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Review in Azo Compounds and its Biological Activity

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Azo Compound

Introduction

Organic chemical compound in which the azo group (—N=N—) is part of the molecular structure. The atomic groups attached to the nitrogen atoms may be of any organic class, but the commercially important azo compounds, those that make up more than half the commercial dyes, have the benzene group or its derivatives as the attached groups (aromatic azo compounds).

Most aromatic azo compounds are prepared by the reaction of a diazonium salt with an organic substance that contains easily replaced hydrogen atoms. The synthesis of azobenzene from nitrobenzene by treatment with certain oxygen-removing reagents is an example of an alternate method useful for symmetrical azo compounds.

Azo compounds in which the attached groups are aliphatic organic groups are usually made by dehydrogenation of the corresponding hydrazo compounds (containing the group —HN—NH—) made from hydrazine, N_2H_4 . An important reaction of the aliphatic azo compounds is their decomposition by heat into nitrogen and free radicals; the latter often are used to initiate polymerization reactions.

Azo compounds are used to make a number of azo dyes and pigments which are used in a variety of industries. These commercial dyes have the benzene group or its derivatives attached instead of the usual nitrogen. The attachment of the benzene groups gives the azo compound an aroma and is referred to as the aromatic azo compound.

Mechanism of Azo Coupling

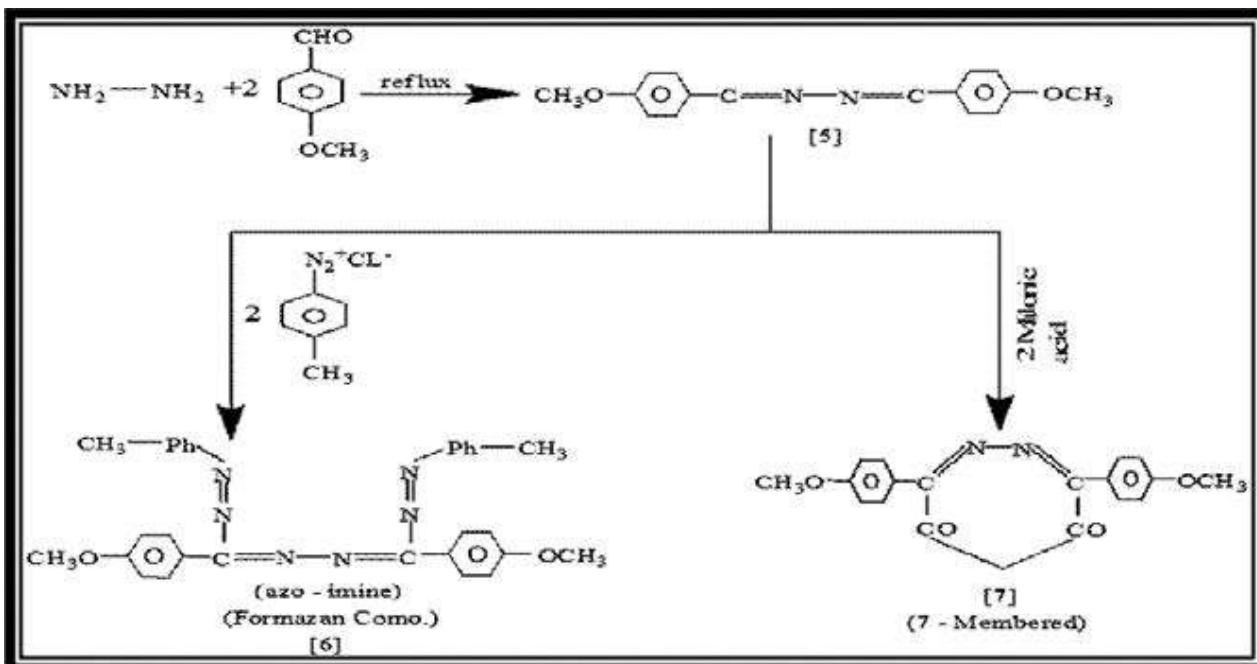


Figure (3): Synthesis of Azo compounds by coupling reaction

synthesized various membered rings containing Azo group

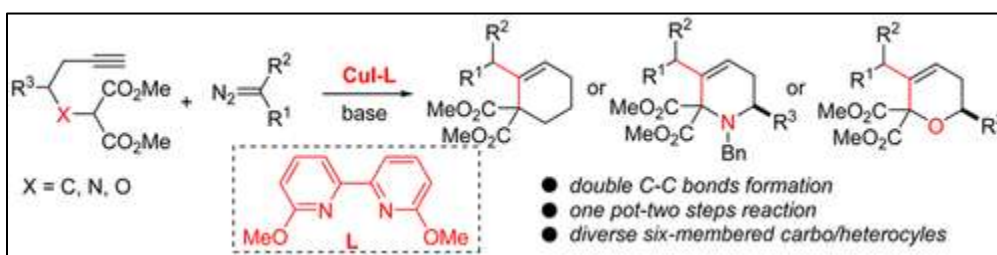


Figure (4): Synthesis of six member ring

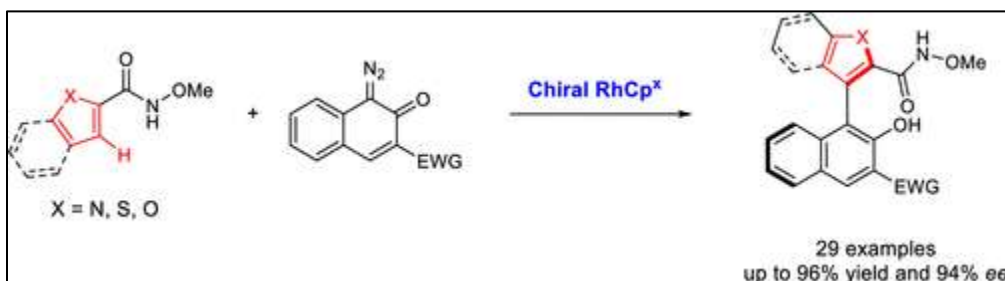


Figure (5): Synthesis of five member ring

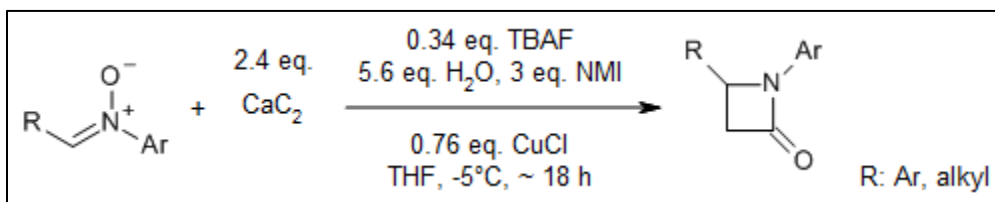


Figure (6): Synthesis of four member ring

Azo dyes

Abstract

Azo dyes, which are substances with two nitrogen atoms linked by a double bond, are frequently found as the primary scaffold in a vast library of chemical species that display promising commercial and biological features. Due to the azo function's wide range of potential applications, there has been a sharp increase in the creation of new azo dyes, the introduction of sophisticated synthetic methods for their production, the investigation of their many properties, and the search for potential new uses for this class of molecules. Due to the significant contamination that textile industry effluents cause to water resources, they have become a major source of worry in the modern world. Because of its chemical makeup, which includes aromatic rings, azoic linkages, and amino groups, azo dyes are one of the more harmful families of synthetic dyes that are emitted in effluents from textile manufacturers. In this review essay, we discuss how dyes are used to color materials, particularly clothes. These dyes are colored by chromophores, which are functional groups that absorb light. Azolo, nitro, and carbonyl groups are the most prevalent chromophores. Another crucial component of dyes is auxochromes, which are functional groups that intensify color. Hydroxyl, amino, sulfate, and carboxylate groups are the most typical chromophores. Nitrogen to nitrogen double bond serves as the chromophore in azo dyes. Diazonium salt is combined with a highly active aromatic system to produce these colors.

It is represent the largest production volume of dye chemistry today, and their relative importance may even increase in the future. They play a crucial role in the governance of the dye and printing market. These dyes are synthesized from a simple method of diazotization and coupling. Different routes and modifications are made to obtain the desired color properties, yield and particle size of the dye for improved dispersibility [1].

Azo dyes are the most used dyes and account for more than 60 % of total dyes [2, 3]. Approximately 70 % of all the dyes used in industry are azo dyes [4, 5]. These compounds are characterized by the functional group (-N=N-) uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals [6].

Azo dyes are the most important synthetic colorants which have been widely used in textile, printing, paper manufacturing, etc. [7].

As well as their harmful effects of azo dyes on humans and aquatic life, have aroused urgent calls for the treatment of effluents containing azo dyes to eliminate them or convert them into useful and safe products, [8, 9].

In addition, the distribution of dyes in water increased with the increase in the molecular weight of the azo dyes, probably caused by the increase in the molecular weight of the azo dyes in the form of increased azo bonds, resulting in a decrease in the rate degradation of azo dyes.

Synthesis of azo dyes

Most azo dyes are synthesized by diazotization of an aromatic primary amine, followed by coupling with one or more electron-rich nucleophiles such as amino and hydroxy [2]. There are other methods of synthesis of azo dyes among these are [10, 11]:

reduction of nitroaromatic derivatives in alkaline medium, reduction of nitroso compounds by AlLiH_4 , oxidation of primary amines by permanganate potassium or lead tetraacetate, condensation of hydrazines and quinones, condensation of primary amines with nitroso derivatives, etc.

The azo group may be bonded to benzene rings, naphthalenes, aromatic heterocycles or to enolizable aliphatic groups [12]. These are essential to give the color of the dye, with their shades of different intensities.

In general, the chemical structure of an azo dye is represented by a backbone, the auxochrome groups, the chromophoric groups and the solubilizing groups according to Figure 1, [13,14,15]. The color of the azo dyes is determined by the azo bonds and their associated chromophores and auxochromes, [2, 16].

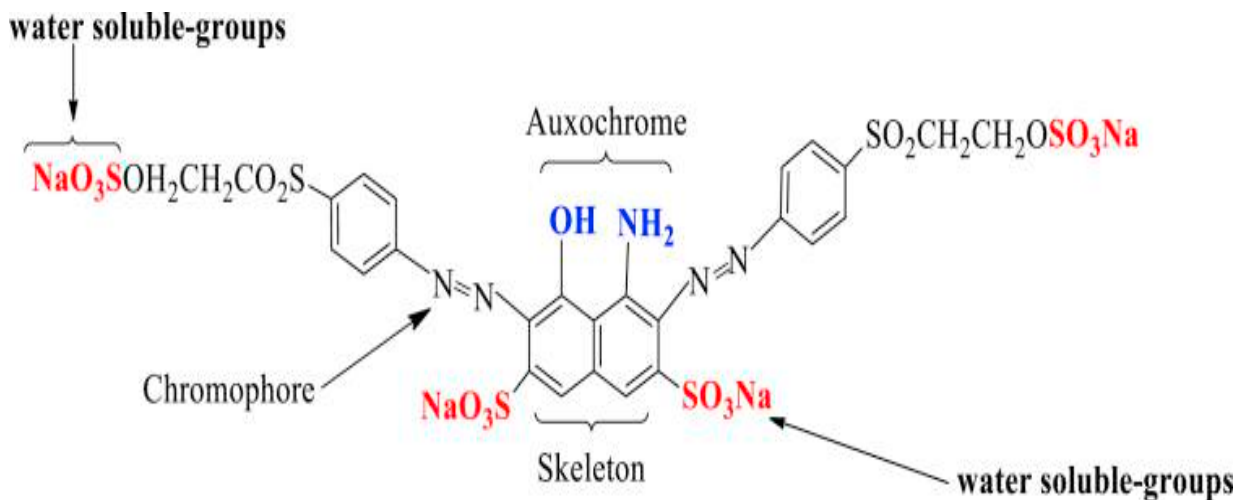


Figure 1

Structure of the azo reactive dye.

The azo dyes are generally characterized by a chemical groups capable of forming covalent bonds with the textile substrates. The energy required for the rupture of these bonds is similar to that

used to degrade the support itself. The objective of this review is to describe a chemical classification of azo dyes and their structural characteristics. It is presented by synthesis of some azo dyes according to the most common method, which comprises the diazotization of a primary aromatic amine and the coupling of the diazonium salt obtained with a generally aromatic substrate on the one hand and the synthesis of symmetrical azo dyes and asymmetric (1), the synthesis of azo dyes contains chemical groups hydrazone (2), the synthesis of azo dyes contains chemical groups chromene (3), the synthesis of azo dyes derived from 2-aminothiophene and 2-aminothiazoles (4) on the other hand. This review also presents the concept of conjugation of azo dyes to polymers and finally the use of the Gewald reaction in the synthesis of azo dyes.

diazotization–diazo coupling

The protonation of nitrous acid is often used to perform the diazotization and diazo coupling reactions under extremely acidic conditions, while the azo coupling reaction is typically carried out at low temperature in the presence of nucleophilic coupling components. A nucleophilic substrate becomes more reactive as its basicity rises. (8). These traditional acid-base catalyzed processes work well for producing the desired azo-products in nearly quantitative amounts. However, the primary drawback of such synthetic processes is that they are incompatible with the environment. The ecosystem is permanently harmed by the acidic and basic waste products from industry and laboratories, which also upset the ecological balance(9). Solid acids have received a lot of attention in recent years due to their use in organic synthesis since they not only make purification procedures simpler but also help to avoid the environmental release of reaction wastes. Recently, several solid acids have been used to create azo hues.

Despite the fact that good product yields are frequently achieved, the diazotization and diazo coupling reactions are difficult due to the presence of numerous competing reactions. (10). For instance, in aqueous media, reaction temperatures above 10 °C typically increase the synthesis of phenol and azophenols are produced when the phenol reacts with unreacted diazonium salts.. The popularity of azo colorants is attributed to how easily they are made by diazotization and azo coupling. By varying the diazo and coupling components, virtually endless possibilities are described. In comparison to other commercial dyes, phenolic azo dyes have a variety of benefits, such as a wide color spectrum, good color fastness, and the capacity to absorb light. These groups are also known as matrix resins or binding resins due to their wide range of uses, accessibility, and extraordinary properties including strong thermal binding stability, great acid resistance, high fire retardancy, etc. Additionally, it has been asserted that naphthols are used as acknowledged intermediates in the production of colors. They can also be made at a low cost because the starting materials are readily available, inexpensive chemicals, the majority of the chemistry is performed at or below room temperature, and water is employed as a solvent in every reaction. (11).

Diazonium Salts

Given their adaptability and the abundance of the necessary starting ingredients, diazo compounds and diazonium salts are crucial intermediates in organic chemistry. If not properly regulated, these nitrogen-rich substances could leak nitrogen gas(12). In addition to the heat released, thermal runaways are harmful because a significant amount of gas is evolved, which increases pressure. Utilizing flow methods to prepare and consume them in-place is one way to manage this. Only a minimal quantity

of these dangerous intermediates are present at any given time, and the temperature is controlled very well as a result(13). Using flow methods, dangerous substances can be produced and consumed in-situ, such. Since safer reaction performance is made possible by this and improved temperature control, numerous reactions involving diazonium salts and diazo compounds are known to occur under continuous flow circumstances. An amine, typically an aromatic aniline, is treated with a nitrite source to produce diazonium salts in most cases. When those are present, they can then carry out a variety of additional reactions in which the diazonium group is substituted either through a nucleophilic substitution, a radical mechanism, or by a nucleophile intermediate(14).

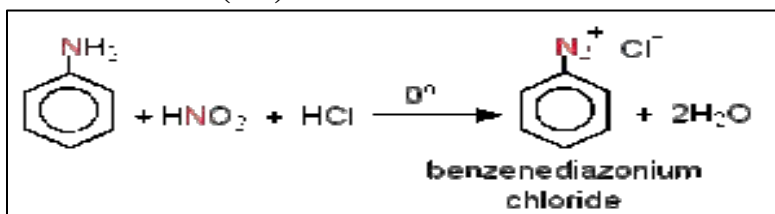


Figure (2): Synthesis of Diazonium salt

Food azo dyes

Azo dyes are the largest group of artificial food dyes, including 70% of the organic dyes generated in the world. Moreover, the commonest azo dyes in the food industry have been considered to be the yellow dyes (sunset yellow and tartrazine) and red dyes (azorubine, ponceau, amaranth, and allura red).

In a majority of cases, they are utilized to color jams, candies, confectionery, ice cream, jellies, alcoholic beverages, soft drinks, and so on. Despite their widespread utilization, some negative impacts on human health have been specified in the output of multiple investigations . So there is enough information stating that the decay of azo dyes gives off products like aromatic amines that have been considered poisonous and carcinogenic. Current investigations have confirmed interactions between human serum albumin and azo dyes and hemoglobin . With

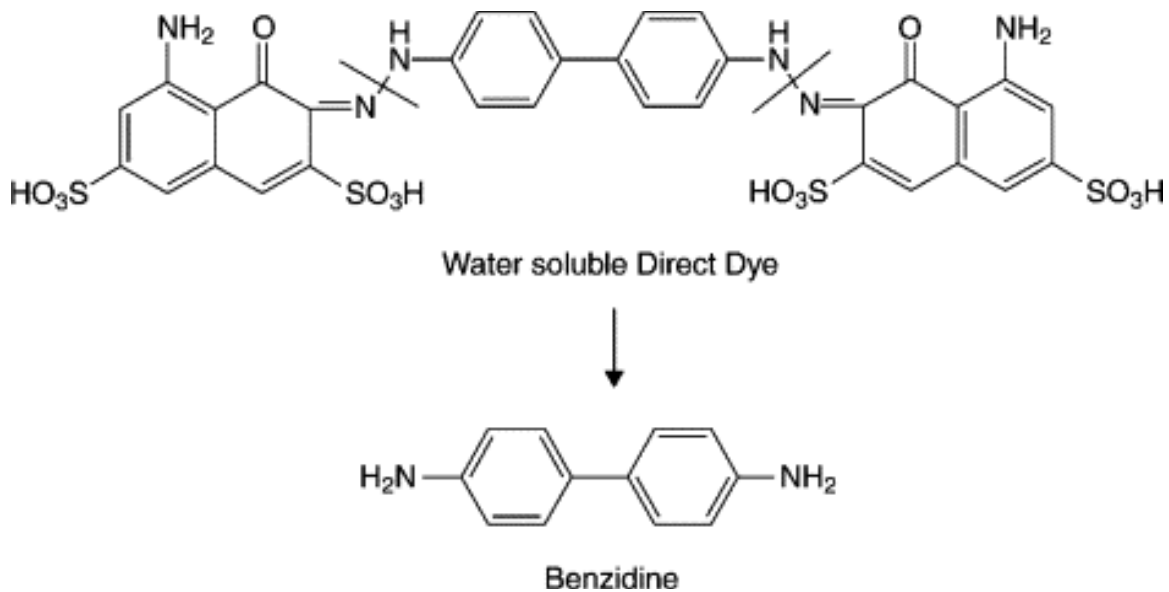
regard to some investigations, synthetic food colorants could result in superexcitation and hyperactivity in children, particularly in the case of excessive application. Moreover, they could result in asthmatic and allergic diseases. Consequently, controlling the content of azo dyes in foodstuffs is of high importance.

Genotoxicity of different dye classes

Azo dyes are by far the most important class of dye, accounting for over 50% of world annual production. Not surprisingly, toxicity of azo dyes has been studied extensively. As early as 1895 increased rates in bladder cancer were observed in workers involved in dye manufacturing. Since that time, many studies have been conducted showing the toxic potential of azo dyes. A broader understanding of the problem can be found in the works of Brown and DeVito⁴⁰ as well as Levine.⁴¹ The carcinogen may be the dye itself, or it may be a metabolite of the dye. For water-insoluble, but solvent-soluble dyes, such as solvent dyes and disperse dyes, the dye is normally the carcinogen. For water-soluble dyes, it is a metabolite of the dye which is the carcinogen. Water-soluble azo dyes based on H-acid, J-acid and Gamma-acid represent a very important class of dyes for dyeing hydrophilic textiles such as cotton and viscose rayon. Cotton is the world's most widely used textile fabric so the tonnages of these water-soluble dyes are extremely large. The dyes are conveniently divided into two types:

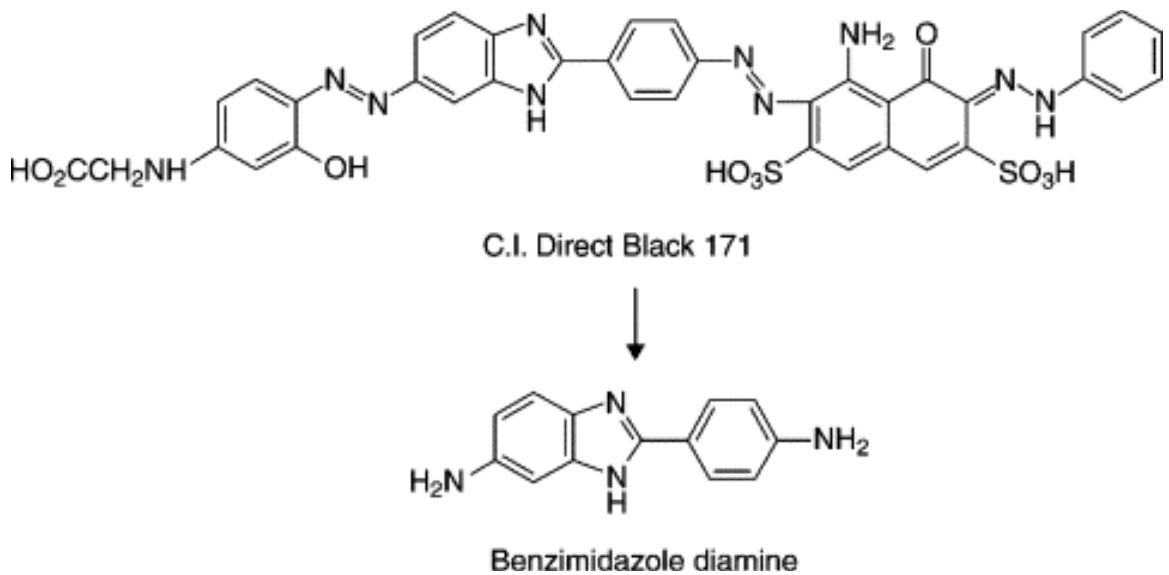
- 1-Those which are capable of generating a carcinogenic metabolite.
- 2-Those that are not.

The workers who developed bladder cancer from handling dyes based on benzidine or 2-naphthylamine got the disease not from the dyes themselves, but from the benzidine and 2-naphthylamine metabolites. Figure 16.4 shows a typical water-soluble dye that can generate carcinogenic benzidine metabolite upon reduction in the animal body.



16.4. Typical water-soluble azo dye that generates carcinogenic benzidine.¹⁶

There are two main methods to circumvent the carcinogenicity of such dyes. The first is to use non-carcinogenic analogues of the amines in question, such as benzidine or its derivatives. For example, in Fig. 16.5, C.I. Direct Black 171 uses a non-carcinogenic aromatic benzimidazol diamine instead of benzidine.

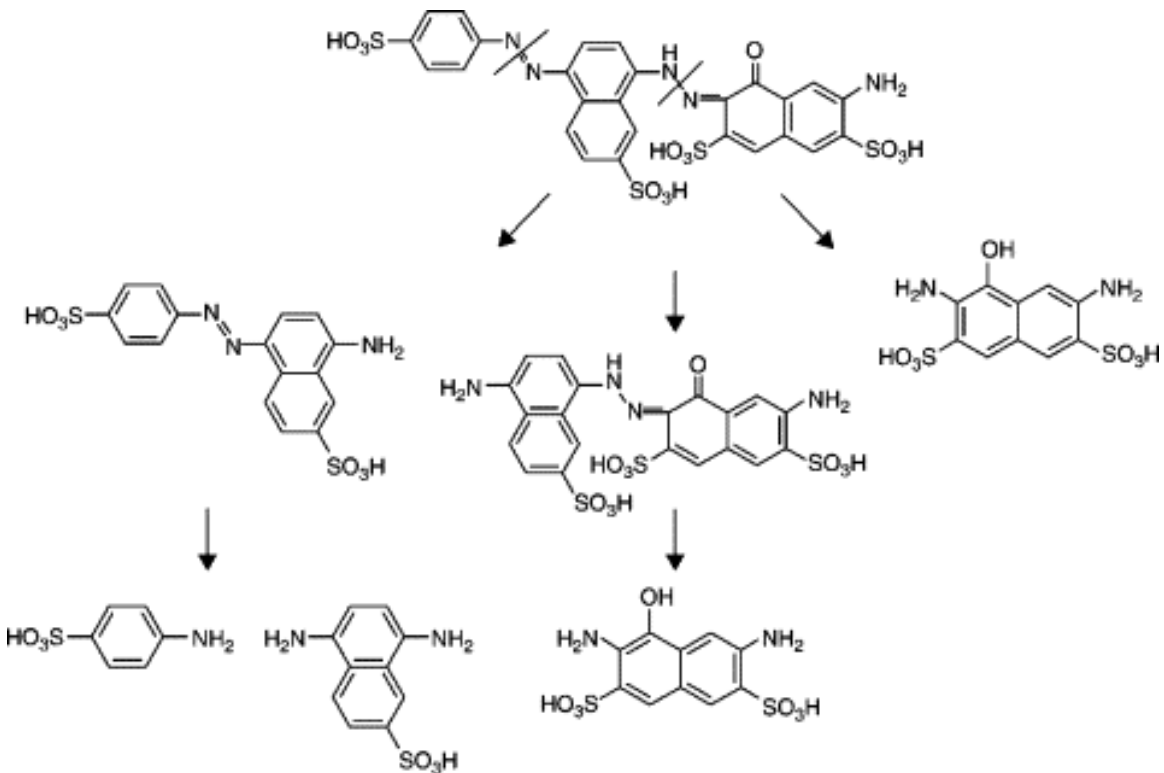


16.5. Typical water-soluble dye that generates non-carcinogenic aromatic

benzimidazole diamine.¹⁶

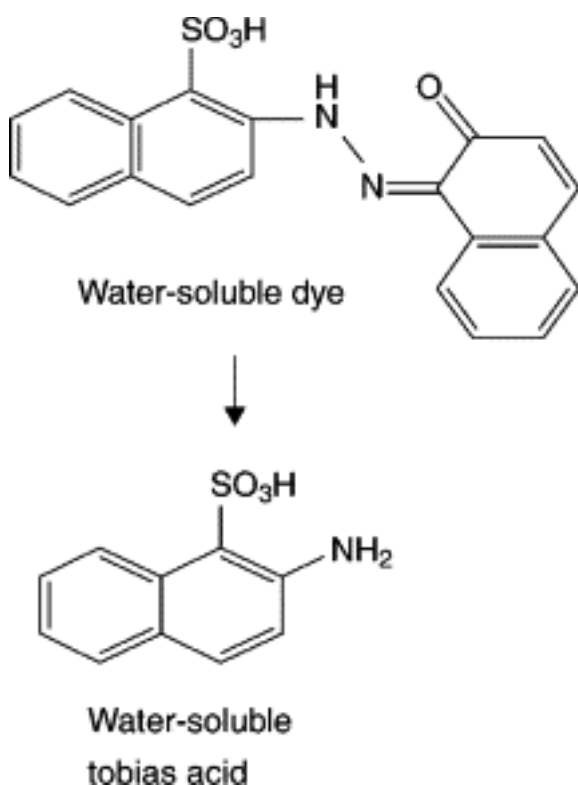
Freeman and Rinde observed that when the C.I. Direct Black 38 based on benzidine was fed to Rhesus monkeys, benzidine was detected in their urine.³⁷

The second way to avoid carcinogenicity is to ensure that all possible metabolites of the dye are water soluble. An excellent example of this principle is shown in Fig. 16.6, where the degradation of C.I. Food Black 2, a dye used in black inks for ink-jet printers, gives metabolites of the dye which contain at least one water-solubilising sulphonic acid group. This ensures that the dye itself, plus any of its metabolites, are water-soluble.



16.6. Probable degradation products of C.I. Food Black 2.¹⁶

Further examples of water-soluble dyes that generate water-soluble metabolites and are non-carcinogenic are given by Gregory.³⁴ The power of the water-solubilising sulphonic acid group to detoxify dyes and intermediates is beautifully demonstrated by the dye in Fig. 16.7. This dye is non-carcinogenic. Upon reductive cleavage, it would produce, as one metabolite, 2-naphthylamine-1-sulphonic acid (Tobias acid). As seen earlier, 2-naphthylamine is a potent human bladder carcinogen. However, the presence of just one sulphonic acid group renders it harmless. Indeed, the sulphonic acid group is an excellent detoxifying group both for dyes and their intermediates.³⁴



16.7. Use of a water-solubilising sulphonic acid group in reductive cleavage

of dyes to give a non-carcinogenic metabolite.¹⁶

The position of a genotoxic group within a dye also determines whether or not the dye expresses genotoxicity. Care has to be exercised when using isomers of carcinogens. Thus, 1-naphthylamine is non-

carcinogenic. However, during its synthesis, some of the isomeric 2-naphthylamine, a known carcinogen, is produced. This carcinogenic impurity must be removed to a level below which it is not a problem. For dyes that use 1-naphthylamine, every batch must be checked to ensure that the level of 2-naphthylamine is below the recommended level.¹⁶

In Germany, bladder cancer is recognised as an occupational disease for textile workers.⁴⁶ Some dyes have the potential to release an aromatic amine that is known to be a rodent carcinogen upon metabolism in an organism and this has prompted some authorities to conclude that such dyes should be considered to be carcinogenic.⁴⁷ This knowledge is the reason for the recommendation of the German MAK Kommission to handle the dyes in the same way as the amines which can be released under reducing conditions. Subsequently, the German, Dutch and Austrian authorities prohibited the use of such dyes in some consumer articles. Such dyes may not be used for textile, leather or other articles which have the potential for coming into direct and prolonged contact with human skin, e.g. clothing, bedding, bracelets, baby napkins, towels, wigs, etc. The ban, which applies across the EU, also covers the import and marketing of the above-mentioned articles dyed with these dyes. Table 16.4 lists the amines that are classified as carcinogenic and formed through cleavage of azo bonds of the azo dyes.

Table 16.4. Carcinogenic aromatic amines defined by German MAK Kommission⁴⁸

S no.	C.I. name	Category of carcinogen*
1	4-Aminobiphenyl	1
2	Benzidine	1
3	4-Chloro-o-toluidine	1
4	2-Naphthylamine	1
5	4-Aminoazobenzene	2
6	o-Aminoazotoluene	2
7	6-Methoxy-m-toluidine	-

S no.	C.I. name	Category of carcinogen*
8	o-Anisidine	2
9	p-Chloroaniline	2
10	5-Nitro-o-toluidine	3
11	4,4'-Diaminodiphenylmethane	2
12	3,3'-Dicholobenzidine	2
13	3,3'-Dimethoxybenzidine	2
14	3,3' Dimethylbenzedine	2
15	4,4'-Methylenedi-o-toluidine	2
16	3,3'-Dichlorobenzidine	2
17	4,4'-Methylene-bis-[2-chloroaniline]	2
18	4,4'-Oxydianiline	2
19	4,4'-Thiodianiline	2
20	o-Toluidine	2
21	4-Methyl-m-phenylenediamine	2
22	2,4,5-Trimethylaniline	2

Classification azo dyes according to azo grouping number

The azo dyes are distributed according to the number of azo linkages which is in the same molecule of the dye such as monoazo, disazo, trisazo, polyazo and azoic. In the Color Index (CI) system, azo dyes are supplied with numbers ranging from 11,000 to 39,999 in correspondence with the chemical structure (Table 1). The color index number, developed by the society of dyers and colorists, is used for dye classification [17].

Table 1

Classification of azo dyes in Colour Index [2, 18].

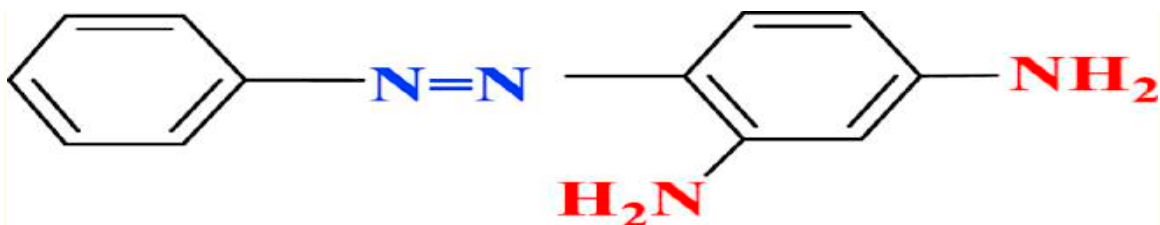
Chemical class	CI no
Monoazo	11000–19999
Disazo	20000–29999
Trisazo	30000–34999
Polyazo	35000–36999
Azoic	37000–39999

1. Monoazo

The monoazo dyes can be schematically represented by the following formula: $Z-N=N-W$ [19].

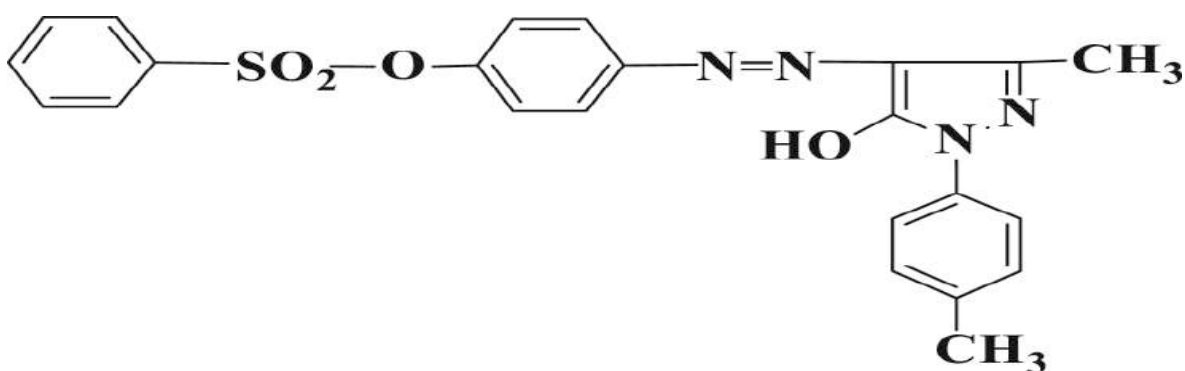
2.1.1. *Z and W the benzene or heterocyclic derivatives*

Figure 2 gives an ancient analog of this family which dyes cotton [20], it is characterized by their orange color.



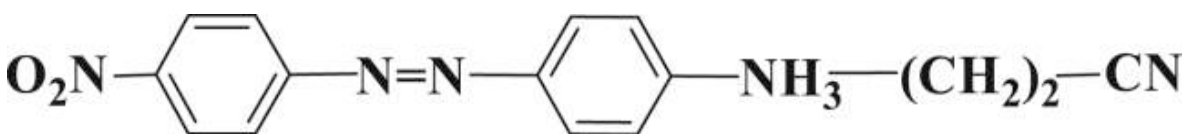
[Figure 2](#)
Structure of chrysoidine.

Other homologs ([Figure 3](#)), were characterized by better light fastness and washing and used for coloring cellulosic fibers.



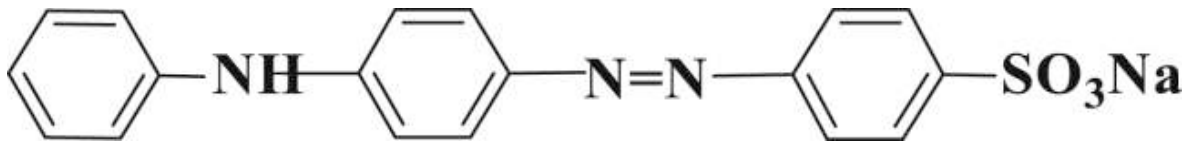
[Figure 3](#)
Yellow basic dye.

Among the dispersed mono azo dyes are the orange dye ([Figure 4](#)) which is used for dyeing cellulose acetate, polyamides, polyesters, and polyacrylonitrile.

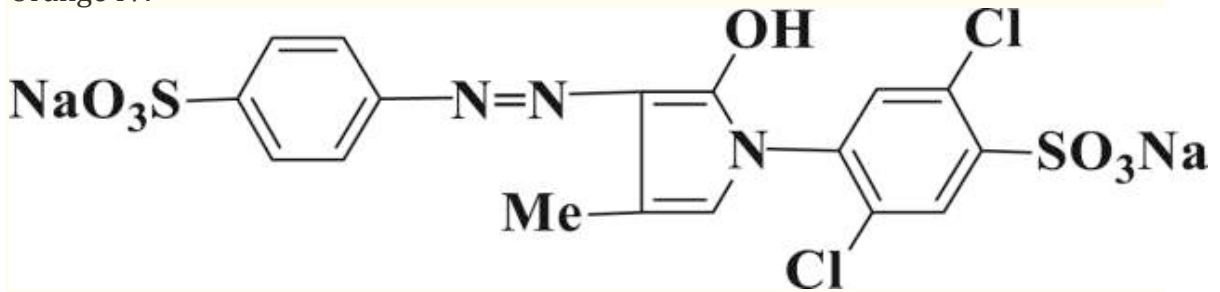


[Figure 4](#)
Structure of the orange dye.

Among the mono azoic acid dyes, mention may be made of orange IV ([Figure 5](#)) and the yellow dye ([Figure 6](#)), which is used for dyeing wool and nylon.



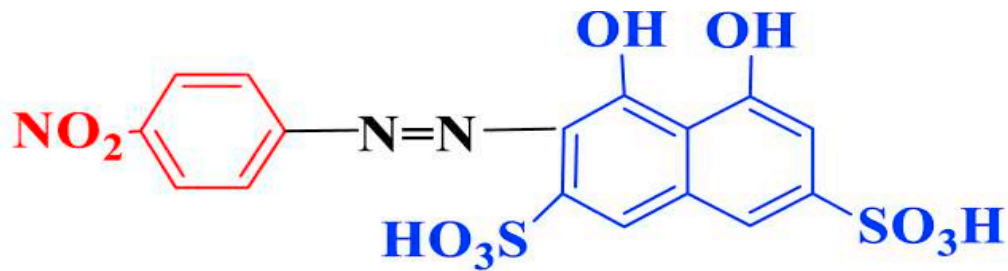
[Figure 5](#)
Orange IV.



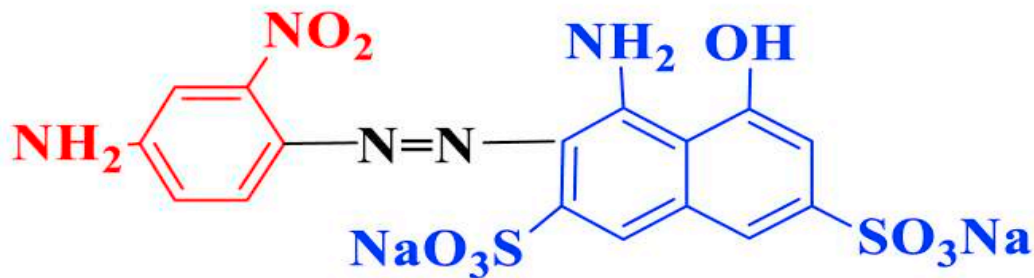
[Figure 6](#)
Structure of the yellow dye.

1.2. *Z* benzene and *W* naphthenic

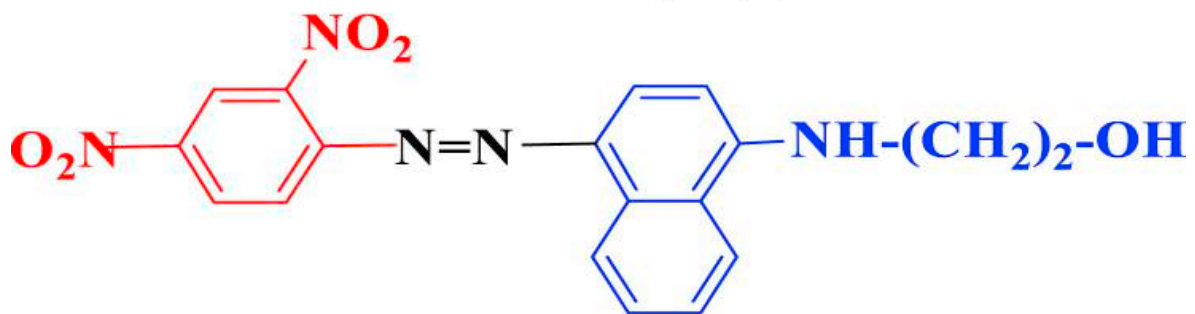
[Figure 7](#) illustrates some analogs of this group of dyes, such as the red dye with mordant (a), as well as the blue dye (b) for wool derived from H acid and blue dye (c).



Mordant Red (a)



Blue dye (b)



Blue dye (c)

Figure 7

Illustrates the red dye with their mordant (a), the blue dye (b) and the blue dye (c).
 1.3. Z and W are naphthalene

They are widely used for dyeing polyamide substrates in black and gives a chromium complex, an example of this family is the the textile dye Mordant Black 17, [CI No.15705], a monosulfonated

aromatic azo compound widely used in a large scale by several textile and dyeing industries was obtained from Sigma-Aldrich, USA [21, 22], (Figure 8).

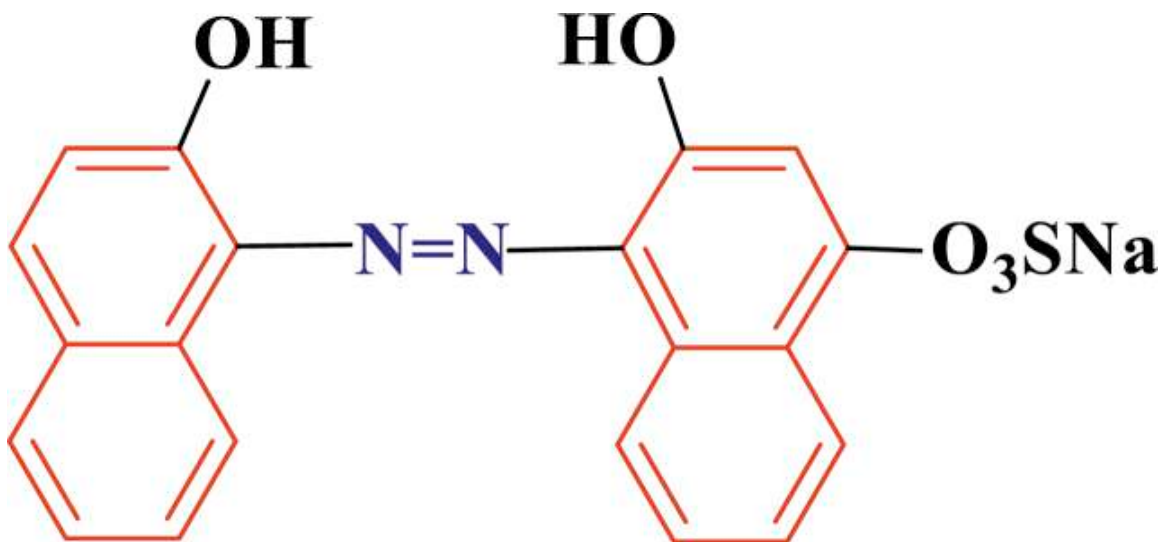


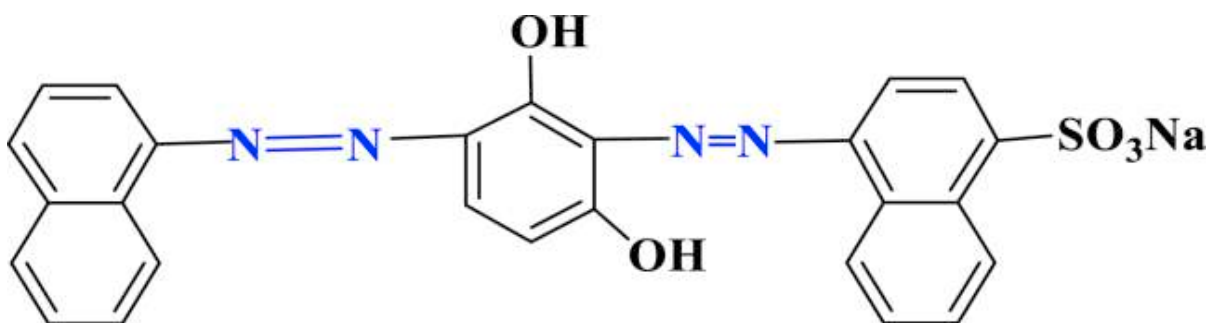
Figure 8
Mordant black 17.

2. Disazo

In general, the diazo dyes contain two groups $-N=N-$, they are obtained according to the following three methods [23].

2.1. Primary diazo

The synthesis of this type of dye was made by a coupling reaction of two moles of di azoic acid on the same coupling term. Globally, these dyes are derivatives of resorcinol and m-phenylenediamine, they are brown, green, matt blue and black. Figure 9 shows an example of a brown dye used to dye wool.



[Figure 9](#)

Brown dye structure.

2.2. Secondary diazoic « symmetrical »

Also, this type has a large number of direct dyes with respect to the small number of acid and mordant dyes. They are derived from a diamine which is diazotized twice and copulated with identical or different terms. [Figure 10](#) shows the structure of the blue direct dye contains benzidine function.



[Figure 10](#)

Structure blue direct dye.

Figure 11 shows an example of a synthesis of an asymmetric azo dye [24, 25].

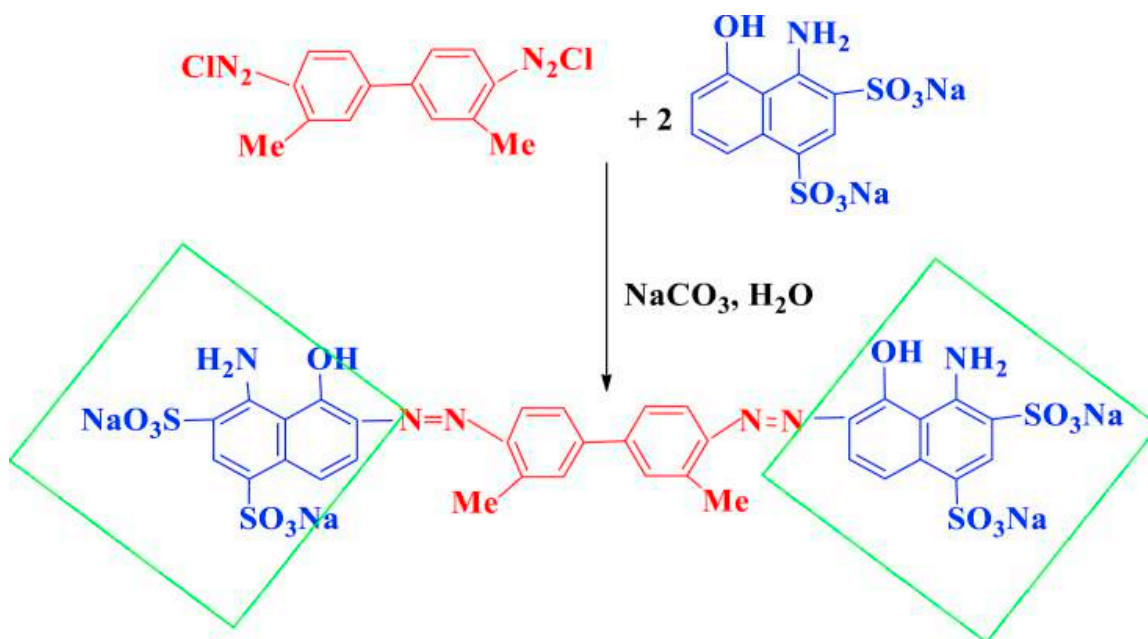


Figure 11

Exemple de synthèse du colorant asymétrique.

2.2.3. Secondary diazoic « asymmetrical »

According to the same author, this type of dye was synthesized by the coupling of an amino azoic acid with a phenolic coupler. Figure 12 shows an analogue of this type of dye [26].

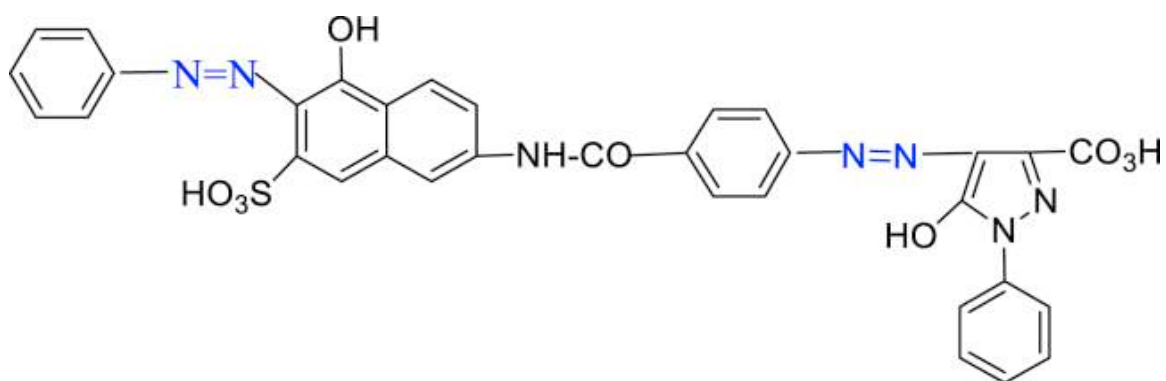


Figure 12

Structure of the orange direct dye.

3. Polyazo

Polyazo dyes are complex dyes characterized by the repetition of the azo group from three or more times in the same molecule. They are intended for dyeing leather, with dark shades: red, brown and dark black. The most common dye for this kind of dye is direct red (Figure 13), [26,27,28]. The latter can be synthesized by the phosgenate of the appropriate diazo dye. This can be achieved by diazotising 6-amino-3,4'-azodibenzenesulfonic acid following acid coupling of N-acetyl-. The acetyl group is hydrolysed before the phosgenation step.

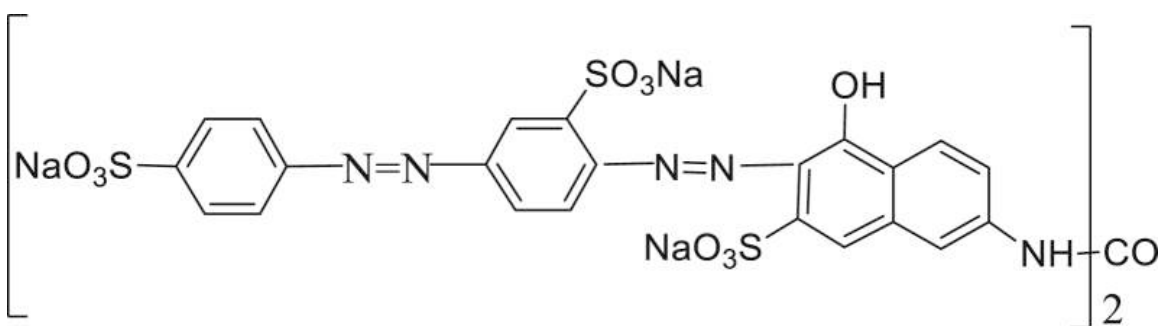


Figure 13

Structure of the direct red dye.

Classification of azo dyes according to reactive functional groupings

1. Mono and dichlorotriazine

A synthetic route of a homologue of mono chlorotriazine dyes is shown in Figure 14, [29].

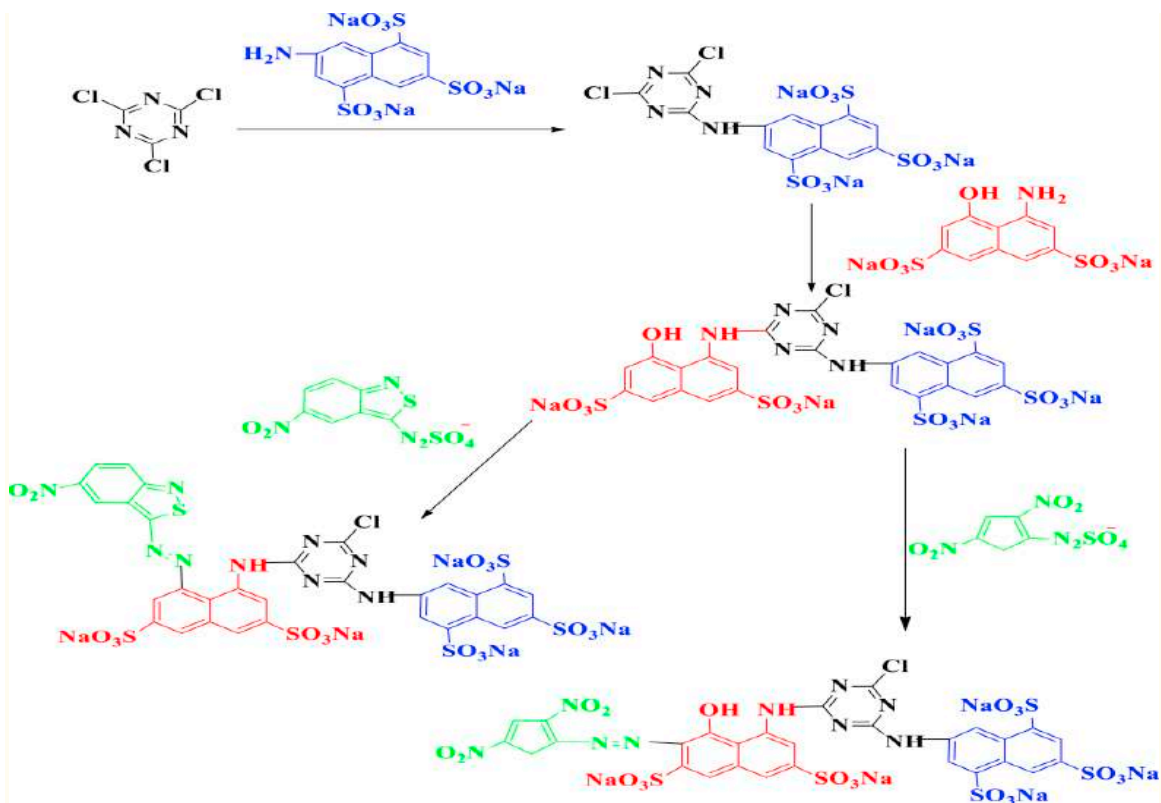


Figure 14
Synthesis route of an example of monochlorotriazine dyes.

Figure 15 shows the chemical structure of the monofunctional azo dye which carries the dichlorotriazine function [30, 31].

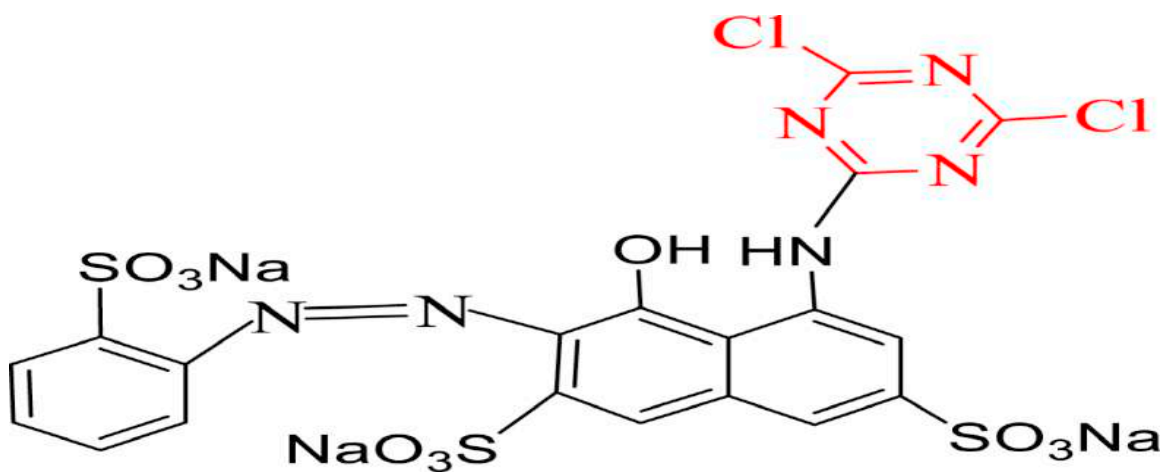


Figure 15
Mordant red procion M-2B.

These dyes have a good affinity for cellulose at a temperature of 20 °C–30 °C. The replacement of a single chlorine by the hydroxyl ion or the cellulosic ion leads to a remarkable decrease in the reactivity of the second chlorine. In an alkaline medium, the ionization of the hydroxyl group results in a relocation of the negative charge of the atoms of the triazine ring, while the chlorine atom is inactivated and the carbon which bonds to the chlorine becomes less electrophilic.

2. Mono-amino-chlorotriazine

It has the same chromophoric groups of dichloro triazine. It carries an active chlorine and the group NH_2 (Figure 16). These groups are less active with respect to dichloro triazine. The link $-\text{NH}-$ linking the chromophore and the reactive group have an influence on the dyeing properties and the solubility of the dye [32].

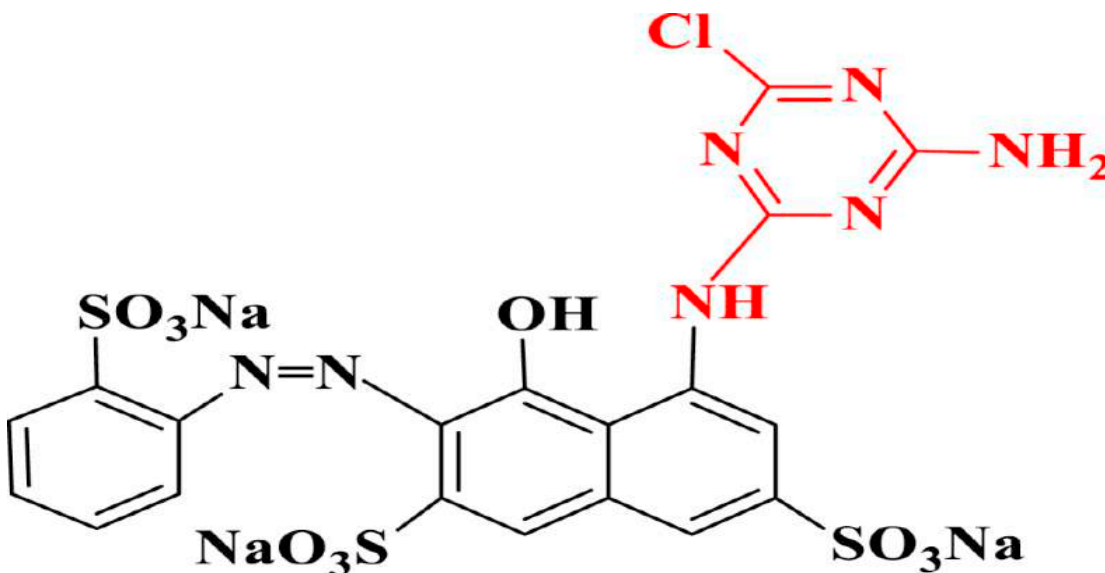


Figure 16

Structure of the Cibacron shiny red dye B.

The binding of mono and dichloro triazine is effected by a nucleophilic substitution mechanism due to the attracting electron

effect of the nitrogen atoms of the triazine nucleus [33, 34]. In an alkaline environment. The reaction of the hydrolysis was deactivated the carbon carries the atom of chlorine. The electronic doublets of the triazine nucleus have been delocalized by the negative charge of the hydroxyl ion, so the carbon enclosure becomes rich by electrons, (Figure 17).



Figure 17

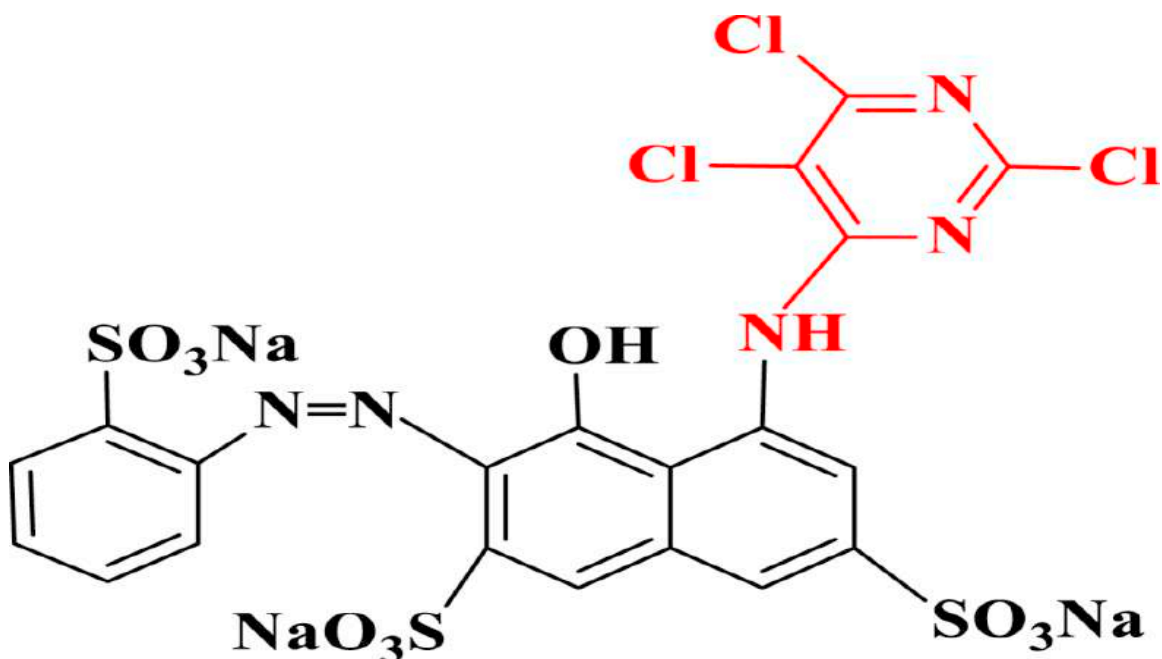
Mechanism of fixing and hydrolysis of the mono and dichloro triazine dye.

3. Pyrimidines

In general, include the di and tri-chloro pyrimidine derivatives, chlorfluoropyrimidine and fluoropyrimidine derivatives as follows:

3.1. Trichloro pyrimidine

The synthesis of dichloro pyrimidine was obtained, on the one hand, by the reaction of trichloro pyrimidine with an arylamine less reactive and more resistant to hydrolysis in acid and alkaline medium [32]. Trichloropyrimidine (Figure 18) was synthesized by a nucleophilic substitution of chlorine in tetrachloro pyrimidine by an arylamine. These types of dyestuffs require a more light temperature range which can reach boiling point, in order to have a good fixation on a cellulosic type textile material. This type of dye was formed by a bond with the textile material more resistant to hydrolysis.



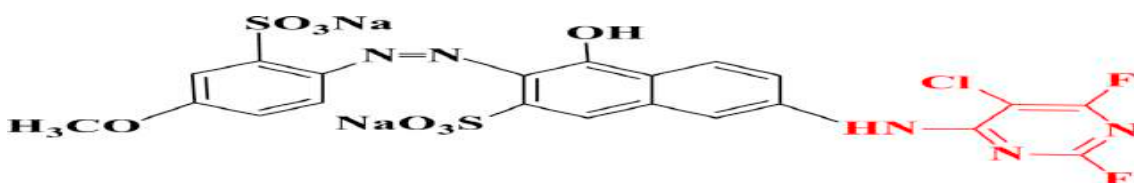
[Figure 18](#)

C.I.Reactive red 17.

3.3.2. Chlorofluoropyrimidine

The increase in the reactivity of this kind of dyes was made by the substitution of chlorines by fluorine. The bond formed with the textile fiber has been more stable in an acid medium, but in the presence of light, this bond becomes sensitive to oxidation by the peroxide compounds [32]. The ideal temperature for a good fixation of this type of dye is between 40 °C and 50 °C.

[Figure 19](#) gives an example of these dyes which have belonged to the range of commercial dyes of the Drimaren K or Levafix E-A type.



[Figure 19](#)

Dye type 5-chloro-2,4-difluoropyrimidine.

4. Dichloroquinoxaline

This type of dye has been characterized by high reactivity to dichloro pyrimidine dyes, dichloro triazine dyes, and difluoro pyrimidine dyes [32]. Under the effect of peroxides and in the presence of light and/or heat, the fiber-dye bond has been less resistant to strength. The optimum temperature for a good fixation is of the order of 50 °C. These dyes belong to the Levafix E range (Figure 20) or to Levafix E-A.

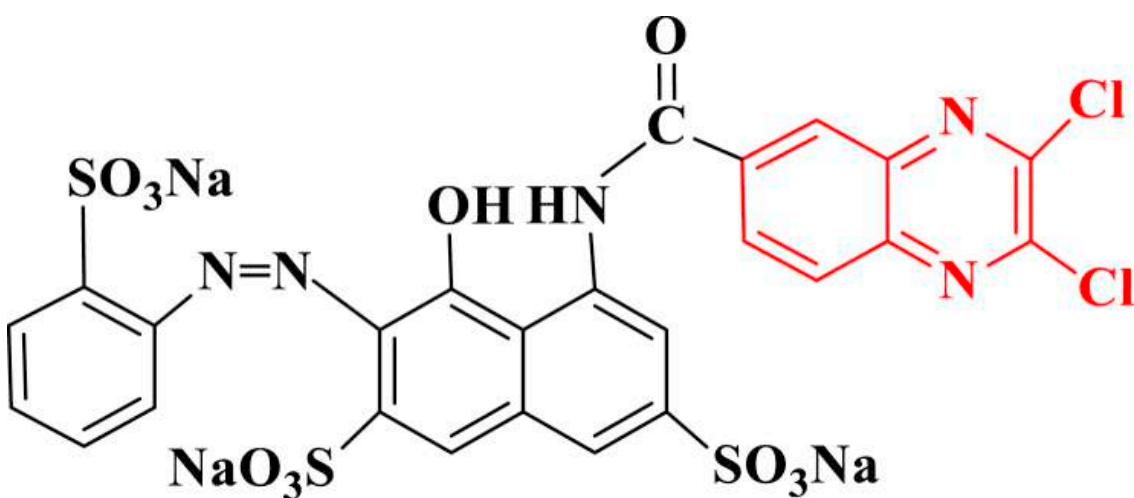
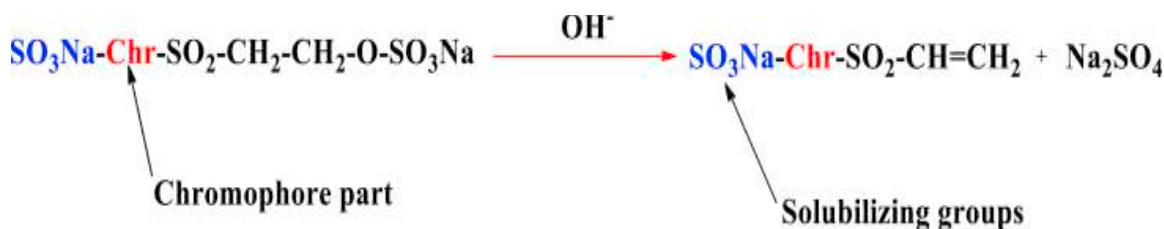


Figure 20

Azo red dye réactif Levafix E.

5. Vinylsulfone

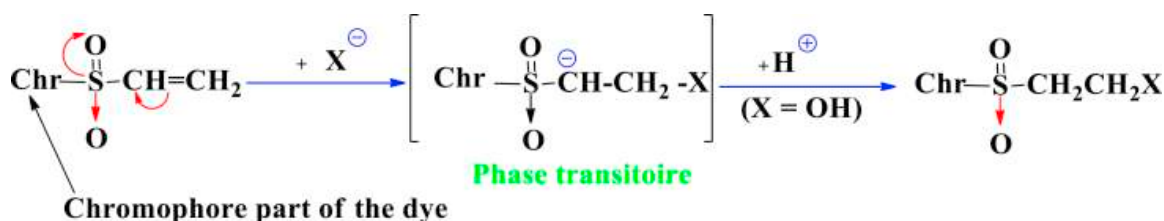
The reactive part of these types of cores comprises the β -sulfatoethylsulphone functional group ($\text{SO}_2\text{-(CH}_2\text{)}_2\text{-O-SO}_3\text{Na}$). The latter was inactive in an acidic and neutral medium and became active in an alkaline medium according to the reaction shown in Figure 21.



[Figure 21](#)

Reaction of the active part of the vinyl sulfone-type.

The attachment mechanism with the cellulosic fibers was carried out by a reaction of the nucleophilic addition, which produces a cellulose ether ([Figure 22](#)). As the hydrolysis reaction produces a hydroxyethyl sulfone [32, 35].



[Figure 22](#)

Fastening mechanism with cellulose fiber.

In terms of reactivity, this type of dye was positioned between high-reactivity heterocyclic systems such as dichloro triazines and difluoro pyrimidines on the one hand. And that of low reactivity based on mono chlorotriazine or trichloro pyrimidine on the other hand. The affinity of these dyes was low compared to that of halohydrocyclics. It is characterized by good water fastness in an acid medium, its optimum pH-binding temperature was given in an interval of 40 °C–60 °C. Among the trade names which represent this type of dye, Remazol is found ([Figure 23](#)).

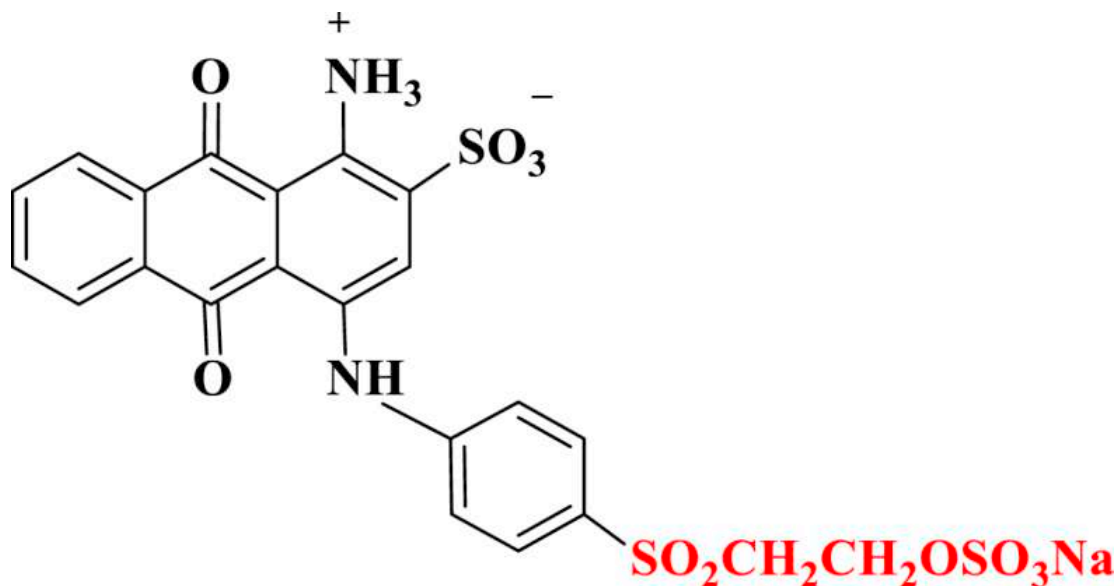


Figure 23

Structure of the reactive blue dye 19.

The sulphatoethylsulfone group results in a better water solubility due to the presence of the group (-O-SO₃Na). This solubility has been decreased and the affinity for cellulose increases after the reaction of removal of the sulfone group in an alkaline medium.

6. Bis-mono chlorotriazine

This type of dye was applied to the cellulosic fiber substrates because of its better affinity for depletion at a temperature of 80 °C, which makes it possible to obtain a fixation rate between 70 and 80 %. The molecules of this kind of dye have been characterized by a twofold dimension to its homo-functional counterpart [32, 36], (Figure 24).

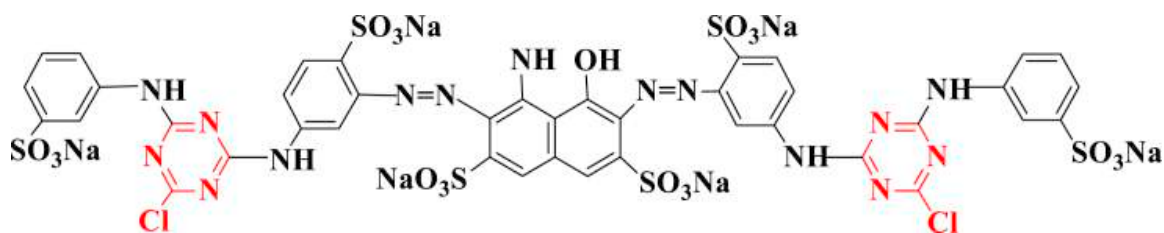


Figure 24

Structure of the dye C.I. Reactive Blue 171.

7. Bis-amino nicotinotriazine

These dyes were obtained by a substitution reaction of the chlorine in the triazine ring by a carboxy pyridine acid. The application temperature at depletion is higher than boiling in a neutral medium and can also be applied at 80 °C at pH = 11 as in the case of mono chlorotriazine. The coloring and the solidity of these dyes with the cellulosic substrates are similar to those of the mono chlorotriazine dyes.

The reactivity of bis aminonicotinotriazine (Figure 25) is higher than that of vinyl sulfones and chlorodifluoropyrimidines, plus beneficial reagents than dichloro triazines and dichloro quinoxalines.

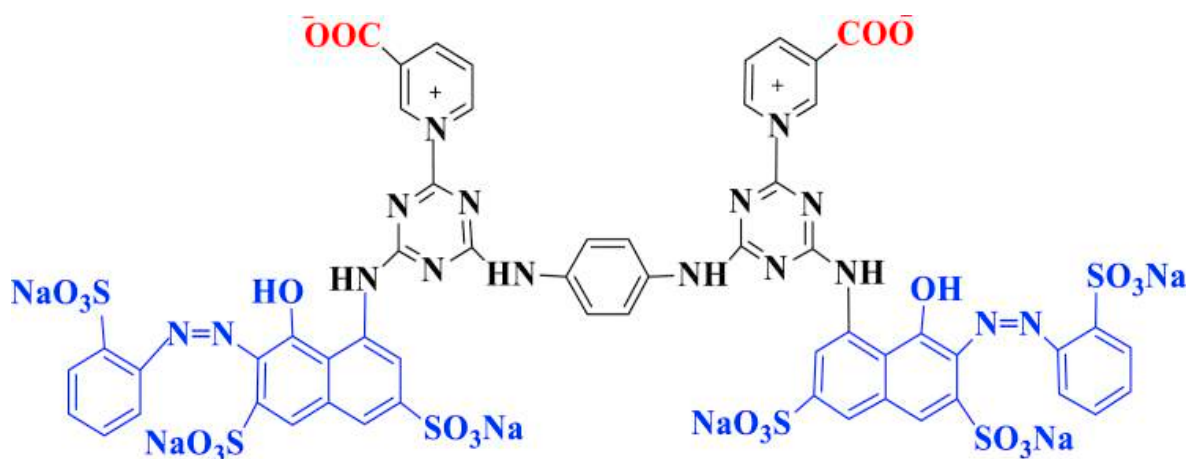


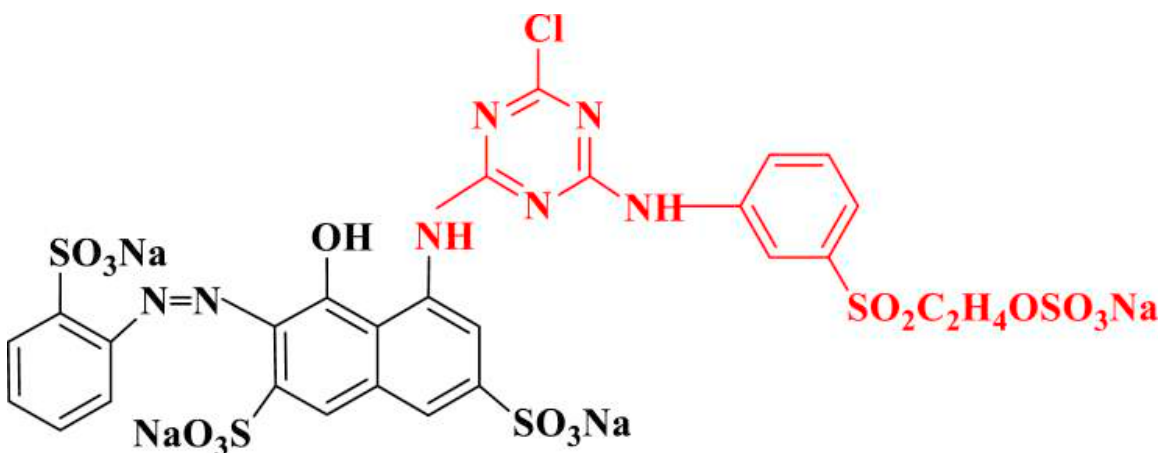
Figure 25

Structure of the dye C.I. Reactive Red 221.

8. Monochlorotriazine -sulphatoethylsulphone

The Monochlorotriazine-sulphatoethylsulphone can be synthesized by the reaction of dichloro triazine with the arylamine containing the sulphatoethylsulphone group [37]. The reactive groups favor good attachment to the cellulosic fibers.

Triazine causes sulphatoethylsulphone to adsorb to fibers in a bifunctional form, because of their high affinity. The existence of two types of fiber-dye bonds promotes different degrees of solidity. While the bonds formed by this type of dye have more acid fastness than for dichloro-triazines and dichloro quinoxalines, hence a better fastness to washing with peroxides than for difluoro pyrimidines and dichloquinoxalines. [Figure 26](#) illustrates an example of supra-gloss Sumifixe red 2BF (NSK) [38, 39].



[Figure 26](#)

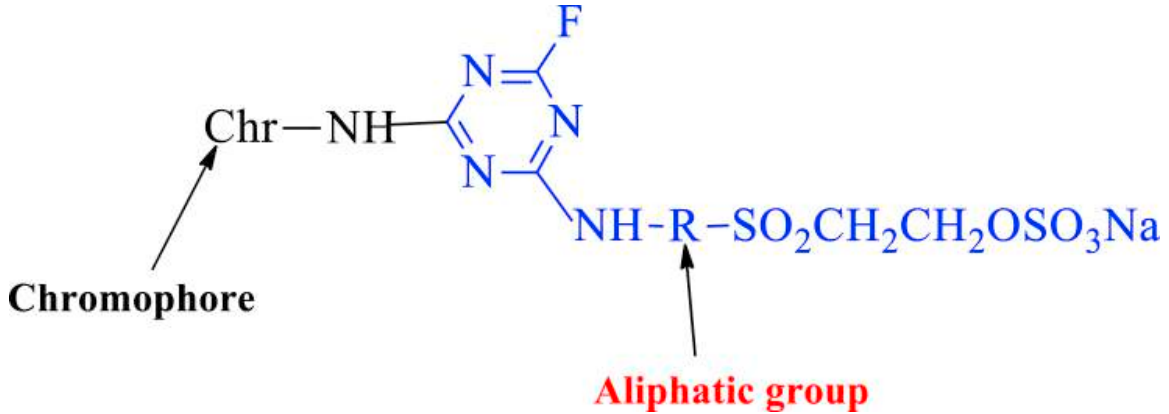
Structure of the C.I. Reactive Red dye 194.

9. Monofluorotriazine - sulphatoethylsulphone

Generally synthesized by an aliphatic moiety bonded to the sulphatoethylsulphone moiety and attached to the second reactive moiety of mono fluoro triazine [32]. The cost of making these dyes is high compared with the other dyes, but this cost is compensated

by their higher yield in semi-continuous dyeing (Pad-Batch or Pad-Roll), their medium to high Their performance washability, high fixation and stability in the cold dyeing bath.

[Figure 27](#) gives an example of these dyes, which were presented by Ciba C from the company Ciba-Geigy which appeared in 1988, [[32](#)].



[Figure 27](#)

Structure of the mono fluoro triazine-sulphatoethylsulfone dye.

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