Review article

Classifications, properties, recent synthesis and applications of azo dyes

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ABSTRACT

In this work, we have presented a very detailed review of the different classification of azo dyes as a function of the number of azo groups and the appropriate functional groups. Then we pointed out some chemical properties of these dyes such as reactivity, isomerization and tautomerism and listed. In the following, we have summarized some recent syntheses of azo dyes and the mechanism of azo dye/polymer conjugation. Finally, we indicate the principle of Gewald's reaction and its application to the synthesis of new azo dyes.

1. Introduction

Azo dyes 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.

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 nitro-aromatic 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].

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
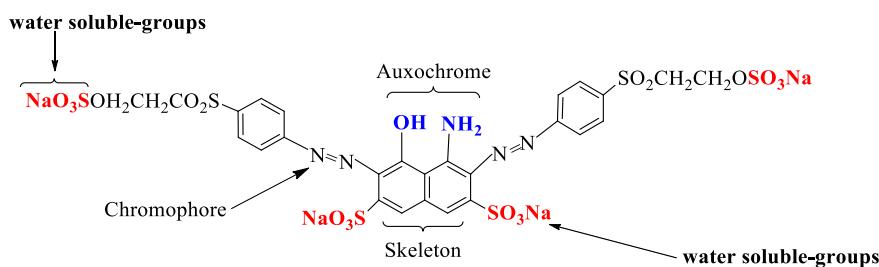

Figure 1. Structure of the azo reactive dye.

Table 1. Classification of azo dyes in Colour Index [2, 18].

| Chemical class	CI no
Monozo	11000–19999
Disazo	20000–29999
Trisazo	30000–34999
Polyazo	35000–36999
Azoic	37000–39999
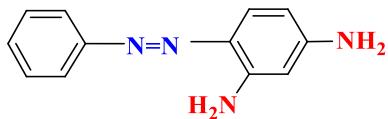
**Figure 2.** Structure of chrysoidine.
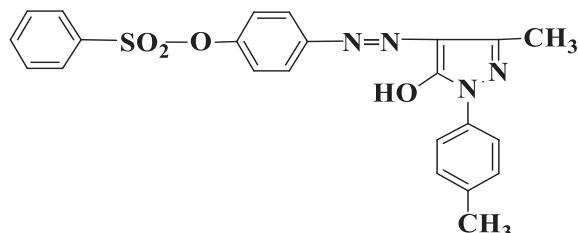
Figure 3. Yellow basic dye.
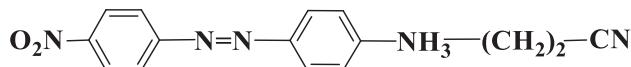


Figure 4. Structure of the orange dye.
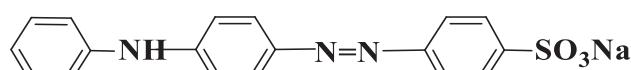
Figure 5. Orange IV.
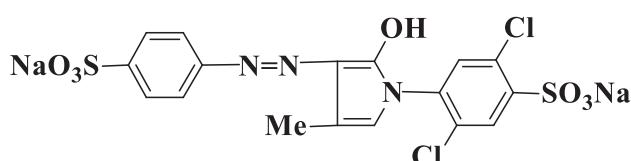
Figure 6. Structure of the yellow dye.
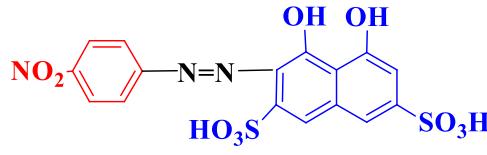
Mordant Red (a)
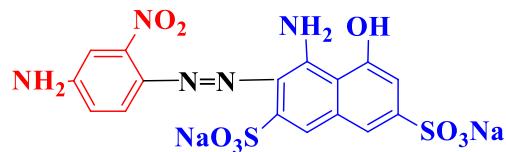
Blue dye (b)
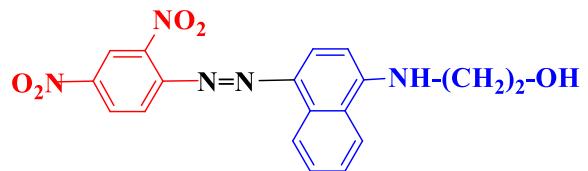
Blue dye (c)

Figure 7. Illustrates the red dye with their mordant (a), the blue dye (b) and the blue dye (c).
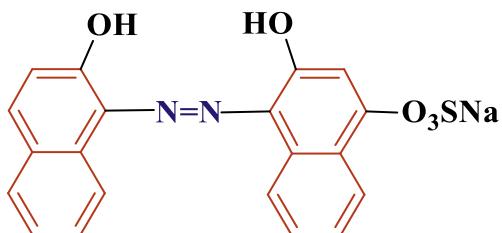
Figure 8. Mordant black 17.

concept of conjugation of azo dyes to polymers and finally the use of the Gewald reaction in the synthesis of azo dyes.

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].
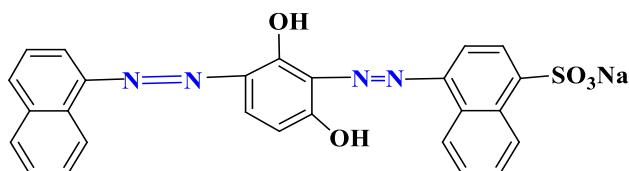
Figure 9. Brown dye structure.

2.1. 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.

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

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

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.

2.1.2. 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).
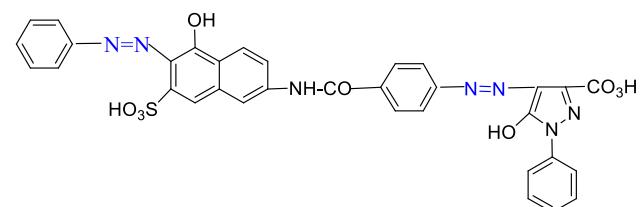
Figure 12. Structure of the orange direct dye.
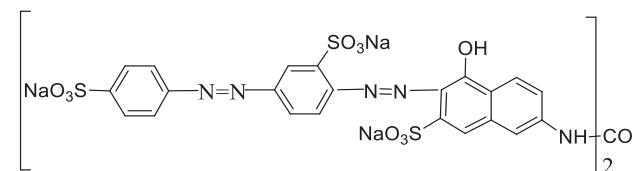
Figure 13. Structure of the direct red dye.

2.1.3. 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).

2.2. Disazo

In general, the diazo dyes contain two groups –N=N-, they are obtained according to the following three methods [23].
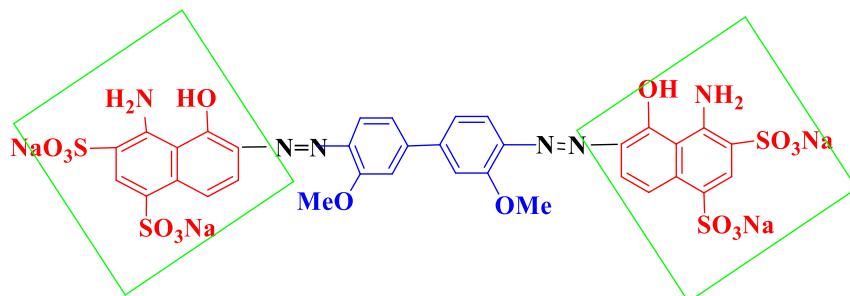
Figure 10. Structure blue direct dye.
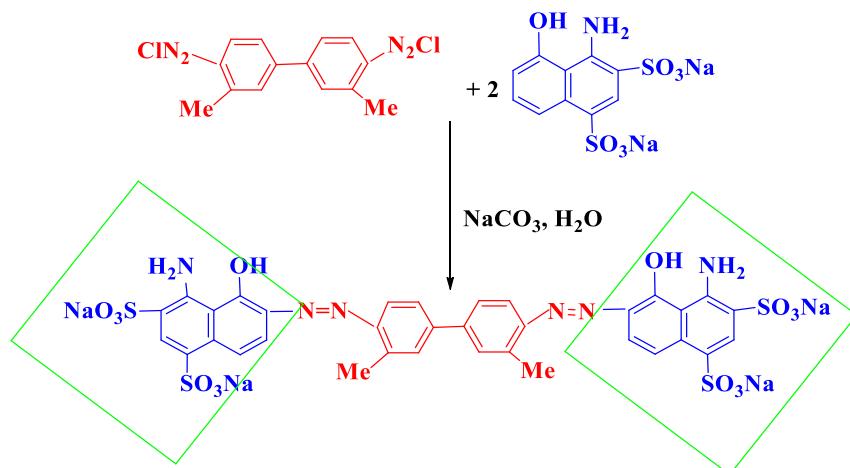
Figure 11. Exemple se synthèse du colorant asymétrique.
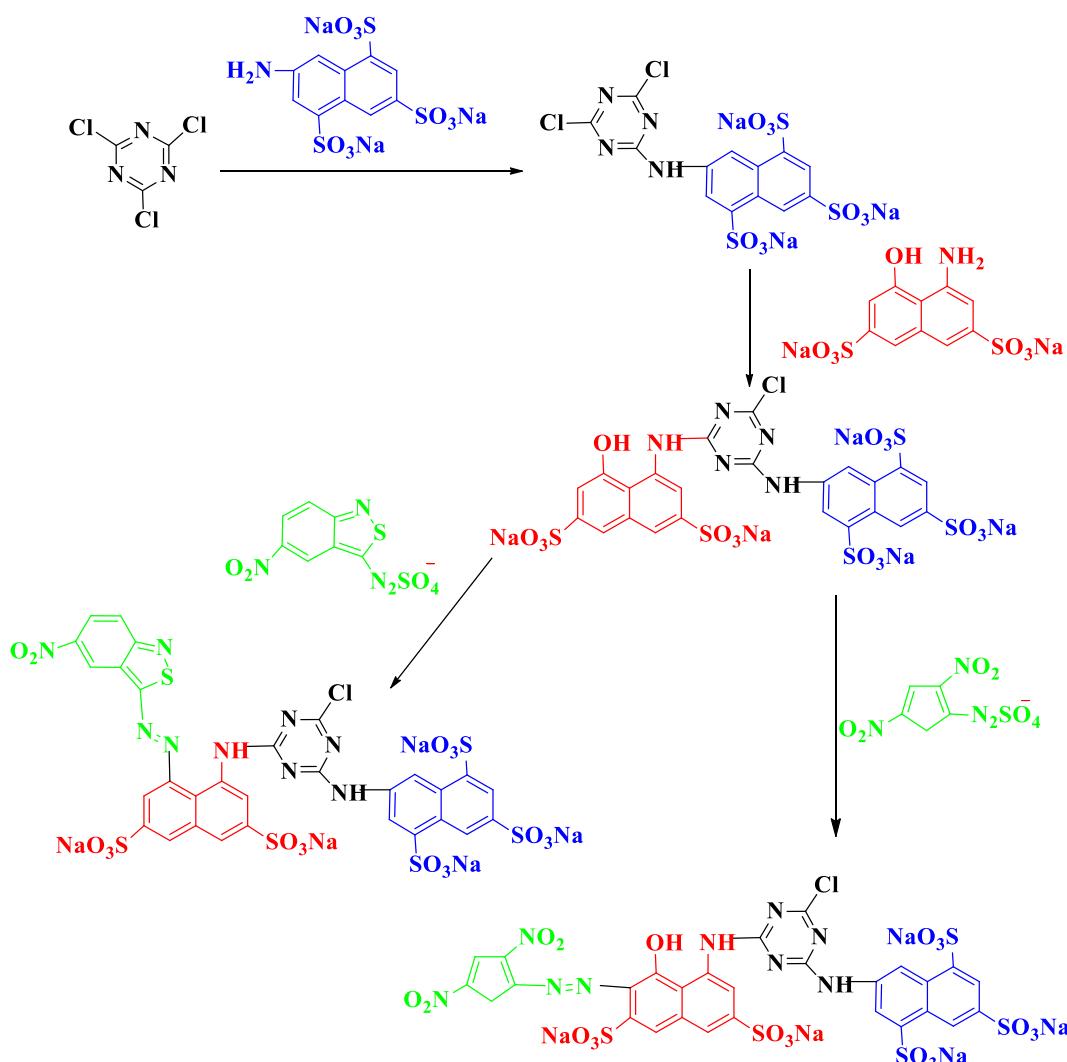
Figure 14. Synthesis route of an example of monochlorotriazine dyes.
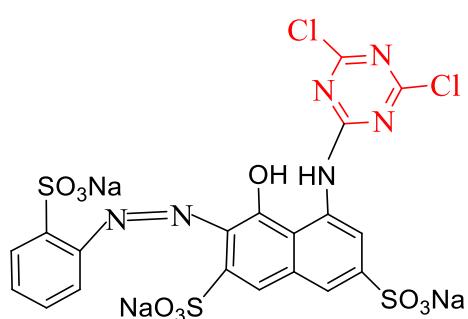
Figure 15. Mording red procion M-2B.

Figure 16. Structure of the Cibacron shiny red dye B.

2.2.1. 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.

2.2.2. 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 11 shows an example of a synthesis of an asymmetric azo dye [24, 25].

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].
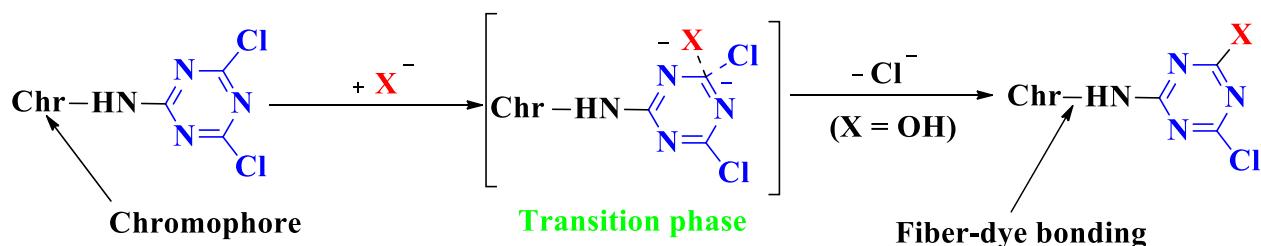
Figure 17. Mechanism of fixing and hydrolysis of the mono and dichloro triazine dye.
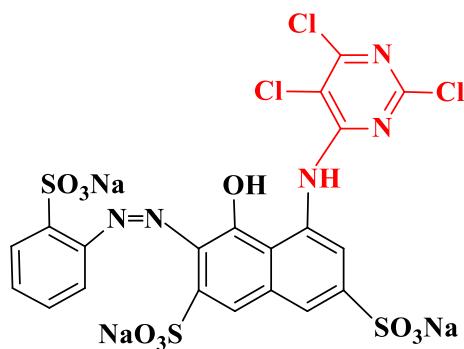
Figure 18. C.I.Reactive red 17.
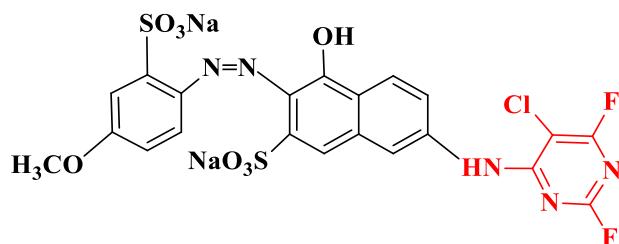
Figure 19. Dye type 5-chloro-2, 4-difluoropyrimidine.
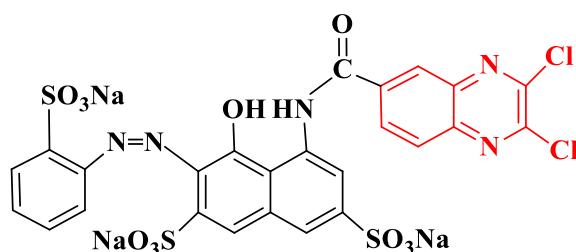
Figure 20. Azo red dye réactif Levafix E.

2.3. Polyazo

Polyazo dyes are complex dyes is 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-J. The acetyl group is hydrolysed before the phosgenation step.

3. Classification of azo dyes according to reactive functional groupings

3.1. Mono and dichlorotriazine

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

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

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.

3.2. 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 -NH- linking the chromophore and the reactive group have an influence on the dyeing properties and the solubility of the dye [32].

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).

3.3. Pyrimidines

In general, include the di and tri-chor pyrimidine derivatives, chlorfluoropyrimimidine and fluoropyrimidine derivatives as follows:

3.3.1. Trichloro pyrimidine

The synthesis of dichloro pyrimidine was obtained, on the one hand, by the reaction of trichloro pyrimidine with an arylamine less reactive
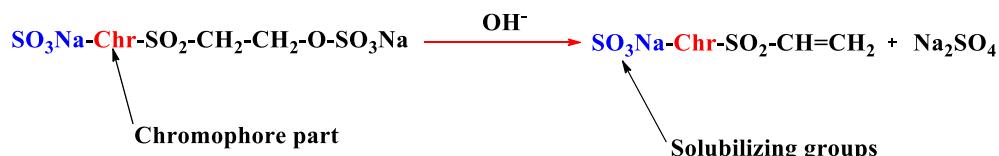
Figure 21. Reaction of the active part of the vinyl sulfone-type.
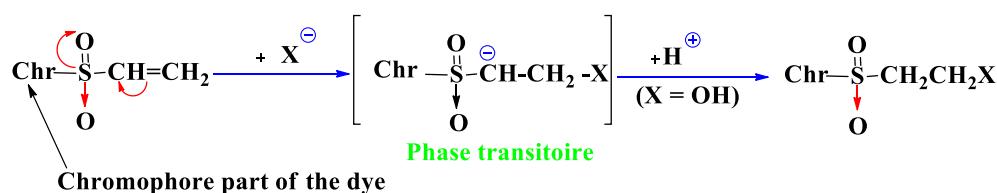
Figure 22. Fastening mechanism with cellulose fiber.
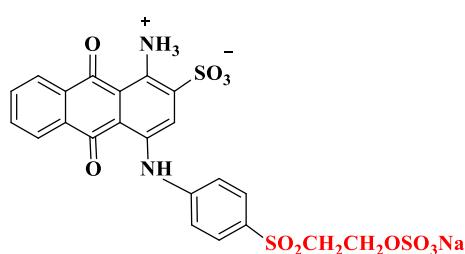
Figure 23. Structure of the reactive blue dye 19.

Figure 26. Structure of the C.I. Reactive Red dye 194.

and more resistant to hydrolysis in acid and alkaline medium [32]. Tri-chloropyrimidine (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.

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 27. Structure of the mono fluoro triazine-sulphatoethylsulfone dye.

3.4. 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.
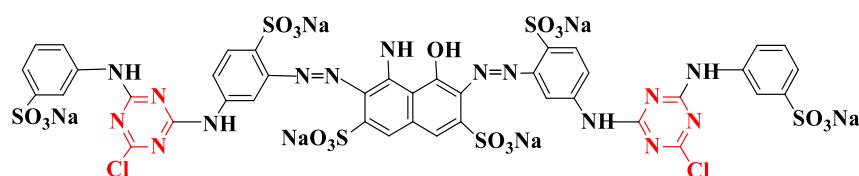
Figure 24. Structure of the dye C.I. Reactive Blue 171.
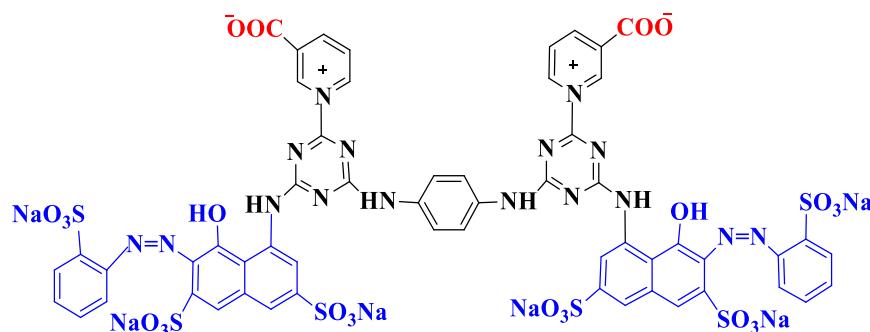
Figure 25. Structure of the dye C.I Reactive Red 221.
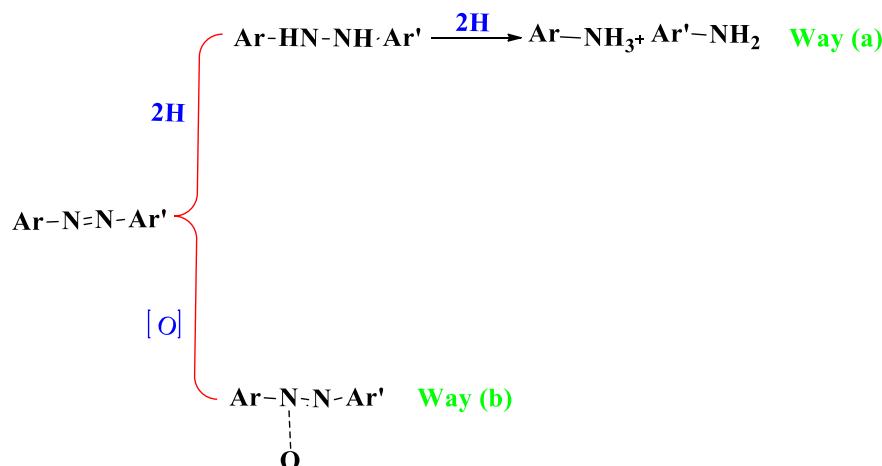
Figure 28. Addition reactions on the azo group.
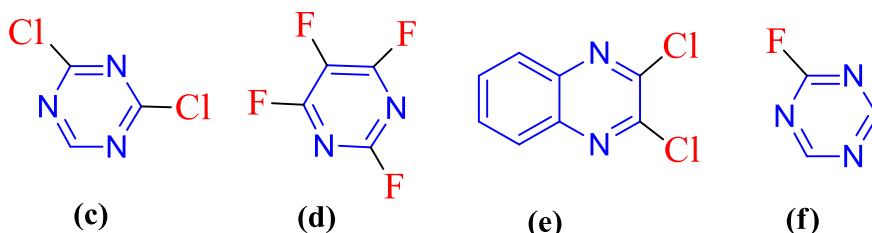
Figure 29. Chemical structures of (c), (d), (e) and (f).

3.5. Vinylsulfone

The reactive part of these types of cores comprises the β-sulfatoethylsulphone functional group (SO_2- $(CH_2)_2$ –O–SO_3Na). 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.

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].

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).

The sulphatoethylsulfone group results in a better water solubility due to the presence of the group (-O-SO_3Na). This solubility has been decreased and the affinity for cellulose increases after the reaction of removal of the sulfone group in an alkaline medium.

3.6. 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).

3.7. Bis-amino nicotinotriazine

These dyes was 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.

3.8. Monochlorotriazine –sulphatoethylsulphone

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

Triazine causes sulphatoethylsulfone 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 dichlorotriazines 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].

3.9. Monofluorotriazine - sulphatoethylsulfone

Generally synthesized by an aliphatic moiety bonded to the sulphatoethylsulfone 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

**Degree sense of increasing substantivity**
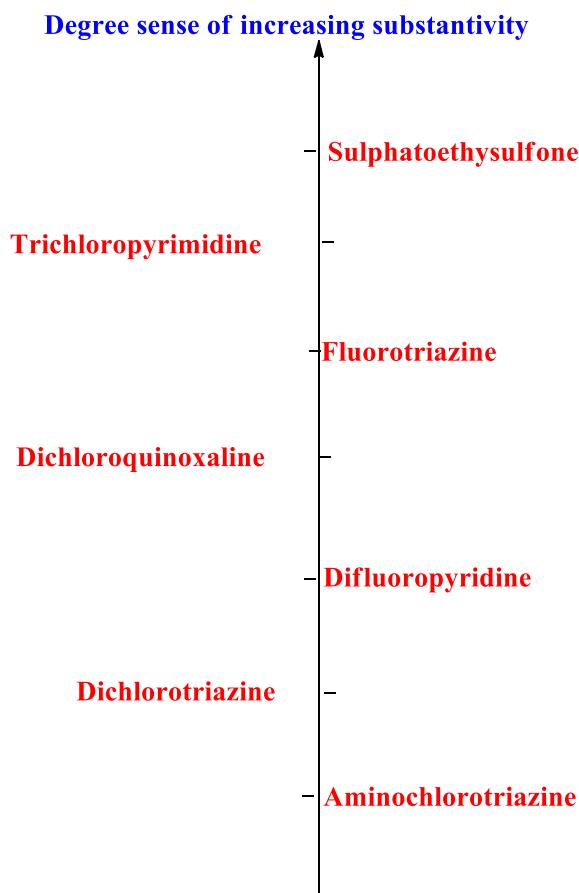
**Figure 30.** Diagram of the substantivity of azo dyes according to their reactive part.
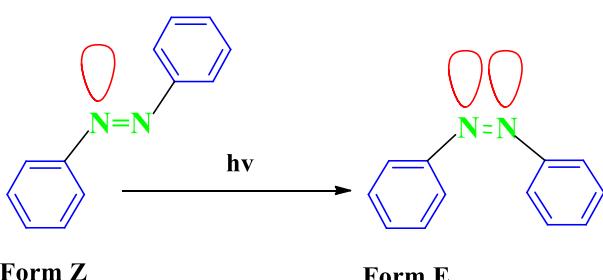
Figure 31. Form Z and E of the azobenzene molecule.
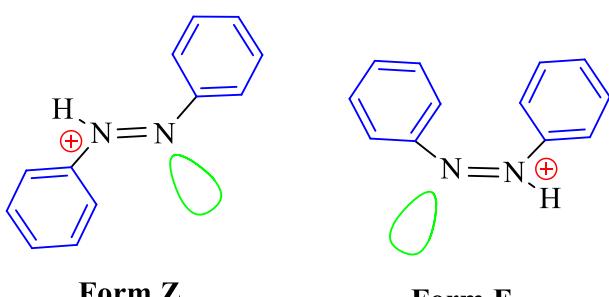

Figure 32. Trans and Cis conjugated acids.

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].

4. Properties chemical of azo dyes

4.1. Reactivity

Among the addition reactions of the azo group, the hydrogenation leading to hydrazo benzene (a) and oxidation by hydrogen peroxide and peracids which promote the compound (b) have been reported in the Figure 28. The frequency of vibration of the N=N bond of some azo compounds was reported between 1630-1575 cm^{-1}. This frequency may be absent in the case of the existence of asymmetric azo derivatives [40, 41].

In general, the reactivity of a dye depends on the structure of its reactive part. Dichlorotriazines [42] (**c**) are the most reactive, followed by di or tetrafluoropyrimidines [43] (**d**) and dichloroquinoxalines [44] (**e**) followed by monofluorotriazines [45] (**f**). The dyes of medium reactivity are represented by vinylsulfones, the bifunctional dye type monochlorotriazine/vinylsulfone. Next, the oxymethylchlorotriazines derived from the structure of aminochlorotriazines having low reactivity are found. Finally, the trichloropyrimidines have the lowest reactivity (Figure 29).

Substantivity is the power to absorb a dye on a textile support surface, depending on the reactive part of the dye being studied [46]. Figure 30 shows the diagram of substantivity in ascending order according to the reactive part of azo dyes [47].

4.2. Isomerism Z/E

The azobenzene molecule admits two isomeric forms Z and E. The form E being unstable, it is obtained from the trans form by photo-isomerization (Figure 31) [26,48].

In general, isomerization is the process by which a molecule is transformed into another molecule that has exactly the same atoms, but the atoms have a different layout. In some molecules and under certain conditions, isomerization occurs spontaneously.

The key to the interesting applications of azobenzene is the isomerization of the azo bond between the more thermally stable E configuration and the metastable Z form [49,50,51,52,53]. In an acid medium, the two Trans and Cis forms of the azobenzenes cause the formation of conjugated acids of different conformation (Figure 32).

In the same sense, the migration of the amino-azobenzenes gives a resonance-stable ammonium-azonium tautomerism (Figure 33).

Azo phenol quinone hydrazone tautomerism is the well-known phenomenon in the case of azo-substituted azobenzenes in ortho or para in an azo moiety [54].

Figure 34 illustrates an example of hydroxyazobenzene tautomerism of hydroxy azobenzene rings [55].

4.3. Tautomerism

The azo/hydrazone tautomerism results in the intramolecular migration of the proton from one element to another [56, 57, 58]. This allomerism tautomerism is of importance for azo dyes by the development of certain characteristics such as light fastness, dye tinctorial power, and the like. The latter determines the profitability of the dye. Therefore the azo dyes must be in the form of an abundant tautomer which is the hydrazone [59, 60]. This phenomenon was discovered in 1884 by Zincher et al. [25] is intended for the hydroxy azo structure. There are other tautomers, such as azo/imino [61] for amino azo and azonium/ammonium [62] dyes in the case of the protonation of azo dyes [63].
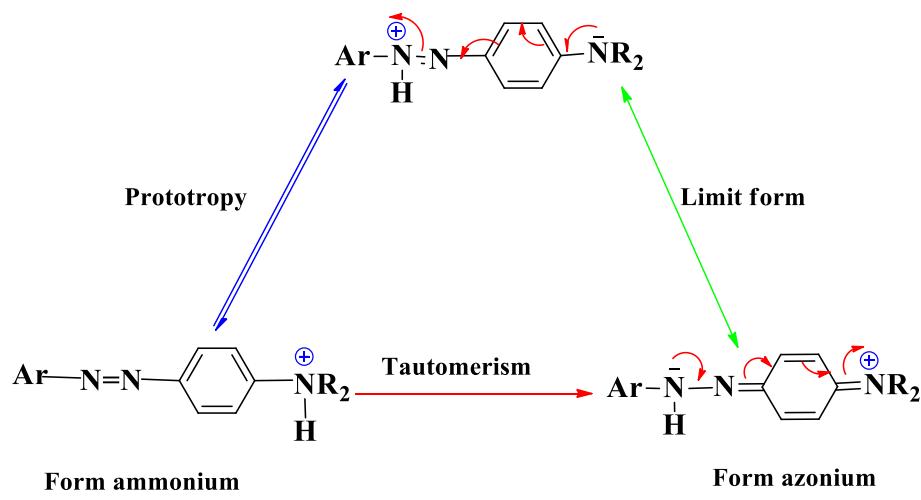
**Figure 33.** Ammonium-azonium tautomerism.
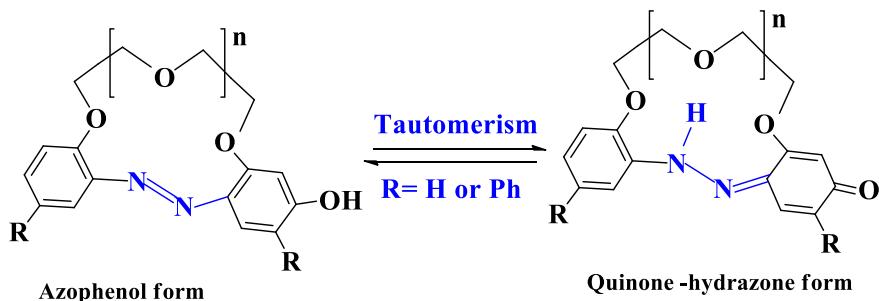
Figure 34. Azophenol-quinone hydrazone tautomerism.
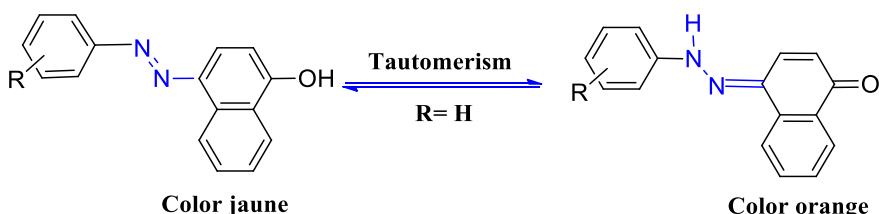

**Figure 35.** Form of tautomerism.
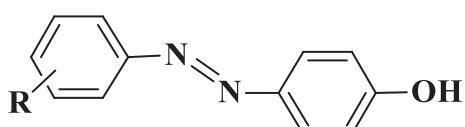
Figure 36. Azophenol dye.

An experiment was carried out on an orange dye synthesized from the coupling of benzene diazonium chloride with 1-naphthol and then a condensation of phenylhydrazine with 1, 4-naphthoquinone. In general, the tautomerization reaction occurs by migration of a hydrogen atom accompanied by a change in the location of a double bond. The results obtained show that there is a tautomerism (Figure 35), [64].


Azo-acetoacetanilide

Azo-pyrazolone
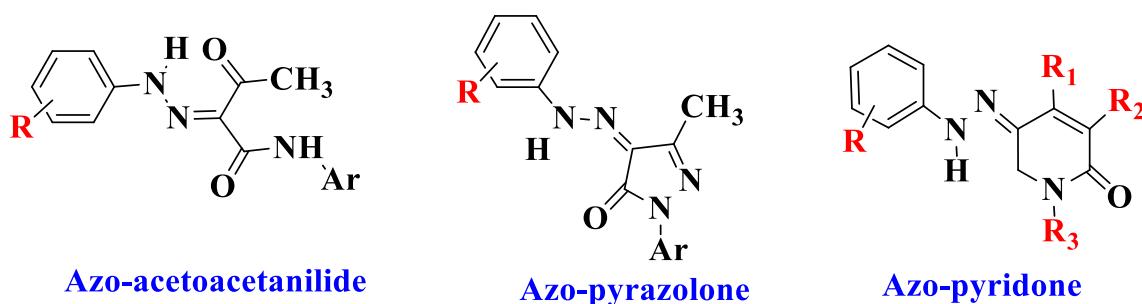
Azo-pyridone

Figure 37. Strucure of azo-acétoacétanilide, azo-pyrazolone and azo-pyridone.
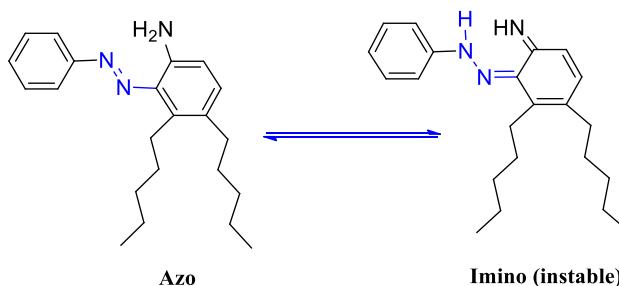
Figure 38. Imino and azo form.
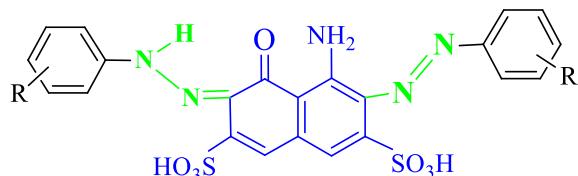
Figure 39. Protonated tautomerism.

Depending on the medium, the hydroxy azo dyes give at the same time different percentages of the tautomers azo and hydrazone, as well as azo phenol dyes which exist in azo form, with the exception of certain particulars cases [63, 65], (Figure 36).

Figure 37 gives the different main classes of dyes which are in hydrazone form azo-acétoacétanilide [66, 67], azo-pyrazolone [68] and azo-pyridone [69].

Moreover, the instability of the imino group entails the azo form of the different kinds of dyes, (Figure 38).

Regarding diazo dyes derived from amino-naphthol. We observe a coexistence between the two groups, one in azo form and the other in hydrazo form (Figure 39).

In the case where the protonation is carried out at the level of the nitrogen carried by β, it favors an azonium tautomer stabilized by resonance. The protonation tautomerism of the azo colorants is done only in the colored indicators.


R$_1$= H, CH$_3$ and NHCOCH$_3$
R$_2$= H
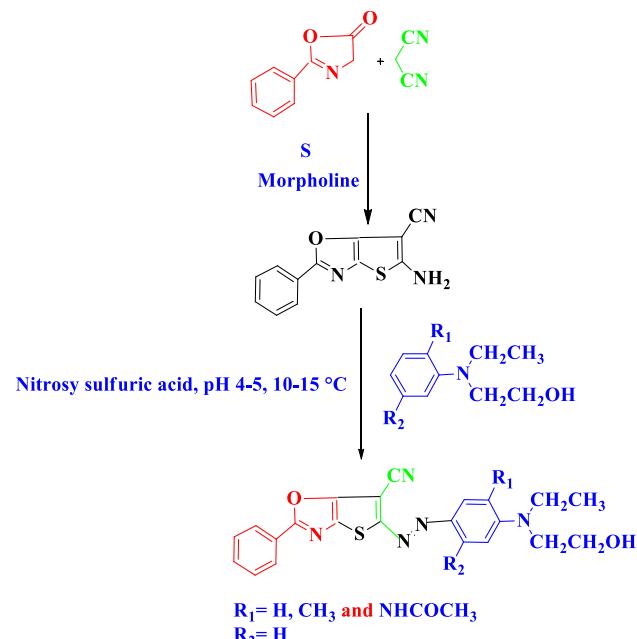
Figure 41. 5-azo-thieno [2, 3-d] oxazoles dyes 27.

5. Synthesis of azo dye by Gewald reaction

This section will deal with the use of the Gewald reaction in the synthesis of conventional and functional dyes [122,133]. This reaction has applications in several fields, such as peptide analogues, dyes and electronic materials; Conjugated carbohydrates, agrochemicals, pharmaceuticals/biomedicine, cane masters, etc.

According to Ram W. Sabnis [71], the condensation of benzo-thiophene-3 (2H) -one-1,1-dioxide with ethyl cyanoacetate was subsequently diazotised using nitrosyl sulfuric acid and coupled with Aryl amines substituted with N, N-dialkyl (acid coupling) gave azo dyes 26 (Figure 40), [71].
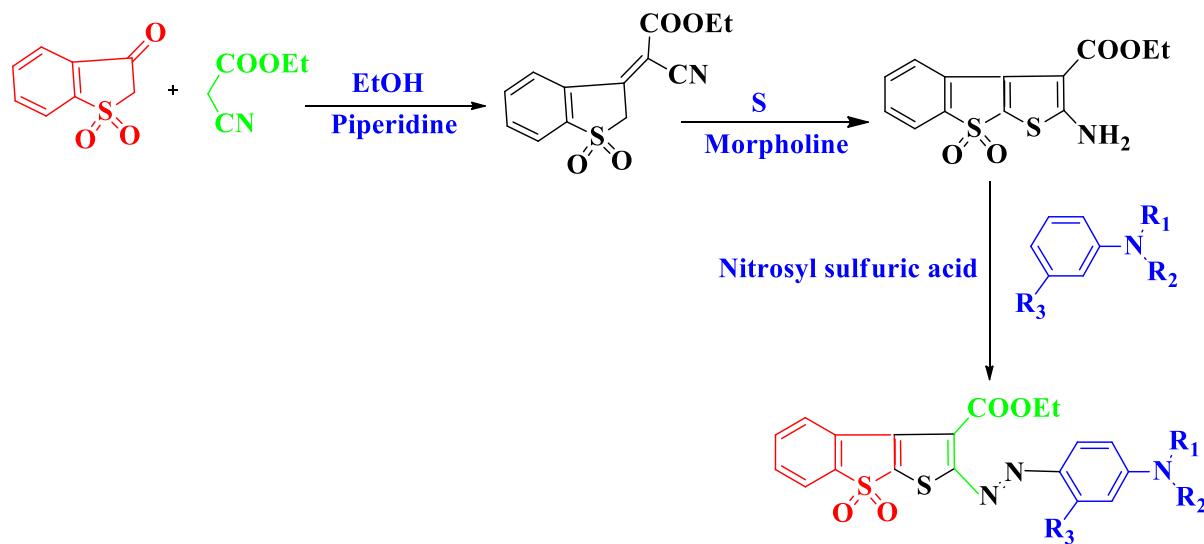
R$_1$, R$_2$ and R$_3$ = Alkyl, Acetyl and Benzyl respectively

Figure 40. Azo dyes 26.

Figure 42. Dispersed diazo dyes 38.

R₁= CN, COOEt;
R₂= H;
R₃= Aryl.

R₁= CN or COOEt;
R₂= Aryl or hetaryl.
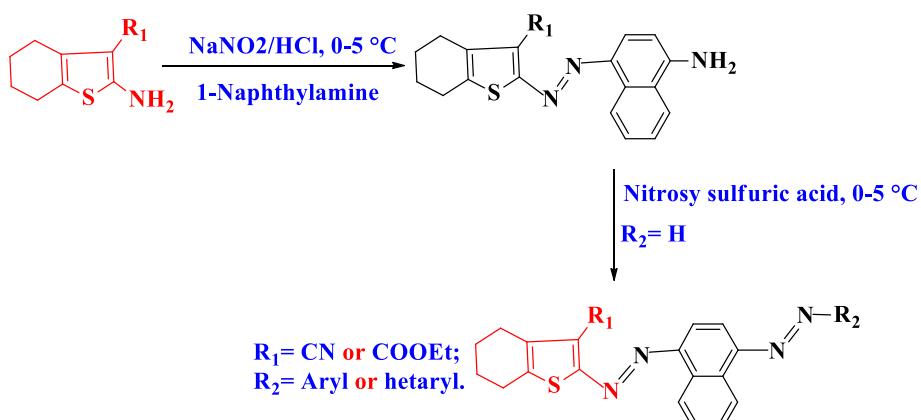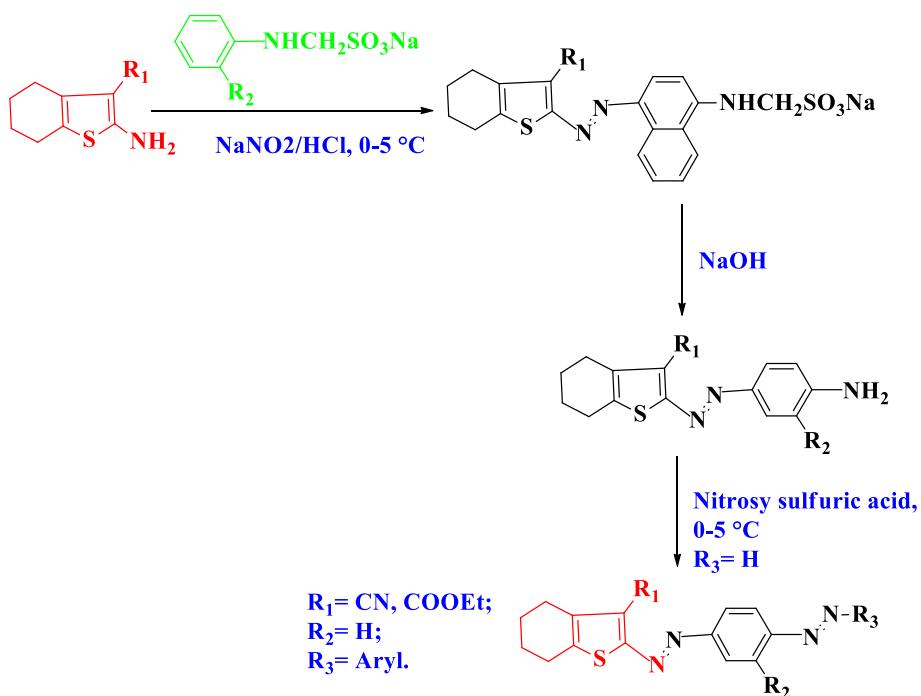
Figure 43. Disazo disperse dyes 39.

According to same author [71], A series of novel azo dispersed dyes were synthesized from 4, 5-hetero-2-aminothiophenes.

The key intermediate is 5-amino-6-cyano-2-phenylthienooxazole. The latter was prepared from 2-phenyl-5-4H-oxazolone, sulfur and malononitrile by the Gewald reaction, which was diazotized with nitrosyl sulfuric acid and coupled with N, N. The substituted arylamines with a dialkyl group at acid pH gave dyes -azo-thieno-oxazoles 27 [72], (Figure 41).

Rangnekar et al. [71], have been demonstrated the using of 2-amino-thiophenes via the Gewald reaction for synthesized dispersed diazo dyes 38. 2-amino-3-cyano- and 2-amino-3-carbethoxy-4, 5, 6, 7-tetrahydro-benzothiophene diazotised with hydrochloric acid and sodium nitrite in the cold and Coupled with N, N-dialkyl-substituted aryl amines to obtain monoazo dyes. The alkaline hydrolysis of monoazo dyes resulted in arylamino monoazothiophenes, which were diazotized with nitrosylsulfuric acid and coupled to 2-naphthol and N, N-dimethylaniline, gave deeply coloured disazo disperse dyes 38 (Figure 42), [71].

According to Rangnekar et al. [71], another series of disazo disperse dyes 39 have been reported using 2-aminothiophene via the Gewald reaction, as illustrated in Figure 43, [71].

R₁= H, Me, MeO
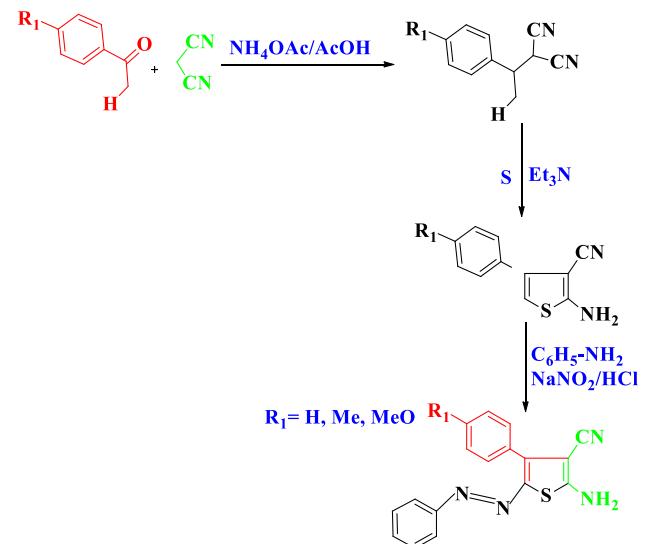
Figure 44. Azothiophene dyes 42.
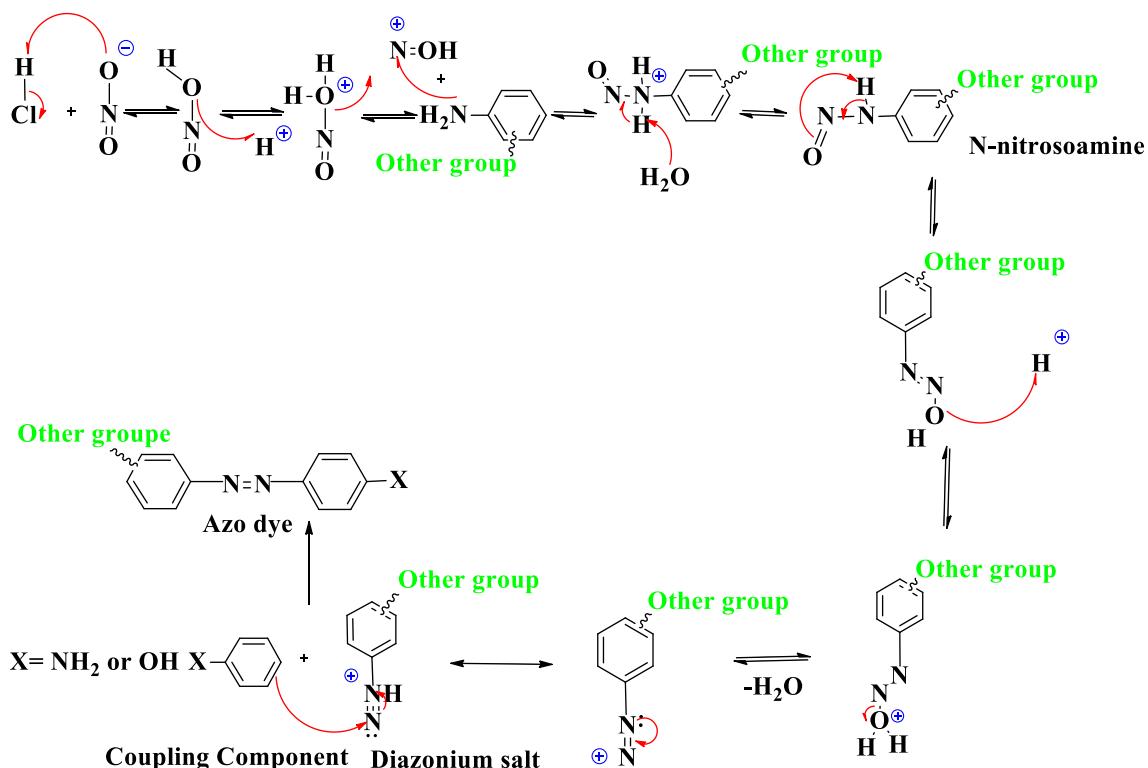
Figure 45. Synthesis of azo dye.
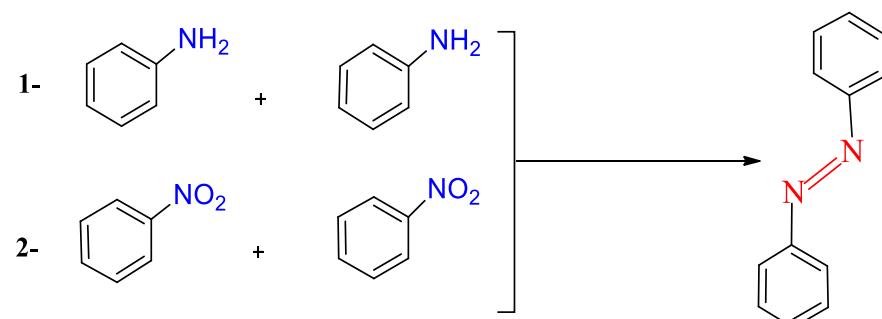
Figure 46. Represents the preparation of symmetrical azo compounds.

Figure 47. Azo compound.

Figure 48. Simple reaction of the synthesis of azo dyes.
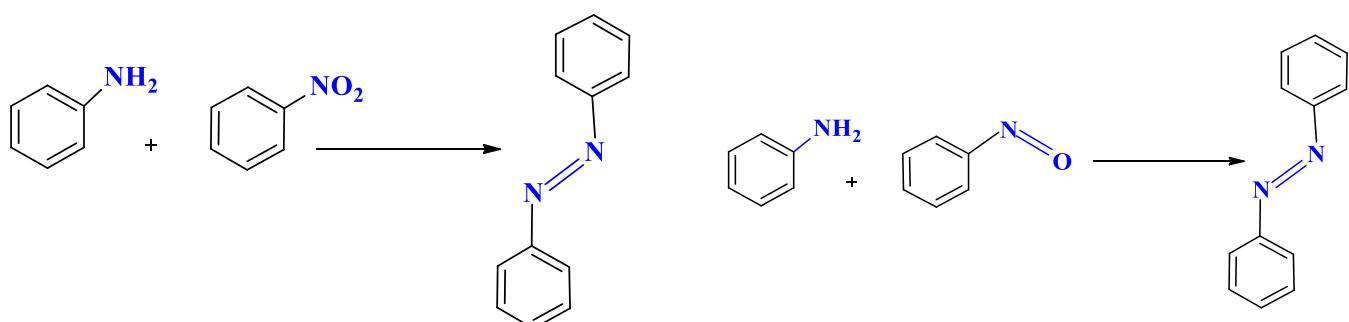
According to Wardakhan et al. [73], aniline was diazotised and coupled with the corresponding 2-amino-3-cyano-4-aryl-substituted thiophenes at the 5-position of the thiophene moiety, yielding azothiophene dyes 42 [73], (Figure 44).

6. Synthesis of azo dyes by the diazotization/coupling reaction

Azo dyes are synthetic compounds containing an azo bond –N=N-, obtained mainly from the aromatic amine substrate, nitro and nitroso. The synthesis processes rely on the use of an appropriate oxidizing/reducing
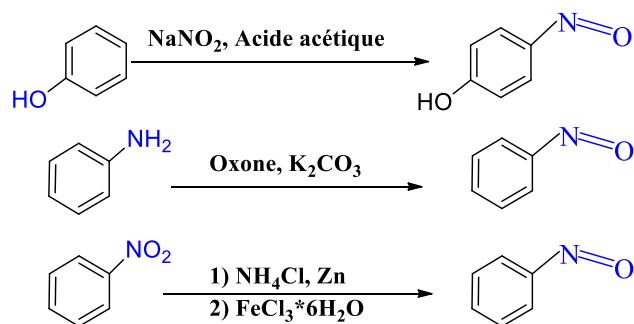
Figure 49. Synthesis of nitrosated derivatives.
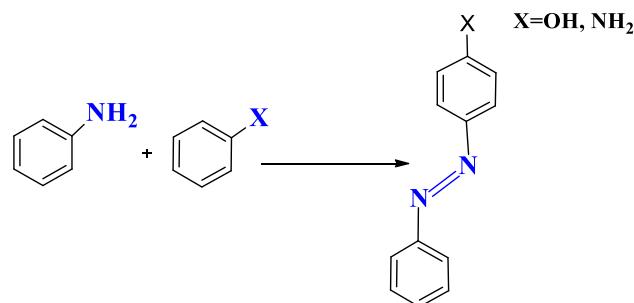
Figure 50. Electrophilic aromatic substitution mechanism.

reaction or a diazotization/coupling reaction. This is considered one of the most important reaction in the development of industrial organic chemistry. The synthesis requires a diazonium salt and a coupling component. Figure 45 shows the general synthesis of an azo dye, [31, 32].

Most diazonium salts are unstable and can be explosive when they are dry. They are always prepared in an acid medium with good stirring at 0 °C to minimize contact with water to produce phenol and are used immediately in the coupling reaction. To complete the synthesis of the azo dye, the diazonium salt reacts as an electrophile with a coupling component is rich in electrons (a phenol or an aniline). This reaction was carried out by an electrophilic aromatic substitution mechanism. The hydroxyl or amine group directs the aryl diasonium ion to the para site in the event that this site is not occupied, otherwise it will be attached to the ortho position. There are other methods for the synthesis of azo dyes [26, 75] among which we found the reduction of the nitroaromatic derivatives in alkaline medium, the reduction of the nitrosated compounds by $AlLiH_4$, the oxidation of the primary amines by the potassium permanganate or lead tetraacetate, condensation of hydrazines and quinones and condensation of primary amines of nitrosated derivatives.

The azo dyes and pigments are manufactured on an industrial scale by the same reaction sequence in two stages, diazotization and azo coupling. Overall, there are five strategies for the synthesis of azo dyes based on the diazotization/coupling reaction. Each strategy has certain restrictions associated with the availability of substrates. The two reactions 1 and 2 below are intended for the preparation of symmetrical azo compounds (Figure 46). In the case where the two substrates are different, the product obtained consists of two symmetrical azo compounds and one asymmetric.

The oxidizing coupling reaction of two amines used can be carried out by oxygen in the presence of a catalyst (CuCl/Pyridine) [76] under photocatalytic conditions promoted by TiO_2 [77], Fe_2O_3 [78] HgO [79] or oxidizing agents such as $KMnO_4$ [80], MnO_2 [81], $NaBO_3$ [82], KO_2 [83], K_2FeO_4 [84], AgO [85], Pb $(OAc)_4$ [86]. The reduction reagents used are zinc or $SnCl_2$ in a basic medium [87,88], $LiAlH_4$ [89], ethylenediamine [90], Na_2Te [91] or lead either with triethylammonium formate or acetate of ammonium [51, 52]. Another method was published in 1906 which is based on the reaction of p-nitrophenol in an alkaline medium at 200 °C [94].

According to Węglarz-tomczak [95], the reaction presented in the Figure 47 could yield a reasonable yield of the azo compound due to their application conditions by heating the substrates used in KOH/DMF solution for 12–48 h at a temperature of 150 °C under a nitrogen atmosphere [96,97]. Previously, a shorter time and a lower temperature did not allow productivity to be less than 20 % [97,98].

The simplest reaction in the synthesis of azo dyes has been illustrated in the Figure 48.

This reaction can be carried out by three different methods [99,100], (Figure 49).

Subsequently, the amino and nitroso substrates are simply mixed in glacial acetic acid at room temperature [101]. A modification of this method involving the in situ generation of the nitroso derivative from the starting amine under the action of H_2O_2 and its subsequent reaction with an unoxidized reagent can lead to the symmetrical product [102].

Figure 50 shows an electrophilic aromatic substitution mechanism such that the diazonium salt formed from aniline is the electrophilic
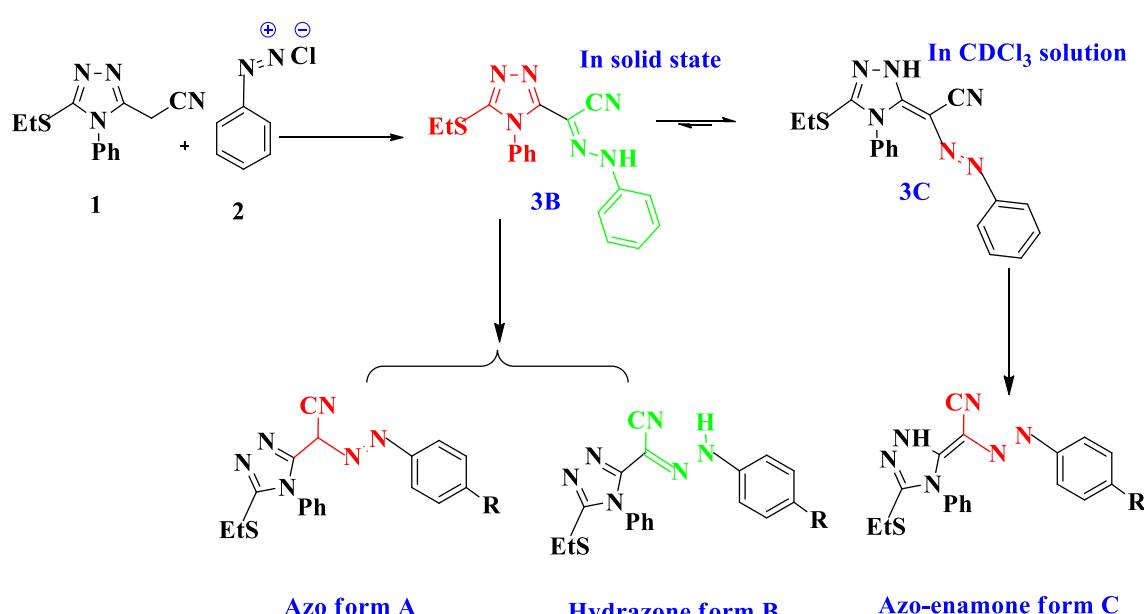

Figure 51. Compound 1 coupling reaction with benzene diazonium chloride and forms A, B, and C.
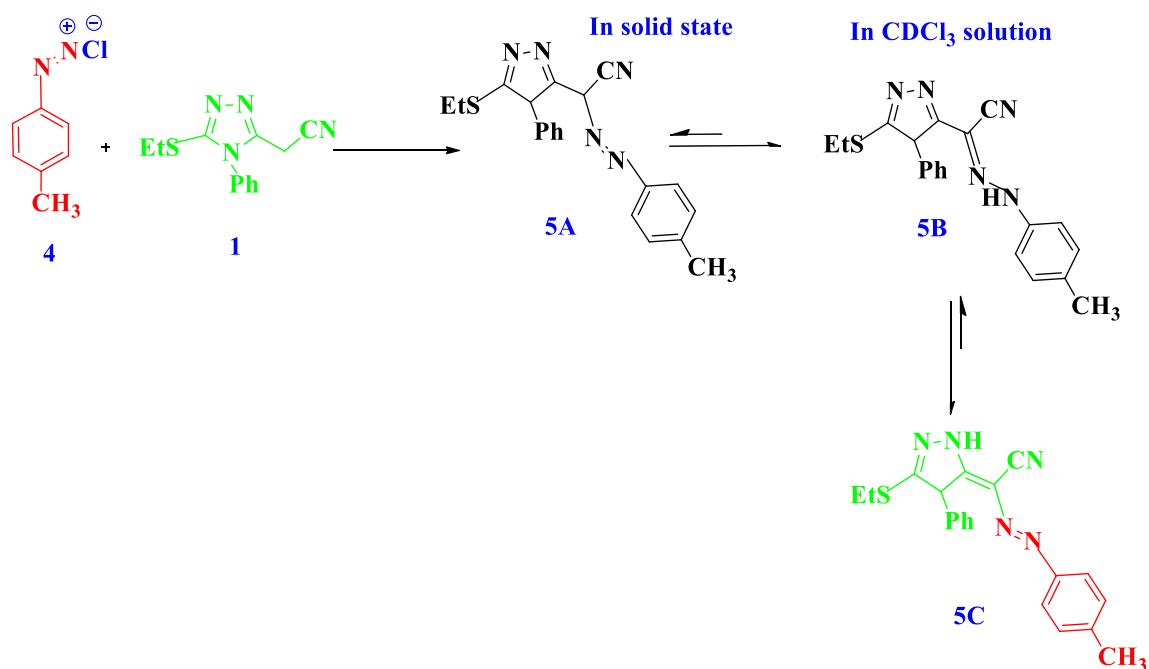
**Figure 52.** Coupling reaction of 1 with diazotized 4-methylaniline.
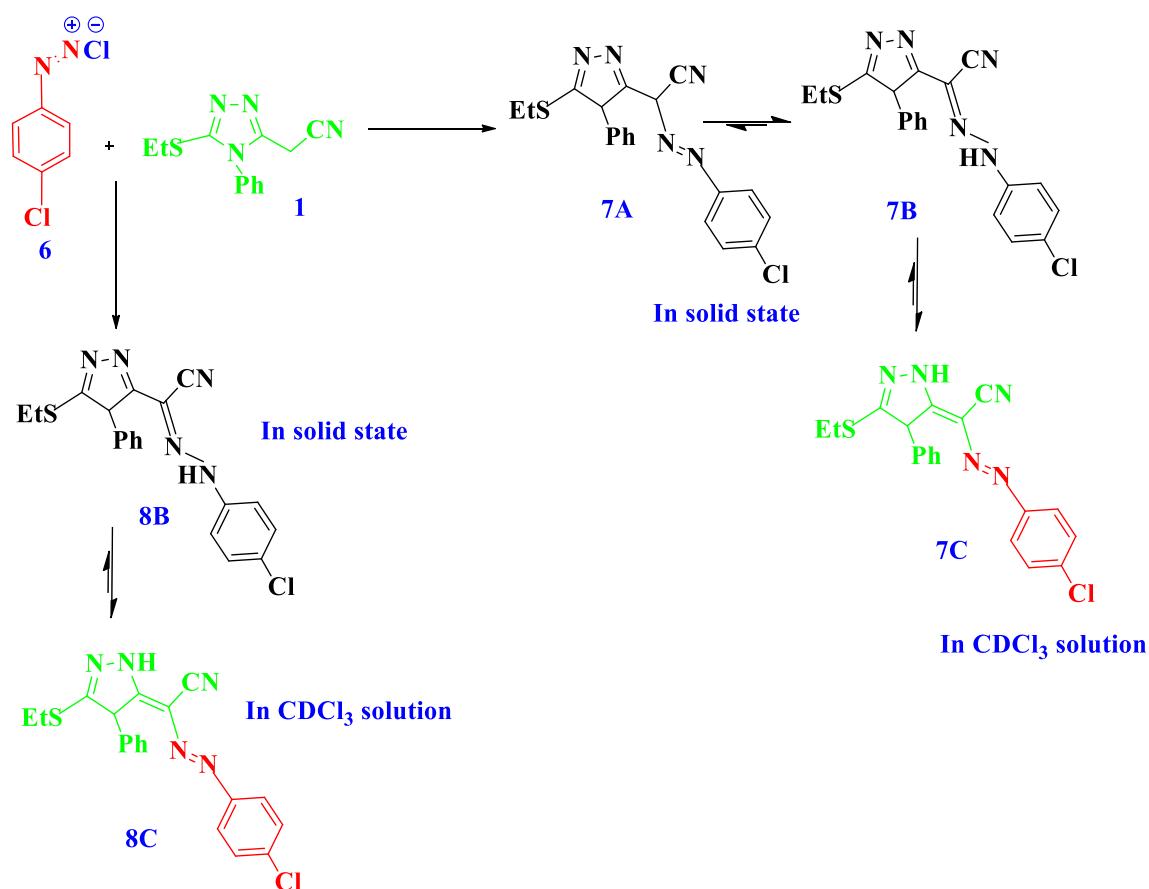
**Figure 53.** Coupling reaction of 1 with diazotized 4-chloroaniline.
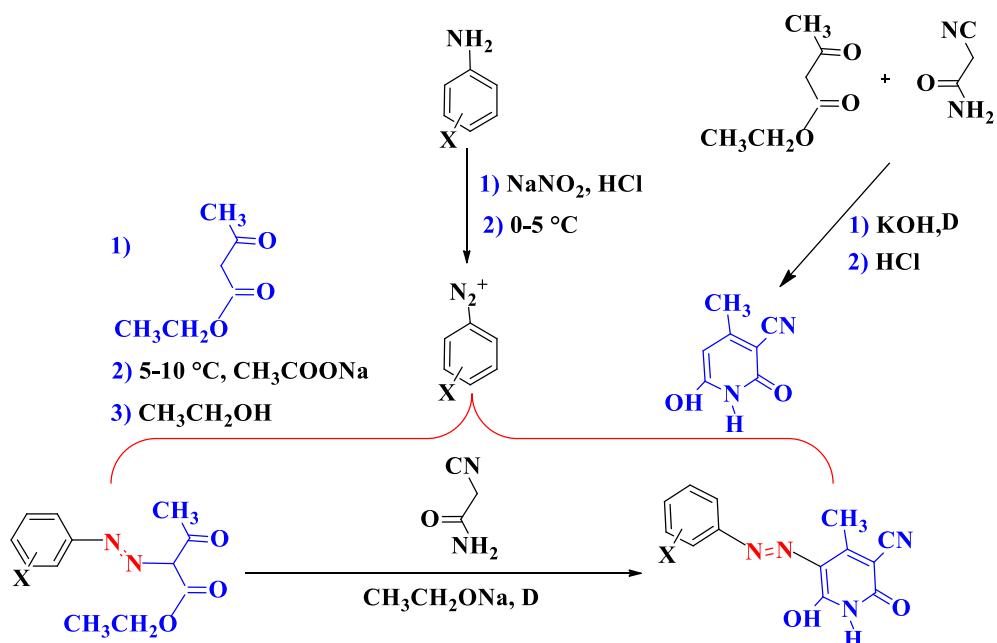
**Figure 54.** Synthesis of arylazo pyridone dye.
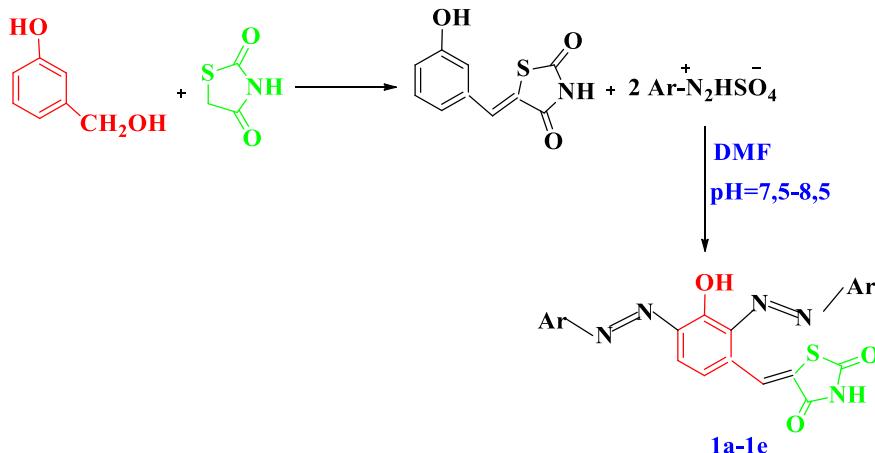
Figure 55. New azo– hydrazone tautomerism in azo dyes.

reagent, while an aromatic system substituted by an electron donor group (OH, NH$_2$ or their derivatives) is the corresponding nucleophile [89, 103].

The coupling reaction can take place when an alkyl-substituted aromatic derivative which is the nucleophilic reagent, in which case the electrophile must contain an electron withdrawing substituent. For example, Nitro group increases the electronic deficit of the diazonium group. This allows the coupling of 2, 4, 6-trinitroaniline with 1, 3, 5-trimethylbenzene, 1, 2, 3, 5-tetramethylbenzene or pentamethylbenzene [103,104]. Typically, the diazonium salt received is immediately subjected to the coupling reaction, because after separation and drying become explosive [105]. In the reaction of diazonium salts with phenols, the product is substituted in the para position with respect to the hydroxyl group. If this site is occupied, the ortho isomer is obtained. In the case of unsubstituted aniline, an azo aminobenzene compound is preliminarily formed (-N=N–NH-) and then rearranged to the mixture of the para and ortho isomers of the amino azobenzene product [106]. To avoid this disadvantage, protection of the amino group can be applied for coupling and eliminated after the reaction, for example, by hydrolysis [107]. The direct method of obtaining the amino azobenzene structure

(avoiding rearrangement) is thus to effect the reaction in formic acid and sodium formate [108].

7. Some reaction patterns of the most recent azo dyes

New generations of azo dyes have been synthesized by different synthetic methods, [109,110,111,112]. In this part we have cited some syntheses of the azo dyes containing chemical groups hydrazone, chromene and derivatives of 2-aminothiophene and 2-aminothiazoles [70,113,114,115].

7.1. Synthesis of azo dyes contain chemical groups hydrazone

The azo dyes can be theoretically included in azo-hydrazone tautomerism which is a very important propertie in the industrial application of the azo dyes [56]. The physical (solution and solid) states of the azo-hydrazone tautomery are of theoretical and practical interest because the two tautomers have different technical properties and different dyeing performance [116].

According to Al-Sheikh et al. [114], the coupling reaction of 3-ethyl-thio-5-cyanomethyl-4-phenyl-1,2,4-triazole (1) with benzene diazonium

Aromatic part

Structure of bis-azo dyes 1a-1e
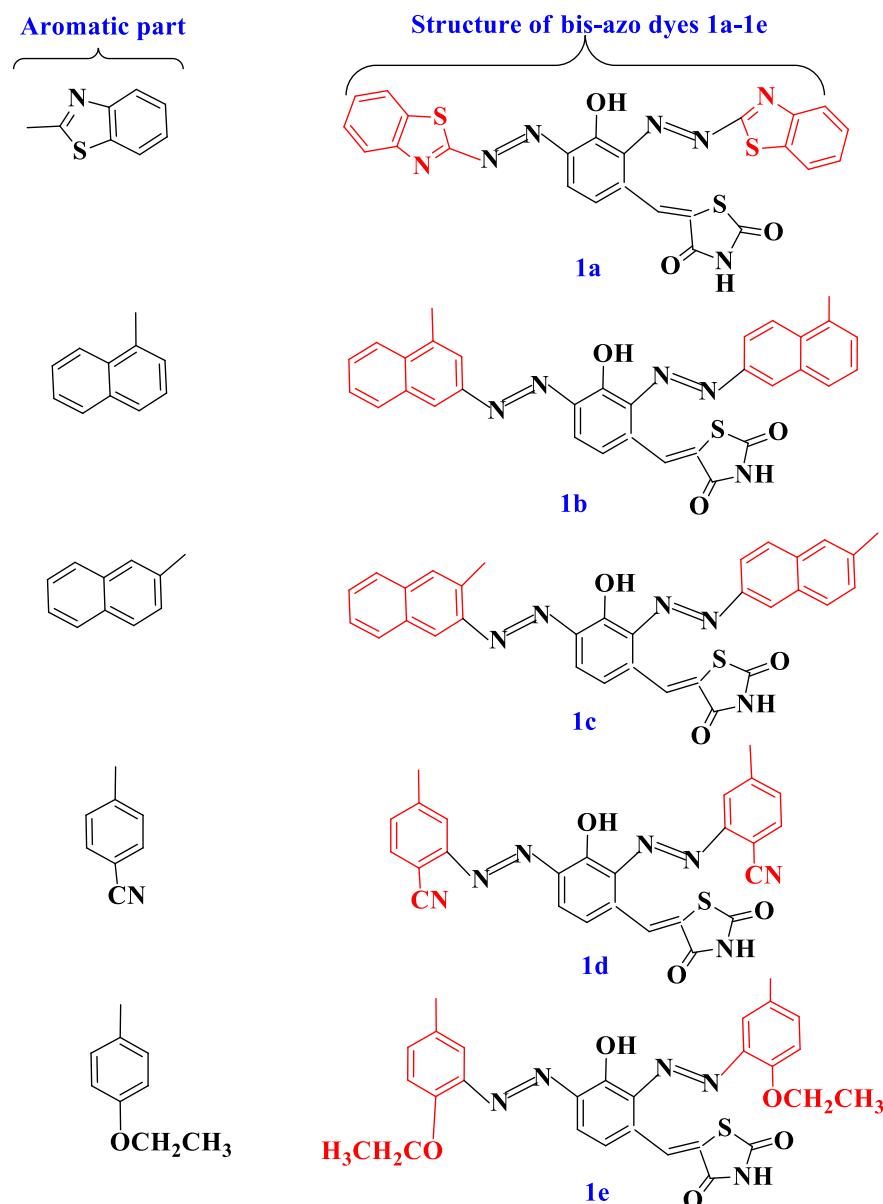
Figure 56. Shows different possibilities of the structure of 1a-1e.

chloride 2 and then coupling of the diazonium salt with compound 1 in an aqueous solution of ethanol in the presence of a buffered solution of sodium acetate. This reaction yields 5-ethylthio-N ′, 4-diphenyl-4H-1, 2, 4-triazole-3-carbohydrazonoyl (3B) with excellent yield. The dye prepared can exist in three possible tautomeric forms, The azo form A, the hydrazone form B and the azo-enamine form C, (Figure 51).

Then, the effect of substitution at the para position of the benzene ring of the diazonium salt on the equilibrium between the three forms **A**, **B**, and **C** is taken into account. A study was made by Pavlović et al. [117], which reported that the electron-releasing substituents in the para position of the diazonium benzene salt increase the azo form content. While the electron-withdrawing groups promote the content of the hydrazone form. In accordance with these results, we have succeeded in predicting that the coupling reaction of compound 1 with diazotized 4-methylaniline 4 under similar reaction conditions to the above gives 5-ethyl-thio-3- (1- (4-methylphenylazo) -4-phenyl-acetonitrile) -4H-1, 2, 4-triazole (**5A**), in 82 % yield (Figure 52).

While the coupling reaction of the diazonium salts induces electron withdrawing substituents in the para position of the benzene ring with **compound 1**. Surprisingly, Compound 1 was coupled to the diazotized 4-

chloroaniline 6 in the same Reaction conditions above it gives two tautomers, **7A** (major product) and **8B** (minor product), (Figure 53).

According to Mirković et al. [56], the arylazo pyridone dyes were synthesized by two routes following the reaction sequence below, (Figure 54).

Mohammadi et al. [118], have been synthesized of certain novel azo-hydrazone tautomeric dyes according to the reaction sequence shown in Figure 55, [118,119,120].

Figure 56 shows different possibilities of the structure of bis-azo dyes according to the aromatic part **1a-1e**.

The benzothiazolyl azo dye 1a may exist in five possible tautomeric models, as shown in Figure 57.

The possible tautomeric structures of dyes **1b-1e** are shown in Figure 58.

7.2. Synthesis of azo dyes contain chemical groups chromene

According to kamazani et al. [113], this dye was obtained by the diazotization of the substituted aniline and the coupling reaction of 2-hydroxybenzaldehyde, (Figure 59).
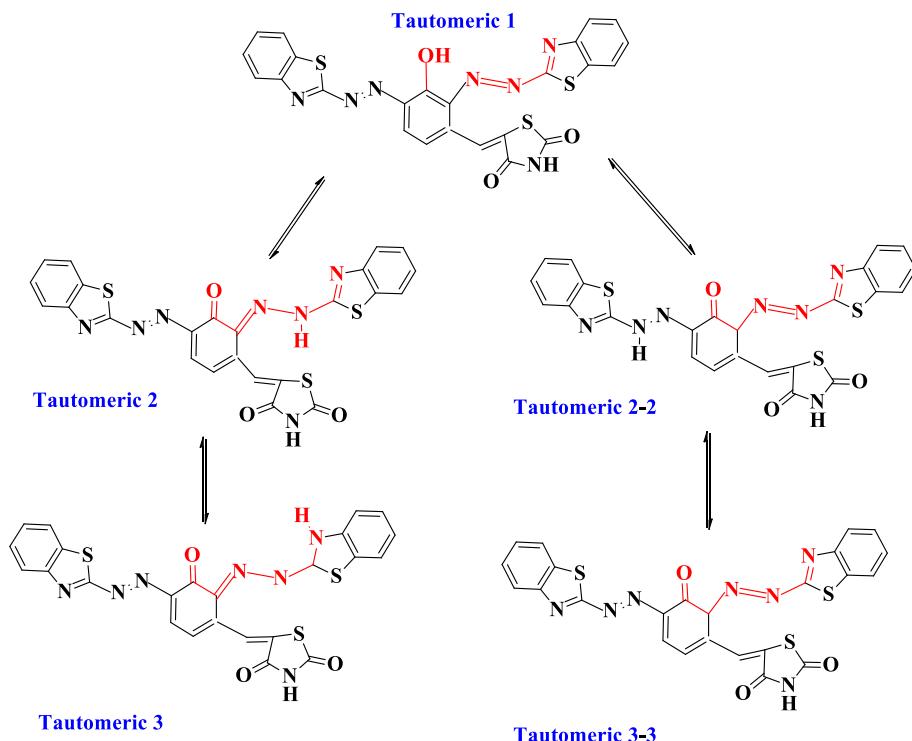
Figure 57. Possible tautomeric structures of dye 1a.
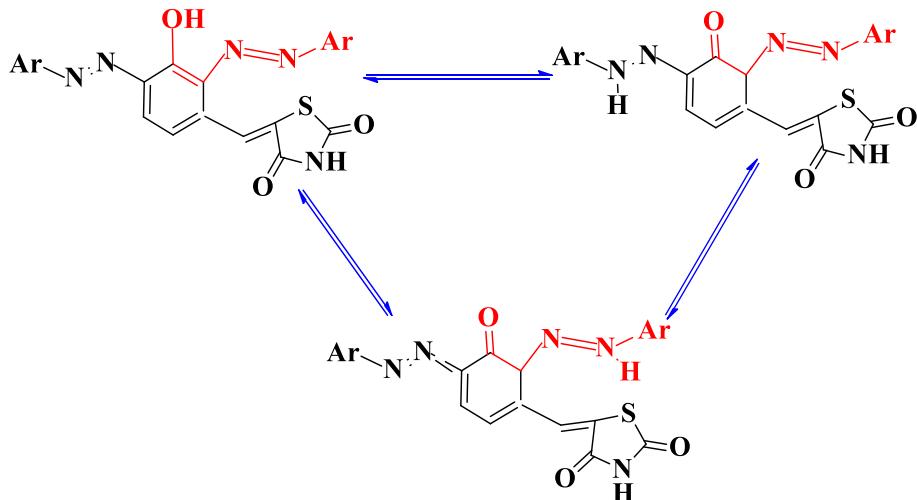
Figure 58. Possible tautomeric forms of prepared dyes 1b–1e.

Figure 60 shows different possible dye a structures according to **R₁** and **R₂** substitutions.

Badrey et al. [115], have been reported that the synthesize of azo dyes based on 2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile [124,125] has been reached by two routes. 2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile was coupled to various diazonium salts which make it possible to obtain the corresponding dyes and then react with cyanuric chloride, (Figure 61).

7.3. Synthesis of azo dyes derived from 2-aminothiophene and 2-aminothiazoles

According to Hallas et al. [70], the following sequence represents the synthesis of azo dyes derived from 2-aminothiophene and 2-aminothiazoles, (Figure 62).

Figures 63 and 64 illustrating different possible IV and V dye structures according to substitutions A, B, and X, [70].

8. Applications of azo dyes

These dyes are the most diverse group of all synthetic dyes (-N=N-) they are widely used in the fields of pharmacy, plastics, hypnotic medicine, living cells cancer and pharmacological activities [123], biological [2,124], in high-tech applications such as lasers and nonlinear optical systems [125], thermal transfer printers and fuel cells [126]. Also sensitized to solar cells [127], photodynamic therapy [126], metallochromic indicators [128], dyeing of textiles [129], leather, paper, food [130,131,132,133], cosmetics [7,134] and medicines [135,136]. The latter result from the combination of the properties of the azo group and of types of substituted aromatic ligands. These dyes are also known to be
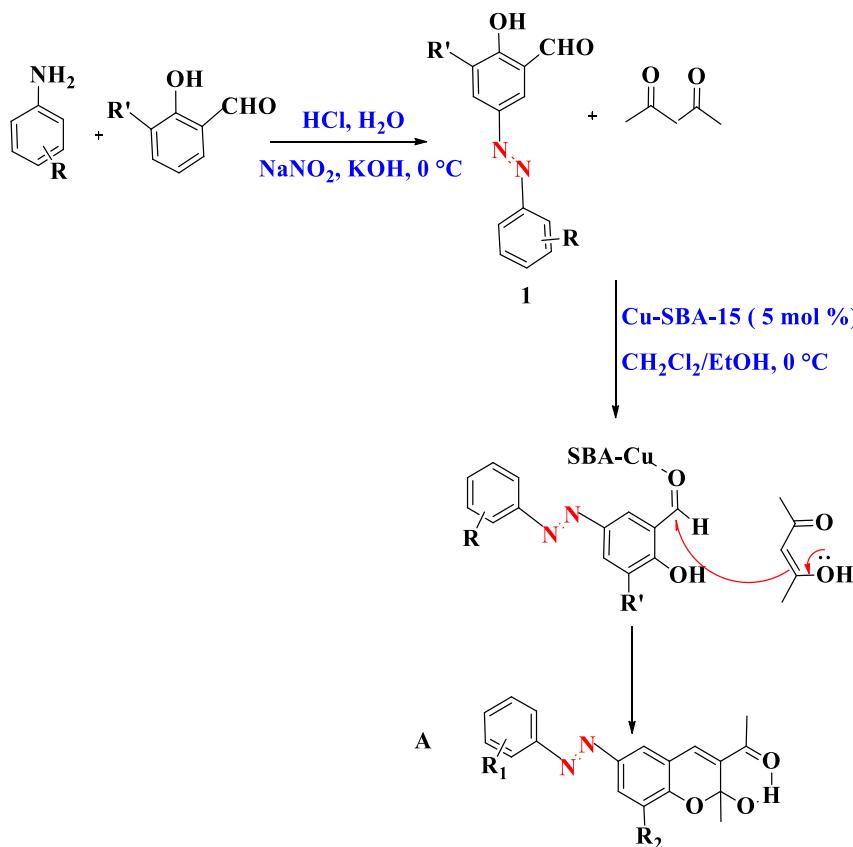
Figure 59. Synthesis of azo-chromene.

involved in a number of biological reactions such as DNA inhibition, RNA and protein synthesis, carcinogenesis and nitrogen fixation, [137].

Furthermore, the azo dyes are characterized by their physicochemical stability [138] and optical properties [139,140] with various applications in liquid crystals [141] and the nanotubes [142]. In recent years, azo-functionalized dyes bearing aromatic heterocyclic compounds have attracted increasing attention due to their wide range of colors, luminosity, the simplicity of manufacture and good dyeing performance [143, 144,145,146].

In the following paragraph, we have presented some recent applications of azo dyes such as azo-polymer conjugation. The types of bond which favor this conjugation can be covalent or non-covalent [146].

The preparation of polymeric dyes for technical and industrial applications is mainly carried out by the polymerization routes of colored monomers and polymer-like fixing of dye molecules to preformed polymers since the corresponding materials contain a higher dye concentration. Then, a tinctorial resistance is higher than the molecular weight derivatives of the unique chromophores [147].

8.1. Preparation of polymeric dyes by copolymerization of colored monomers

As reporeted in [148], the modification of dye molecules into polymerizable derivatives followed by their copolymerization is an interesting approach for the preparation of dye containing polymers. The general procedure is illustrated in Figure 65 [149].

8.2. Azo acrylic dye prototype

A synthesis was performed by azo coupling of 6-(methyl (phenyl) amino) hexan-1-ol and a 4-nitrobenzenediazonium salt. Subsequently, this methacrylate dye was treated with acryloyl chloride and meth acryloyl chloride. Copolymerization with methyl methacrylate as well as

homopolymerization of each coloring monomer gave linear soluble polymers. These dyes are commonly used in materials applied in nonlinear optics [150].

Another example is the performance of azo coupling with N-aryl maleimides for the generation of polymerizable azo polyester radicals [140,141]. For the preparation of structurally different azo dyes, 2, 6-dibromo-4-nitroaniline and 2-amino-3, 5-bis (ethoxy carbonyl)-4-methylthiophene have been converted into the corresponding diazonium salts (Figure 66), [152].

These were then coupled with several N-aryl maleimides giving the desired coloring monomers which readily polymerize under free radical conditions. The preparation of a methacrylate-based azo dye monomer in three reaction steps was addressed in another study (Figure 67), [151]. In the first step, tyramine was methacrylate by treatment with methacrylic anhydride. Subsequently, the diazotization of 3-aminopyridine was carried out. The product obtained therefrom is then coupled to the methacrylate tyramine. The resulting azo dye monomer was incorporated into polymers by copolymerization with N, N-dimethyl acrylamide. In addition, the copolymer has been studied with regard to its complexing behavior in the presence of copper ions [153].

8.3. Fixation of molecule dye to preformed polymer

Dye-polymer-like binding requires the presence of functional side groups linked to the polymer backbone which can readily react with small molecule functional groups. Figure 68 shows the mechanism for binding a molecule of the dyes to a polymer [154,155].

These molecules can be dyes themselves or a constituent element established by several steps and by fixing a chromophore. Depending on the molecular structure of the dye and the nature of the reactive side group, this attachment can lead to significant changes in the chromophore system.

R₁ and R₂

Structure of compound A

R₁= H ; R₂= H

R₁= H ; R₂= OMe

R₁= 4-Me ; R₂= H

R₁= 4-Et ; R₂= H

R₁= 3, 4-Me ; R₂= H

R₁= 4-Et ; R₂= OMe
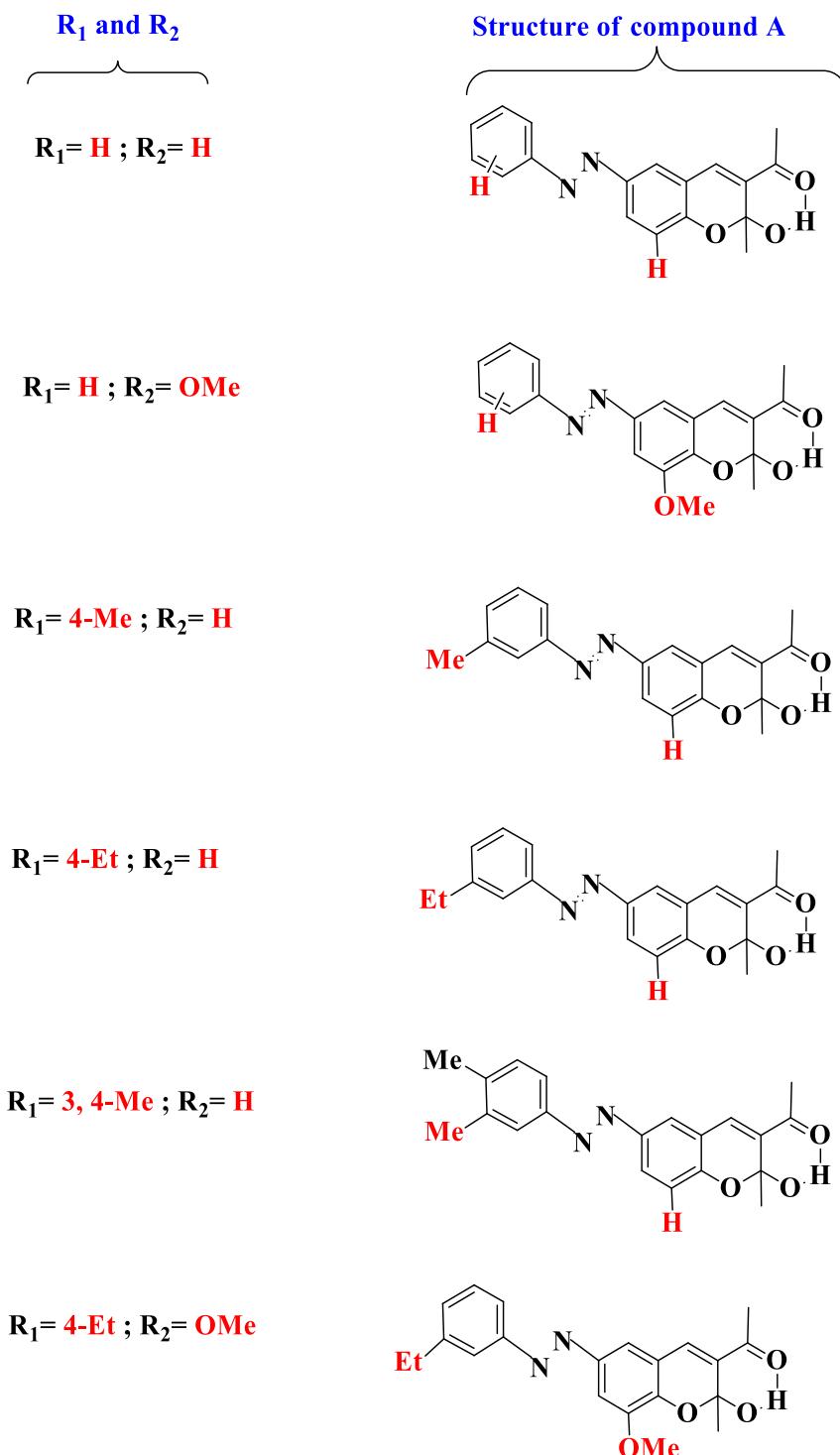
Figure 60. Different structure of compound A.

The polymer backbone was synthesized from the copolymerization of poly (N-isopropyl acrylamide and N-acyloxy succinimide), which gave linear polymers bearing active ester side groups. These were reacted with a catalyst derivative and amino-terminated methyl orange, which resulted in the formation of polymeric catalysts, including a colored "phase label [155].

In general, to preformed polymers, several varieties of examples of attachment of azo dyes have been published [151]. It has been observed that poly-electrophiles such as poly (epichlorohydrin) and poly (chloromethyl styrene) make it possible to attach nucleophilic building blocks which can be further converted into azo dyes, but the problem with these compounds is their tendency to Crosslinking. By using poly-morphonuclear agents, the effective fixation of N-acetylsulfanilyl chloride has demonstrated poly (vinylamine). The polymeric azo dyes were then obtained by the deprotection and diazotization of the sulfanilic acid fractions followed by azo coupling with a sufficient aromatic amount (Figure 69), [151].
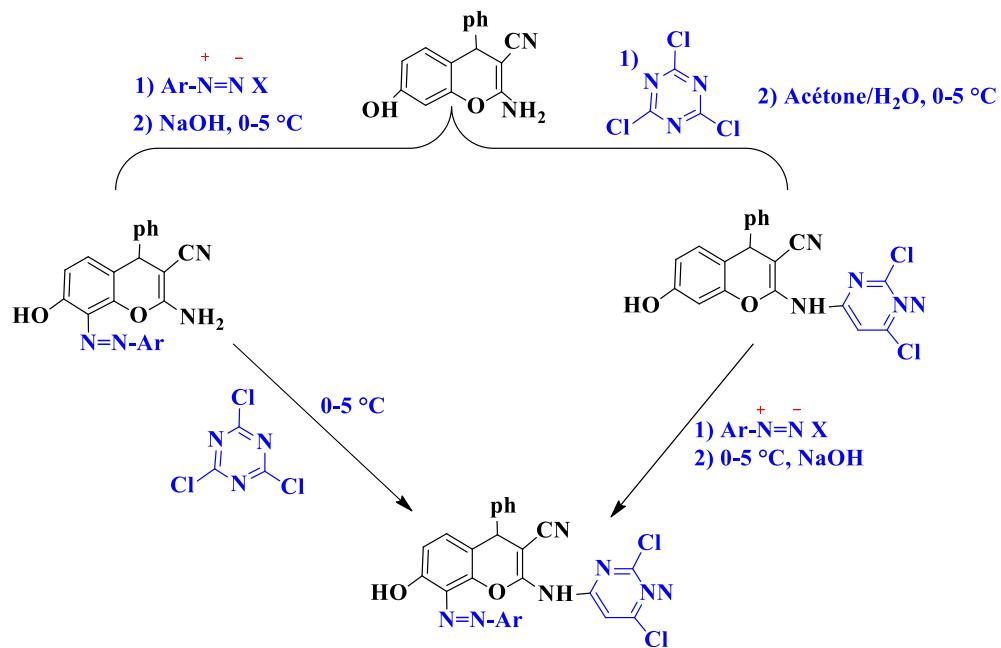
Figure 61. Synthesis of reactive azo dyes from 2-amino-7-Hydroxy-4-phenyl-4H-chromene-3-carbonitrile through various alternative routes.
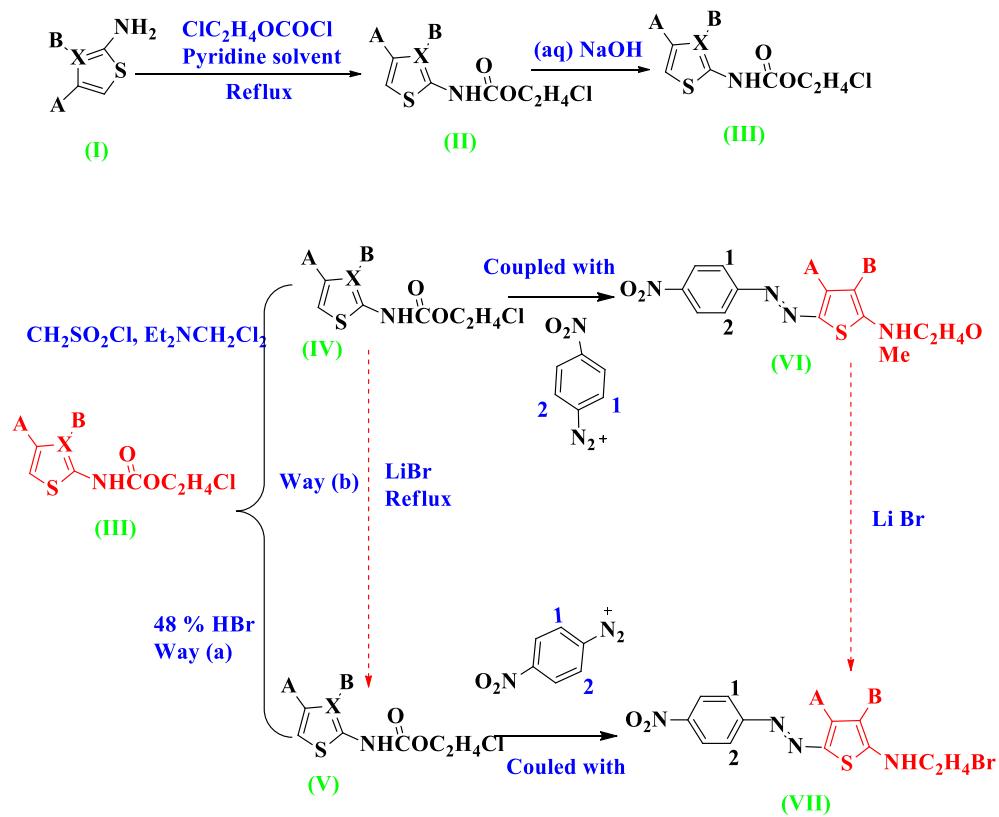
Figure 62. Synthetic routes to some azo dyes from 2-amino- thiophenes and 2-aminothiazole.

8.4. Conjugation by a non-covalent bond

Non-covalent binding can occur through different types of interactions such as ion dipoles, dipole interactions and inclusion complexes, and so on.

● Dye - Sugar-based polymers

There are a large number of polar substituents that enable the formation of dipolar interactions with adequate substrates, sugar-based macromolecules are suitable materials for supramolecular attachment of dye. Such oligo-polysaccharides can be obtained from natural products such as starch, cellulose, chitosan and the like [145,146]. Figure 70 illustrates a schematic of a non-covalent dye bound to polymeric materials [157].

A   B   X   **1= Cl ; CF$_3$; CN ; NO$_2$ or Br ; 2= H or Br**

Ph CN C

Me CN C

H CN C

Me CONH$_2$ C

Me H N
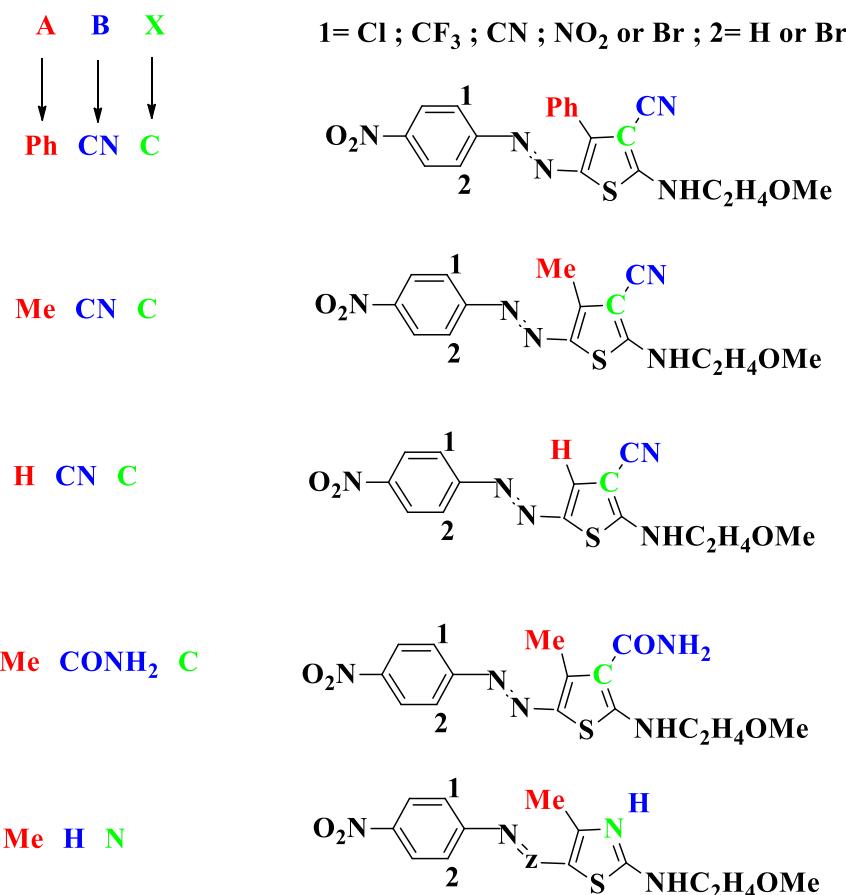
Figure 63. Different structure of compound IV.

A   B   X   **1= Cl, CF$_3$, CN, NO$_2$ or Br, 2= H or Br**

Ph CN C

Me CN C

Me H N
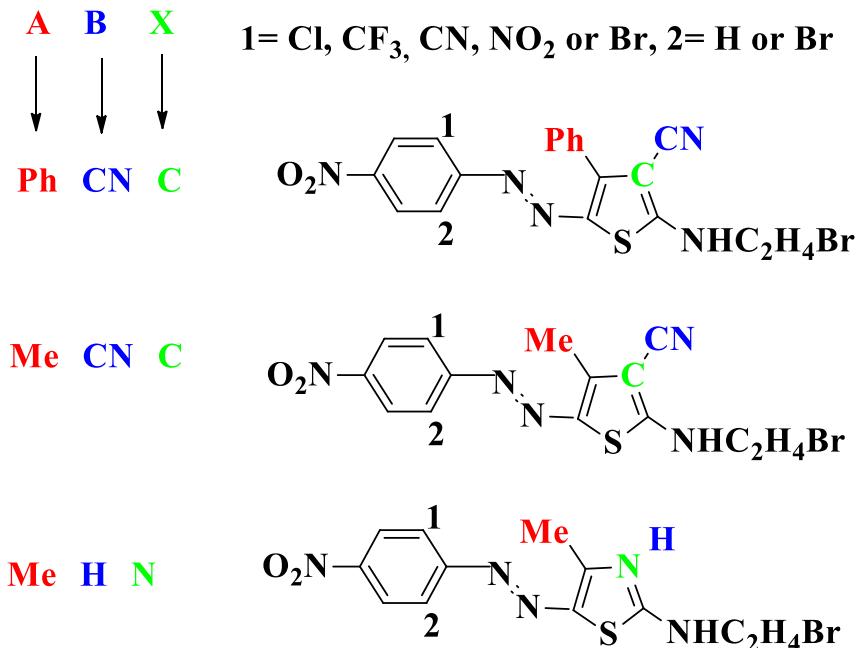
Figure 64. Different structure of compound V.

Sugar-based macromolecules are suitable materials for the supramolecular fixation of dyes. Adsorption was effective for anionic azo dyes which carried sulfonate moieties for starch and β-cyclodextrin polymers [158]. The principal effects resulting from the adsorption of the dyes have been found to be hydrogen bonds formed between hydroxyl and amine groups located in polymers and in the sulphonate groups of azo dyes. In addition, cyclodextrins are known to form inclusion complexes
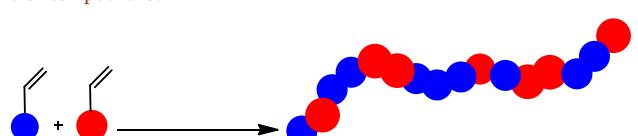
Figure 65. Diagram of the preparation of polymeric dyes by copolymerization of colored monomers.
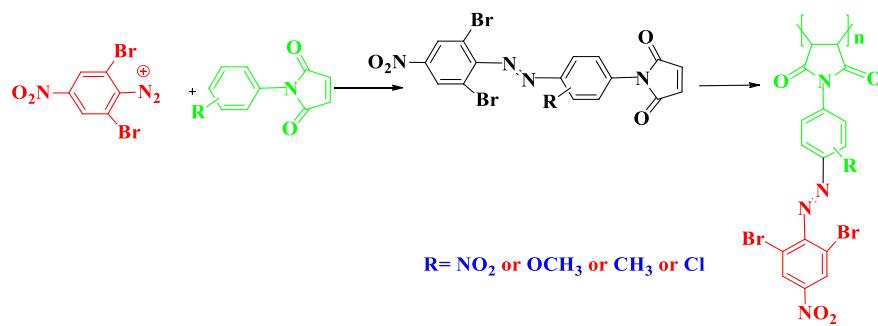
Figure 66. Synthesis of an azo dye bearing N-aryl maleimides and their free radicals of polymerization.
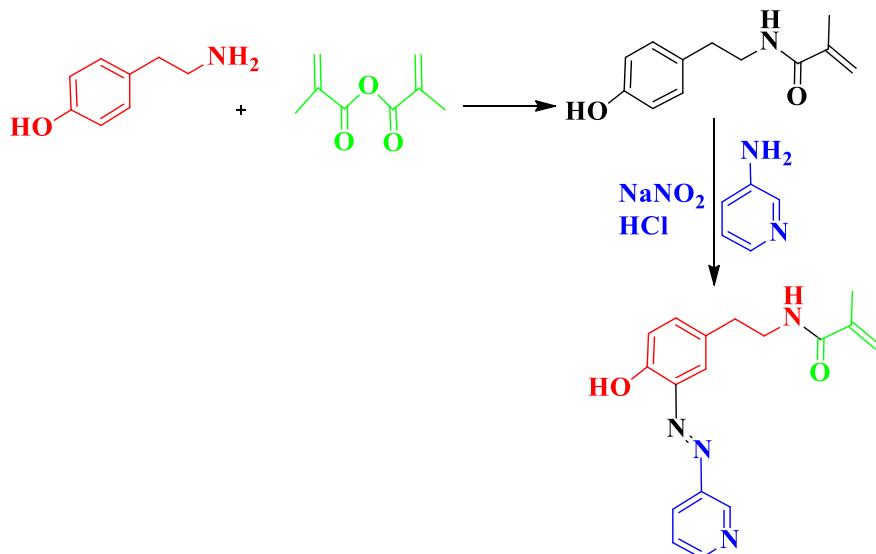
Figure 67. Synthesis of a derivative of polymerizable azo dye.

Reactive side group
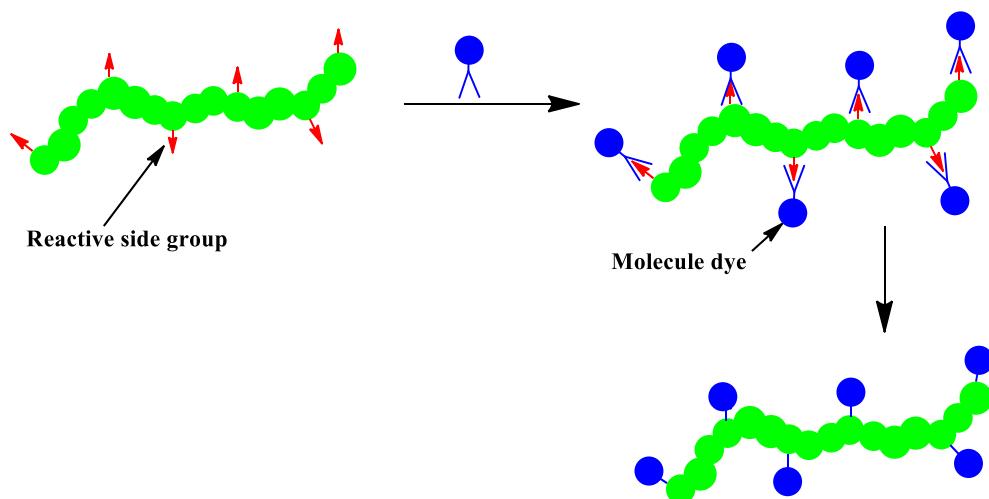
Molecule dye

Figure 68. Fixing molecule of the dye on polymer.
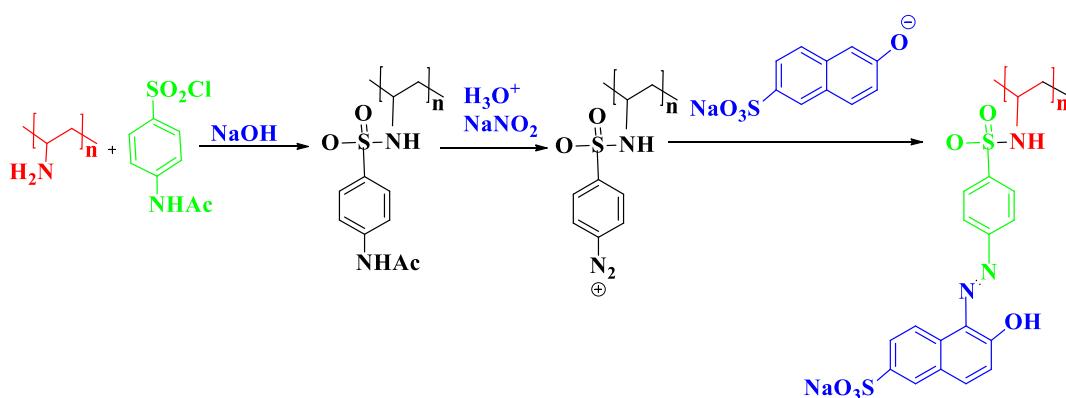
Figure 69. Step-wise fixing of an azo dye to poly (vinylamine).
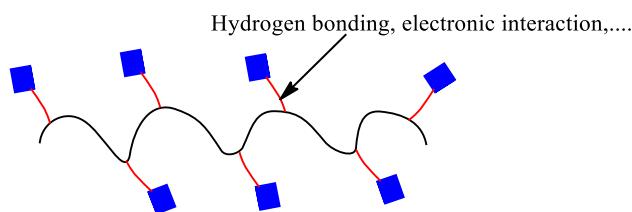
Figure 70. Diagram of a noncovalent dye-polymer bond.

with azo dyes and complex formation which should, therefore, contribute to the sorption of the dyes from the corresponding cyclodextrin-based polymers.

It has been found that the adsorption of the dyes to the polymer takes place by bonding hydrogen or dipole-dipole. In addition, β-cyclodextrin polymers have an efficient adsorption of cationic dyes [159].

9. Conclusion

Azo dyes represent the largest production volume of dye chemistry today, and their relative importance may even increase in the future. Azo dyes are regularly used in a variety of applications in the food, pharmaceutical, paper, cosmetics, textile and leather industries and others. They make up about half of all synthesized dyes.

In addition, the data presented in this review show that azo dyes have reached the widest range of uses, as variations in chemical structure are easily synthesized by the reaction of an azo coupling component containing an atom active hydrogen bonded to a carbon atom. This reaction proceeds according to the electrophilic aromatic substitution mechanism rich in electrons. More than 60 % of the synthesized dyes are produced by this reaction.

The reaction of azo coupling, taking place between diazonium salts and aromatic amines, phenols, or naphthols, results in deep-colored products (azo dyes).

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Author contribution statement

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