy preparation of dye solutions at concentrations of importance to printers and continuous dyers. High reactivity coupled with rapid diffusion allows level dyeing to be achieved at room temperature in practical dyeing times [24]. Reactive dyes can also be applied using a variety of commercial machines with no major alterations in the machine used [88, 93, 94].

5. These dyes have a moderate cost. This has enabled them to gain their market share mainly at the expense of azoic dyes. Reactive dyes have also achieved limited market penetration against vat dyes, which offer excellent fastness at a higher price, and against direct dyes, which offer low cost and easy application but have duller shades and poor wetfastness properties [63, 89, 95].

Although reactive dye technology has become mature, there are still important technological problems needing to be resolved.

1. The major problem to be overcome is the loss of dye due to the competing hydrolysis process [25, 73]. The hydrolyzed dye formed can not react with the fiber [88]. This problem reduces dye fixation levels, which is

clearly uneconomical and can give rise to effluent problems. Fixation accelerators, short liquor ratio dyeing and low temperature dyeing techniques have received attention and are gradually being reduced to practice.

2. The fastness of reactive dyes to light, in the presence and absence of chlorine, is still a matter of concern. With regard to perspiration lightfastness, it has been shown that in the case of metal-complex dyes, the color loss is due to demetallization of dyes by the action of histidine in perspiration [96]. In case of metal-free dyes, the mechanism associated with color loss is not clear.

Reactive dyed fabrics have moderate to poor chlorine fastness. Chlorine fastness problems can arise from the action of trace amounts of active chlorine used in the sterilization of tap water and in the bleaching process associated with laundering. Some after-treatment fixatives designed to improve the bleach resistance of reactive dyes have been developed. The scope of utility of these agents has not been determined [25, 96, 97].

3. Reactive dyeing processes always produce high volumes of wastewater of varied composition, often containing salt, urea, metal ions and dye [98]. Since it is possible that such chemicals contribute to the toxicity of the effluents, approaches to the design of eco-friendly coloration process for reactive dyes have involved using low salt reactive dyes, machinery suitable for dyeing at low liquor ratio, padding at reduced volumes, replacement of urea with dicyandiamide, implementation of the E-control process, etc [16].

4. A lengthy washing sequence is often needed to remove the unfixed hydrolyzed dyes from the fabric surface [25, 60]. While reactive dyes with

improved exhaustion and fixation are generally effective in increasing substantivity, such dyes are more difficult to wash off. Since in reactive dyes that are applied by an addition reaction, e.g. sulfatoethylsulphones, the active forms (vinylsulphone dyes) possess high substantivity but the hydrolyzed forms (hydroxyethylsulphone dyes) possess lower substantivity. Therefore, wash off is easier to achieve [96].

5. A problem from the bleeding of dyed goods can occur following cleavage of the dye-fiber bond during distribution or use and storage [96].

Main causes of this problem may be as follows:

5.1 Acid hydrolysis by the action of acidic gases such as carbon dioxide, sulfur oxides and nitrogen oxides in the atmosphere

5.2 Oxidative decomposition by oxidizing agents such as active chlorine in tap-water and sodium percarbonate and sodium perborate in detergent.

5.3 Thermal decomposition by hot pressing

7. RECENT DEVELOPMENTS IN REACTIVE DYES

The major driving forces associated with recent reactive dye research and product development fall into three broad categories.

7.1 Products with Greater Economy

This has been accomplished by means such as developing more efficient dye manufacturing processes, shortening dyeing cycles, increasing

the percentage of right-first-time dye house production, the use of more fixation efficient dyes and the use of chromophores with high molar extinction coefficient, E_{\max} .

7.2 Products with Better Environmental Performance

The introduction of products and processes intended for providing improved environmental performance has been another important development. Typical of these approaches have been dyes that function efficiently in the presence of reduced quantities of electrolyte and dyes that have higher fixation levels, thus reducing the amount of colored effluent.

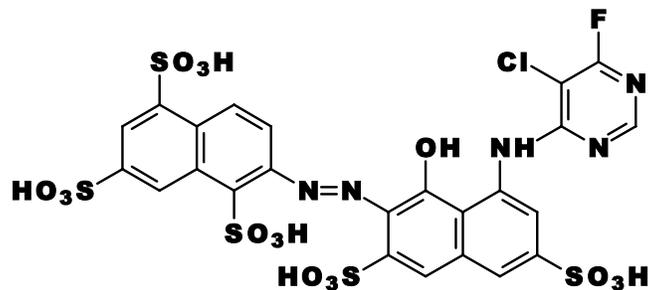
7.3 Products with Improved Technical Properties

Many new products have been designed to achieve technical properties such as high color strength, lightfastness, and washfastness. Patents relating to reactive dyes continue to be awarded, but very few relate to the production of novel chromogens. Most concern novel combinations of existing chromophores and reactive groups.

These developments often overlap. For example, products with greater economy may also have stronger chromophores, higher fixation efficiency, and faster overall dyeing and wash off cycles.

Much of the work has followed the approach of Sumitomo, by introducing heterobifunctional products, usually involving a haloheterocyclic in combination with a vinylsulphone group. Dyes containing a 4-fluoro-5-chloropyrimidinyl reactive group were developed by Bayer. These dyes are

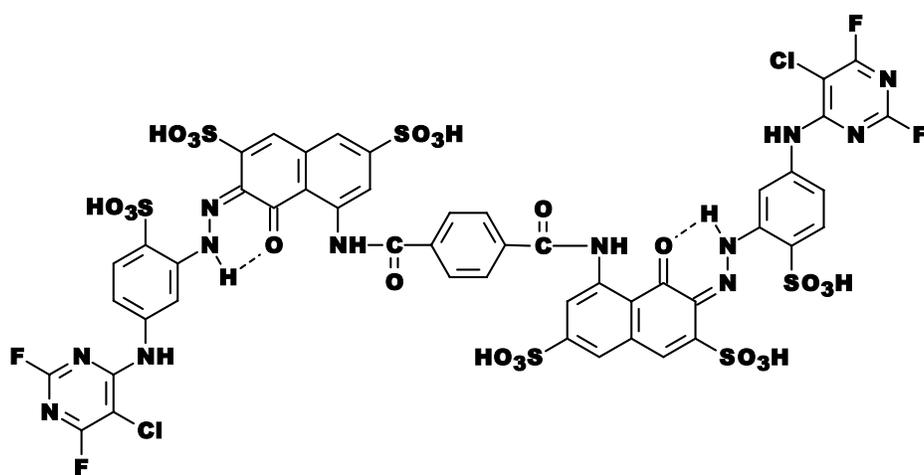
claimed to give high color yields on cotton. For example, dye (29) in which the chromophore is a conventional H-acid-derived red was claimed to produce bluish-red dyeing with excellent washfastness [51].



(29)

Other heterobifunctional reactive dyes include vinylsulphone with monofluorotriazine [99, 100], 2,4-difluoropyrimidine with monofluorotriazine [101] and vinylsulphone with 2,4-difluoropyrimidine [102].

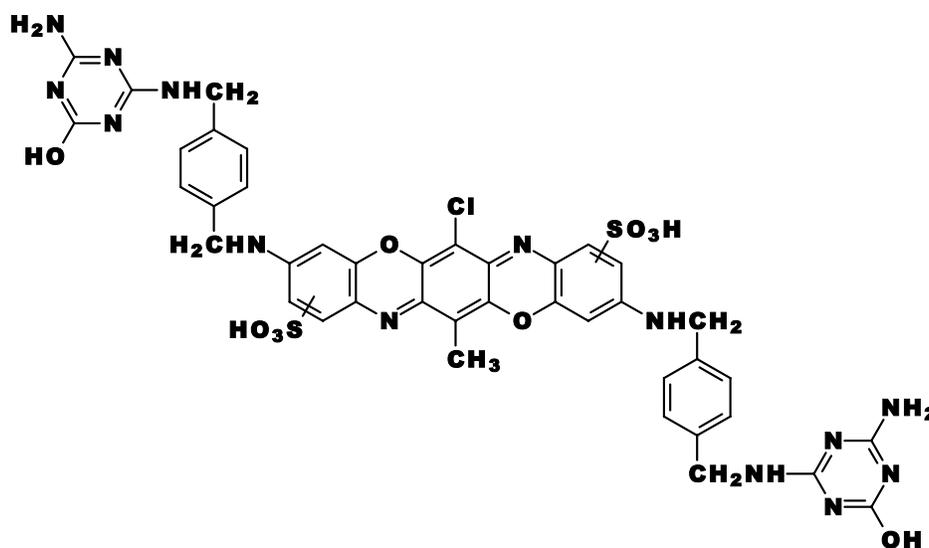
In addition to heterobifunctional types, novel homobifunctional products continue to be introduced, for example, bis-difluorochloropyrimidine dyes (30) disclosed by Bayer [103]. These dyes were claimed to efficiently bond with cellulose.



(30)

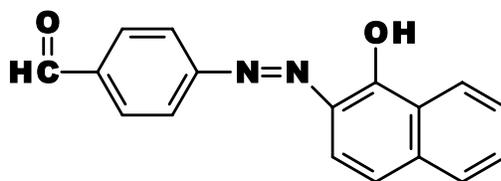
In the case of triphenodioxazine dyes, the introduction of an alkyl group in place of chlorine atoms in the 6 and 13 positions leads to a hypsochromic shift and allow in strong bright reddish-blue triphenodioxazine dyes (**31**) [104]. These modified dyes were also claimed to have less substantivity with consequential enhancements in wash off performance.

Dystar introduced aluminum phthalocyanine reactive dyes for cellulose. These were claimed to be environmental friendly, having excellent lightfastness and better strength on the fabric than analogous copper and nickel phthalocyanine dyes [35].

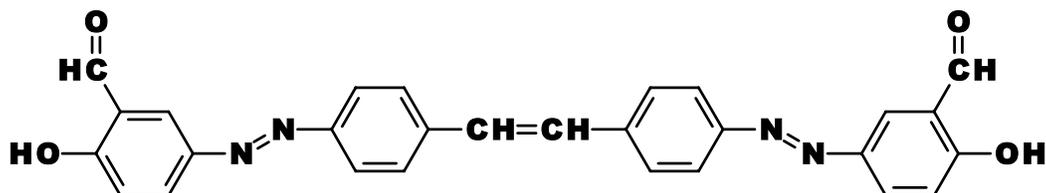


(31)

The synthesis of the azo dyes that contain an aldehyde reactive group has been described. Such dyes are capable of forming covalent bonds with wool and cellulose. It is possible to synthesize a reactive dye structure with either one (**32**) or two (**33**) aldehyde groups [65, 105].

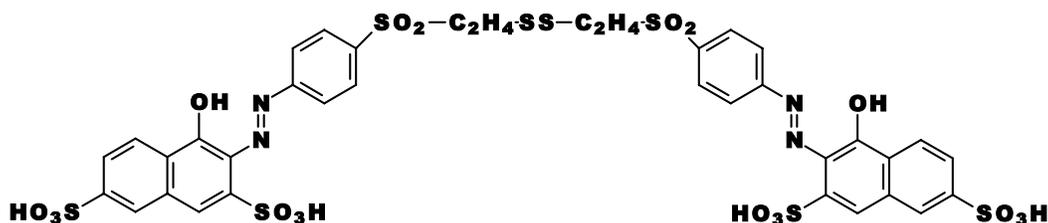


(32)



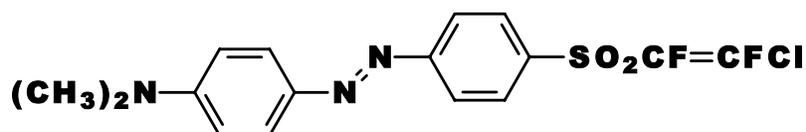
(33)

A new reactive dye containing a bis-ethylsulphone-disulfide (34) has been synthesized. This dye is able to separate into two small vinylsulfone dye molecules under alkaline conditions. When applied to cotton fabrics the bis-ethylsulphone-disulfide dye shows higher primary exhaustion than a corresponding model sulphatoethylsulphone dye and can be covalently bonded to the substrate by raising the pH to 11.5. Any hydrolysed dye produced is approximately half the size of the starting dye molecule and therefore the wash off properties are the same as the normal sulphatoethylsulphone dye [22].



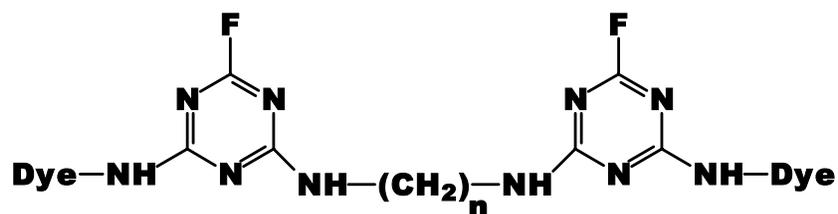
(34)

Another new reactive dye (**35**) has been developed by introducing fluorine atoms into the vinylsulphone group of conventional reactive dyes. This new reactive center for dyes which form a covalent link with the fiber is the $\text{SO}_2\text{CF}=\text{CFCl}$ group. The dyes derived using this reactive system color polyamide from an alkali dyebath with good affinity [106].

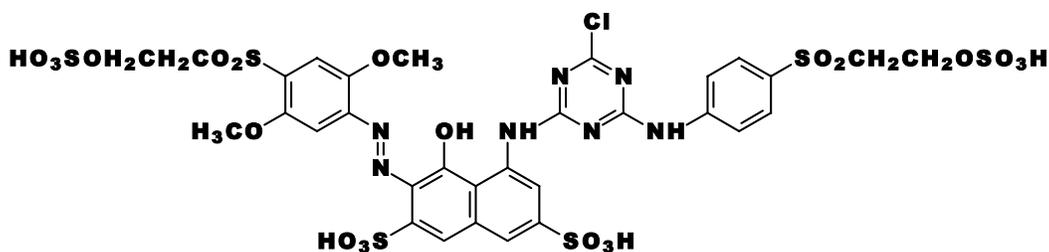


(35)

Several manufacturers have recognized the environmental and economic benefits arising from reduction in the usage of electrolytes and have introduced dyes that function efficiently in the presence of reduced amount of salt. Only a few of the many approaches have reached commercial success, for example, the Cibacron LS range (**36**). The ability of these dyes to function effectively in the presence of reduced quantities of salt reflects their high affinity for cellulose [35, 81]. Other reactive dyes with reduced salt levels have been exploited including dyes such as (**37**) those possessing two sulphatoethylsulphone groups and monochlorotriazine [107].



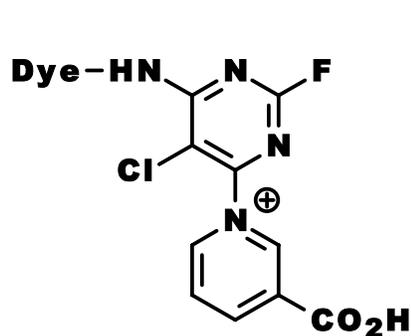
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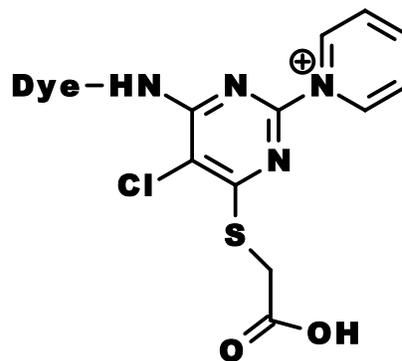
(37)

Hoechst has introduced the Remazol EF range, which includes dyes that are claimed to dye cellulose efficiently in the presence of reduced quantities of salt. The Procion XL+ ranges are also suggested to offer several environmental benefits, including high fixation efficiency, easy wash off, and reduced overall consumption of energy, electrolyte and water [51].

Procter and Gamble disclosed pyridinium salts derived from fluoropyrimidines (38) and N-(2-pyrimidinyl) pyridinium salts (39) that are claimed to display exceptionally high fixation, even up to an efficiency value of about 99% or greater [51].



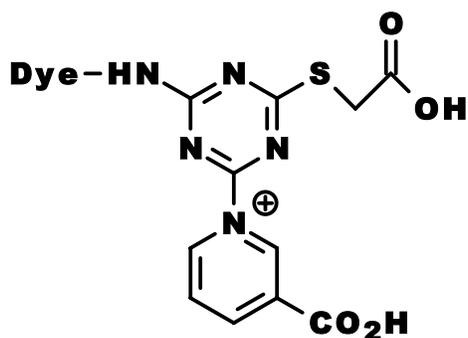
(38)



(39)

In addition to pyrimidinyl derivatives, Procter and Gamble has also disclosed the triazinyl analogs of (40) as reactive dyes for cellulose. These

materials are claimed to display fixation values of greater than 95% on cotton. Fixation at 25°C results in reduced quantities of unfixed dyes. Moreover, they provide intense dyeings with lower amounts of salt required for dyeing cotton, compared with conventional types. These dyes are suitable for dyeing other substrates, such as wool and nylon fabrics as well [51].

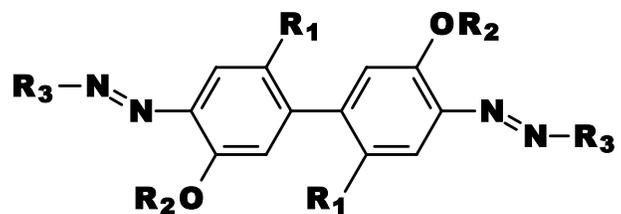


(40)

8. PROPOSED RESEARCH

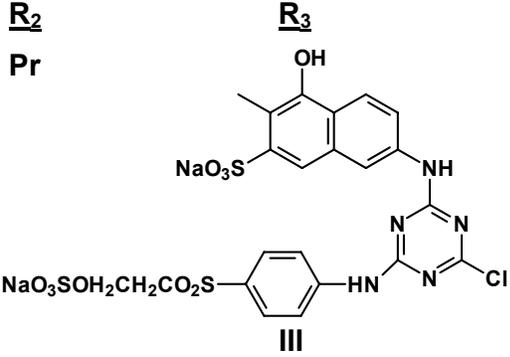
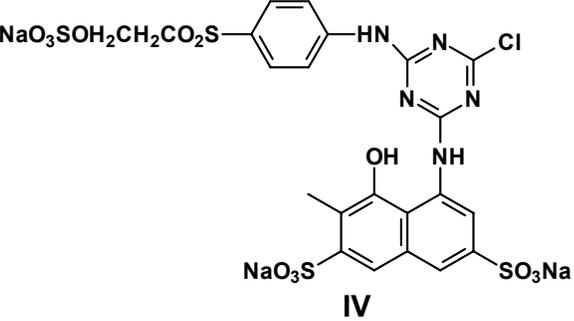
The objectives of this research are to design and synthesized reactive dyes with high fixation and easy wash off properties, and to apply these dyes to cotton fabric and determine the fastness and wash off properties of the dyed cotton.

In this study, the approach involves lowering the substantivity of the hydrolyzed dye by reducing the planarity usually required for dyes to have high substantivity on cotton. In this regard, disazo reactive dyes **1-20** derived from twisted and untwisted benzidines (i) are synthetic targets.



(i)

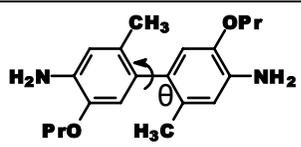
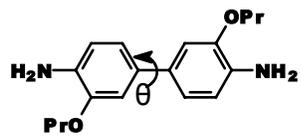
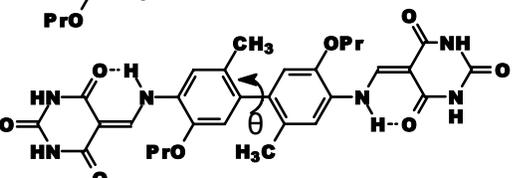
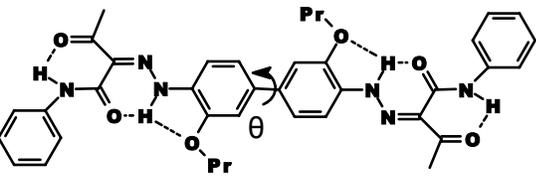
<u>Group</u>	<u>Dye</u>	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>
a	1	Me	Pr	 I
	2	H	Pr	I
	3	Me	Me	I
	4	H	Me	I
	5	Me	Et	I
b	6	Me	Pr	 II
	7	H	Pr	II
	8	Me	Me	II
	9	H	Me	II
	10	Me	Et	II

<u>Group</u>	<u>Dye</u>	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>
c	11	Me	Pr	 III
	12	H	Pr	III
	13	Me	Me	III
	14	H	Me	III
	15	Me	Et	III
<hr/>				
d	16	Me	Pr	 IV
	17	H	Pr	IV
	18	Me	Me	IV
	19	H	Me	IV
	20	Me	Et	IV

Dyes in groups **a** and **b** are bis-DCT bifunctional reactive dyes while those in groups **c** and **d** are bis-(MCT/SES) tetrafunctional reactive dyes. It is anticipated that both types will give good fixation levels and that the latter groups will also have lower sensitivity to dyeing parameters such as temperature and pH, since they contain two different reactive systems.

El-Shafei [108] reported the dihedral angles (θ) across the biphenyl linkage of benzidines and pigments from X-ray data (cf. Table 10). Methyl groups in the 2 and 2' positions of the biphenyl group cause the benzidine **21** and pigment **23** to have a twisted structure. Benzidine **22** and pigment **24** have hydrogen atoms in the 2 and 2' positions of the biphenyl group. Benzidine **22** is essentially planar while pigment **24** is slightly twisted.

Table 10. Dihedral angles of benzidines **21-22** and pigments **23-24**.

Compound	Dihedral angle (θ)
21 	68.30
22 	0.24
23 	73.66
24 	20.20

Reactive dyes which have methyl groups in the 2 and 2' positions (R_1) of the biphenyl group are anticipated to have a twisted geometry at the biphenyl linkage. These dyes should have lower substantivity to the fibers, and better wash off properties than their non-twisted counterparts.

Dyes having hydrogen atoms in the 2 and 2' positions (R_1) of the biphenyl group should be planar. The substantivity of the resultant reactive dyes should be higher than dyes having methyl groups in these positions because of their planarity. Thus, the wash off process for the hydrolyzed forms is expected to be less efficient than the twisted structures.

The effects of the alkyl group (R_2) in the 5 and 5' positions of biphenyl moiety will also be compared in the dye application process. $R_1 = \text{Me, Pr, Me}$ and Et will be employed in these positions.

The results of this study should enhance our ability to generate reactive dyes with high fixation and easy wash off properties. Such dyes would give the advantages of reduced effluent color and shorter wash off times, reducing water consumption, saving energy, and allowing a faster dye cycle.

II. EXPERIMENTAL PROCEDURES

1. GENERAL INFORMATION

All of the chemicals used as solvents and reagents in this study were obtained from Aldrich Chemical Company. In addition, compound **39** was purchased from Aldrich Chemical Company. Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was conducted using Whatman 250 μm silica gel 60A plates. The structures of dye intermediates were evaluated by $^1\text{H-NMR}$, and CI- or EI-mass spectrometry. $^1\text{H-NMR}$ spectra were recorded on Varian Mercury 300 and 400 MHz spectrometers and Varian VNMR software using $\text{d}_6\text{-CDCl}_3$ and $\text{d}_6\text{-DMSO}$. The chemical shifts were reported in ppm using tetramethylsilane (TMS) as the internal reference. Reactive dye samples were sent to Prof. Michal Holčápek, at the University of Pardubice, Czech Republic, for analysis by ESI mass spectrometry. The instrument used was an Esquire 3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany). The samples were dissolved in 50% MeCN/ H_2O (Merck, Darmstadt, Germany) and analyzed by direct infusion at the flow rate of 1 - 3 $\mu\text{L}/\text{min}$. Mass spectra were recorded in the range m/z 15 - 1000 in the negative-ion ESI mode. The ion trap analyzer was tuned to give an optimum response for m/z 400 - 600 according to the expected m/z values of doubly charged ions; i.e. the tuning parameter "target mass" was set to m/z 400 - 600. The ion source temperature was 300°C and the flow rate and the pressure of nitrogen were 4 L/min and 10 psi, respectively. Visible absorption spectra were recorded on a Varian Cary 3 UV-Visible spectrophotometer.

4-Methyl-2-nitro-n-propoxybenzene (**27**), 2-nitro-n-propoxybenzene (**28**), 2,2'-dimethyl-5,5'-di-n-propoxybenzidine (**35**) and 3,3'-di-n-propoxybenzidine (**36**) were obtained using published procedures [109].

The bleach and mercerized cotton fabric was obtained from Test Fabrics, Inc. Exhaust dyeing of cotton fabric was conducted using a Gibbs machine. A standard lab padder was used for pad-batch and pad-dry-cure experiments. Washfastness, lightfastness and crockfastness were performed by using an Atlas Launder-ometer, an Atlas 3SUN Hi 35 high irradiance Xenon Weather-ometer and an Atlas crockmeter, respectively. In these cases, AATCC test methods 61, 16E and 8 were used, respectively. Colorimetric data were measured using a Datadolor International Spectroflash SFX and SLI-form N/G software (GretagMacbeth, Greensboro, USA). The spectrophotometer setup was as follows: specular included, illuminant D65, 10° standard observer. Measurements were made on 4-ply fabric and each sample was measured twice and the data averaged.

2. SYNTHESIS OF DYES AND DYE INTERMEDIATES

2.1 Synthesis of 4-methyl-2-nitro-n-propoxybenzene (27)

4-Methyl-2-nitrophenol (15.3 g, 0.10 mol) and 2-methoxyethanol (50 ml) were stirred at 25°C in a 250 ml 3-necked round bottom flask equipped with a reflux condenser and thermometer. 1-Bromopropane (18.5 g, 0.15 mol) and finely ground anhydrous K₂CO₃ (13.8 g, 0.1 mol) were added to the stirred solution to give a deep red mixture. The mixture was stirred under reflux at 105-110°C for 6 h. The resultant pale yellow mixture was allowed to

cool and was filtered. The collected solid was washed with EtOAc. The combined filtrate and washings were concentrated using a rotary evaporator. The dark brown crude liquid from evaporation was dissolved in EtOAc (100 ml) and then the solution was washed twice with 5% (w/w) NaOH (25 ml) and twice with water (25 ml). The solvent was concentrated and the dark brown liquid was purified by vacuum distillation. The clear yellow liquid product (16 g, 82%) had bp 120°C (30 in Hg) (lit. [109], 104°C (3 mm Hg)), $R_f = 0.52$ (PhMe:hexane/4:1). $^1\text{H-NMR}$ (CDCl_3): δ 1.05 (3H, t, $J=7.5$), δ 1.80-1.95 (2H, m), δ 2.32 (3H, s), δ 4.02 (2H, t, $J=6.9$), δ 6.94 (1H, d, $J=8.4$), δ 7.28 (1H, dd, $J=2.1, 8.7$), δ 7.58 (1H, d, $J=2.1$).

2.2 Synthesis of 2-nitro-n-propoxybenzene (28)

The synthesis of 2-nitro-n-propoxybenzene was carried out using 2-nitrophenol (13.9 g, 0.10 mol) and the procedure described above for 4-methyl-2-nitro-n-propoxybenzene was employed. The product was obtained as a clear yellow liquid (15.7 g, 87%) bp 115°C (30 In Hg) (lit. [109], 112°C (3 mm Hg)), $R_f = 0.55$ (PhMe:hexane/4:1). $^1\text{H-NMR}$ (CDCl_3): δ 1.07 (3H, t, $J=7.5$), δ 1.80-1.91 (2H, m), δ 4.05 (2H, t, $J=6.6$), δ 6.95-7.06 (2H, m), δ 7.45-7.51 (1H, m), δ 7.78 (1H, dd, $J=1.8, 8.1$).

2.3 Synthesis of 4-methyl-2-nitroethoxybenzene (29)

The solution of 4-methyl-2-nitrophenol (23 g, 0.15 mol) in MeOH (70 ml) was stirred at room temperature as 20% NaOH (30 ml, 0.15 mol) was

added. After stirring for 20 min, the solvent was removed to give a deep orange solid (18.8 g). A solution of the phenolate salt in DMSO (180 ml) was stirred in a 500 ml 3-necked round bottom flask equipped with a reflux condenser and a thermometer as EtBr (27.3 g, 0.25 mol) and finely ground anhydrous K_2CO_3 (15.2 g, 0.11 mol) were added under reflux. The reaction was carried out for 6 h to give a pale orange mixture. The resultant mixture was poured into water (200 ml) and extracted with EtOAc (200 ml). The EtOAc solution was concentrated, and the resultant dark brown solution was purified by vacuum distillation to give a clear yellow liquid (18.6 g, 96%) bp 110°C (30 In Hg), $R_f = 0.46$ (PhMe:hexane/4:1). 1H -NMR ($CDCl_3$): δ 1.45 (3H, t, $J=6.9$), δ 2.33 (3H, s), δ 2.32 (3H, s), δ 4.14 (2H, q, $J=6.9$), δ 6.94 (1H, d, $J=8.4$), δ 7.28 (1H, dd, $J=2.1, 9$), δ 7.60 (1H, d, $J=2.1$).

2.4 Synthesis of 2,2'-dimethyl-5,5'-di-n-propoxybenzidine (35)

4-Methyl-2-nitro-n-propoxybenzene (13.7 g, 70 mmol) and ligroin (25 ml) were placed in a 250 ml 3-necked round bottom flask and stirred at room temperature. Zinc dust (13.7 g, 0.21 mol) was added to this stirred yellow solution and the mixture was heated to reflux (80-85°C) with vigorous stirring. NaOH (50% (w/w), 1 g, 1.3 mmol) was slowly added dropwise, followed by the slow dropwise addition of water (0.9 g, 49 mmol) at the same temperature range. The mixture gradually turned from yellow to orange and finally to red. After about 15 h, zinc (2.7 g) was added and the mixture was allowed to stir until the organic layer turned colorless. TLC (PhMe:hexane/4:1) was used to follow the disappearance of starting material. The reaction mixture was

diluted by the addition of ligroin (100 ml, bp 90-110°C), filtered and the filtrate was allowed to cool. The organic layer was washed twice with 1% (w/w) HCl (30 ml) and twice with distilled water (30 ml).

The organic layer was collected and the benzidine rearrangement was effected by the dropwise addition of 15% (w/w) HCl (34.1 g, 0.14 mol) to the vigorously stirred organic layer at room temperature. After stirring for 2 h, the gray solid was collected and washed repeatedly with acetone. The white product was dried and recrystallized from MeOH/EtOAc to provide 2,2'-dimethyl-5,5'-di-n-propoxybenzidine dihydrochloride (8.4 g, 60%).

The dihydrochloride salt (8.4 g, 20 mmol) was slurred with water (80 ml), and stirred as 5% NaOH (32 g, 40 mmol) added dropwise to give the free base. After stirring a further 30 min, the precipitate was extracted into EtOAc (100 ml), and the organic layer was collected, washed with distilled water (100 ml) and dried over MgSO₄. The solvent was removed by rotary evaporation to give a tan colored solid (5.7 g, 50%), mp 126-127°C. TLC: R_f = 0.70 (PhMe: EtOAc/3:1). ¹H-NMR (DMSO): δ 0.97 (6H, t, J=7.6), δ 1.66-1.75 (4H, m), δ 1.84 (6H, s), δ 3.82 (4H, t, J=6.8), δ 4.52 (4H, s), δ 6.41 (4H, s), δ 6.50 (4H, s). CI mass spectrum: m/z (relative intensity) 329 ([M+H]⁺, 100%).

2.5 Synthesis of 3,3'-di-n-propoxybenzidine (36)

The synthesis was carried out using 2-nitro-n-propoxybenzene (14.4 g, 80 mmol) and the procedure described above for 2,2'-dimethyl-5,5'-di-n-propoxybenzidine. This gave an off-white solid (10.7 g, 70%) that was converted to the free base of 3,3'-di-n-propoxybenzidine, a tan colored solid

was obtained (7.9 g, 66%), mp 140°C. TLC: $R_f = 0.62$ (PhMe:EtOAc/3:1). $^1\text{H-NMR}$ (DMSO): δ 1.02 (6H, t, $J=7.6$), δ 1.72-1.81 (4H, m), δ 3.97 (4H, t, $J=6.4$), δ 4.62 (4H, s), δ 6.40 (2H, d, $J=2.0$), δ 6.88 (2H, dd, $J=2.0, 8.0$), δ 6.94 (2H, d, $J=2.0$). CI mass spectrum: m/z (relative intensity) 301 ($[\text{M}+\text{H}]^+$, 100%).

2.6 Synthesis of 2,2'-dimethyl-5,5'-diethoxybenzidine (37)

The procedure described above for 2,2'-dimethyl-5,5'-di-n-propoxy benzidine was employed, with 4-methyl-2-nitroethoxybenzene (27.2 g, 0.15 mol) used as the starting compound. The white solid obtained (13.1 g, 47%) afforded the free base a brown solid (8.1 g, 36%), mp 172 °C. TLC: $R_f = 0.67$ (PhMe:EtOAc/3:1). $^1\text{H-NMR}$ (DMSO): δ 1.30 (6H, t, $J=6.8$), δ 1.84 (6H, s), δ 3.11 (4H, q, $J=6.8$), δ 4.52 (4H, s), δ 6.41 (2H, s), δ 6.50 (2H, s). EI mass spectrum: m/z (relative intensity) 300 ($[\text{M}]^+$, 100%).

2.7 Synthesis of 2,2'-dimethyl-5,5'-dimethoxybenzidine (38)

The procedure described above for 2,2'-dimethyl-5,5'-di-n-propoxy benzidine was employed using 4-methoxy-3-nitro-toluene (30 g, 0.18 mol) as the starting material. The white solid obtained (12.4 g, 40%) was converted to the free base form to give a tan colored solid (7.3 g, 30%), mp 154°C. TLC: $R_f = 0.52$ (PhMe:EtOAc/3:1). $^1\text{H-NMR}$ (DMSO): δ 1.85 (6H, s), δ 3.69 (6H, s), δ 4.55 (4H, s), δ 6.43 (2H, s), δ 6.50 (2H, s). CI mass spectrum: m/z (relative intensity) 273 ($[\text{M}+\text{H}]^+$, 100%).

2.8 Synthesis of reactive dyes

2.8.1 Preparation of tetrazonium salt solution

2,2'-Dimethyl-5,5'-di-n-propoxybenzidine (0.66 g, 2 mmol) was stirred in a mixture of water (10 ml), conc. HCl (3 ml) and ice (5 g). The reaction mixture was cooled to 0-5°C using an ice bath and then NaNO₂ (0.28 g, 4 mmol) dissolved in water (3 ml) was added dropwise. The solution was stirred for 30 min, and excess HNO₂ was decomposed by adding sulfamic acid. Activated carbon was added with stirring, and the mixture was filtered at 0-5°C to give the clear yellow solution.

Similarly, 3,3'-di-n-propoxybenzidine (0.60 g, 2 mmol), 2,2'-dimethyl-5,5'-dimethoxybenzidine (0.54 g, 2 mmol), 2,2'-dimethyl-5,5'-diethoxybenzidine (0.60 g, 2 mmol) and a commercial sample of 3,3'-dimethoxybenzidine (0.49 g, 2 mmol) were used to prepare the corresponding tetrazonium salt solutions.

2.8.2 Coupling components

2.8.2.1 Synthesis of compound 40

J-acid (1.3 g, 5 mmol) in water (15 ml) was adjusted to pH 7.5 using 20% (w/v) Na₂CO₃ to give a clear brown solution. A solution of cyanuric chloride (0.97 g, 5.25 mmol) in acetone (5 ml) was cooled to 0-5°C, and added dropwise to the stirred J-acid solution at 0-5°C. After 10 min, the solution was adjusted to pH 4 by adding 20% (w/v) Na₂CO₃, and the reaction was continued for 0.5 h at 0-5°C. The progress of the reaction was followed

by TLC using n-PrOH:n-BuOH:EtOAc:H₂O/2:4:1:3 where the product had R_f = 0.72.

2.8.2.2 Synthesis of compound 41

H-acid (1.7 g, 5 mmol) in water (20 ml) was adjusted to pH 7.5 using 20% (w/v) Na₂CO₃ to give a clear brown solution. A solution of cyanuric chloride (0.97 g, 5.25 mmol) in acetone (5 ml) was cooled to 0-5°C, and added dropwise to the stirred J-acid solution at 0-5°C. After 10 min, the solution was adjusted to pH 4 by adding 20% (w/v) Na₂CO₃, and the reaction was continued for 0.5 h at 0-5°C. Activated carbon was added and the mixture was filtered to give a clear solution of **41**. The progress of the reaction was followed by TLC using n-PrOH:n-BuOH:EtOAc:H₂O/2:4:1:3 where the product had R_f = 0.75.

2.8.2.3 Synthesis of compound 42

To a well stirred solution of **40** (5 mmol), 4-β-sulphatoethylsulphonyl aniline (1.5 g, 5.5 mmol) was added. The solution was stirred for 1 h at 40°C, after adjusting to pH 6.5 using 20% (w/v) Na₂CO₃. The progress of the reaction was followed by TLC (n-PrOH:n-BuOH:EtOAc:H₂O/2:4:1:3), where the product had R_f = 0.35.

2.8.2.4 Synthesis of compound 43

To a well stirred solution of **41** (5 mmol), 4-β-sulphatoethylsulphonyl aniline (1.5 g, 5.5 mmol) was added. The solution was stirred for 1 h at 40°C,

after adjusting to pH 6.5 using 20% (w/v) Na₂CO₃. The progress of the reaction was followed by TLC (n-PrOH:n-BuOH:EtOAc:H₂O/2:4:1:3), where the product had R_f = 0.39.

2.8.3 Synthesis of dyes 1-5

To well stirred solutions of **40** (5 mmol), freshly prepared tetrazonium salt solutions (2 mmol) of **35-39** were added dropwise. The pH was maintained at 9 by using 20% (w/v) Na₂CO₃ and the couplings were continued for 4 h at 0-5°C. Then, 10% (w/v) urea was added, to help stabilize the dyes [110]. The dyes were isolated by salting out of solution with KCl (3 g). The pH was adjusted to 7 using 6% (w/v) HCl and stirring was continued for 2 h. The dyes were collected by filtration and washed with 5% (w/v) KCl. Salt was removed by stirring the crude dyes with DMF, followed by precipitation by adding EtOAc. The dyes were collected, washed with EtOAc and air-dried. This gave dyes **1** (2.3 g, 97%), **2** (1.2 g, 53%), **3** (2.2 g, 98%), **4** (1.4 g, 64%) and **5** (2.2 g, 97%). The eluent system for TLC was 2-BuOH:EtOH:NH₄OH:pyridine/4:1:3:2. Dyes **1-4** had R_f = 0.54, with impurities at R_f = 0.38, 0.40, 0.43 and 0.40, respectively. Dye **5** had R_f = 0.51, with an impurity at R_f = 0.38.

2.8.4 Synthesis of dyes 6-10

To well stirred solutions of **41** (5 mmol), freshly prepared tetrazonium salt solutions (2 mmol) of **35-39** were added dropwise. The pH was maintained at 9 by using 20% (w/v) Na₂CO₃ and the couplings were continued

for 4 h at 0-5°C. Then, 10% (w/v) urea was added to the reaction. The dyes were isolated by salting out of solution with KCl (12 g). The pH was adjusted to 7 using 6% (w/v) HCl and stirring was continued for 2 h. The dyes were collected by filtration and washed with 20% (w/v) KCl. Salt was removed by stirring the crude dyes with DMF, followed by precipitation by adding EtOAc. The dyes were collected, washed with EtOAc and air-dried. This gave dyes **6** (2.7 g, 98%), **7** (1.8 g, 67%), **8** (2.1 g, 80%), **9** (2.4 g, 95%) and **10** (1.6 g, 60%). The eluent system for TLC was the same as for dyes **1-5**. Dyes **6-10** had $R_f = 0.56$. Dyes **7**, **8** and **10** had impurities at $R_f = 0.47$, 0.50 and 0.47, respectively.

2.8.5 Synthesis of dyes 11-15

To well stirred solutions of **42** (5 mmol), freshly prepared tetrazonium salt solutions (2 mmol) of **35-39** were added dropwise. The coupling procedure and conditions described for preparing dye **1** were employed, giving dyes **11** (3.3 g, 97%), **12** (1.4 g, 43%), **13** (2.7 g, 82%), **14** (2.3 g, 71%) and **15** (3.3 g, 98%). The eluent system for TLC was the same as for dyes **1-5**. Dyes **11-15** had $R_f = 0.56$, with impurities at $R_f = 0.39$, 0.42, 0.42, 0.42 and 0.44, respectively.

2.8.6 Synthesis of dyes 16-20

To well stirred solutions of **43** (5 mmol), freshly prepared tetrazonium salt solutions (2 mmol) of **35-39** were added dropwise. The coupling procedure and conditions described for preparing dye **2** were employed,

giving dyes **16** (1.8 g, 47%), **17** (2.5 g, 67%), **18** (1.0 g, 27%), **19** (1.2 g, 33%) and **20** (2.0 g, 53%). The eluent system for TLC was the same as for dyes **1-5**. Dyes **16**, **18**, **19** and **20** had $R_f = 0.48$, while dye **17** had $R_f = 0.51$. Dyes **17-19** also had impurity at $R_f = 0.37$.

3. VISIBLE ABSORPTION DATA

Dye solutions (5×10^{-5} mmol) were prepared by dissolving the reactive dyes in DMF (50 ml) and diluting 1 ml with DMF (24 ml) to give a final concentration 4×10^{-5} mol/l. From the resultant absorption spectra λ_{\max} and E_{\max} values were recorded. Two commercial reactive dyes, Procion Red MX-8B and C.I. Reactive Red 198 (Figure 11), were used for comparisons in this study.

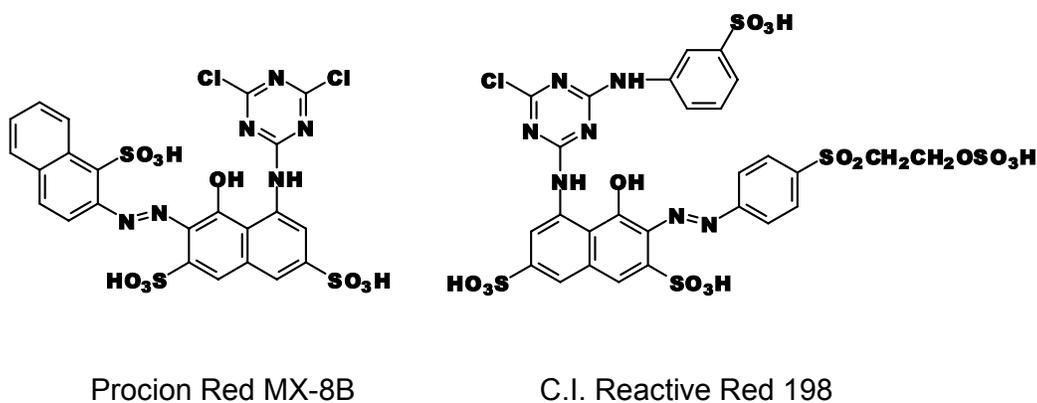


Figure 11. Structures of commercial reactive dyes used in this study.

4. DYEING PROCEDURES

4.1 Exhaust dyeing

Cotton fabric samples (5 g) were dyed in a Gibbs machine, using 2% (owf) dye, and a dye liquor to fabric ratio of 80:1. Dye solutions were

prepared by grinding each dye and urea together before adding warm water (20 ml) and stirring the solutions while they sat in an ultrasonic machine. The fabrics were wet out in water at 80°F for 5 min. Then, dye solutions and NaCl (30 g, granular) were added and the temperature was held at 80°F for 10 min. Na₂CO₃ (0.5 g, powder) and 50% NaOH (0.2 g) were added to the dyebath and the temperature was raised to 140°F and held for 30 min. The same amounts of alkali were added just prior to increasing the temperature to 165° and to 180°F. The dyebaths were held at each temperature for 30 min. The dyed fabrics were rinsed in warm water and scoured with 2 g/l AATCC detergent at 160°F for 5 min, then rinsed again in warm water and dried.

4.2 Pad-Batch

This dyeing procedure was used for reactive dyes based on couplers **40** and **41**. A stock solution of urea (100 g), Na₂CO₃ (10 g) and Ludigol (5 g) was prepared in warm water (385 ml) and cooled. Superclear[®] 80 (0.5 g) was added with stirring. Reactive dye (0.3 g) was dissolved in 15 ml of this solution. Bleach-mercerized cotton fabric samples (2 g) were padded with these 2% dye solutions. The padded fabrics were placed in separate plastic bags and batched at 160°F for 24 h. The fabrics were rinsed in warm water and scoured with 2 g/l AATCC detergent at 160°F for 5 min. After that, the fabrics were rinsed again in warm water and dried.

4.3 Pad-Dry-Cure

This procedure was used for reactive dyes derived from couplers **42** or **43**. Using the same dye solutions prepared in section 4.2, bleach-mercerized cotton fabrics (2 g) were padded. The dyed fabrics were dried at 212°F for 5 min, and then cured at 390°F for 2 min. The fabrics were rinsed in warm water and scoured with 2 g/l AATCC detergent at 160°F for 5 min, then rinsed again in warm water and dried.

5. FASTNESS TEST

5.1 Washfastness Test

The washfastness of dyed fabrics was evaluated using AATCC test method 61-2001, test No. 2A [111] using the conditions shown below.

Temperature:	49°C
Bath volume:	150 ml
% Detergent of total volume:	0.15%
No. of steel balls:	50
Time:	45 min

The dyed fabrics employed were 2.0x6.0 in cotton samples and multifiber test fabrics from Test Fabrics, Inc., were attached to each fabric sample to assess staining. The resultant fabrics were evaluated spectrophotometrically for color change and staining of attached multifiber fabrics using AATCC Evaluation Procedure 7 [112]. The rating system used was 1 (poor) to 5 (excellent).

5.2 Lightfastness Test

The lightfastness of the dyed fabrics were evaluated according to the conditions of AATCC test method 16-1998 option E [113] using the conditions shown below.

Light source:	Xenon
Lamp cooling:	Water
Black panel temperature:	$63 \pm 1^{\circ}\text{C}$
Dry bulb temperature:	$43 \pm 2^{\circ}\text{C}$
% Relative humidity:	$30 \pm 5\%$
Duration of test:	20 h

The fabrics employed were 7.0x12.0 cm samples, and were exposed for 20 h. The resultant fabrics were evaluated for color change using the Data Color spectrophotometer and the rating system used was 1 (poor) to 5 (excellent).

5.3 Crockfastness Test

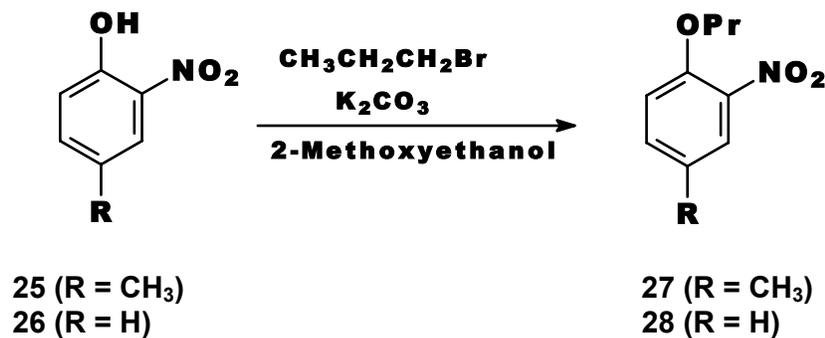
Crockfastness assessment was carried out in accordance with AATCC test method 8-2001 [114]. The fabric samples were evaluated in dry and wet tests. Color transferred to the white test square was measured using a spectrophotometer and the rating system used was 1 (poor) to 5 (excellent).

III. RESULTS AND DISCUSSION

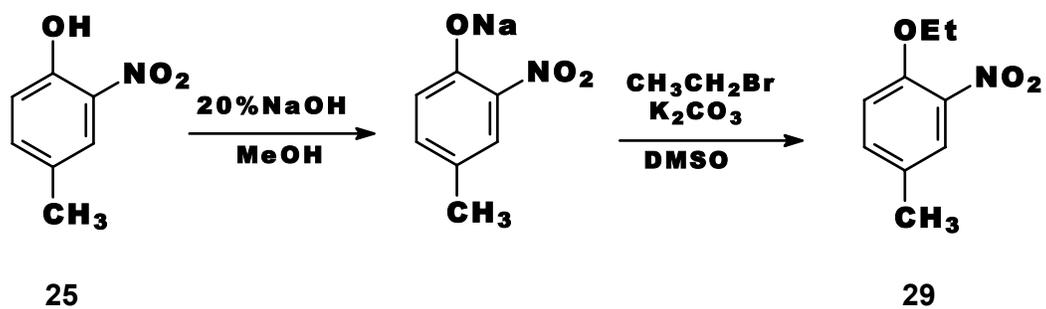
This section provides results pertaining to the synthesis and evaluation of the target reactive dyes. In this regard, visible absorption, mass spectral, ¹H-NMR and fastness data are presented.

1. SYNTHESIS OF DYES AND DYE INTERMEDIATES

Nitropropoxybenzenes **27** and **28** were obtained from nitrophenols **25** and **26**, by alkylation with 1-bromopropane (Scheme 1). 4-Methyl-2-nitrophenol (**25**) was also used as the starting compound to prepare compound **29**. In the latter case, compound **25** was converted to the phenolate sodium salt and then alkylated with bromoethane as shown in Scheme 2. The ¹H-NMR spectra shown in Figure 11-13 were consistent with the structures of **27-29**.



Scheme 1. Alkylation reaction used to prepare compounds **27** and **28**.



Scheme 2. Reaction sequence used to prepare compound 29.

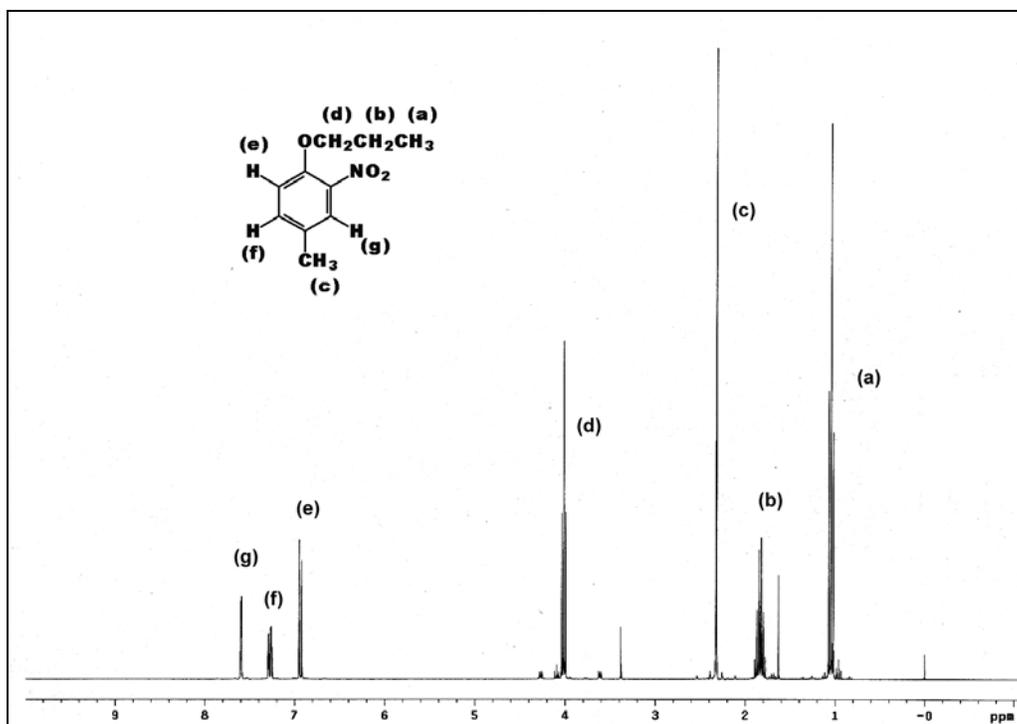


Figure 12. ¹H-NMR spectrum of compound 27.

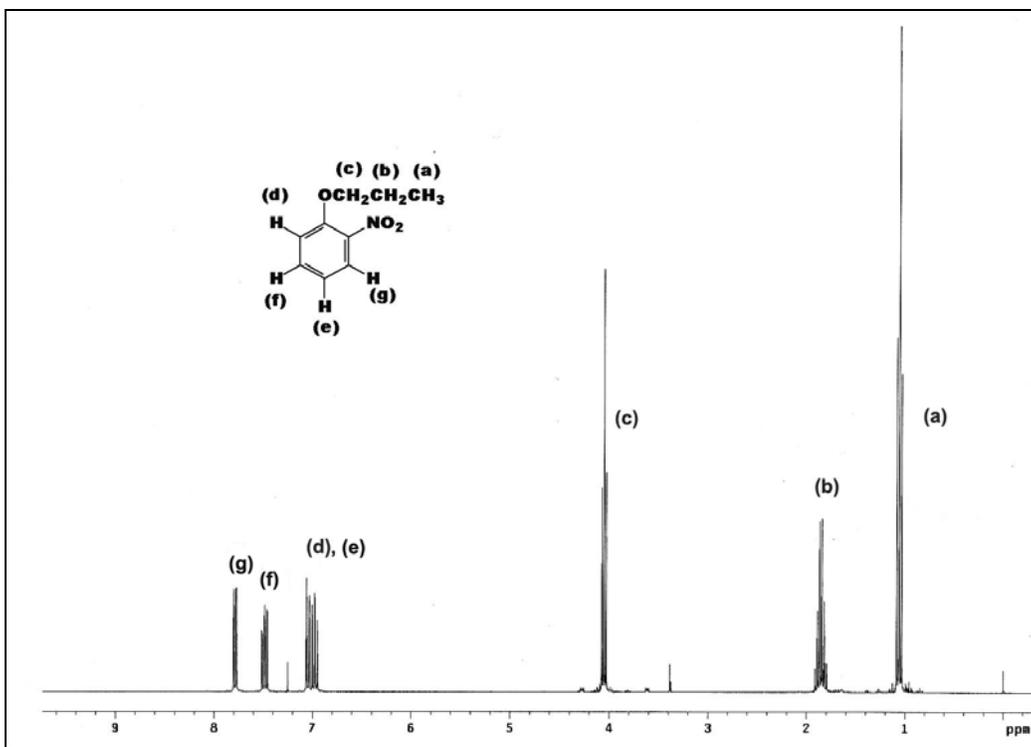


Figure 13. ¹H-NMR spectrum of compound 28.

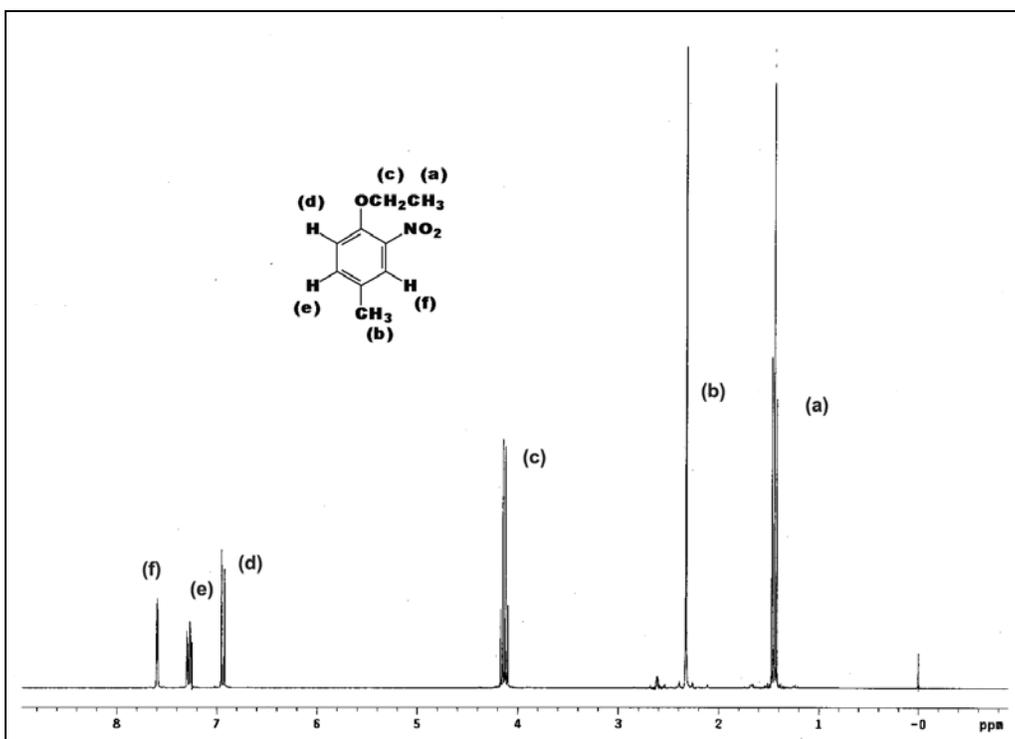
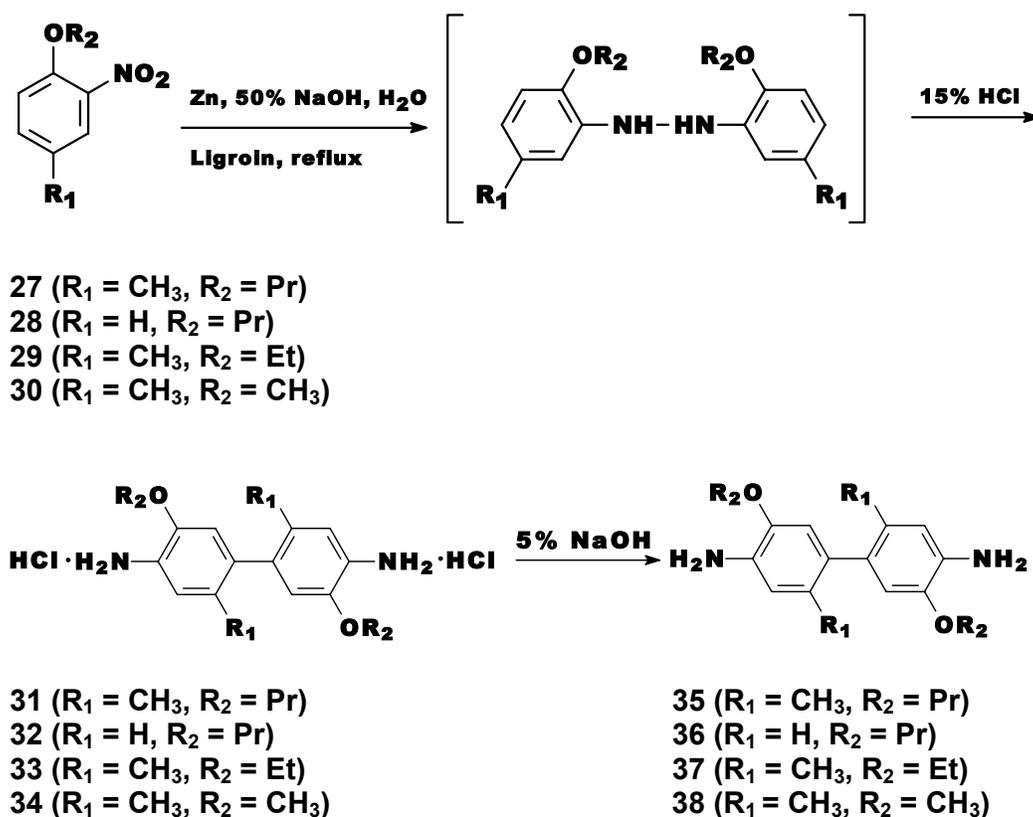


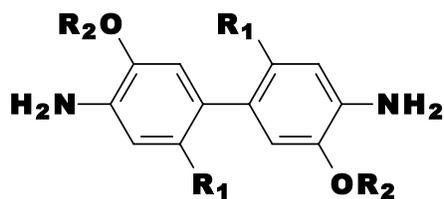
Figure 14. ¹H-NMR spectrum of compound 29.

Benzidine dihydrochlorides **31-34** were obtained in two steps from compounds **27-30** as shown in Scheme 3. In the first step, compounds **27-30** were used in an alkaline reduction reaction to give the corresponding hydrazo compounds. The second step was the benzidine rearrangement which was achieved by the addition of 15% HCl to the hydrazo compounds to give benzidine dihydrochlorides **31-34**. The free amines (**35-38**) were prepared by treatment of **31-34** with 5% NaOH solution. A summary of data pertaining to benzidines **35-38** is shown in Table 11, where the reaction yields corresponding to the overall yields for the conversion of compounds **27-30** to diamines **35-38** and are the yields for purified products.



Scheme 3. Reaction sequence used to prepare benzidine analogs **35-38**.

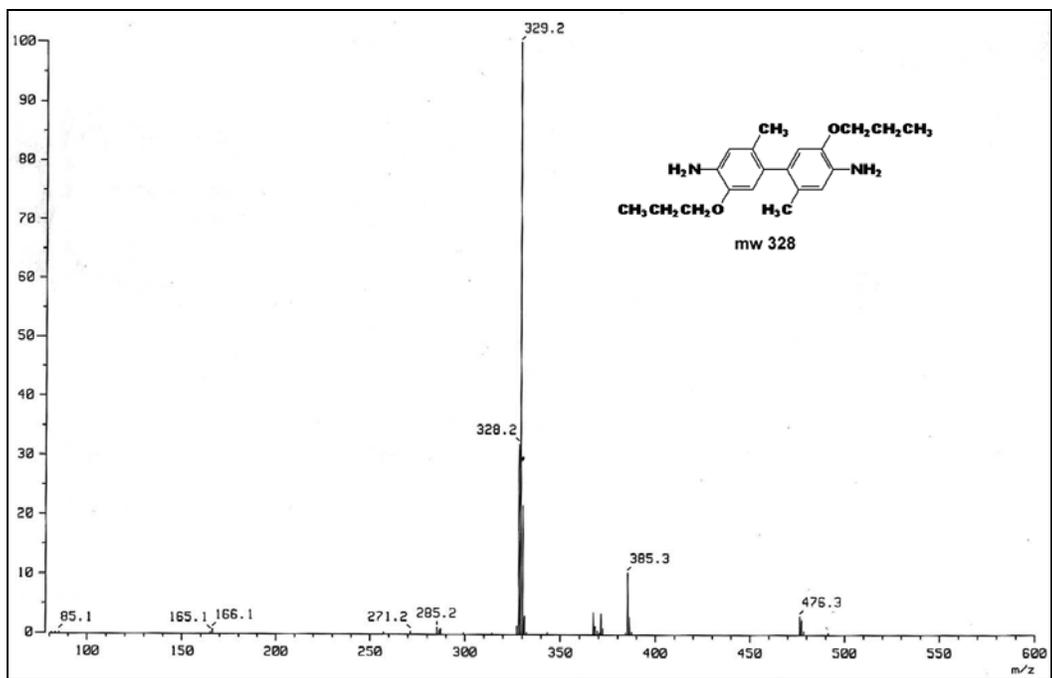
Table 11. Summary of data pertaining to benzidines **35-39**.



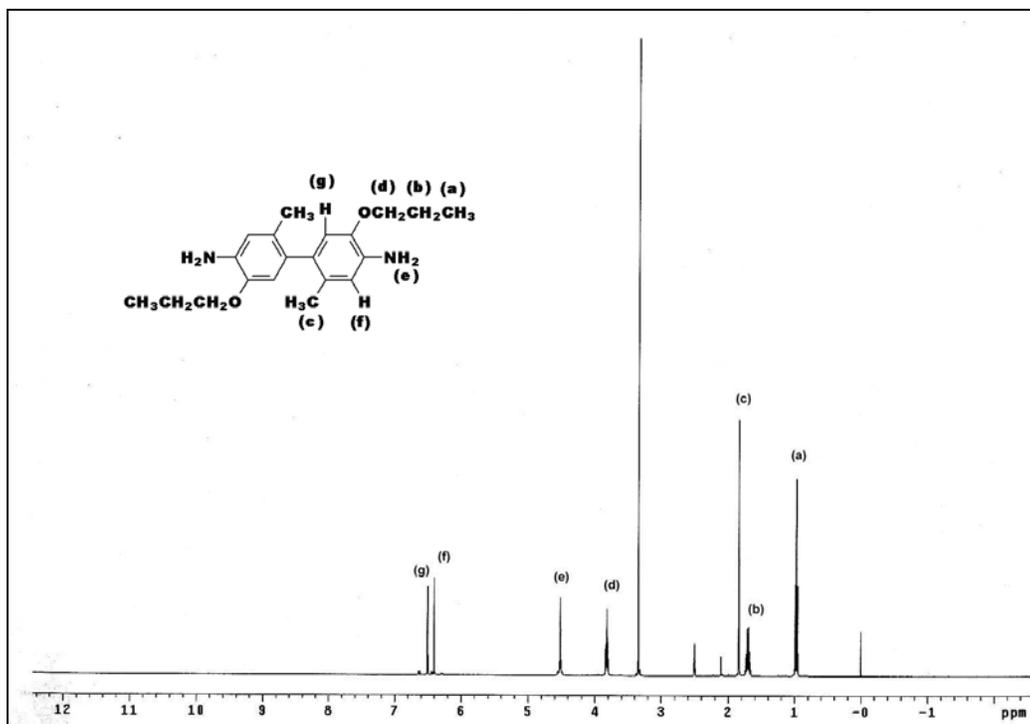
Compound	R ₁	R ₂	Yield (%)	m.p. (°C)
35	CH ₃	Pr	50	126-127
36	H	Pr	66	140
37	CH ₃	Et	36	172
38	CH ₃	CH ₃	30	154
39	H	CH ₃	- ^a	137-138

^a Purchased from Aldrich

The yields for benzidines **35** and **36** obtained from the syntheses in this study were comparable to those reported previously [109]. In that case, compounds **35** and **36** were obtained in 63% and 51%, respectively. The structures of **35-38** were confirmed by ¹H-NMR and mass spectrometry (cf. Figures 15-18). ¹H-NMR spectra were recorded using d₆-DMSO, and the peak at δ 3.3 was due to a small amount of water in the solvent.

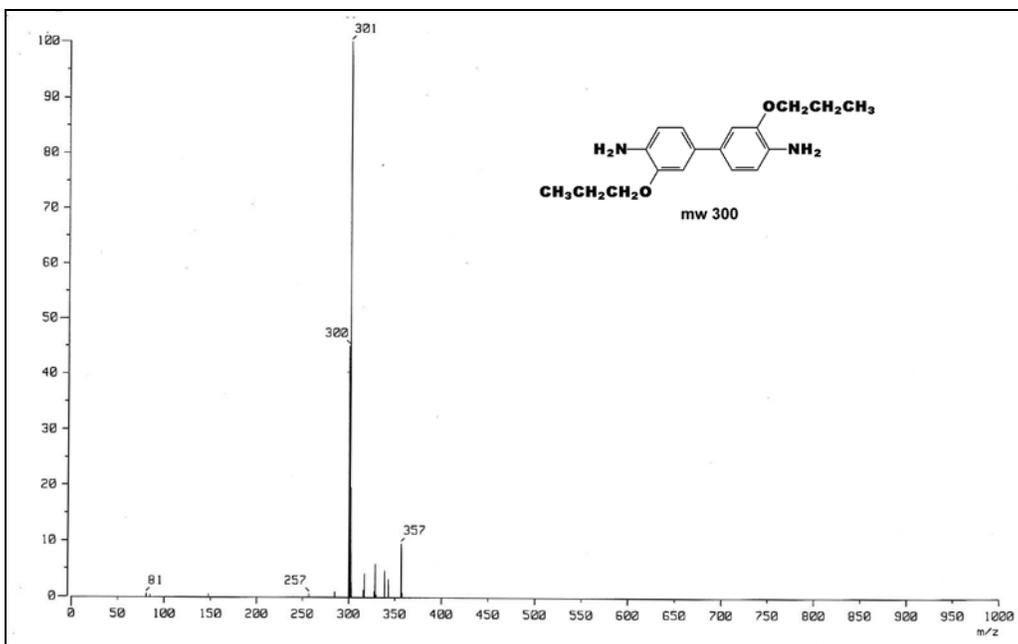


(a)

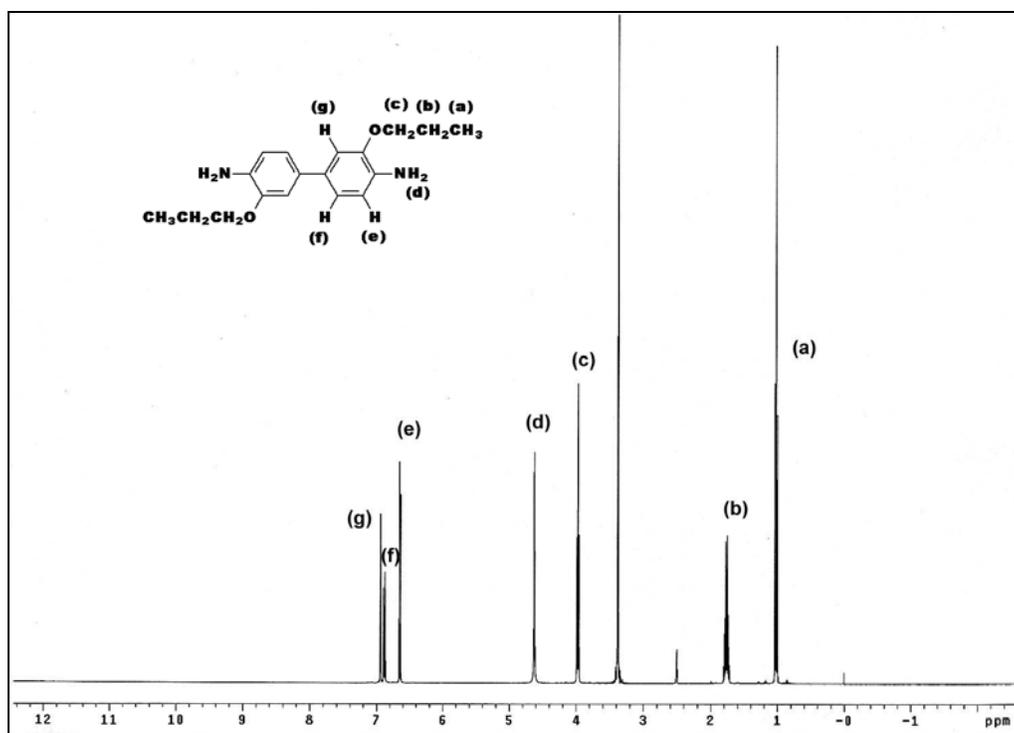


(b)

Figure 15. Cl mass spectrum (a) and $^1\text{H-NMR}$ spectrum (b) of compound 35.

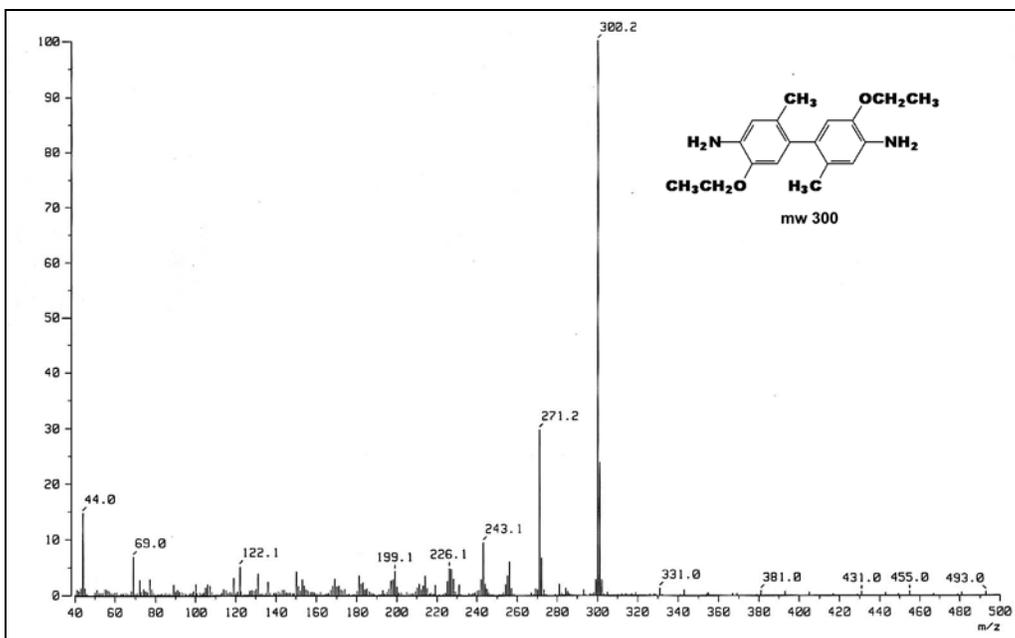


(a)

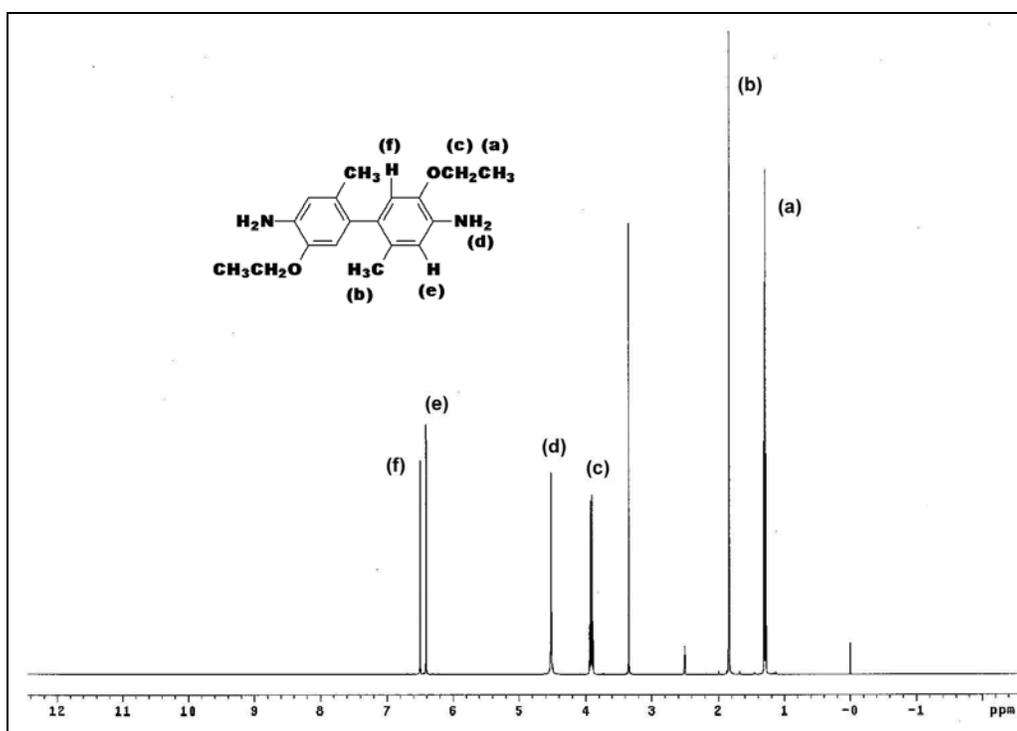


(b)

Figure 16. CI mass spectrum (a) and $^1\text{H-NMR}$ spectrum (b) of compound 36.

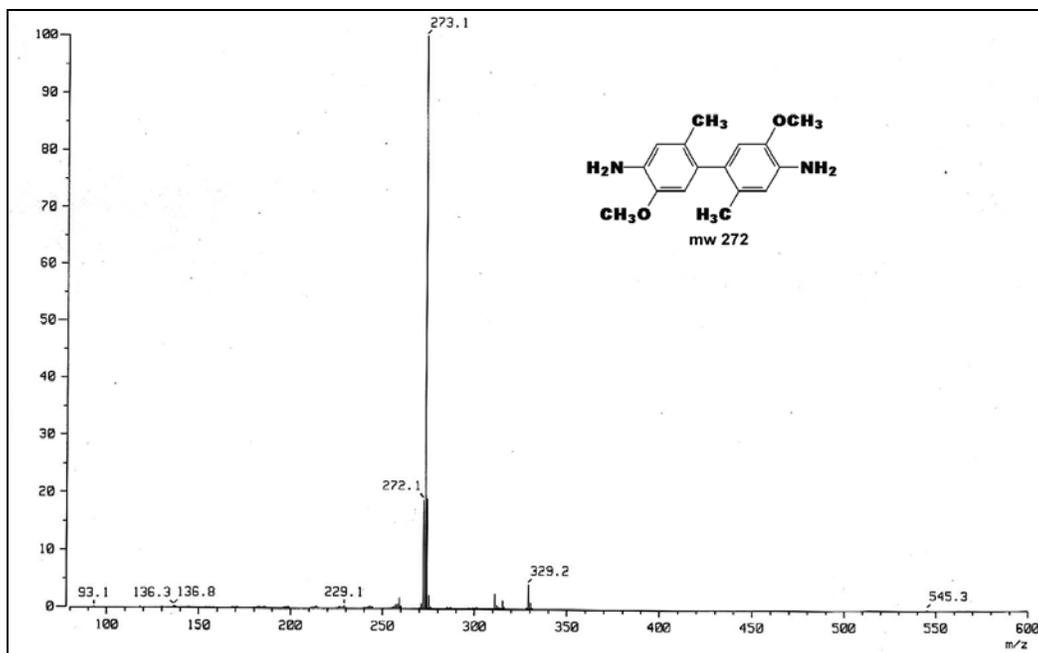


(a)

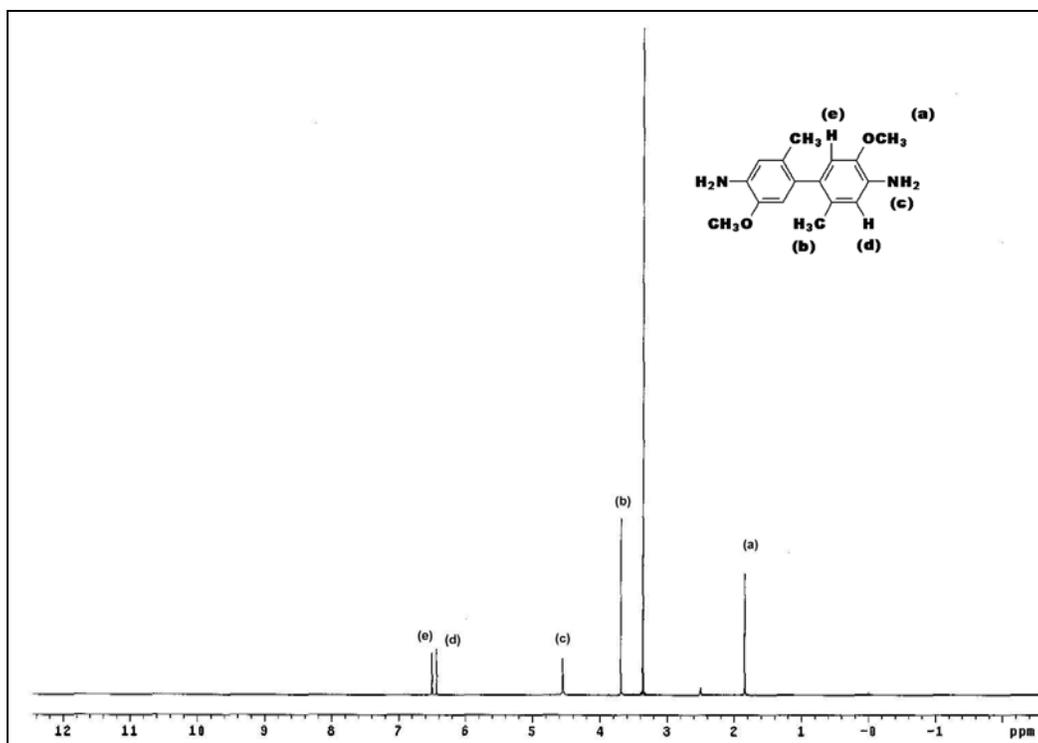


(b)

Figure 17. EI mass spectrum (a) and $^1\text{H-NMR}$ spectrum (b) of compound 37.



(a)

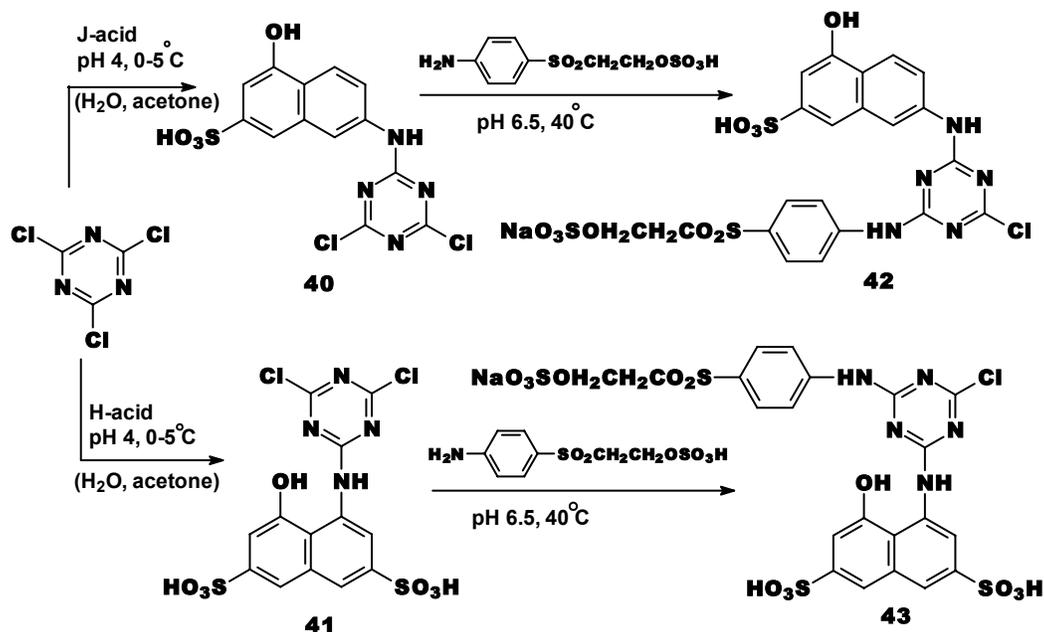


(b)

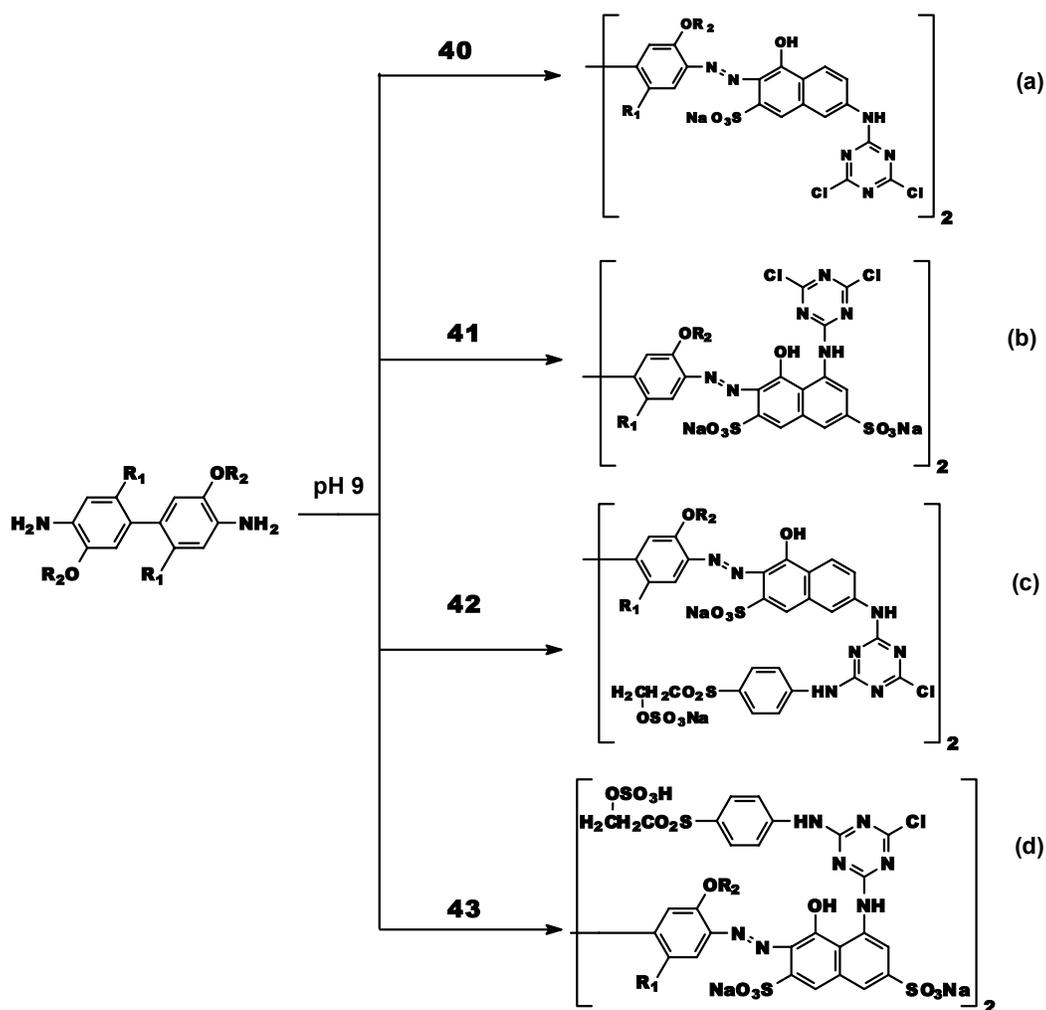
Figure 18. Cl mass spectrum (a) and ¹H-NMR spectrum (b) of compound 38.

Dye synthesis began with the preparation of couplers **40-43**, according to the steps outlined in Scheme 4. Couplers **40** and **41** were synthesized from the reaction of cyanuric chloride with J-acid and H-acid, respectively, at pH 4. Then, couplers **40** and **41** were used in a reaction with 4- β -sulphato ethylsulphone aniline at pH 6.5 to prepare couplers **42** and **43**, respectively. The progress of the reaction was followed by TLC using n-PrOH:n-BuOH:EtOAc:H₂O/2:4:1:3. TLC showed complete conversion of both starting acids to the target couplers.

Tetrazotization of diamines **35-38** and commercial diamine **39** was carried out using NaNO₂/HCl at 0-5°C. Then, the tetrazonium salt solutions were added to individual coupler solutions at pH 9 to give the target bis-DCT bifunctional reactive dyes of groups (a) and (b) and Bis-(MCT/SES) tetrafunctional reactive dyes of groups (c) and (d), as shown in Scheme 5.



Scheme 4. Reactions used to prepare couplers **40-43**.



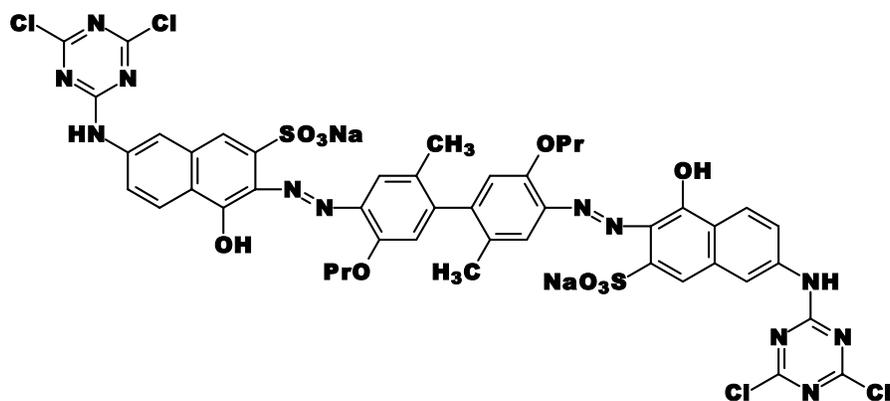
Scheme 5. Synthesis of reactive dyes.

- | | |
|--|--|
| <p>(a) Dye 1 ($R_1 = \text{CH}_3$, $R_2 = \text{Pr}$)
 Dye 2 ($R_1 = \text{H}$, $R_2 = \text{Pr}$)
 Dye 3 ($R_1 = \text{CH}_3$, $R_2 = \text{CH}_3$)
 Dye 4 ($R_1 = \text{H}$, $R_2 = \text{CH}_3$)
 Dye 5 ($R_1 = \text{CH}_3$, $R_2 = \text{Et}$)</p> | <p>(b) Dye 6 ($R_1 = \text{CH}_3$, $R_2 = \text{Pr}$)
 Dye 7 ($R_1 = \text{H}$, $R_2 = \text{Pr}$)
 Dye 8 ($R_1 = \text{CH}_3$, $R_2 = \text{CH}_3$)
 Dye 9 ($R_1 = \text{H}$, $R_2 = \text{CH}_3$)
 Dye 10 ($R_1 = \text{CH}_3$, $R_2 = \text{Et}$)</p> |
| <p>(c) Dye 11 ($R_1 = \text{CH}_3$, $R_2 = \text{Pr}$)
 Dye 12 ($R_1 = \text{H}$, $R_2 = \text{Pr}$)
 Dye 13 ($R_1 = \text{CH}_3$, $R_2 = \text{CH}_3$)
 Dye 14 ($R_1 = \text{H}$, $R_2 = \text{CH}_3$)
 Dye 15 ($R_1 = \text{CH}_3$, $R_2 = \text{Et}$)</p> | <p>(d) Dye 16 ($R_1 = \text{CH}_3$, $R_2 = \text{Pr}$)
 Dye 17 ($R_1 = \text{H}$, $R_2 = \text{Pr}$)
 Dye 18 ($R_1 = \text{CH}_3$, $R_2 = \text{CH}_3$)
 Dye 19 ($R_1 = \text{H}$, $R_2 = \text{CH}_3$)
 Dye 20 ($R_1 = \text{CH}_3$, $R_2 = \text{Et}$)</p> |

2. MASS SPECTROMETRY

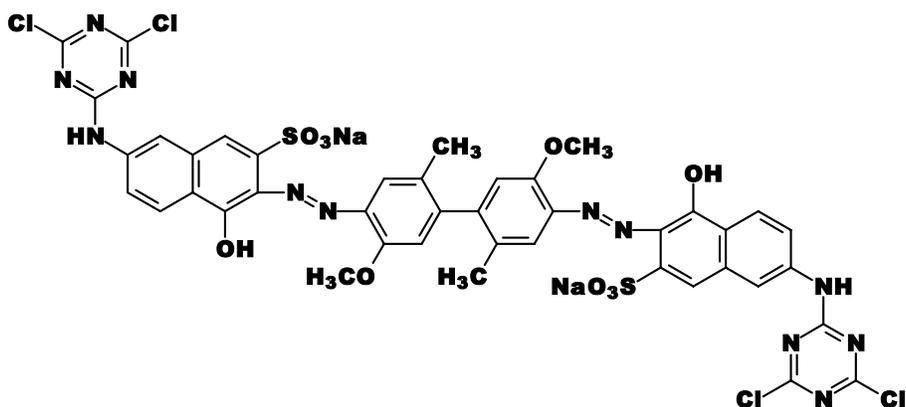
Dyes synthesized in this study have molecular masses in the 1000 – 1800 amu range. The preliminary report received from Prof. Holčápek indicated that the background noise level in the ESI spectra of the bis-MCT dyes covered a broad range of masses, which is usually an indication of the presence of inorganic salts. While samples containing dyes such as **13**, **14** and **15** give signals for ions that could correspond to the expected molecules, further work was needed to validate the results. This work included the use of ion exchange resins to reduce inorganic salts to the lowest possible levels. Following the efficient removal of salt, the best results were obtained for dyes **1**, **3**, **4** and **5** derived from J-acid, since they had fewer $-\text{SO}_3\text{Na}$ groups. A summary of the results is provided in the discussion below and in Table 12.

Dye 1



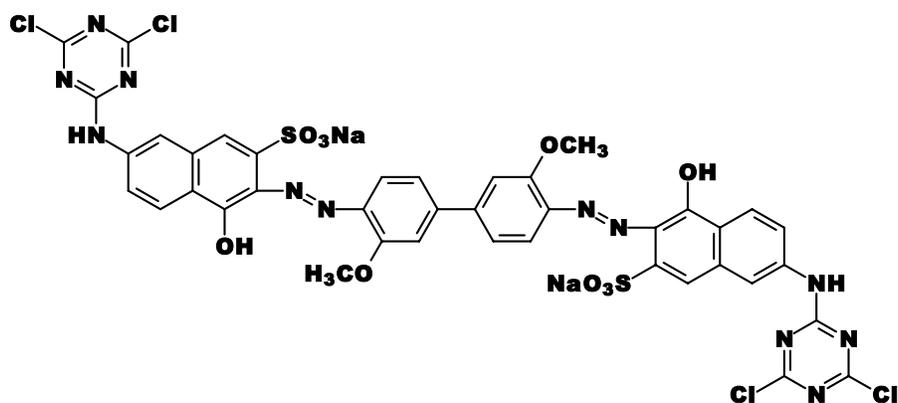
Dye 1 has MW = 1168, based on the formula $C_{46}H_{36}N_{12}O_{10}S_2Cl_4Na_2$. With the loss of 2 Na^+ ions, the signal corresponding to $m/2 = 561$ was observed in the spectrum (Figure 19). In addition to the molecular ion peak, key fragment ions were observed at $m/z = 709$ and $m/z = 383.8$. Structures assigned to these ions are listed in Table 12, where it is suggested that they were produced by cleavage at C-N bonds adjacent to the azo linkage.

Dye 3



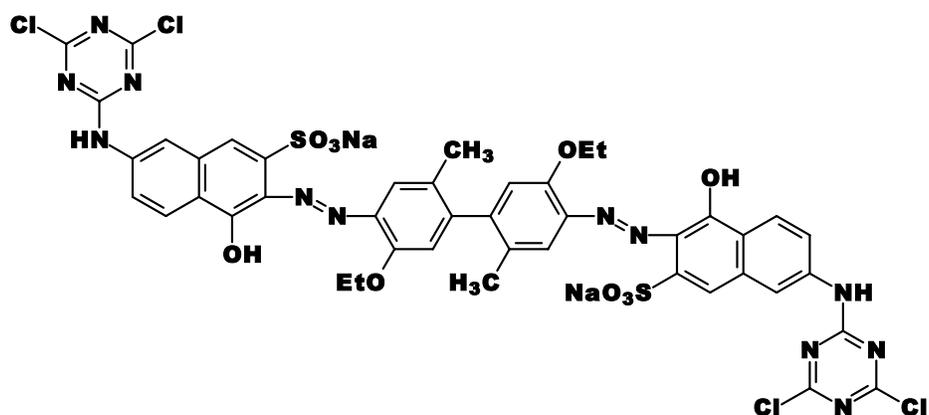
Dye 3 has MW = 1112, based on the formula $C_{42}H_{28}N_{12}O_{10}S_2Cl_4Na_2$. With the loss of 2 Na^+ ions, the signal corresponding to $m/2 = 561$ was observed in the spectrum (Figure 20). In addition to the molecular ion peak, key fragment ions were observed at $m/z = 653$ and $m/z = 383.8$. Structures assigned to these ions are listed in Table 12, where it is suggested that they were produced by cleavage at C-N bonds adjacent to the azo linkage.

Dye 4



Dye **4** has MW = 1084, based on the formula $C_{40}H_{24}N_{12}O_{10}S_2Cl_4Na_2$. With the loss of 2 Na^+ ions, the signal corresponding to $m/z = 519$ was observed in the spectrum (Figure 21). In addition to the molecular ion peak, key fragment ions were observed at $m/z = 624.9$, $m/z = 383.8$ and $m/z = 348.8$. Structures assigned to these ions are listed in Table 12, where it is suggested that they were produced by cleavage at C-N bonds adjacent to the azo linkage, and by hydrolysis of the chlorotriazine group. In this case, the signal at $m/z = 624.9$ is very small.

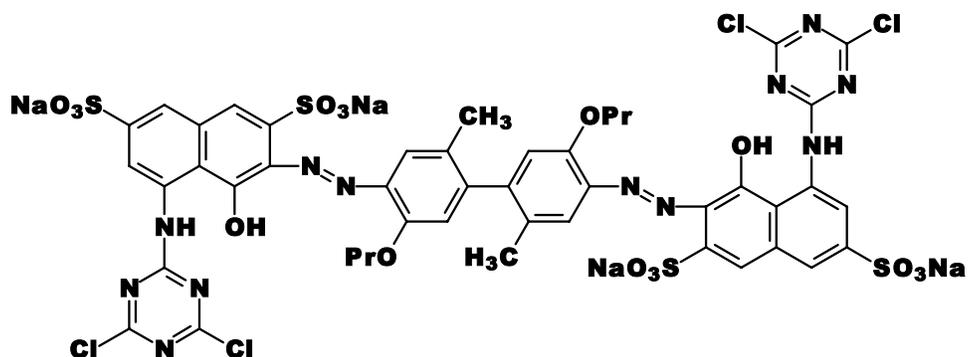
Dye 5



Dye **5** has MW = 1140, based on the formula C₄₄H₃₂N₁₂O₁₀S₂Cl₄Na₂. The expected signal corresponding to m/2 = 547 was not observed in the spectrum (Figure 22). However, key fragment ions were observed at m/z = 681, m/z = 696.9, m/z = 383.8 and m/z = 348.8. Structures assigned to these ions are listed in Table 12, where it is suggested that they were produced by cleavage at C-N or N=N bonds and by hydrolysis of the chlorotriazine group.

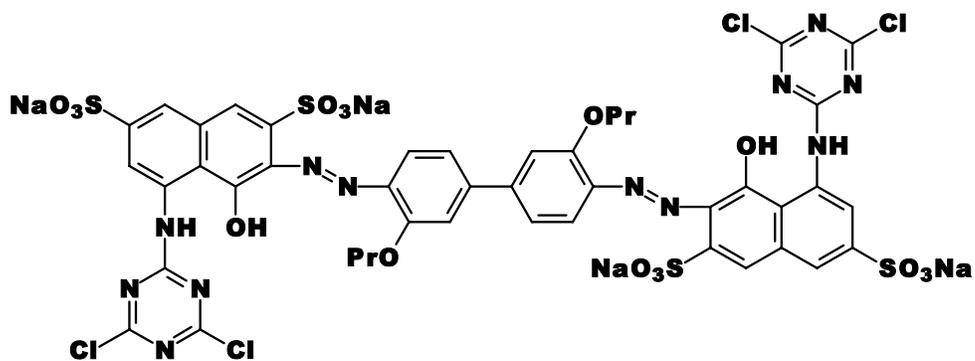
Dyes **6-10** contain 4 sulphonic acid groups. Producing mass spectral data was more complicated since the increase in ionic groups usually leads to higher salt concentrations and failure to make useful MS measurements.. Consequently, the mass spectra of dyes **6-10** (Figures 23-27) did not show direct evidence of target dye structures. It is also possible that hydrolysis is a major factor in the lack of success, as there are signals consistent with hydrolyzed dye structures.

Dye 6



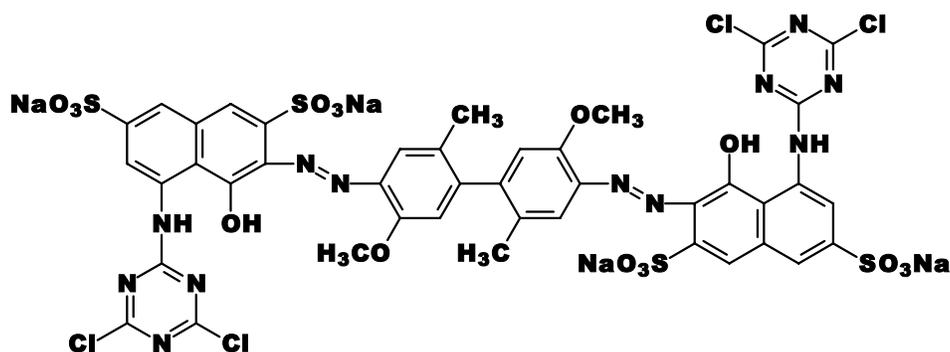
Dye **6** has MW = 1372, based on the formula C₄₆H₃₄N₁₂O₁₆S₄Cl₄Na₄. The loss of Na⁺ ions would give signals corresponding to m/2 = 640, m/3 = 426.7 and m/4 = 320, neither of which was observed in the spectrum (Figure 23). In this case, a fragment ion at m/z = 466.5 was observed. It is believed that this ion was produced by cleavage at a C-N bond adjacent to the azo linkage.

Dye 7



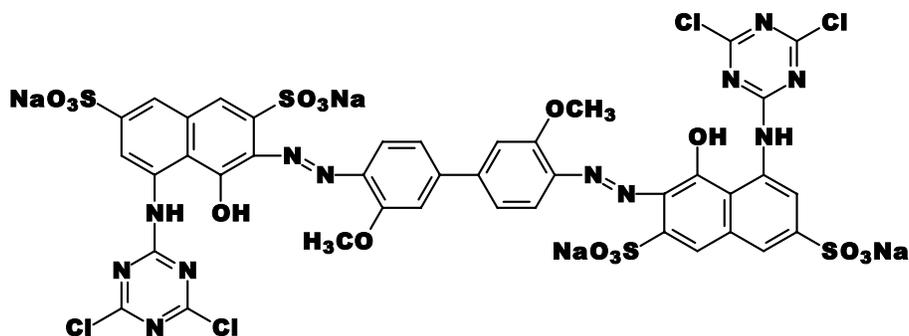
Dye 7 has MW = 1344, based on the formula $C_{44}H_{30}N_{12}O_{16}S_4Cl_4Na_4$. The loss of Na^+ ions would give signals corresponding to $m/2 = 626$, $m/3 = 448$ and $m/4 = 313$, neither of which was observed in the spectrum (Figure 24). A fragment ion at $m/z = 724.6$ was observed. It is believed that this ion was produced by cleavage a C-N bond between the azo group and H-acid, and replacement of both chlorine atoms by hydroxyl groups (Table 12).

Dye 8



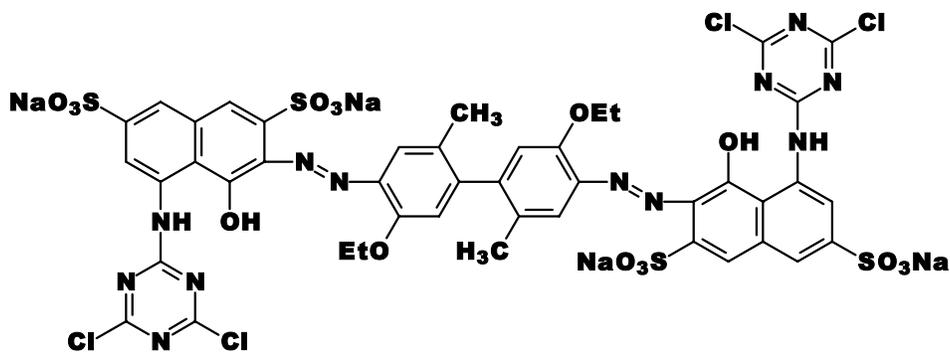
Dye 8 has MW = 1316, based on the formula $C_{42}H_{26}N_{12}O_{16}S_4Cl_4Na_4$. The expected signals corresponding to $m/2 = 612$, $m/3 = 438.7$ and $m/4 = 306$ were not observed in the spectrum (Figure 25). In this case a fragment ion at $m/z = 734.9$ was observed. This fragment would arise from cleavage at C-N bonds adjacent to the azo linkage (Table 12).

Dye 9



Dye 9 has MW = 1288, based on the formula $C_{40}H_{22}N_{12}O_{16}S_4Cl_4Na_4$. The expected signals corresponding to $m/2 = 598$, $m/3 = 398.7$ and $m/4 = 299$ were not observed in the spectrum (Figure 26). The fragment ions at $m/z = 666.9$ and $m/z = 722$ were produced by cleavage at C-N or N=N bonds, and in the former case two chlorine atoms were replaced by hydroxyl groups (Table 12).

Dye 10



Dye **10** has MW = 1344, based on the formula $C_{44}H_{30}N_{12}O_{16}S_4Cl_4Na_4$. The expected signals corresponding to $m/2 = 626$, $m/3 = 417.3$ and $m/4 = 313$ were not observed in the spectrum (Figure 27). However, the fragment ions at $m/z = 762.9$ and $m/z = 722.9$ were observed, and were probably formed by cleavage at C-N bonds adjacent to the azo linkage, and in the latter case two chlorine atoms were replaced by hydroxyl groups (Table 12).

Table 12. Fragment ions corresponding to signals from ESI-MS analyses.

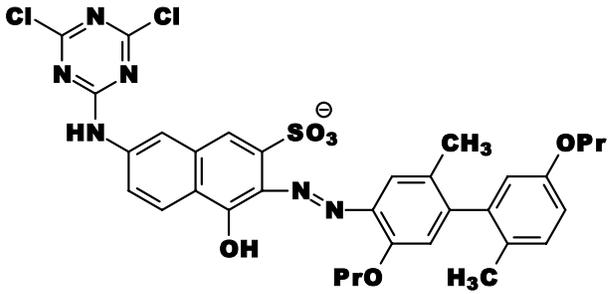
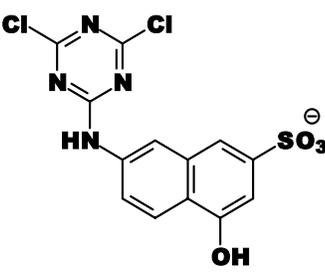
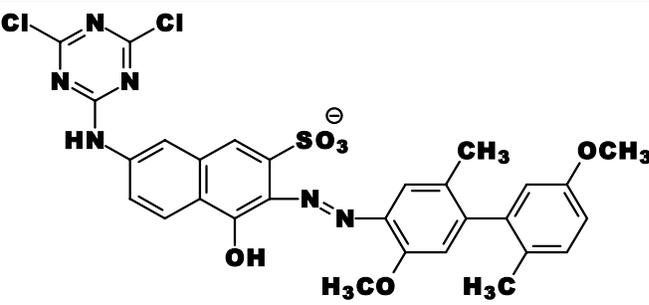
Dye	m/z	Structure
1	709	
	383.8	
3	653	

Table 12 (continued)

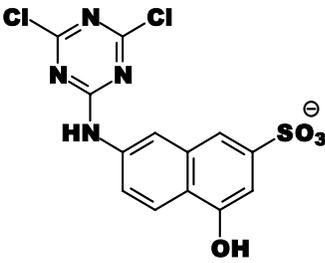
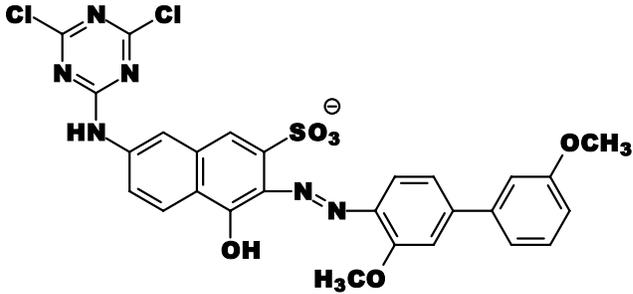
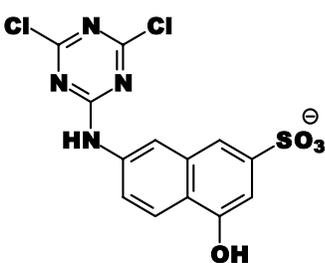
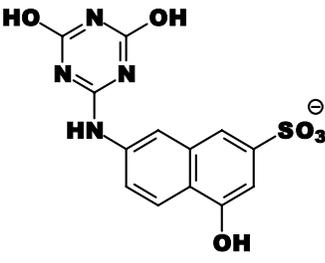
Dye	m/z	Structure
3	383.8	
4	624.9	
	383.8	
	348.8	

Table 12 (continued)

Dye	m/z	Structure
5	681	
	696.9	
	383.8	
	348.8	
6	466.5	

Table 12 (continued)

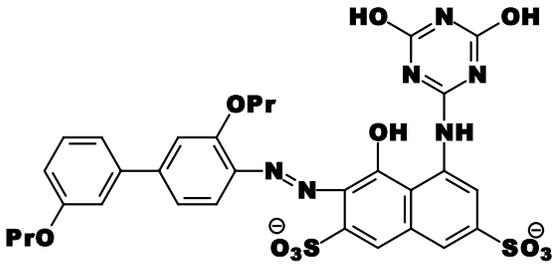
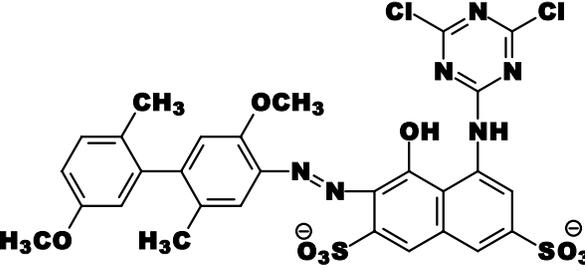
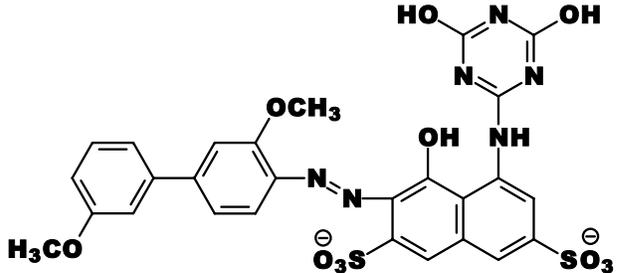
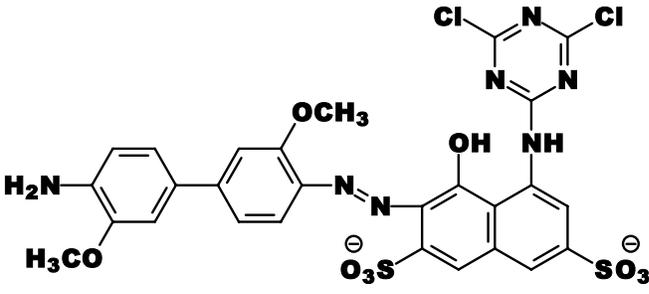
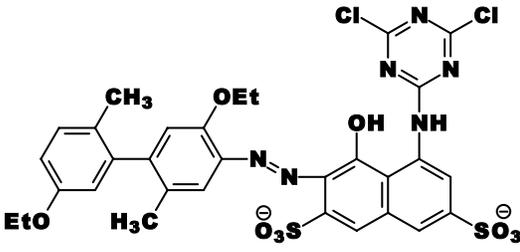
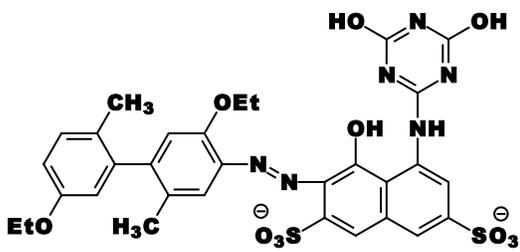
Dye	m/z	Structure
7	724.6	
8	734.9	
9	666.9	
	722	

Table 12 (continued)

Dye	m/z	Structure
10	762.9	 <p>The structure shows a central naphthalene ring system. At the 1-position, there is a hydroxyl group (OH) and a quinoxaline ring. The quinoxaline ring has chlorine atoms (Cl) at the 2 and 8 positions and an NH group at the 5-position. At the 4-position of the naphthalene ring, there is a sulfonate group (SO₃⁻). At the 8-position, there is another sulfonate group (SO₃⁻). A diazo group (-N=N-) is attached to the 6-position of the naphthalene ring. This diazo group is linked to a benzene ring that has an ethoxy group (OEt) at the 1-position, a methyl group (CH₃) at the 2-position, and another methyl group (H₃C) at the 4-position. An ethoxy group (EtO) is also attached to the 3-position of this benzene ring.</p>
	722.9	 <p>The structure is identical to the one above, but the quinoxaline ring is replaced by a dihydroquinoxaline ring. The dihydroquinoxaline ring has hydroxyl groups (OH) at the 2 and 8 positions and an NH group at the 5-position.</p>

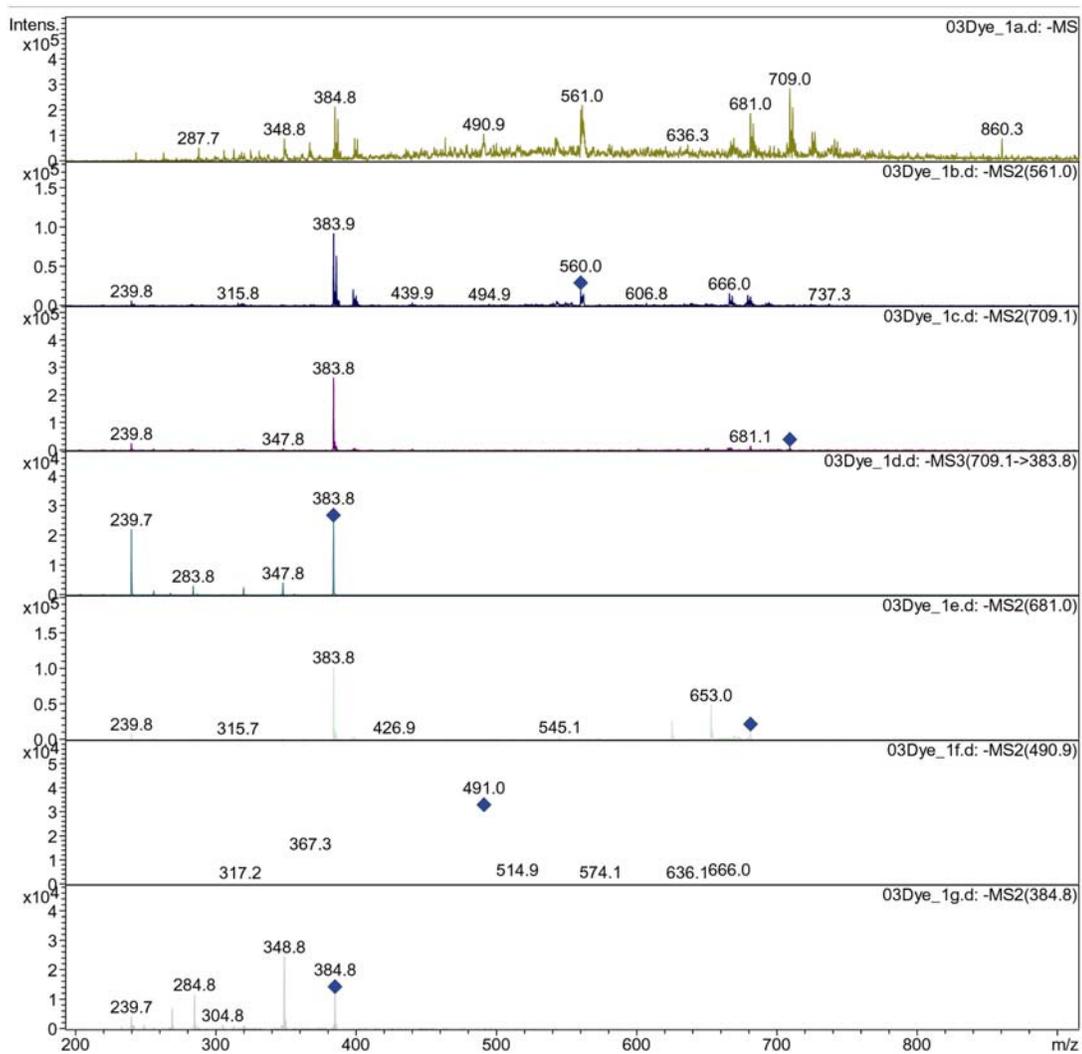


Figure 19. ESI mass spectra of dye 1.

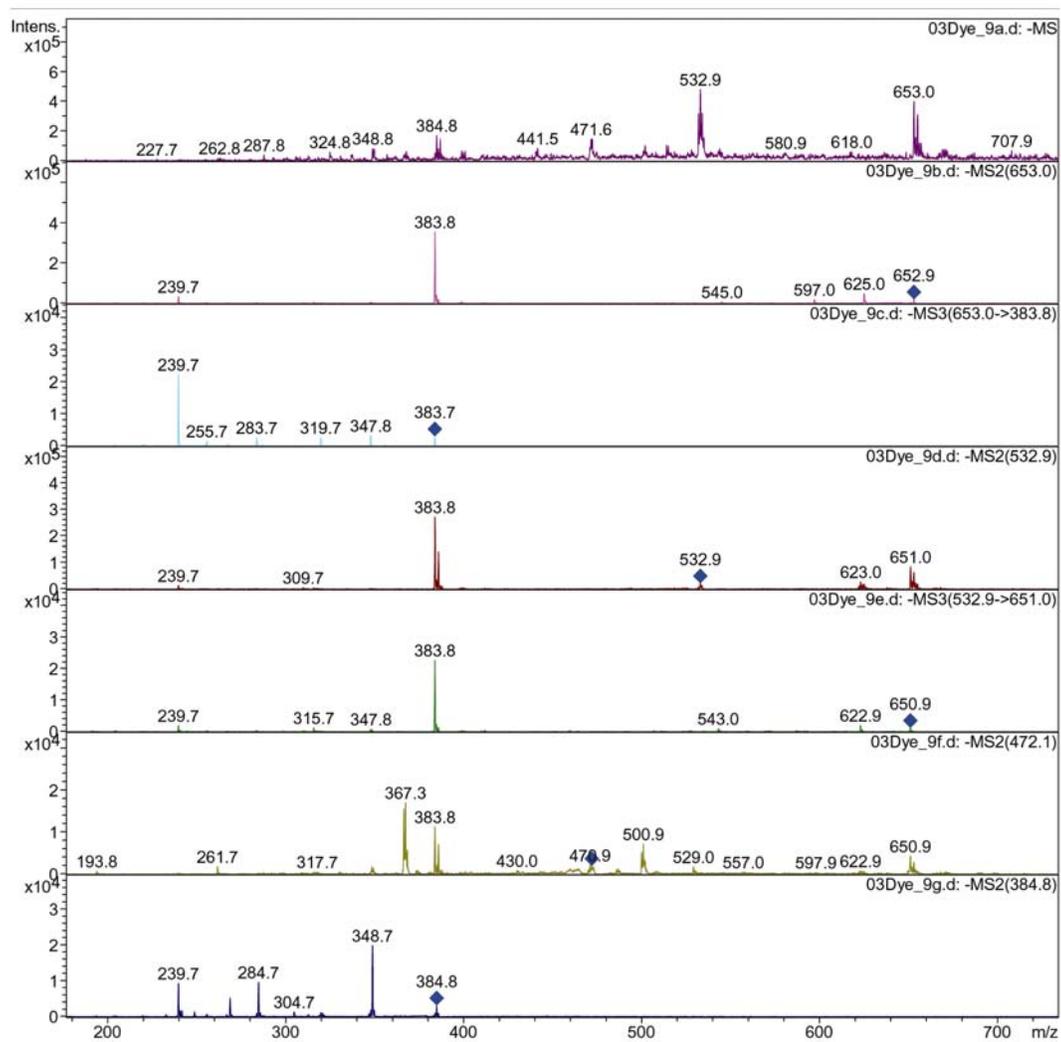


Figure 20. ESI mass spectra of dye 3.

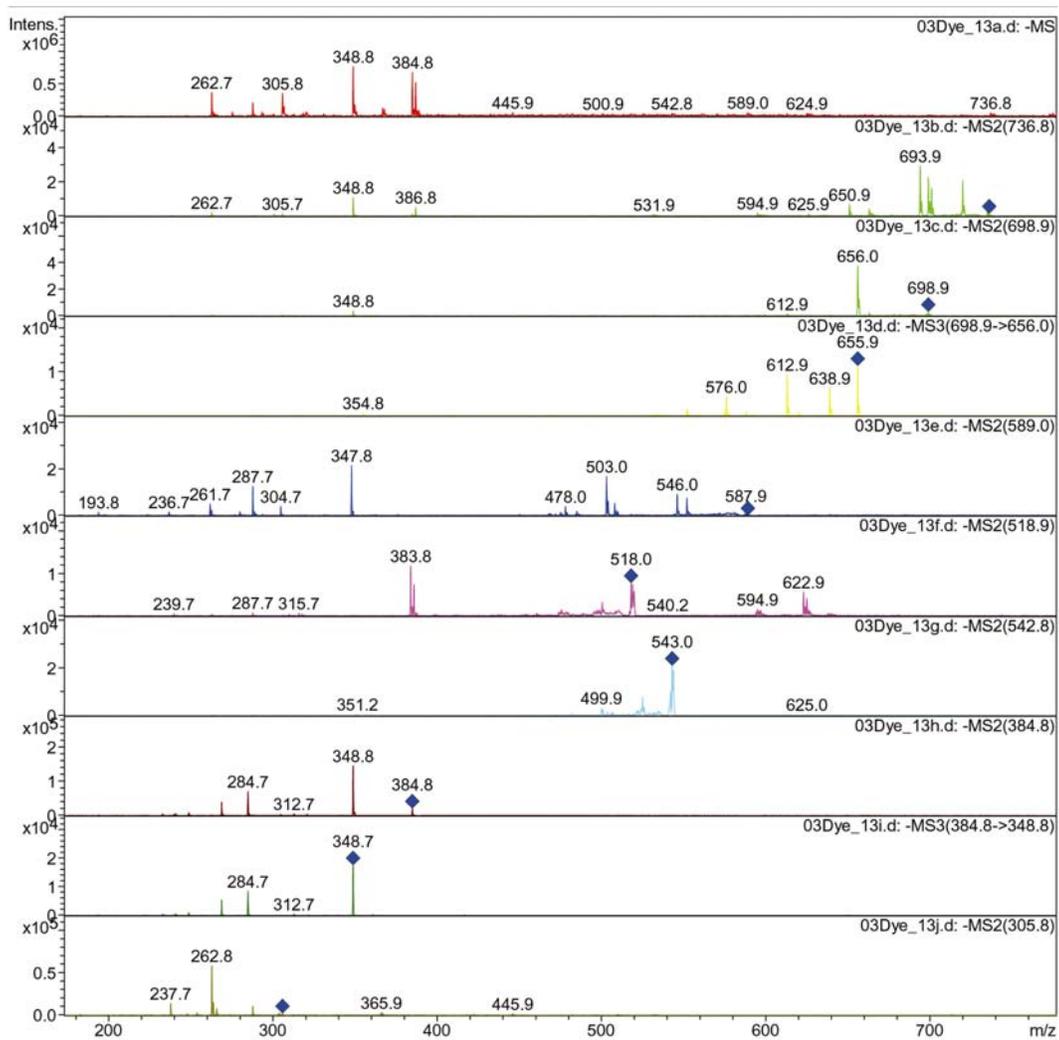


Figure 21. ESI mass spectra of dye 4.

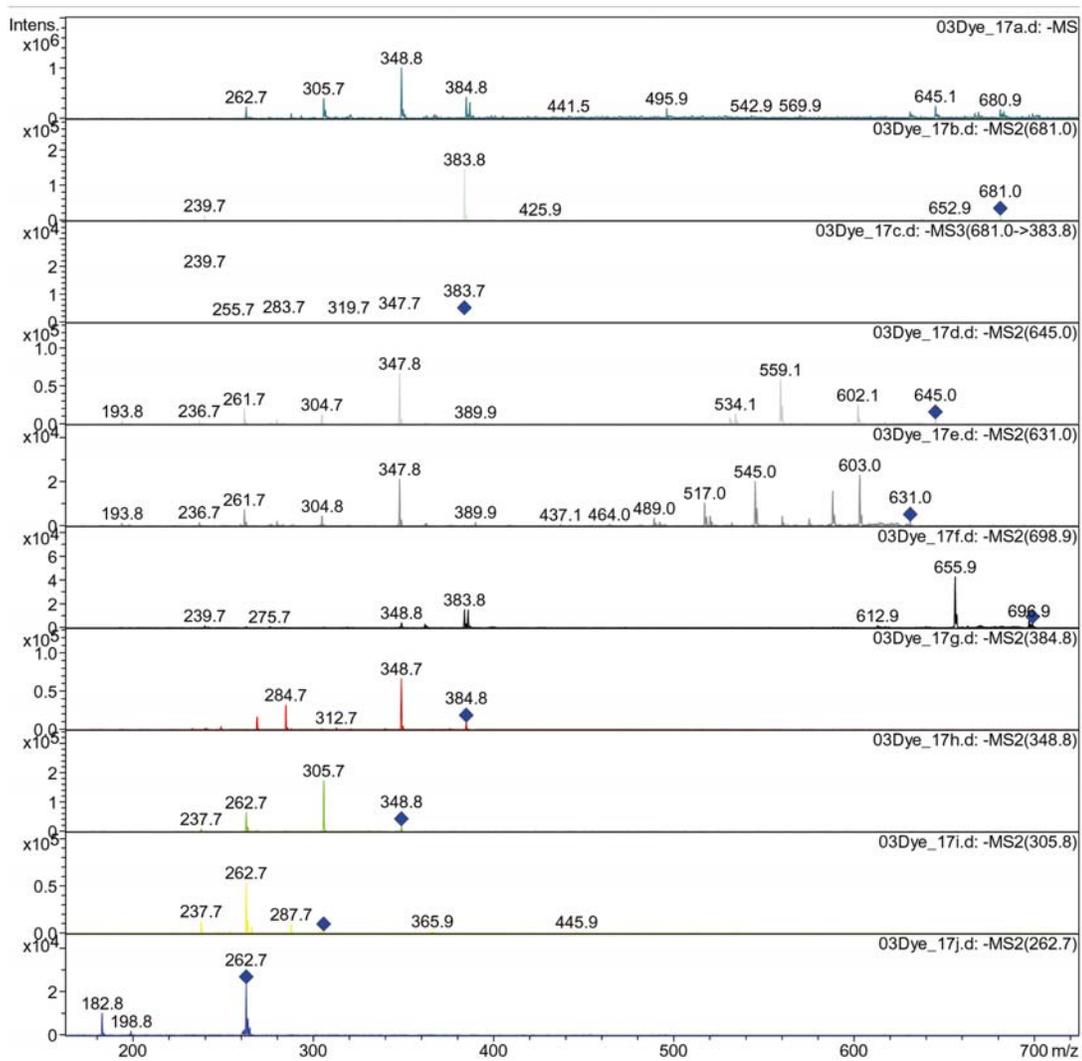


Figure 22. ESI mass spectra of dye 5.

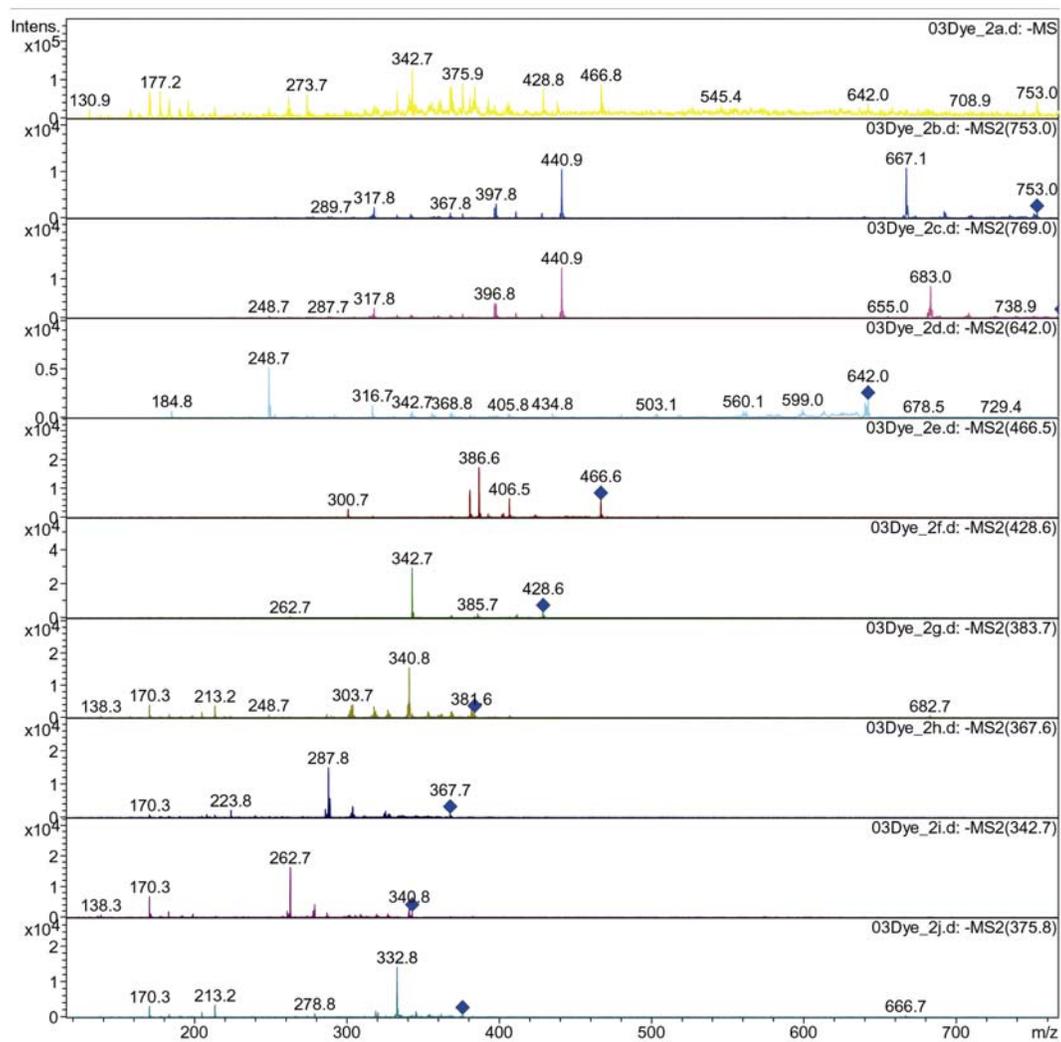


Figure 23. ESI mass spectra of dye 6.

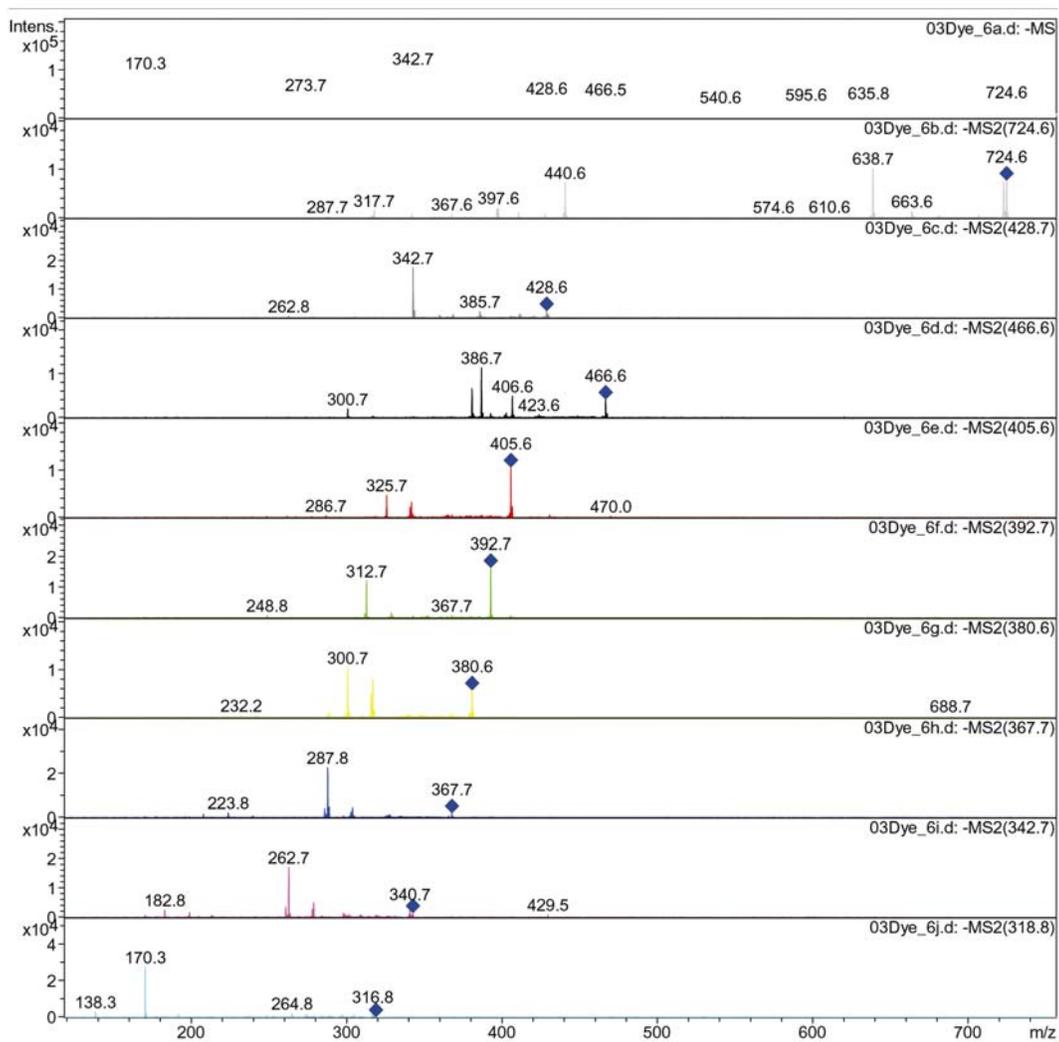


Figure 24. ESI mass spectra of dye 7.

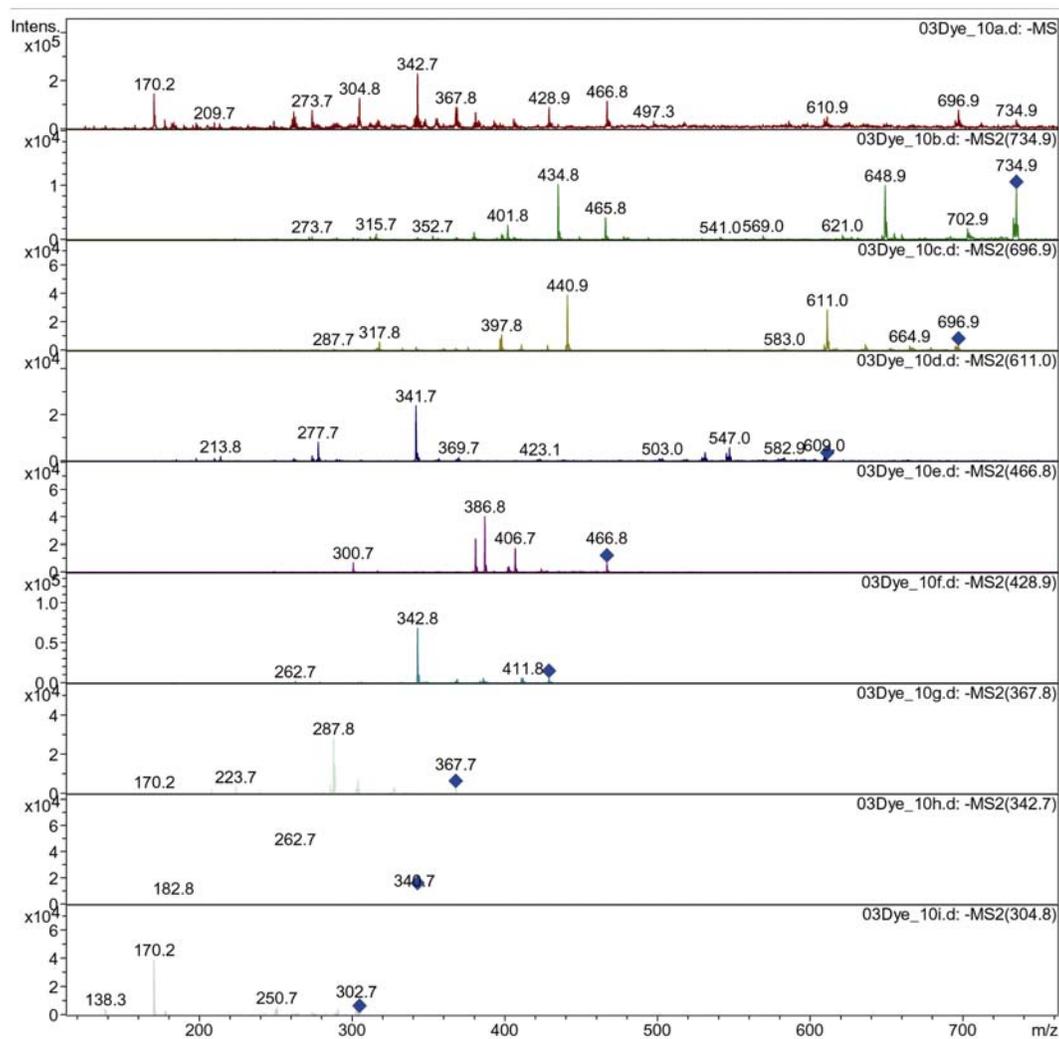


Figure 25. ESI mass spectra of dye 8.

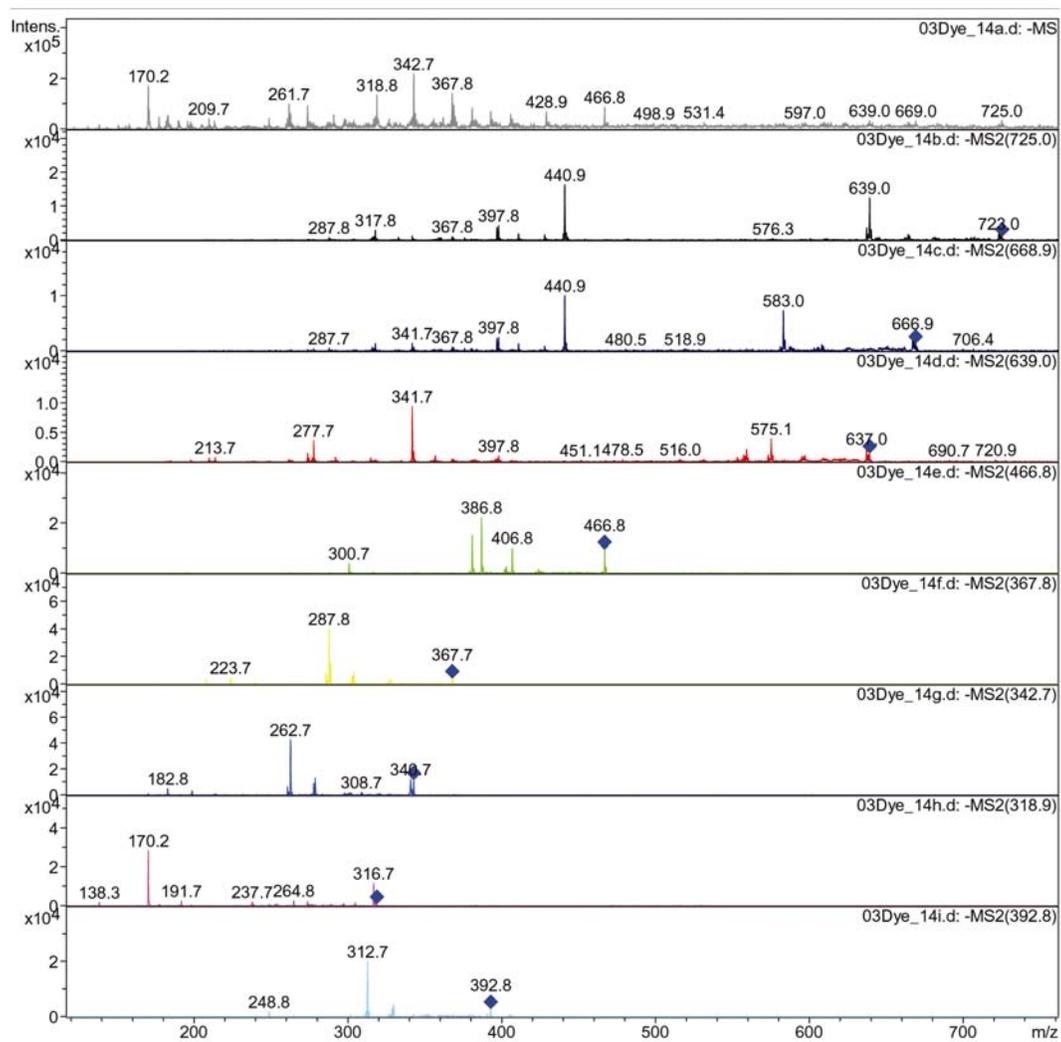


Figure 26. ESI mass spectra of dye 9.

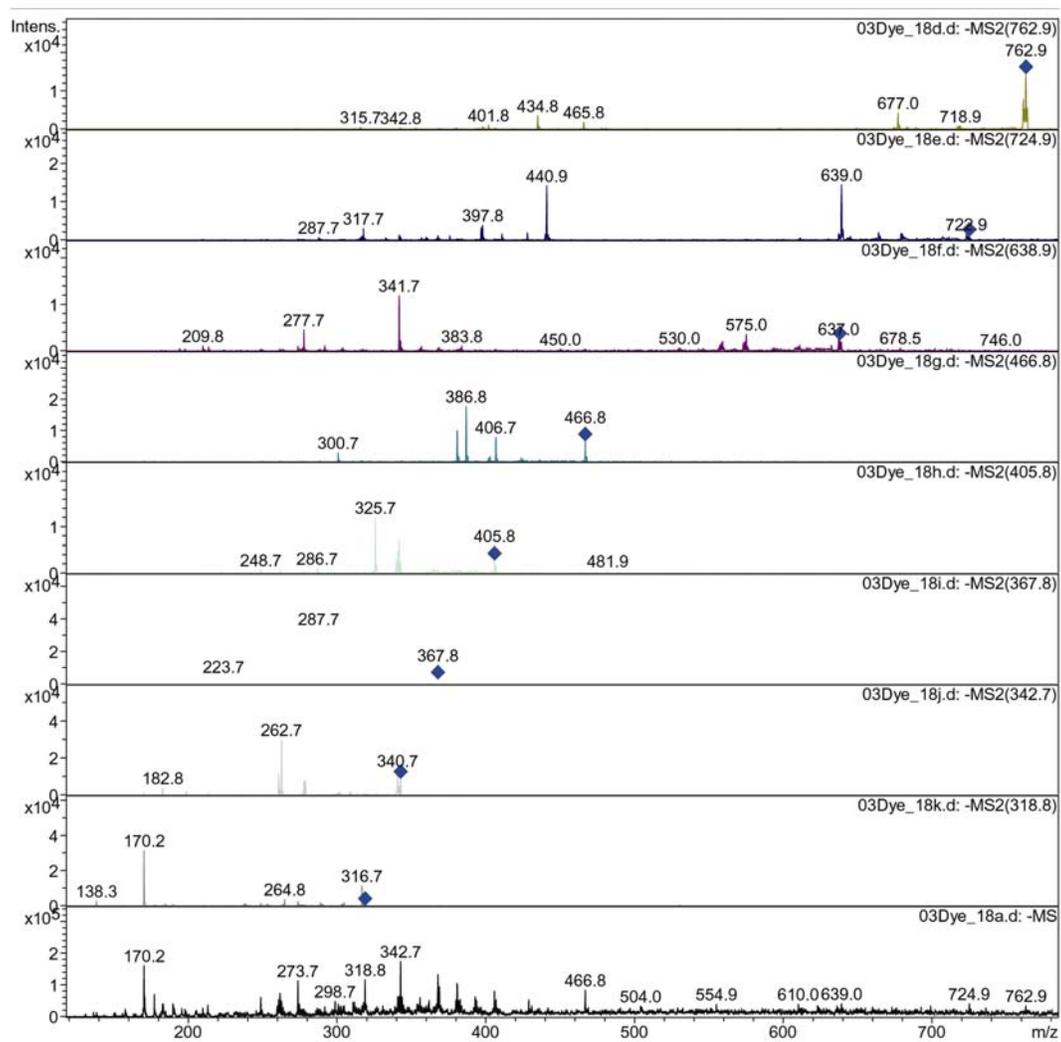


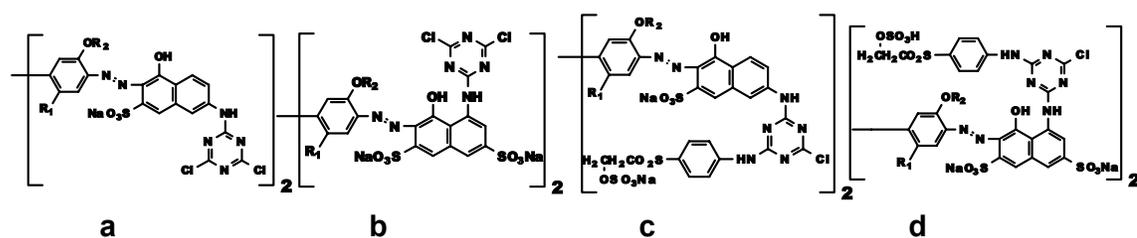
Figure 27. ESI mass spectra of dye 10.

3. VISIBLE ABSORPTION DATA

The visible absorption spectra of dyes **1-20** were recorded in DMF (cf. Figure 28-31), the results of which are summarized in Table 13. Most spectra showed two peaks because these dyes exist in azo and hydrazone forms. The hydrazone form is bathochromic compared to the azo form. The dyes are capable of undergoing azo-hydrazone tautomerism because they have the hydroxyl groups of J-acid or H-acid conjugated to the azo groups. The data showed that reactive dyes containing H-acid in groups **b** and **d** have higher λ_{\max} values than their counterparts containing J-acid (groups **a** and **c**). For example, dye **6** (λ_{\max} = 560 nm) absorbed at a longer wavelength than dye **1** (λ_{\max} = 542 nm). The spectra of dyes in groups **b** and **d** which contain H-acid showed that these dyes exist predominantly in the hydrazone form.

Dyes from twisted benzidines generally had lower λ_{\max} values (hypsochromic) than the non-twisted counterparts. For example, dyes **6** and **8** in group **b** had lower λ_{\max} than dyes **7** and **9** (Figure 29). The twisted structure interrupts the extended conjugated system and causes the dyes to absorb light at a shorter wavelength. Color strengths (E_{\max}) of reactive dyes in groups **a** and **b** were comparable to that of Procion Red MX-8B which also has dichlorotriazine as a reactive group. Likewise, color strengths of reactive dyes in group **d** was comparable to that of C.I. Reactive Red 198 which has MCT/SES as the reactive group. While color strength values of most dyes in group **c** were a little lower than that of C.I. Reactive Red 198. Dye **2** had quite low color strength. This might be because of residual salt content.

Table 13. Absorption spectral data of dyes 1-20.



Group	Dye	R ₁	R ₂	λ_{\max}	E_{\max} ($\times 10^4$ l mol ⁻¹ cm ⁻¹)
a	1	Me	Pr	542	2.3
	2	H	Pr	524	0.6
	3	Me	Me	545	2.5
	4	H	Me	553	1.8
	5	Me	Et	514	4.2
b	6	Me	Pr	560	2.5
	7	H	Pr	572	2.6
	8	Me	Me	561	2.6
	9	H	Me	568	2.7
	10	Me	Et	563	2.8
c	11	Me	Pr	513	3.1
	12	H	Pr	525	1.4
	13	Me	Me	512	1.6
	14	H	Me	543	1.5
	15	Me	Et	540	1.6
d	16	Me	Pr	560	2.8
	17	H	Pr	570	2.4
	18	Me	Me	561	2.6
	19	H	Me	565	2.6
	20	Me	Et	559	2.7
Procion Red MX-8B				544	2.9
C.I. Reactive Red 198				523	2.9

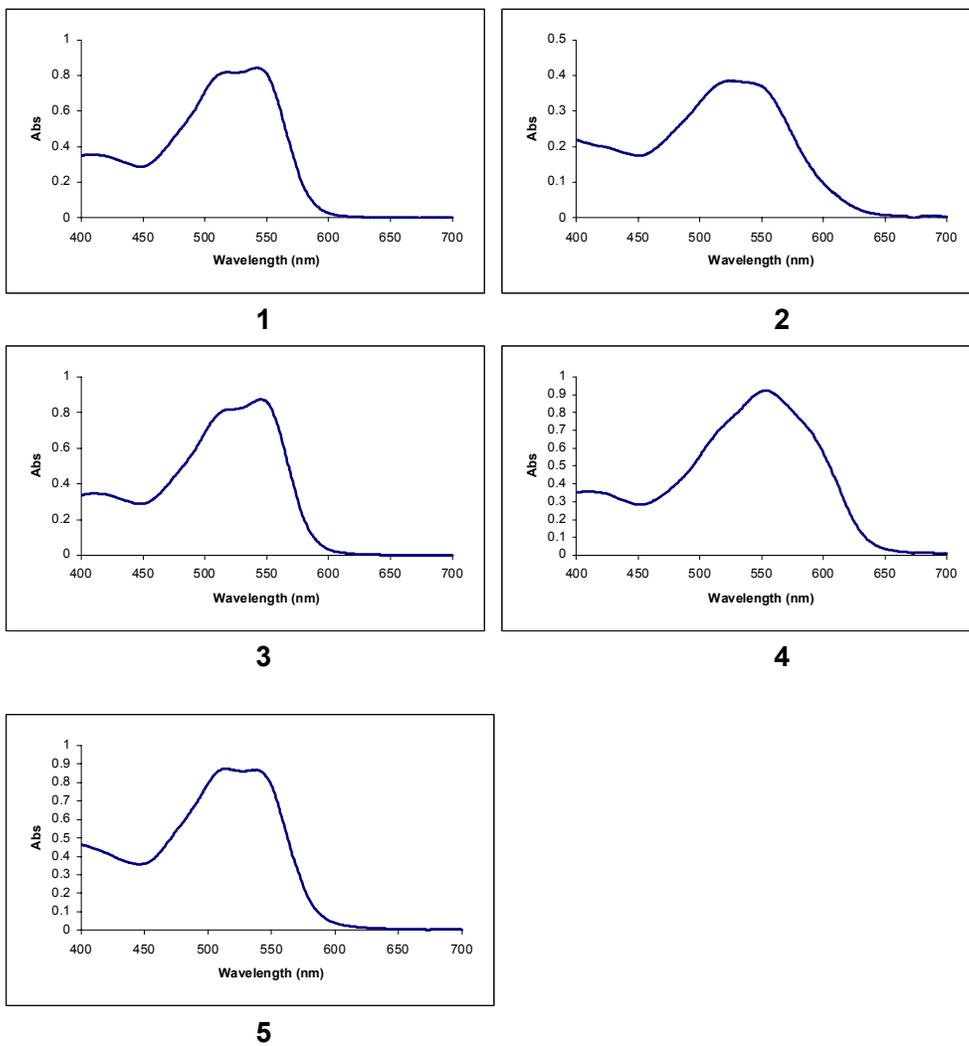
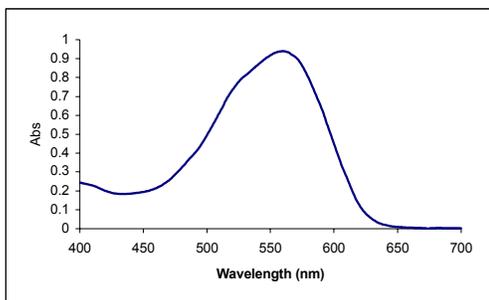
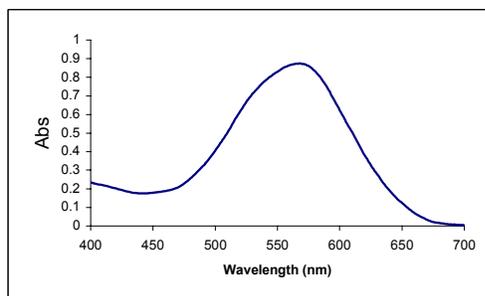


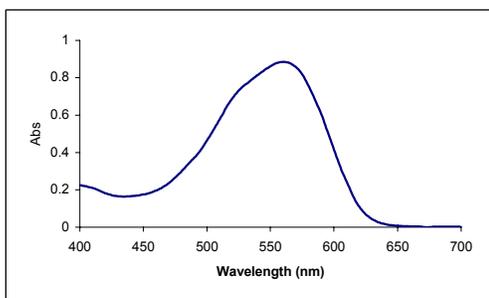
Figure 28. Absorption spectra of dyes 1-5 (group a).



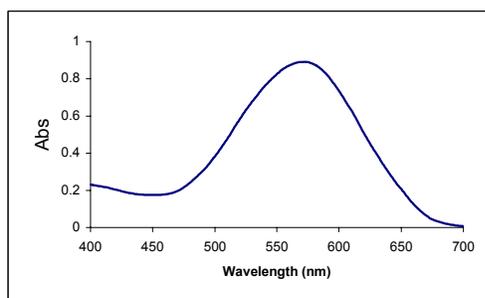
6



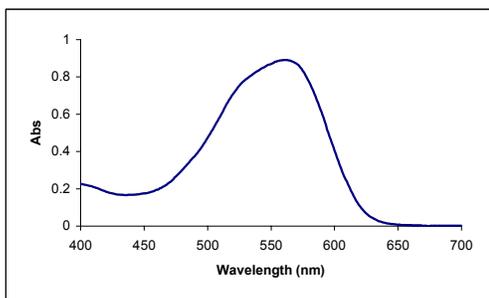
7



8

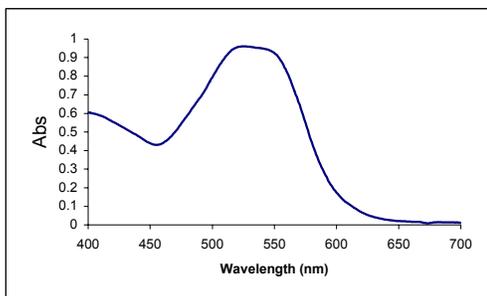


9

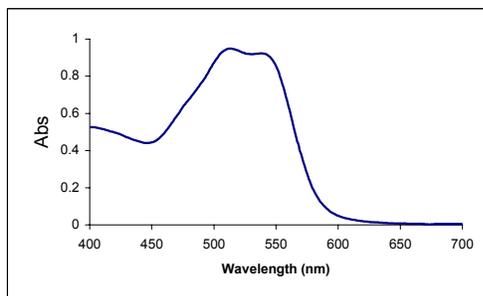


10

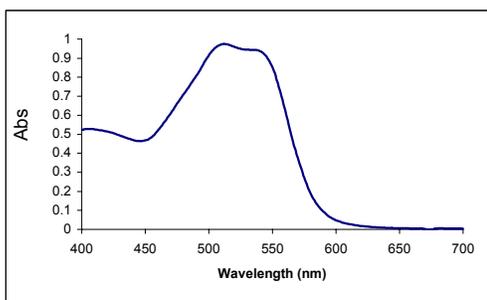
Figure 29. Absorption spectra of dyes **6-10** (group **b**).



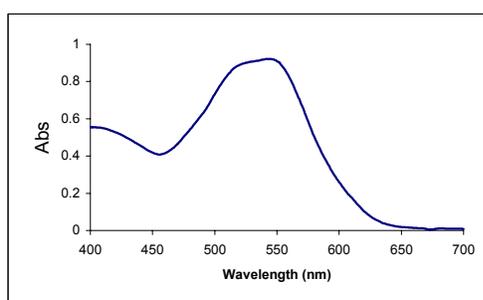
11



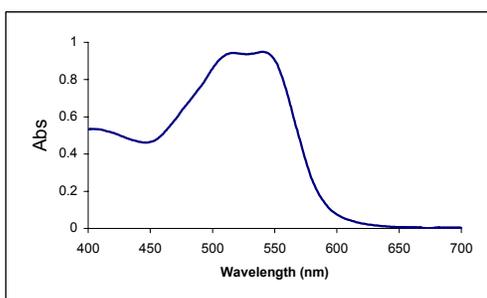
12



13

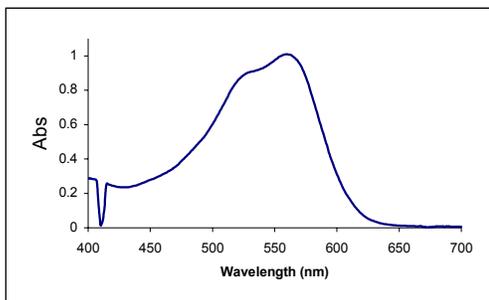


14

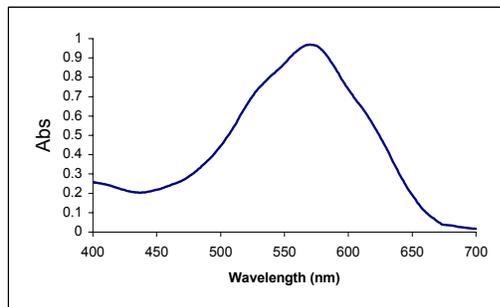


15

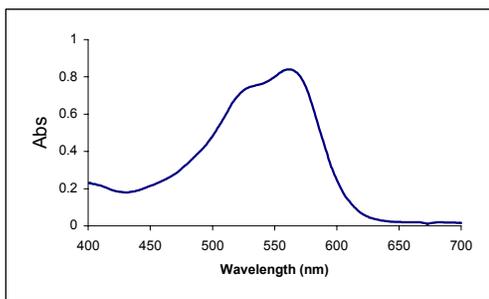
Figure 30. Absorption spectra of dyes 11-15 (group c).



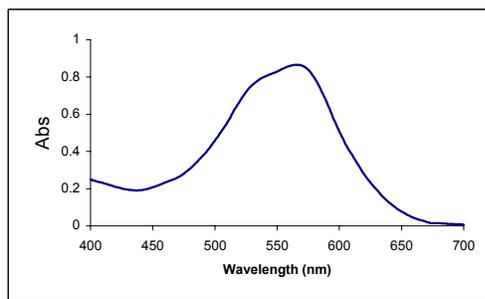
16



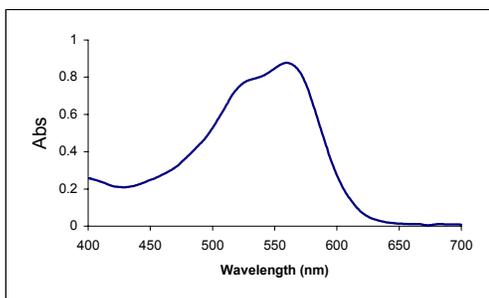
17



18



19



20

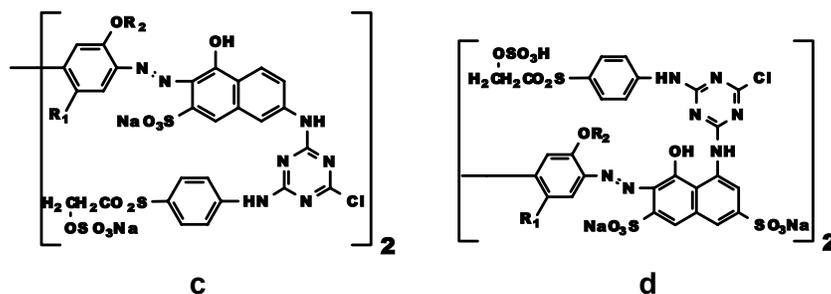
Figure 31. Absorption spectra of dyes **16-20** (group d).

4. COLORIMETRIC DATA

4.1 Colorimetric data from exhaust dyeing

Table 14 shows the colorimetric data for the dyed fabrics from exhaust dyeing with dyes in groups **c** and **d**. The fabric samples all had a very light shade (high L^* value), making exhaust dyeing unsuitable for these reactive dyes. Dyebath exhaustion of the dyes from the dyebath to fabric samples was not good, and only small amounts of dye were fixed to the fabric.

Table 14. Color values from exhaust dyeing.



Group	Dye	R ₁	R ₂	L [*]	a [*]	b [*]	K/S
c	11	Me	Pr	73.60	20.96	2.21	0.55
	12	H	Pr	68.53	18.50	-3.96	0.77
	13	Me	Me	72.29	20.36	-0.94	0.58
	14	H	Me	63.06	19.01	-8.99	1.05
	15	Me	Et	76.47	15.66	-0.97	0.36
d	16	Me	Pr	61.05	18.20	-11.43	1.24
	17	H	Pr	60.76	5.98	-15.00	1.03
	18	Me	Me	62.83	15.62	-10.86	1.03
	19	H	Me	57.42	10.79	-16.13	1.58
	20	Me	Et	62.67	18.09	-10.05	1.02

4.2 L* a* b* values of dyed cotton fabrics

Padding solutions of reactive dyes and alkali directly on the fabric was a better way to apply the dyes made in this study. Bis-DCT bifunctional reactive dyes in groups **a** and **b** were applied on cotton by pad-batch method since the dichlorotriazine reactive groups are highly reactive and can be applied at room temperature and then batched overnight. Bis-(MCT/SES) tetrafunctional reactive dyes in groups **c** and **d** were applied on cotton by pad-dry-cure since monochlorotriazine reactive groups required higher temperature for fixation.

L* a* b* values of dyed cotton fabrics were calculated and the data are reported in Table 15.

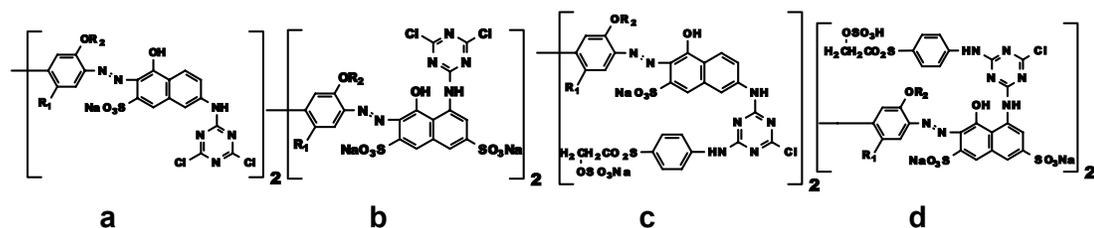
4.2.1 Comparison between dyes from twisted and untwisted benzidines

Dyes from twisted benzidines gave redder (higher a* values) shades on cotton than their planar counterparts. On the other hand, dyes from untwisted benzidines gave bluer (higher -b* values) than those from twisted benzidines. In groups **c** and **d**, dyes from twisted benzidines consistently gave lighter (higher L*) shades than their untwisted counterparts.

4.2.2 Comparison of R₂

For dyes derived from untwisted benzidines and H-acid, R₂ = Me gave lighter, redder and yellower fabrics than when R₂ = Pr. The corresponding dyes from J-acid had lighter, redder and yellower shades than when R₂ = Pr.

Table 15. L* a* b* values of dyes 1-20.

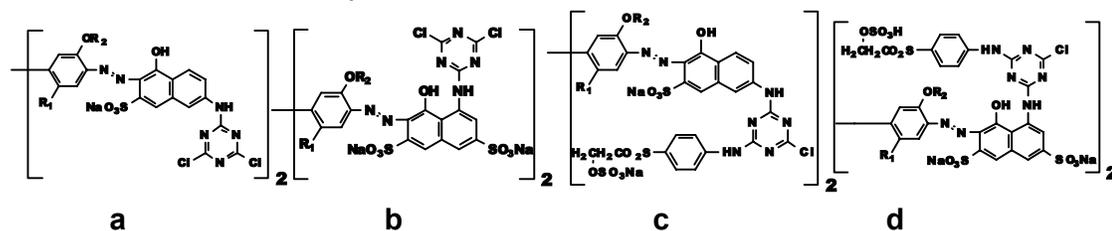


Group	Dye	R ₁	R ₂	L*	a*	b*
a	1	Me	Pr	42.10	31.28	-5.89
	2	H	Pr	54.89	15.70	-9.99
	3	Me	Me	42.13	26.85	-11.63
	4	H	Me	39.80	9.49	-17.22
	5	Me	Et	50.32	30.67	-4.90
b	6	Me	Pr	41.78	17.50	-24.01
	7	H	Pr	45.12	-0.33	-26.33
	8	Me	Me	47.57	13.15	-24.31
	9	H	Me	49.79	-0.36	-25.07
	10	Me	Et	59.64	8.34	-20.37
c	11	Me	Pr	56.29	26.69	0.19
	12	H	Pr	51.62	16.90	-4.05
	13	Me	Me	52.23	25.82	-0.48
	14	H	Me	48.48	13.64	-7.53
	15	Me	Et	51.70	25.33	-1.03
d	16	Me	Pr	45.35	21.22	-13.67
	17	H	Pr	33.96	7.79	-21.29
	18	Me	Me	51.33	17.12	-13.57
	19	H	Me	40.04	9.47	-19.61
	20	Me	Et	46.19	21.13	-12.54

4.3 K/S values

K/S and λ_{\max} values for dyes **1-20** are shown in Table 16. Dyes derived from twisted benzidines had lower λ_{\max} than the non-twisted counterparts. The color of fabrics from dyes based on untwisted benzidines were deeper than fabrics with dyes from twisted counterparts. For example, dye **6** gave violet fabric while dye **7** gave blue. The results of bis-DCT bifunctional reactive dyes in groups **a** and **b** showed that dyes derived from twisted benzidines gave higher K/S values than the non-twisted counterparts. On the other hand, the results of bis-(MCT/SES) tetrafunctional reactive dyes in groups **c** and **d** showed that dyes derived from twisted benzidines gave lower K/S values than the non-twisted counterparts. In the same dye group, dyes from twisted benzidines had the same color and dyes from untwisted benzidines also had the same color. However, the different **R₂** groups gave different shades on the fabrics as shown in Figure 32. Dyes in groups **a** and **b** had K/S values lower than Procion Red MX-8B. Similarly, dyes in groups **c** and **d** had K/S values lower than C.I. Reactive Red 198. Dye **17** had the highest K/S, which was comparable to that of C.I. Reactive Red 198.

Table 16. K/S values of dyes 1-20.



Group	Dye	R ₁	R ₂	Color	λ _{max}	K/S
a	1	Me	Pr	Reddish Purple	540	5.44
	2	H	Pr	Purple	550	1.78
	3	Me	Me	Reddish Purple	550	4.99
	4	H	Me	Violet	570	4.72
	5	Me	Et	Reddish Purple	540	3.11
b	6	Me	Pr	Violet	570	4.86
	7	H	Pr	Blue	600	4.14
	8	Me	Me	Violet	580	3.23
	9	H	Me	Blue	600	2.94
	10	Me	Et	Violet	580	1.34
c	11	Me	Pr	Reddish Purple	535	1.93
	12	H	Pr	Purple	540	2.19
	13	Me	Me	Reddish Purple	530	2.45
	14	H	Me	Purple	545	2.59
	15	Me	Et	Reddish Purple	540	2.48
d	16	Me	Pr	Purple	550	3.57
	17	H	Pr	Violet	575	7.07
	18	Me	Me	Purple	560	2.33
	19	H	Me	Violet	570	4.66
	20	Me	Et	Purple	550	3.38
Procion Red MX-8B				Purple	550	8.09
C.I.Reactive Red 198				Reddish Purple	530	7.50

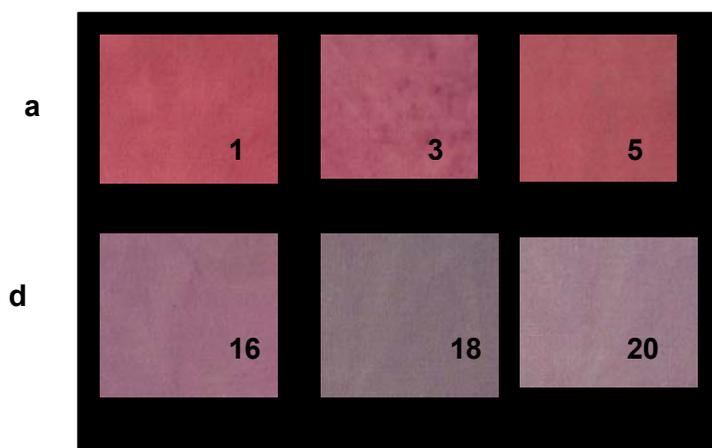


Figure 32. Approximate Fabric shades obtained as the R_2 group was varied.

4.4 Wash off process

The dyed fabrics were rinsed in warm water and scoured with 2 g/l AATCC detergent at 160°F for 5 min, then rinsed again in warm water and dried. This process is important to achieve the high wetfastness. The unfixed dyes were removed.

The dyed fabric gave some color in the first rinse in warm water and less color in scouring process. In the second rinse with warm water, there was almost no color seen. This suggests that the unfixed dyes were easily removed from the fiber surface.

5. FASTNESS PROPERTIES

5.1 Washfastness Studies

The data from washfastness studies are shown in Table 17, where it can be seen that dyed fabric had moderate to good washfastness. The synthesized reactive dyes gave better washfastness than the two direct dyes used in this study (Figure 33) and had comparable washfastness to the commercial reactive dyes. Dyes **44** and **45** were chosen because their structures are based on twisted benzidines containing J-acid and H-acid and are similar to the synthesized dyes.

Most of the observed staining was on cotton in the multifiber fabric, and there was little staining of wool and nylon. In general, staining on cotton by dyes derived from twisted benzidines was less than staining observed from untwisted counterparts.

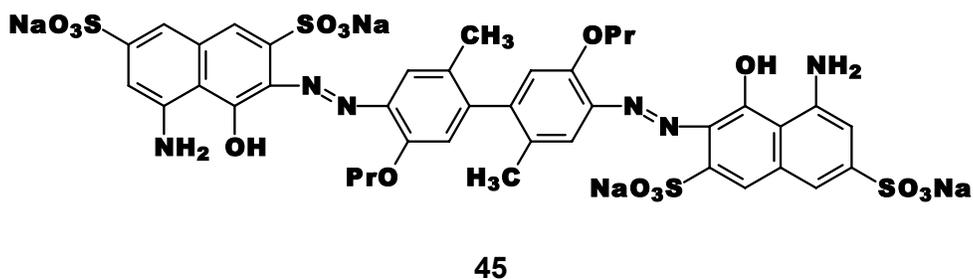
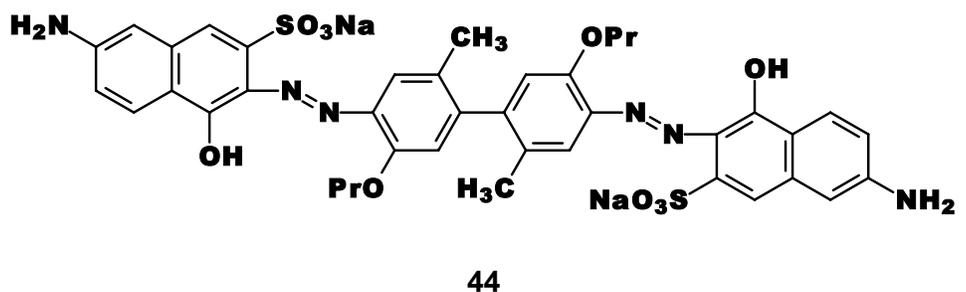
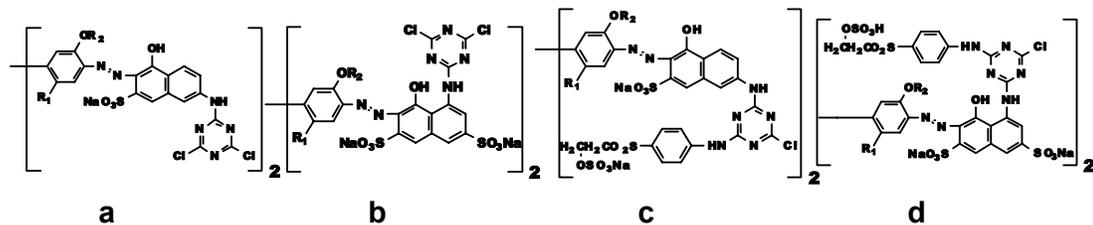


Figure 33. Structures of direct dyes used in washfastness studies.

Table 17. The data from washfastness testing of dyes 1-20.

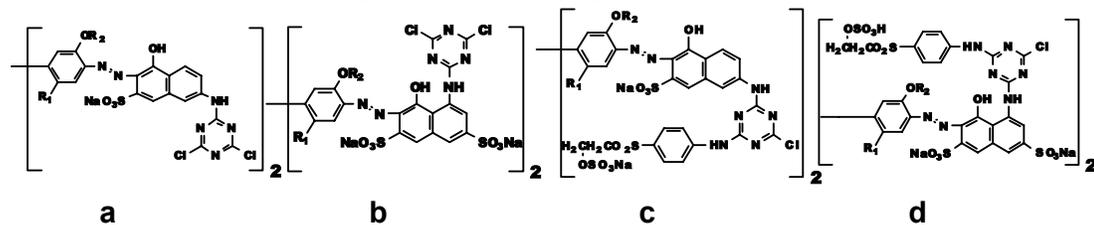


Group	Dye	R ₁	R ₂	Color change	Staining		
					Cotton	Wool	Nylon
a	1	Me	Pr	2.5	2.5	4	2.5
	2	H	Pr	4	3	4.5	3.5
	3	Me	Me	3	3	4.5	3.5
	4	H	Me	4.5	2.5	4.5	4.5
	5	Me	Et	3	3	4	3
b	6	Me	Pr	3.5	4.5	3.5	5
	7	H	Pr	4.5	4	4.5	5
	8	Me	Me	4	4.5	4.5	5
	9	H	Me	3.5	4	4.5	5
	10	Me	Et	3	4.5	4.5	5
c	11	Me	Pr	4.5	4	4.5	4.5
	12	H	Pr	4.5	3	5	4
	13	Me	Me	4.5	3.5	4.5	4.5
	14	H	Me	4.5	3	4.5	4.5
	15	Me	Et	3	4.5	4.5	4.5
d	16	Me	Pr	5	4	4.5	5
	17	H	Pr	3.5	3.5	4.5	4.5
	18	Me	Me	4	4.5	4.5	5
	19	H	Me	4.5	3	4.5	5
	20	Me	Et	4	4	4.5	5
Dye 44				2	1.5	3.5	2
Dye 45				1.5	4	4.5	4.5
Procion Red MX-8B				4	4	4	4.5
C.I.Reactive Red 198				3	4	4.5	4.5

5.2 Lightfastness Studies

The data from lightfastness studies are shown in Table 18. After a 20-hour exposure, dyed cotton fabrics had lightfastness ratings of 1-1.5. Dye penetration might be the reason for such poor colorfastness to light. This suggests that most of the dyes form covalent bonds at or near the fiber surface with little penetration. In related studies, Bae [115] reported the lightfastness properties of direct dyes based on twisted and untwisted benzidine. In his studies, dyes based on untwisted benzidines exhibited better colorfastness to light than the twisted counterparts. The results from group **b** showed that lightfastness of dyes from untwisted benzidines was minimally better than their twisted counterparts, but still unsatisfactory. Dyes **7** and **9** gave a lightfastness rating of 1.5 while their counterparts, dyes **6** and **8**, gave a lightfastness rating of 1.

Table 18. The data from lightfastness testing of dyes 1-20.

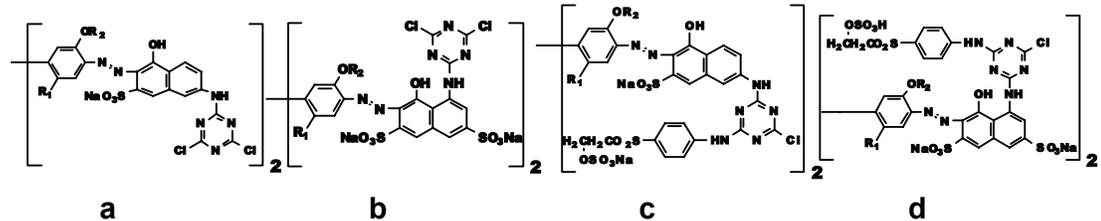


Group	Dye	R ₁	R ₂	Color Change
a	1	Me	Pr	1
	2	H	Pr	1
	3	Me	Me	1
	4	H	Me	1
	5	Me	Et	1
b	6	Me	Pr	1
	7	H	Pr	1.5
	8	Me	Me	1
	9	H	Me	1.5
	10	Me	Et	1
c	11	Me	Pr	1
	12	H	Pr	1
	13	Me	Me	1
	14	H	Me	1
	15	Me	Et	1
d	16	Me	Pr	1
	17	H	Pr	1
	18	Me	Me	1
	19	H	Me	1
	20	Me	Et	1
Dye 44				1
Dye 45				1
Procion Red MX-8B				3
C.I.Reactive Red 198				2

5.3 Crockfastness Studies

The data from crockfastness studies are shown in Table 19. In the dry crockfastness test, reactive dyes based on twisted benzidines in groups **a** and **b** had lower crockfastness than their planar counterparts. On the other hand, reactive dyes based on twisted benzidines in groups **c** and **d** had better crockfastness than their planar counterparts. Similar results were obtained for dyes in groups **a-d** in the wet crockfastness test when comparing dyes based on twisted and untwisted benzidines. However, the crockfastness ratings were lower in the wet crockfastness test. The staining was most likely from the hydrolyzed form on the fiber surface. The hydrolyzed dyes attach to the cotton surface by physical adsorption, which is the case for direct dyes. Direct dyes **44** and **45** have a good crockfastness rating in the dry test but the dyes were rubbed off in the wet test. The synthesized reactive dyes in groups **a** and **b** had crockfastness rating comparable to Procion Red MX-8B. Similarly, the synthesized reactive dyes in groups **c** and **d** had crockfastness rating comparable to C.I. Reactive Red 198.

Table 19. The data from crockfastness testing of dyes 1-20.



Group	Dye	R ₁	R ₂	Dry Test	Wet Test
a	1	Me	Pr	3	2.5
	2	H	Pr	5	3.5
	3	Me	Me	3	2.5
	4	H	Me	4.5	3
	5	Me	Et	5	3.5
b	6	Me	Pr	3.5	3
	7	H	Pr	4	4
	8	Me	Me	5	3.5
	9	H	Me	4.5	4.5
	10	Me	Et	5	4.5
c	11	Me	Pr	5	3.5
	12	H	Pr	4.5	3.5
	13	Me	Me	5	3.5
	14	H	Me	4	4
	15	Me	Et	4.5	3
d	16	Me	Pr	4.5	3
	17	H	Pr	4.5	2.5
	18	Me	Me	4.5	3.5
	19	H	Me	3.5	3
	20	Me	Et	5	3
Dye 44				4.5	2.5
Dye 45				5	3.5
Procion Red MX-8B				5	3.5
C.I.Reactive Red 198				5	3.5

IV. CONCLUSIONS

With the goal of designing reactive dyes that not only provide good fixation on cotton but also relatively low substantivity in the hydrolyzed form, reactive dyes based on twisted benzidines were synthesized. The benzidines employed were non-genotoxic alternatives to benzidine itself and had Me groups in the 2,2' position of the biphenyl moiety. The principal benzidine was 2,2'-dimethyl-5,5'-dipropoxybenzidine and the dyes prepared had either bis-DCT or bis-(MCT/SES) reactive groups and naphthalene-based couplers.

The extinction coefficient for these new reactive dyes was in the range of 16,000-30,000 $\text{l mol}^{-1}\text{cm}^{-1}$. Most of the E_{max} values were comparable to those of commercial dyes used in this study. Dyes from untwisted benzidines absorbed light at a lower wavelength than their twisted counterparts, and dyes from untwisted benzidines were bluer than their twisted counterparts. The twisted structure interrupted the extended conjugated system and caused the dyes to absorb light at shorter wavelengths.

The new reactive dyes based on J-acid did not exhaust or level very well. Dyes containing J-acid had low water solubility which caused a difficulty for level dyeing in some cases. Dyes containing H-acid had better water solubility but they did not give high exhaustion levels. Therefore, bis-DCT bifunctional reactive dyes were applied on cotton fabrics by pad-batch, and bis-(MCT/SES) tetrafunctional reactive dyes were applied by the pad-dry-cure method. Following dye fixation, there were small amounts of dye in the wash off liquors.

Dyed cotton had moderate to good washfastness because the reactive groups formed covalent bonds with the cellulosic fibers. Compared with the direct dyes of similar structures, reactive dyes had superior washfastness. However, the lightfastness of the reactive dyes on cotton fabrics was poor. In this case, dye penetration was less than optimum, and dye on or near the surface was easily degraded by light.

Crockfastness assessments were used to assess the wash off properties of dyed fabrics. It was expected that any hydrolyzed dye on the fabric surfaces would lower crockfastness. For bis-DCT bifunctional reactive dyes, dyes from untwisted benzidines gave less staining than twisted counterparts. In contrast, dyes from twisted benzidines gave less staining than the planar counterparts in the case of bis-(MCT/SES) tetrafunctional reactive dyes. These results were comparable to those from structurally related commercial reactive dyes.

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