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An Overview of Preparation for Different Azo Compounds

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Abstract

Azo compounds are a class of organic materials that have the group R-N=N-R' where the substitution group R and R' are aromatic or heterocyclic sides. The azo compounds have a variety of applications including dyes, pigments, and pharmaceuticals. The preparation and characterization of different azo compounds is an important area of research in organic synthesis. The azo compound synthesis typically involves the diazotization process for coupling between an aromatic amine and another aromatic compound containing an activating group such as -OH, $-NH_2$, or $-NR_2$. The reaction conditions must be carefully controlled to prevent side reactions, such as the formation of unwanted byproducts. Once synthesized, azo compounds can be characterized using a variety of techniques including UV-Vis spectroscopy, NMR spectroscopy, and mass spectrometry. UV-Vis spectroscopy is a commonly used technique for characterizing azo compounds. The absorption spectrum of an azo compound typically exhibits a strong absorption band in the visible region due to the delocalized π-electrons in the azo group. While in FTIR, the loss of the amine peak and showing a weak peak at about 1550 cm^{-1} for the (N = N) group, indicates the presence of Azo. The preparation and characterization of different azo compounds is a significant field of research in organic chemistry, which are applied as acid and base indicators, food coloring, optical switches, liquid crystal and in medicine. By carefully controlling the synthesis conditions and using a variety of characterization techniques, researchers can gain a better understanding of the properties and applications of these compounds.

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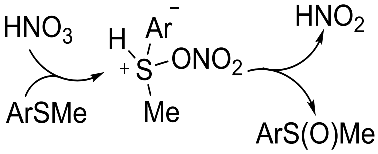
1. Introduction

In the synthesis of aromatic molecules, diazonium salts are considered and they are the critical starting point for azo synthesis [1]. These compounds are extremely helpful in the production of pigments compounds are employed as colorants in the textile industry, but they also have a variety of other uses [2]. For instance, they may be utilized as colorants in digital printing and photography, as well as in food, medicine and cosmetic use. Azo dyes were also employed in the biomedical sector [3]. They are also utilized in photochemistry as chiral switches, liquid crystals, novel glassy compounds, chiral receptors, and liquid crystals [3, 4]. It is well known that the action of nitrous acid on anilines results in the formation of diazonium salts in aqueous acidic sections. Later, they can interact with other substances to produce goods, depending on whether or not the nitrogen of the $[R-N^{+}\equiv N]X^{-}$ group is retained. Azole dyes are specific substances with azo structures connected to unsaturated molecules. The protonation of nitrous acid under very acidic circumstances is the first step in the synthesis of the diazotizing reagent, and the coupling happens in the existence of nucleophilic combinations at low temperatures. The weak diazonium salt electrophiles are often attacked by phenols and aromatic amines with electron donor substituents, and the reactivity of the reaction increases. Diazonium ion reactions are known to produce low yields and a large number of byproducts, which means they do not adhere to the requirements of green chemistry [5]. These concepts were incorporated to solve environmental and health issues at their root by preparing safer chemical procedures for chemical manufacture out of the illustration of novel and eco-friendly chemical synthesis [6]. Because of the important role of azo compounds in many medical and industrial fields, the research for potential synthetic alternatives has become an important matter. For instance, utilizing a CO_2/H_2O device has been suggested as a potential experimental method [7]; diazotization and diazo coupling reactions have also employed clay catalysts such as bentonite, kaolin, and K10 [8]. Numerous reaction media have also been taken into consideration, such as ionic liquids [9], natural solvents such as acetonitrile [10], 1,2-dichlorobenzene [11], dichloromethane [12], and solvent-free circumstances [13]. The preparation of novel, insoluble in aqueous medium azo compound derivatives from amines is an important step that might pave the way for innovative new technologies. Currently, there is a keen interest in conducting a systematic investigation into reactions that can lead to alternative methods of green synthesis [14]. This focus is based on the fundamental and ongoing research regarding the reaction of azo compounds, particularly in the advancement of synthetic planning techniques to facilitate their convenient preparation [15]. According to the proposed mechanism, the catalytic sulfoxidation reaction generates a significant quantity of nitrogen oxides and nitrous acid. In this study, it was observed that 4-(methylthio)aniline produces 4-(methylthio) bromobenzene as a byproduct, indicating the formation of a diazonium salt in the reaction medium through the diazotization of the aromatic amino group [16, 17]. Given the behavior of 4-(methylthio)aniline, we explored potential applications for our catalytic device in this salt production system. Therefore, the sulfoxidation process leads to the production of HNO_2, along with various nitrogen oxides and nitrous acid (Scheme 1) [18, 19].



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Scheme 1. Sulfoxidation process.

More than 60% of all dyes are azo dyes, which are the most often used [20]. Azo dyes make up around 70% of all the dyes used in the business [21]. The functional group (-NN-) joining with two groups, or the non-azo alkyl or different groups such as aromatic radicals, were used to describe these compounds [22]. Azo dyes are the most significant artificial colorants that are widely employed in the production of textiles, prints, and papers, among other things [23]. Azo dyes dangerous influence on people and the environment and these effects require prompt treatment of effluents containing azo dyes to separate them or transform them into helpful and safe compounds [24].

Additionally, when azo dyes' molecular weight grew, the dispersion of colors in water doubled. This phenomenon was likely caused by the presence of more azo bonds in the azo dyes' structure, which reduced the rate at which they degraded. The most of azo compounds are made by diazotizing coupling of an aromatic primary amine and electron-rich nucleophiles which prefer amino or hydroxyl groups. There are several ways to create azo dyes, some of which include [25]. Nitroaromatic derivatives can be reduced in an alkaline medium, nitroso compounds can be reduced by $AlLiH_4$, essential amines can be oxidized using different catalysts can be condensed, and dominant amines can be condensed with nitroso derivatives, among other processes [2]. The double bond of azo may also be linked to aromatic heterocycles, benzene derivatives, or polycyclic aromatic hydrocarbon compounds [26]. These compounds are necessary for providing the dye with its color, as they come in a variety of colors and intensities. According to

Figure 1(see Table 1), an azo dye's chemical form is typically characterized by a backbone, auxochrome groups, chromophoric groups, and solubilizing agents [27]. The azo bonds, together with the chromophores and auxochromes they are connected with, are what give azo dyes their color [28].

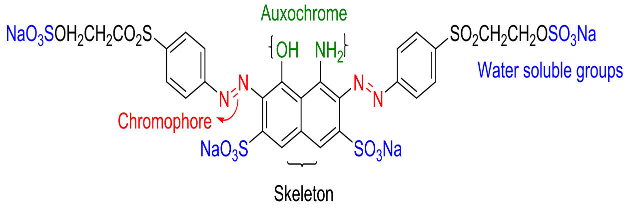

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Figure 1. Chemical structure of compound 2.

Chemical groups that may form connections with the molecules of the materials serve as the primary way by which azo dyes are commonly identified. The capacity needed to release these bonds is equivalent to the capacity required to degrade the assistance. The definition of an azo dye's chemical categorization and structural properties forms the basis of this evaluation. It is demonstrated by the production of a few azo dyes using the most used technique. The process of diazotizing an essential aromatic amine and mixing the resulting diazonium salt with usually aromatic substrate results in the production of both symmetrical and different azo compounds. Chemical groups hydrazone and chromene are produced during the preparation of azo compounds, respectively. The aminothiophene and 2-aminothiazoles are used in the production of azo dyes. Aspects of the coupling of azo compounds with polymers are also discussed in this evaluation, as a process of the Gewald reaction used in the production of azo compounds.

2. The monoazo dyes Z and W

The formula Z-N≡N-W can be used to schematically describe the monoazo dyes [29]. Their orange color (Figure 2a, see Table 1) presents the latest analog of this category that dyes cotton [30]. Other homologs were utilized to color cellulosic fibers and were grouped by superior light fastness and washing (Figure 2b). The isolated orange dye of mono azo compound is applied to color cellulose acetate, polyamides, polyesters, and polyacrylonitrile (Figure 2c). While Wool and nylon are colored using the orange IV and yellow dyes (Figure 2 d and e).

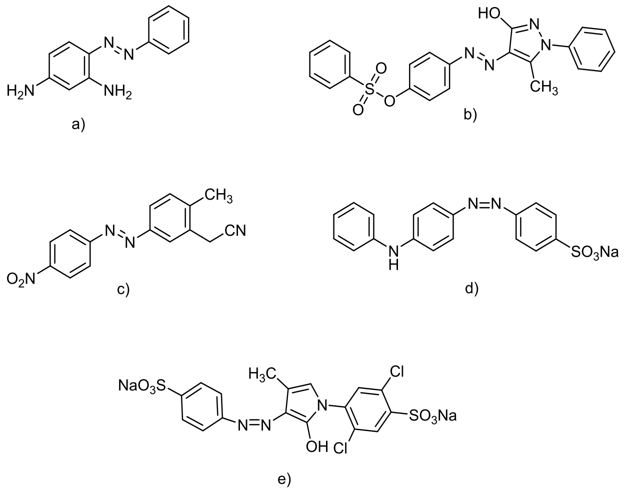
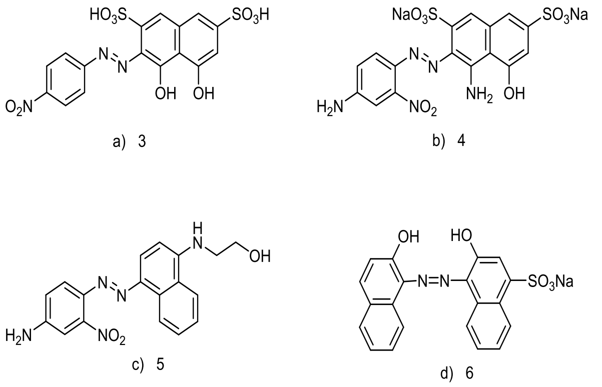


Figure 2.. Structure of a) chrysoidine, b) Yellow basic dye, c) orange dye, d) Orange IV e) yellow dye.

2.1. Z benzene and W naphthenic

Examples of this family of dyes' analogs are the red dye (Figure 3), the blue color (c) made from H acid for wool (Figure 3, see Table 1), and the blue dye. (Z benzene and W naphthenic are two isomers of cyclic hydrocarbons that differ in their molecular structure and physical properties. Z benzene, also known as cis-cyclooctene, is a cyclic hydrocarbon with a double bond between two carbon atoms in the ring [٢٩]. W naphthenic, also known as trans-decalin, is a cyclic hydrocarbon with two fused cyclohexane rings. The structure of Z benzene makes it a useful intermediate in the synthesis of various organic compounds, including fragrances and pharmaceuticals [29]. The cis-double bond in Z benzene makes it more reactive than its trans isomer and allows it to undergo various chemical reactions such as addition and oxidation. Z benzene has a boiling point of 167 °C and a melting point of -8.4 °C. W naphthenic is commonly used as a solvent in the chemical industry due to its low toxicity and high solvency power. The two fused cyclohexane rings in W naphthenic make it more stable than other cyclic hydrocarbons. They have boiling point and melting point of 185°C and -9.7°C respectively. W naphthenic is also used as a lubricant in the petroleum industry due to its excellent thermal stability and low volatility [31]. Z benzene and W naphthenic are two isomers of cyclic hydrocarbons with different physical and chemical properties. Z benzene is more reactive due to its cis-double bond and is used as an intermediate in the synthesis of organic compounds.



a) 3 b) 4 c) 5 d) 6

Figure 3. Chemical structures of red dye (a), blue dye (b & c), d) Mordant black 17.

W naphthenic is used as a solvent and lubricant due to its stability, low toxicity, and high solvency power. The study of these isomers and their properties may result in the creation of novel materials and their applications in various industries. The material dye Mordant Black 17, a mono-sulfonated aromatic azo structure considerably used in a notable scale with the various fabric and dyeing areas. The substance in question is commonly employed for imparting a black color to polyamide compounds and provides a chromium complex [32] (depicted in Figure 3d).

3. Diazo, Primary diazo

Overall, there are two families of diazo dyes, N≡N-, and they can be found using one of these techniques: [33]. Two moles of diazoic acid were coupled together on the same coupling term to complete the synthesis of this type of color. These dyes, which come in various shades of different colors, are all products of m-phenylenediamine. For example, a brown dye is used to color the clothes of wool as shown in (Figure 4).

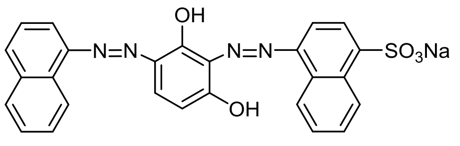


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Figure 4. Brown dye structure.

3.1. Secondary diazoic (symmetrical)

Similar to the previous type, this one has more direct dyes than acid and mordant colors. These originate from the compound with two amine groups that have undergone two diazotizations and have been reacted with indistinguishable or various conditions. (Figure 5, see Table 1) Illustrates the blue color structure with the benzidine functioning. Scheme 2 shows a sample of how an asymmetric azo dye is synthesized [34].

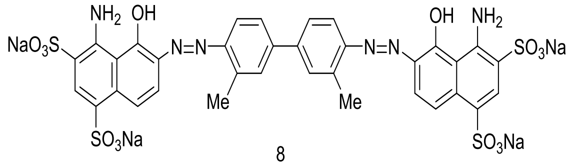

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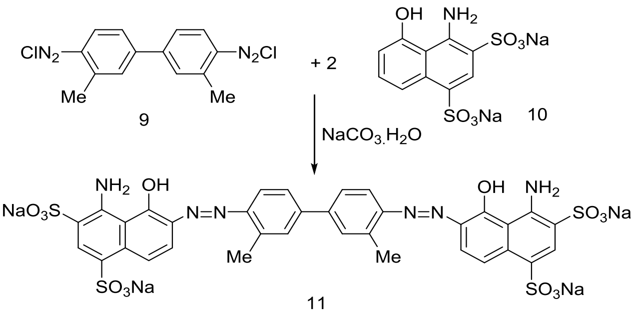
Figure 5. Chemical structure of compound 8.



Scheme 2. Synthesize of compound **11.**

3.2. Secondary diazoic (asymmetrical)

An amino azoic acid and a phenolic coupler were combined to create this particular dye. Figure 6 explains this sort of dye [35].

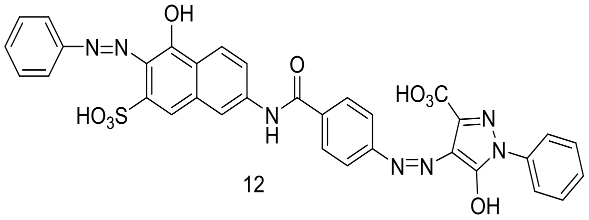

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Figure 6. Chemical structure of compound 12.

3.3. Polyazo dyes

Complex dyes known as polyazos are those in which the azo group appears more than three times in a single structure. These complexes dye fabric a dark shade like dark black, brown, and red [29]. The most popular dye for this sort of color is direct red (Figure 7). A dye can be created by phosgenating the appropriate diazo color. This can be done by diazotizing 6-amino-3,4'-azodibenzenesulfonic acid and acid coupling N-acetyl-J. Acetyl group hydrolysis occurs on phosgenation.

4. Classification of reactive functional azo dyes

4.1. Mono and dichlorotriazine

Scheme 3 explains and demonstrates how a homolog of this type of dye is synthesized [36]. The chemical structure in (Figure 8) shows the mono-functional azo dye, this dye includes the dichlorotriazine function [29].

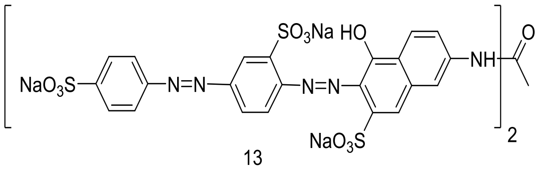
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Figure 7. Chemical structure of compound 13.

At 20°C to 30°C, these dyes are very cellulose-friendly. A significant reduction in the second chlorine's reactivity results from the substitution of chlorine using the ions of hydroxyl or cellulose. The hydroxyl group ionization causes the negative charge in the triazine ring in the basic solution. Therefore, the chlorine atom and carbon atom that are linked become deactivated and have low electrophilicity, respectively.

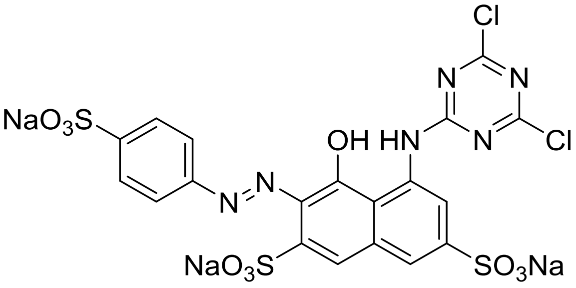
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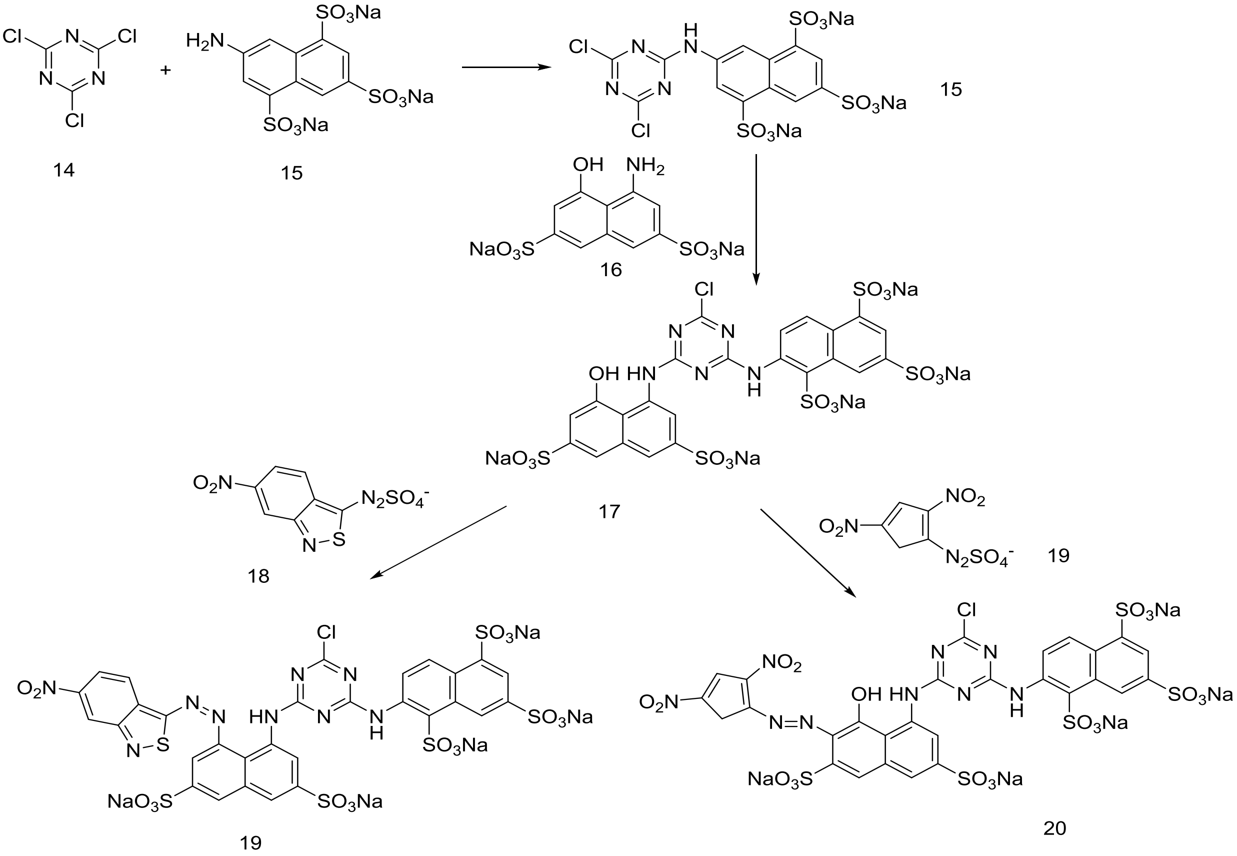
Figure 8. Chemical structure of compound 21.

4.2. Mono-amino-chlorotriazine

This type includes NH_2 and active chlorine groups which have activity fewer than dichlorotriazine (Figure 9). The qualities of dyeing and the solubility of the dye are affected by the link -NH- connecting the chromophore [37]. Due to the ability to capture electrons of nitrogen atoms in the triazine, the mechanism of binding for these compounds is accomplished through a nucleophilic replacement [38]. The carbon atom that contains the chlorine atom blocked the hydrolysis reaction in the alkaline condition and negative charge delocalized the electronic doublets in the triazine center, making the carbon attachment electron-rich (Scheme 4)

4.3. Pyrimidines

Pyrimidine is a six-membered aromatic heterocyclic organic compound as pyridine-like. The two nitrogen atoms are located at positions 1 and 3 in the ring, making it one of the three diazines. Pyrimidines contain fluoropyrimidine, and chlorfluoropyrimidine derivatives, while the following in general [39].



Scheme 3. Synthesis of compounds **19** and **20** **[29]**.

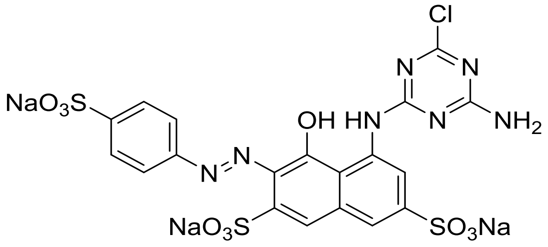


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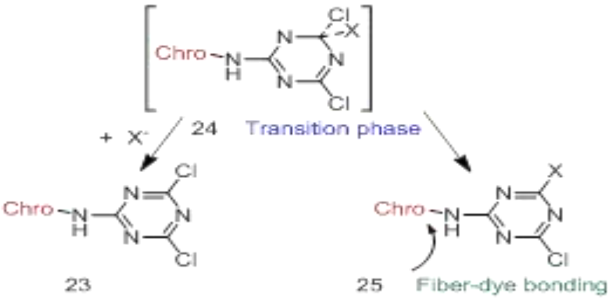
Figure 9. Chemical Structure of compound **22**



Scheme 4. Mechanism of synthesis compound **25**.

4.4. Chlorofluoropyrimidine

The addition of fluorine instead of chlorine increased this type of dye's reactivity. In an acidic environment, the linkage created with the cloth was stabilized but this bond is more sensitive to degradation by the peroxide chemicals in the existence of UV light [37]. Between 40°C and 50°C is the ideal range for this sort of dye to fix well. The Drimaren K kind is an example of these commercial dyes and is illustrated in (Figure 10).

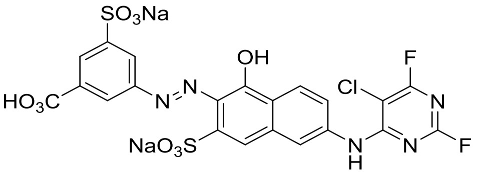


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Figure 10. Chemical structure of compound **26**.

4.5. Trichloropyrimidine

On the one hand, trichloro pyrimidine was reacted with aromatic amines in both conditions (acid and base) and the reactivity and resistance were worked in oppositely to produce dichloro pyrimidine. By nucleophilic substitution, the chlorine in tetrachloropyrimidine with an arylamine, trichloropyrimidine was produced (Figure 11). For these types of dyestuffs to have a good establishment on a cellulosic type of cloth substance, they need harsh conditions. By forming a link with a textile substance that is more resistant to hydrolysis, this type of dye was created [40].

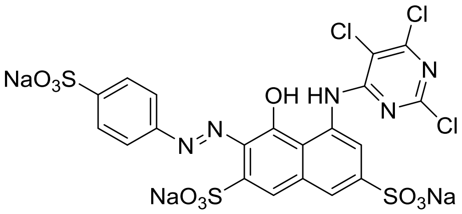

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Figure 11. Chemical structure of compound **27**.

4.6. Dichloroquinoxaline

The exceptional efficiency exhibited by dichloro pyrimidine, dichloro triazine, and difluoro pyrimidine dyes has led to their classification. However, it has been observed that the bond between the dye and the fiber is less stable when exposed to peroxides, light, and/or temperature. To ensure a successful reaction, the optimum temperature is found to be 50°C. These color compounds are compatible with Levafix E or Levafix E-A dyes [29] (illustrated in Figure 12).

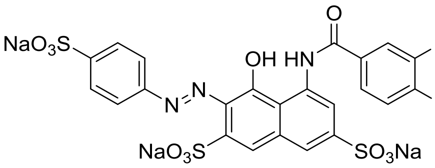

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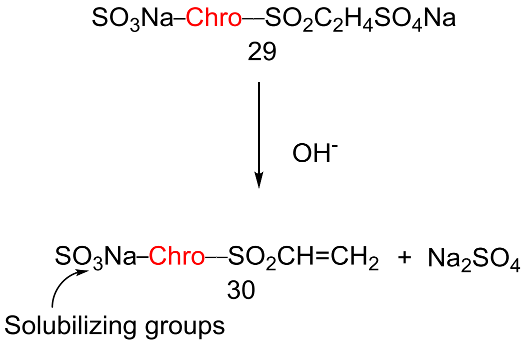
Figure 12. Chemical structure of compound 28 [29].

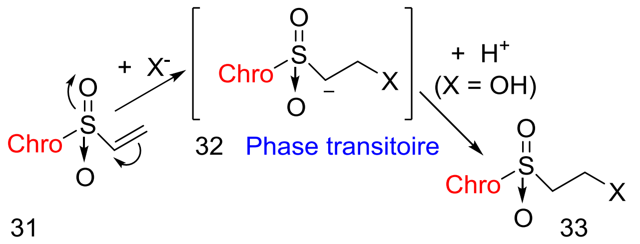
4.7. Vinylsulfone

The functional part of vinylsulfone is SO_2-$(CH_2)_2OSO_3Na$ which is considered the reactive part. According to the reaction depicted in (Scheme 5), the functional group is inert in the non-alkaline environment.



Scheme 5. Prepare compound **30**.

The technique of this reaction includes an addition reaction to form an ether compound of cellulose (Scheme 6). A hydroxyethyl sulfone is produced by the hydrolysis process.



Scheme 6. Fastening mechanism with cellulose fiber

This type of dye was found in classes of high effectiveness of heterocyclic framework like dichloro triazines while low reactivity that are dependent on trichloro pyrimidine. The relationship towards halo-hydrocyclic was weakly associated. It was classified as having strong water resistance in an acidic media and an ideal pH binding temperature range of 40° to 60°C. Remazol can be found between the commercial exchange names that describe this kind of color compound [41] (Figure 13).

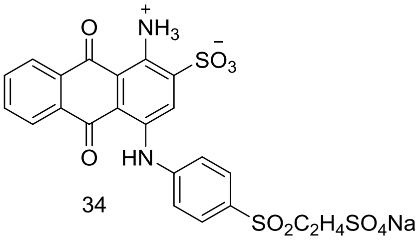


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Figure 13. Chemical structure of compound **34**.

The presence of the part sulphatoethylsulfone leads to the ability to be dissolved, especially in water (-O-SO3Na). The reaction of the elimination of the sulfone part in the base condition makes the solubility has been reduced and the affinity has grown for a cellulose [30].

4.8. Bis-monochlorotriazine

Due to this type of color's improved affinity for reduction at a temperature of 80 °C, which enables the achievement of a fixation rate between 70 and 80 percent, it was used in the cellulosic thread material. In comparison to its homo-functional counterpart, this type of color has been described by a double-distance [29] (Figure 14).

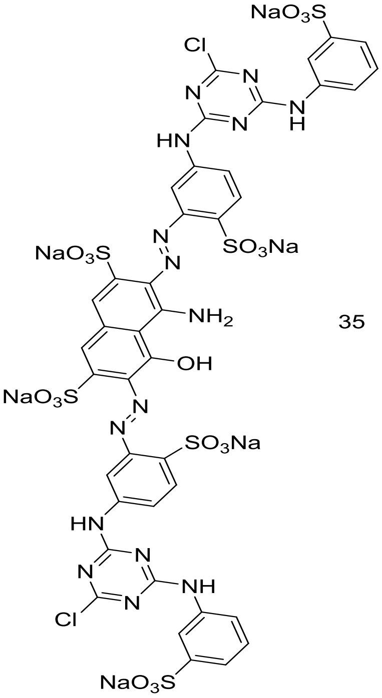

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Figure 14. Chemical structure of compound **35**.

4.9. Bis-amino nicotinotriazine

The compounds of this type were created through a substitution addition between a carboxy pyridine acid and the chlorine with the triazine ring. When a reduction occurs, the required heat, at 80 °C at pH = 11, is greater than the boiling in an equal environment. These dyes behave similarly to mono chlorotriazine dyes in terms of coloring and firmness when used with cellulose substrates [32]. In addition to being more reactive than dichloro triazines and bis aminonicotinotriazine (Figure 15) also has higher reactivity than vinyl sulfones and chlorodifluoropyrimidines [40].

4.10. Monochlorotriazine Sulfato-Ethylsulphone

Dichlorotriazine and an arylamine with a sulphatoethylsulfone group can combine to create monochlorotriazine-sulfatoethylsulfone [42]. Due to their strong affinity, triazine allows sulphatoethylsulfone to bind to threads in two functional shapes. Distinct degrees of firmness are promoted by the presence of two different thread-color linkages. Whereas the linkages created by this kind of color are more resistant to acid than those created by dichlorotriazines and dichloroquinoxalines, they are also more resistant to peroxide washing than those created by difluoropyrimidines and dichloquinoxalines, a compound 37 is an example (Figure 16).

4.11. Monofluorotriazine-sulphatoethylsulfone

Typically, the synthesis of these dyes involves the combination of an aliphatic component with the sulphatoethylsulfone segment, along with another interactive moiety such as mono fluoro triazine. Although these dyes are comparatively more costly to produce than other types, their advantages, including higher productivity during semi-continuous painting processes like Pad-Batch or Pad-Roll, moderate to high instability, and excellent fixation and settlement during cold dyeing and washing, outweigh the additional expenses. A depiction of these compounds, introduced by Ciba C of the Ciba-Geigy Corporation in 1988, can be seen in Figure 17.

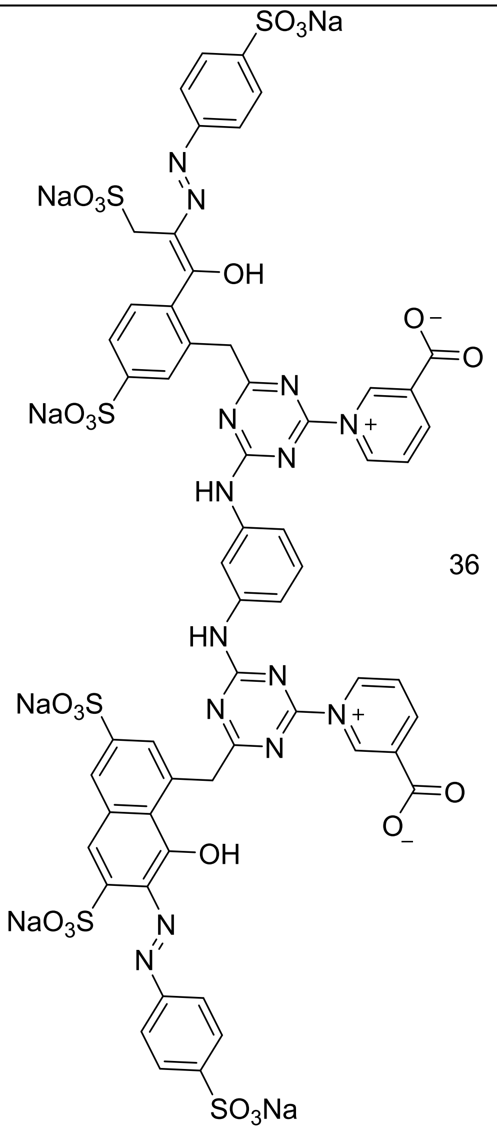

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Figure 15. Chemical structure of compound **36**.

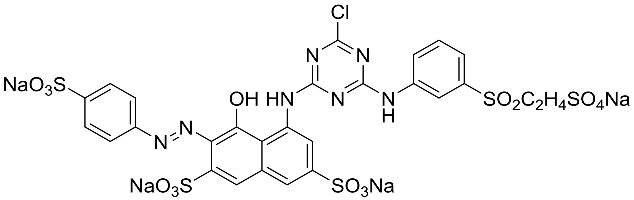

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Figure 16. Chemical structure of compound **37**.

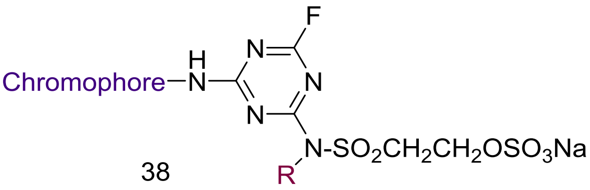

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Figure 17. Chemical structure of compound **38**.

Table 1. List of dyes.

Figure number (Number of compound)	Dyes
Figure 1 (2)	Sodium (((1E,1'E)-(1-amino-8-hydroxy-3,6-disulfonatonaphthalene-2,7-diyl)bis(diazene-2,1-diyl))bis(4,1-phenylenesulfonyl))bis(ethane-2,1-diyl) bis(sulfate)
Figure 2 (a)	(E)-4-(phenyldiazenyl)benzene-1,3-diamine
Figure 2 (b)	(E)-4-((3-hydroxy-5-methyl-1-phenyl-1H-pyrazol-4-yl)diazenyl)phenyl benzenesulfonate
Figure 2 (c)	(E)-2-(2-methyl-5-((4-nitrophenyl)diazenyl)phenyl)acetonitrile
Figure 2 (d)	Sodium (Z)-4-((4-(phenylamino)phenyl)diazenyl) benzenesulfonate
Figure2 (e)	Sodium (Z)-2,5-dichloro-4-(2-hydroxy-4-methyl-3-((4-sulfonatophenyl)diazenyl)-1H-pyrrol-1-yl)benzenesulfonate
Figure 3 ((e) 1)	(E)-4,5-dihydroxy-3-((4-nitrophenyl)diazenyl)naphthalene-2,7-disulfonic acid
Figure 3 ((b) 2)	Sodium (E)-4-amino-3-((4-amino-2-nitrophenyl)diazenyl)-5-hydroxynaphthalene-2,7-disulfonate
Figure 3 ((c) 3)	(E)-2-((4-((4-amino-2-nitrophenyl)diazenyl)naphthalen-1-yl)amino)ethan-1-ol
Figure3 ((d) 4)	Sodium 3-hydroxy-4-((2-hydroxynaphthalen-1-yl)diazenyl)naphthalene-1-sulfonate
Figure 4 (7)	Sodium 4-((2,6-dihydroxy-3-(naphthalen-1-yldiazenyl)phenyl)diazenyl)naphthalene-1-sulfonate
Figure 5 (8)	Sodium 6,6'-((3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(diazene-2,1-diyl))bis(4-amino-5-hydroxynaphthalene-1,3-disulfonate)
Scheme 2 (9)	(E)-1-chloro-2-(3,3',4'-trimethyl-[1,1'-biphenyl]-4-yl)diazene
Scheme 2 (10)	Sodium 4-amino-5-hydroxynaphthalene-1,3-disulfonate
Scheme 2 (11)	Sodium 6,6'-((3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(diazene-2,1-diyl))bis(4-amino-5-hydroxynaphthalene-1,3-disulfonate)
Figure 6. (12)	5-hydroxy-4-((1Z)-(4-((5-hydroxy-6-(phenyldiazenyl)-7-sulfonaphthalen-2-yl)carbamoyl)phenyl)diazenyl)-1-phenyl-1H-pyrazole-3-carboperoxoic acid
Figure 8. (21)	Sodium (E)-5-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-4-hydroxy-3-((4-sulfonatophenyl)diazenyl)naph

	thalene-2,7-disulfonate
Figure 9. (22)	Sodium (E)-5-((4-amino-6-chloro-1,3,5-triazin-2-yl)amino)-4-hydroxy-3-((4-sulfonatophenyl)diazenyl)naphthalene-2,7-disulfonate
Schemeeme 3 (17)	Sodium 6-((4-chloro-6-((8-hydroxy-3,6-disulfonatonaphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-1,3,5-trisulfonate
Schemeeme 3 (19)	Sodium (Z)-6-((4-chloro-6-((8-((6-nitrobenzo[c]isothiazol-3-yl)diazenyl)-3,6-disulfonatonaphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-1,3,5-trisulfonate
Schemeeme 3 (20)	Sodium (E)-6-((4-chloro-6-((7-((2,4-dinitrocyclopenta-1,3-dien-1-yl)diazenyl)-8-hydroxy-3,6-disulfonatonaphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-1,3,5-trisulfonate
Figure 12 (28)	Sodium (E)-3-((3-carboperoxy-5-sulfonatophenyl)diazenyl)-7-((5-chloro-2,6-difluoropyrimidin-4-yl)amino)-4-hydroxynaphthalene-2-sulfonate
Figure 14 (35)	Sodium 4-amino-3,6-bis((E)-(5-((4-chloro-6-((3-sulfonatophenyl)amino)-1,3,5-triazin-2-yl)amino)-2-sulfonatophenyl)diazenyl)-5-hydroxynaphthalene-2,7-disulfonate
Figure 15 (36)	Sodium 1-(4-((3-((4-(3-carboxylatopyridin-1-ium-1-yl)-6-((8-hydroxy-3,6-disulfonato-7-((E)-(4-sulfonatophenyl)diazenyl)naphthalen-1-yl)methyl)-1,3,5-triazin-2-yl)amino)phenyl)amino)-6-(2-((Z)-1-hydroxy-3-sulfonato-2-((E)-(4-sulfonatophenyl)diazenyl)prop-1-en-1-yl)-5-sulfonatobenzyl)-1,3,5-triazin-2-yl)pyridin-1-ium-3-carboxylate

5. Conclusions

In conclusion, azo compounds are a diverse and important class of organic compounds that have found wide-ranging applications in industries such as dyes, pigments, and pharmaceuticals. The preparation and characterization of different azo compounds have been the focus of much research in organic chemistry due to their unique electronic and optical properties. The diazotization and coupling reaction used in the preparation of azo compounds requires careful control to avoid unwanted side reactions and to obtain high yields. Once synthesized, various techniques such as UV-Vis spectroscopy, NMR spectroscopy, and mass spectrometry are used to characterize the properties of azo compounds.

These techniques can provide information about the electronic structure, connectivity, and conjugation of the azo group. The study of azo compounds has led to the growth of novel and improved dyes and pigments, which have played a vital role in various industries. In the future, the synthesis and characterization of new azo compounds may lead to the discovery of novel dyes with even more interesting properties and applications.

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