

Review

The Use of Heterocyclic Azo Dyes on Different Textile Materials: A Review

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Abstract: The art of dyeing textiles has a long history, as natural dyes have been used since prehistoric times. With the development of synthetic dyes in the 19th century, the focus shifted from natural to synthetic dyes due to their superior properties. Recently, however, interest in natural dyes has increased again due to environmental and health concerns. Among industrial dyes, heterocyclic dyes, especially azo dyes, are of great importance due to their color brilliance and fastness. This review examines the synthesis, application, and analysis of azo dyes, especially heterocyclic dyes. It deals with monoazo, diazo, and polyazo dyes and highlights their structures, synthesis methods, and fastness properties. In addition, the ecological impact of azo dyes and practical solutions for their synthesis and application are discussed.

Keywords: heterocyclic azo dyes; textile dyeing; photochromic properties

1. Introduction

The art of textile dyeing is an activity as old as mankind, as colored textiles have been found in archeological excavations in the oldest civilizations. However, it should be emphasized that heterocyclic dyes have also been in use since prehistoric times. At that time, only natural dyes obtained from natural resources of plant, animal, mineral, and microbial origin were used [1]; many of them were, in fact, natural heterocyclic dyes such as indigo (obtained from the leaves of *Indigofera tinctoria*) and Tyrian purple (obtained from the shells of mollusks of the Muricidae family), which were used to dye textiles in blue and purple, respectively (Figure 1).

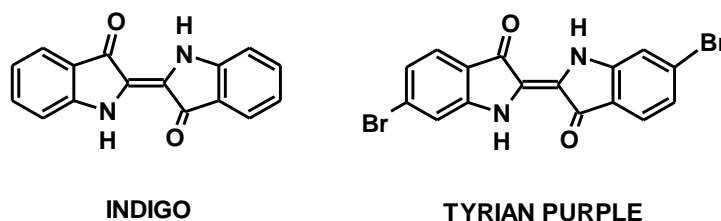


Figure 1. Structure of indigo and Tyrian purple.

Since the second half of the 19th century, more precisely since the invention of synthetic dyes, the use of natural dyes has been almost completely replaced by synthetic dyes due to their ease of use and better fastness properties, although there has been a return to the use of natural dyes in recent decades, not only because they are environmentally friendly, but also due to the fact that many artificial textile dyes are hazardous to human health [2]. Nevertheless, the search for synthetic dyes is still very active, as the requirements of customers around the world are changing rapidly. In the field of industrial dyes, heterocyclic dyes have been increasingly used recently as they have higher color brilliance and strength as



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well as better color fastness compared to benzene analogous dyes. Heterocyclic dyes can be divided into different technical sections according to the type of electronic character of the dye molecule [3]. This overview reports on the most important group among them—the azo dyes. In particular, the synthesis, the applications on different textile materials, and the analyses carried out to verify the fastness properties are reported.

2. The Azo Dyes

Azo dyes are characterized by the functional group $-N=N-$, which connects two symmetrical or asymmetrical substituents, of which at least one, but usually both, are aromatic [4].

They are usually synthesized in a two-step reaction as follows: synthesis of an aromatic diazonium ion from an aniline derivative (diazotization) and coupling of the diazonium salt with an aromatic compound (Figure 2) [5] or by the reduction of nitro aromatic compounds in an alkaline medium and oxidation of aromatic amine with various oxidizing agents such as lead tetraacetate, permanganate, and haloxy acid [6].

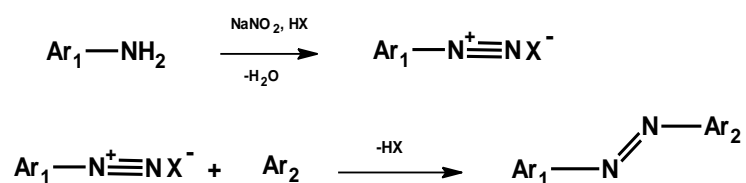


Figure 2. Synthesis of azo compounds.

If both substituents are aromatic substituents, the dyes are referred to as carbocyclic, whereas if they contain one or more heterocyclic substituents, the dyes are referred to as heterocyclic azo dyes.

All azo compounds are classified by Griffiths [7] as donor–acceptor chromogens (D- π -A) (Figure 3), and studies have shown that replacing the benzene ring of the acceptor with a less aromatic heterocycle in these chromogens leads to a significant bathochromic shift (red shift) in the visible absorption band, which results in greater color brilliance and higher color intensity, especially in synthetic materials [8].

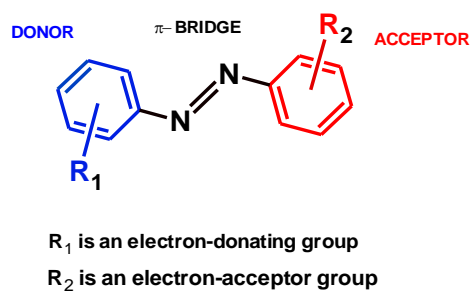


Figure 3. Scheme of D- π -A azo compounds.

Due to the structure of azo compounds, they exhibit photochromic properties.

Photochromism is a phenomenon that occurs when two molecules (A and B) are in chemical equilibrium with each other and can be easily distinguished due to their different absorption spectra. Normally, the more stable isomer (A) can transform into the less stable, higher energy isomer (B) when excited by light. However, the B isomer can spontaneously transform into the former through a thermal or photochemical reaction (Figure 4). It follows that there are the following two types of photochromic systems: Type T, i.e., thermally reversible photochromes, and Type P, i.e., photochemically reversible photochromes [9].

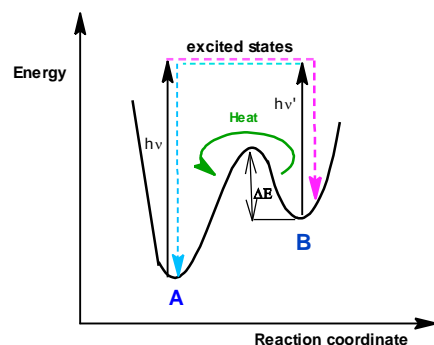


Figure 4. Energy profile for the interconversion between the two isomers A and B [9].

In the case of azo compounds, these two isomers are E and Z isomers (Figure 5).

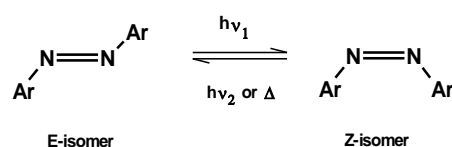


Figure 5. Isomerization E–Z for azo compounds.

The case of isomerization of azobenzene has been extensively studied and analyzed. In this case, the photochromic system is of the T-type, and the azobenzene in the E-configuration is more stable than in the Z-form. The two isomers differ not only in their structure and properties, but they also exhibit different absorption spectra in the UV spectrum (Figure 6). The different spectral position of the bands indicates that not only is the wavelength of light required to induce the reaction different for the two isomers, but they also have different colors [9].

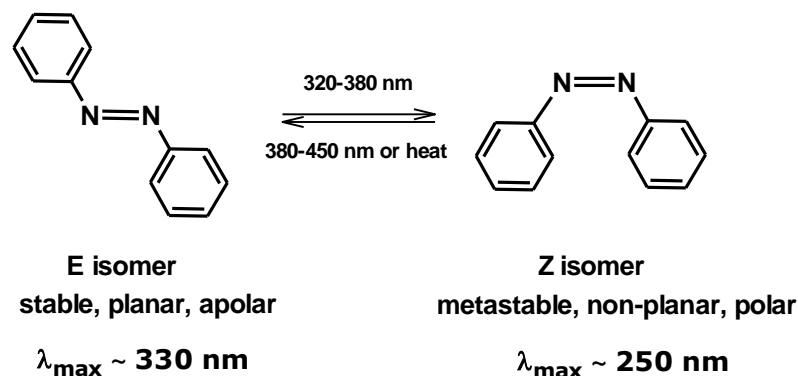


Figure 6. The E and Z isomers of azobenzene.

Changes in the absorption spectra between the two forms are generally not very pronounced due to a small difference in electron delocalization between the two isomers, and the color change is invisible to the naked eye. In contrast, the photochromic reaction induces very significant change in the free volume [10], density, viscosity, electrical conductivity, stiffness, and porosity of the molecule [9].

As early as 1990, Gregory reported that heterocyclic azo dyes are able to “combine the brightness and high fastness properties of anthraquinone dyes with the strength and economy of azo dyes” [11]. It is therefore not surprising that numerous attempts have since been made to synthesize ever more efficient heterocyclic azo dyes.

3. Heterocyclic Azo Dyes

Heterocyclic azo dyes, like all azo dyes, can be divided into three categories according to the number of azo groups in the same molecule as monoazo, diazo, and polyazo dyes.

3.1. Heterocyclic Monoazo Dyes

In 1999, Towns gave an overview of the progress made with heterocyclic diazo components over the past decade [12]. This paper reports on the applications to textiles of heteroazo dyes consisting of five-membered rings containing a sulfur heteroatom, to which a diazotizable amino group is directly attached. These compounds are divided into the following four groups based on the heteroaromatic amine used for diazotization: Thiazoles **1** and Benzothiazoles **2**, Isothiazoles **3** and Benzisothiazoles **4**, Thiadiazoles **5a–5b**, and Thiophenes **6** (Figure 7).

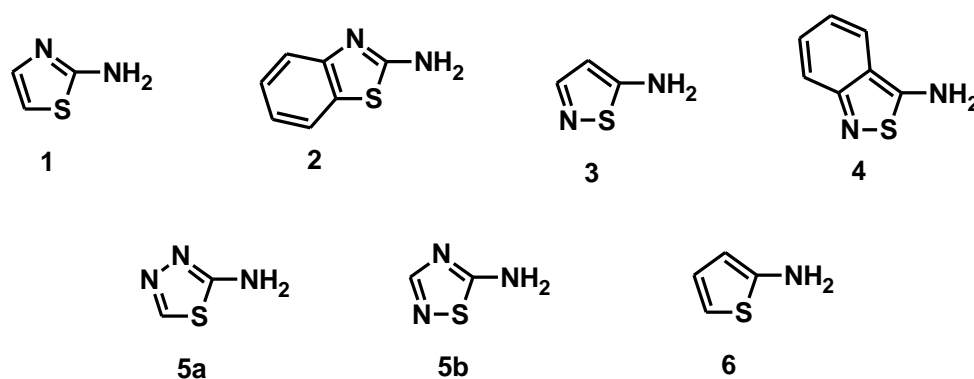


Figure 7. Structures of heteroaromatic amines.

Towns reported that most of the numerous patents filed in the last ten years have mostly been the result of modifications and improvements to existing products, with no real innovation in molecular structures. He also said that the search for brighter and more economical dyes was still ongoing and predicted that disperse dyes from heterocyclic components would be explored in the coming years.

A few years later, the synthesis and application of novel heterocyclic dyes based on a new fused heterocyclic compound, 11-amino-3-bromo-13h-acenaphtho[1,2-e]pyridazino[3,2-b]-quinazolin-13-one, was reported [13]. A series of new azo dyes (**7a–k**) was synthesized by diazotization of this heterocyclic amino compound and coupling with various naphthols (**a–k**), leading to the general structure shown in Figure 8.

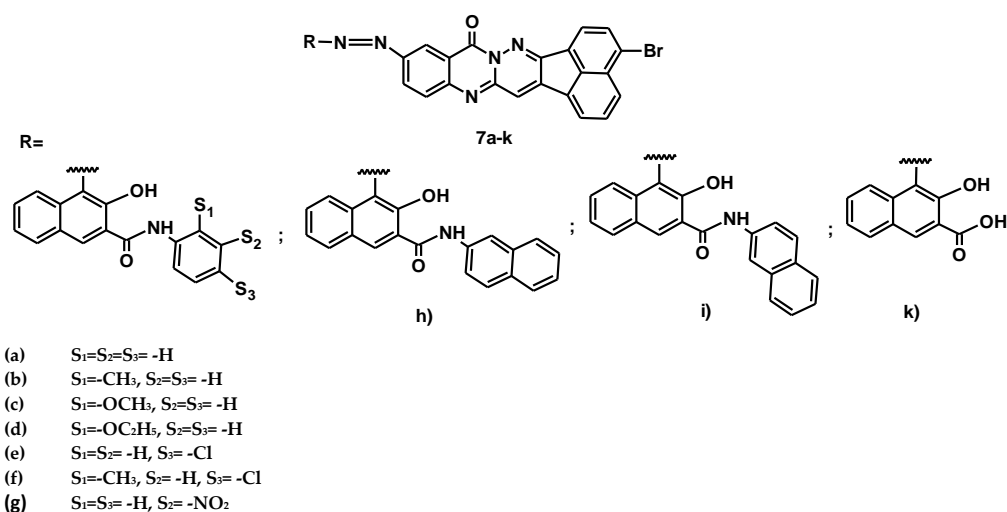
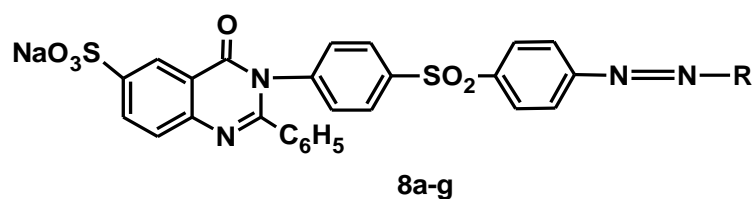


Figure 8. General structure of dyes **7a–k**.

Specifically, these dyes were synthesized by diazotization with sodium nitrite and hydrochloric acid, and coupling was carried out in a moderately alkaline medium at 0–5 °C. After characterization, the dyes were applied as azo dyes to nylon 66 and polyester fibers, resulting in a variety of shades ranging from pink to red and brown. The differences in the shades of the dyed fibers are due to the type and position of the substituent.

The analysis showed that the dyes on both substrates had fairly good to good light fastness and very good to excellent fastness to washing, rubbing, perspiration, and sublimation, while the percentage exhaustion of the dye bath was better on nylon 66 than on polyester, probably due to the better accessibility of the open structure.

In 2010, the same authors reported the synthesis, characterization, and application of another series of heterocyclic monoazo reactive dyes (**8a–g**), which were synthesized by coupling diazotized 2-phenyl-3{4'-[(4''-aminophenyl)sulfonyl]phenyl}-quinazolin-4(3H)-one-6-sulfonic acid with various 2-chloro-4-nitro-anilino-cyanurate coupling components [14], with the general structure shown in Figure 9.



R = various 2-chloro-4-nitro anilino cyanurated coupling components (a-g).

Figure 9. The general structure of dyes **8a–g**.

The 2-chloro-4-nitro anilino cyanurated coupling components used are as follows: H-acid (**a**), Gamma acid (**b**), J-acid (**c**), N-methyl-J-acid (**d**), N-phenyl-J-acid (**e**), Chicago acid (**f**), and Laurant acid (**g**).

When applied to silk, wool, and cotton fabrics, the dyes obtained covered almost the entire visible range and generally produced yellow to violet shades. The differences in the color shades of the dyed fabric result from the change in the coupling components.

All the dyes (**8a–g**) generally show moderate to good light fastness properties, while the fastness to washing and rubbing is very good to excellent. The presence of a quinazolinone structure in all the dyes results in high color strength, as the quinazolinone structure exhibits intrinsic conjugation, leading to excellent color strength. The heteroatoms in the dye structure lead to bathochromicity and brightness of shades. The exhaustion and fixation properties are good for all the dyes, although the introduction of a triazine group improves both properties.

The same authors have published many articles on this type of research, in which they have tested not only the fastness property but also the antimicrobial activity against bacteria and fungi [15,16], which is a new trend in this field, as people's lives have improved and consumers are aware of a hygienic lifestyle and tend to ask for textile products that do not cause toxicity, allergy, or irritation to the users [17–19].

For example, a recent paper reported on the synthesis of new antibacterial dyes for fabric printing [20]. In this work [21], three new azo dyes (**9a–c**) with sulfonamide chromophores were used to dye polyester fibers via azo coupling with nucleophilic precursors (Figure 10).

The analytical results showed that the fastness properties and color evaluation of the printed samples exhibited moderate to excellent results in washing, rubbing, perspiration, sublimation fastness, and light fastness. Antibacterial activity was tested against four bacterial species (*Pseudomonas aeruginosa*, *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*) for the new dyes, but also for the printed fabrics after washing, using ampicillin as a reference, which is normally considered a standard antibacterial agent [22]. The diameter of the inhibition zone (mm/mg sample) as a measure of antibacterial activities

was measured for all samples, and the results are shown in Tables 1 and 2. From the results, it can be seen that the dyes **9a** and **9b** containing sulfate groups showed higher antibacterial activity against all types of bacteria. On the other hand, the dyed polyester fabrics showed moderate antibacterial activity, which, in this case, was also higher in the samples printed with **9a** and **9b**, showing that the antibacterial properties of the dyes were transferred to the corresponding dyed textile samples.

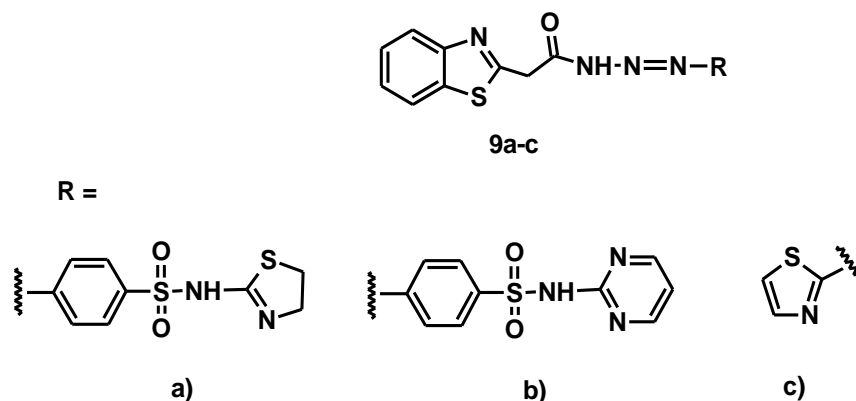


Figure 10. The general structure of dyes **9a-c**.

Table 1. Inhibition zone of **9a-c** as a measure of the antibacterial activities (mm/mg samples).

	9a	9b	9c	Ampicillin
<i>Pseudomonas aeruginosa</i>	29	30	10	26
<i>Escherichia coli</i>	28	30	11	25
<i>Staphylococcus aureus</i>	29	30	9	21
<i>Bacillus subtilis</i>	26	20	9	26

Table 2. The inhibition zone of the fabrics dyed with after 4 washes **9a-c** as a measure of the antibacterial activities (mm/mg samples).

	Polyester Fabric Printed with 9a	Polyester Fabric Printed with 9b	Polyester Fabric Printed with 9c	Ampicillin
<i>Pseudomonas aeruginosa</i>	15	12	8	26
<i>Escherichia coli</i>	12	12	10	25
<i>Staphylococcus aureus</i>	12	14	9	21
<i>Bacillus subtilis</i>	16	12	8	26

These inexpensive, easy-to-synthesize, biologically active dyes could be used to sterilize textiles for future applications.

3.2. Heterocyclic Diazo Dyes

Diazo dyes, which contain two groups $-N=N-$, are divided into the following three groups depending on the synthesis method used for their production [23]:

3.2.1. Primary Diazo Dyes

This type of dye is synthesized by a coupling reaction of two moles of diazoic acid with the same coupling term. An example, a brown dye used for dyeing wool, is shown in Figure 11a.

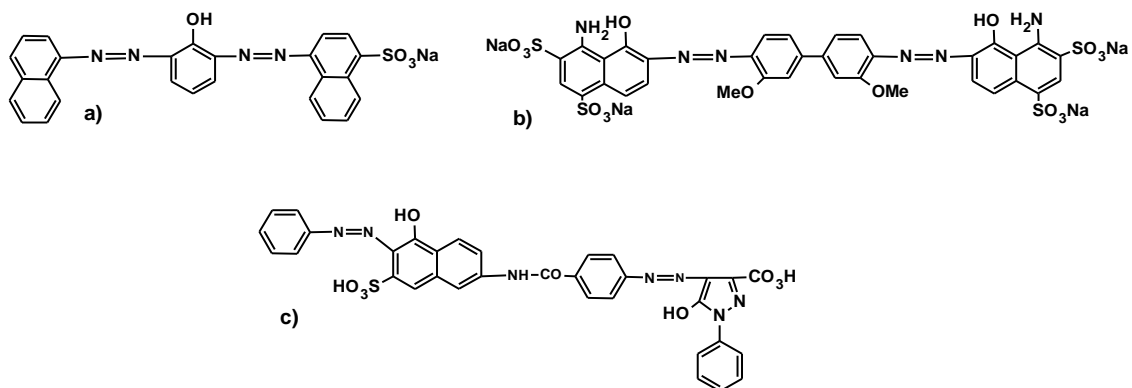


Figure 11. Structure of: (a) a brown dye, (b) a blue dye, (c) an orange dye.

3.2.2. Secondary Symmetrical Diazo Dyes

This type of dye is derived from a diamine that is diazotized twice and coupled with the same or different terms. An example, a blue direct dye with a benzidine function, is shown in Figure 11b.

3.2.3. Secondary Asymmetrical Diazo Dyes

This type of dye is synthesized by the coupling of an amino azoic acid with a phenolic coupler. Figure 11c shows an example, an orange direct dye.

Although a patent [24] for the use of heterocyclic diazo dyes was granted as early as 1954, only a few studies [25,26] were conducted in the literature regarding the comparison with monoazo compounds until 2005. In that year, Karci reported the synthesis of ten novel diazo dyes derived from various heterocyclic coupling components and aminomethylphenylazo pyrazoles [27]. The entire synthesis process begins with the preparation of nitrile 10, then pyrazoles 11a–b, which are finally used for the synthesis of diazo dyes 12a–j (Figure 12).

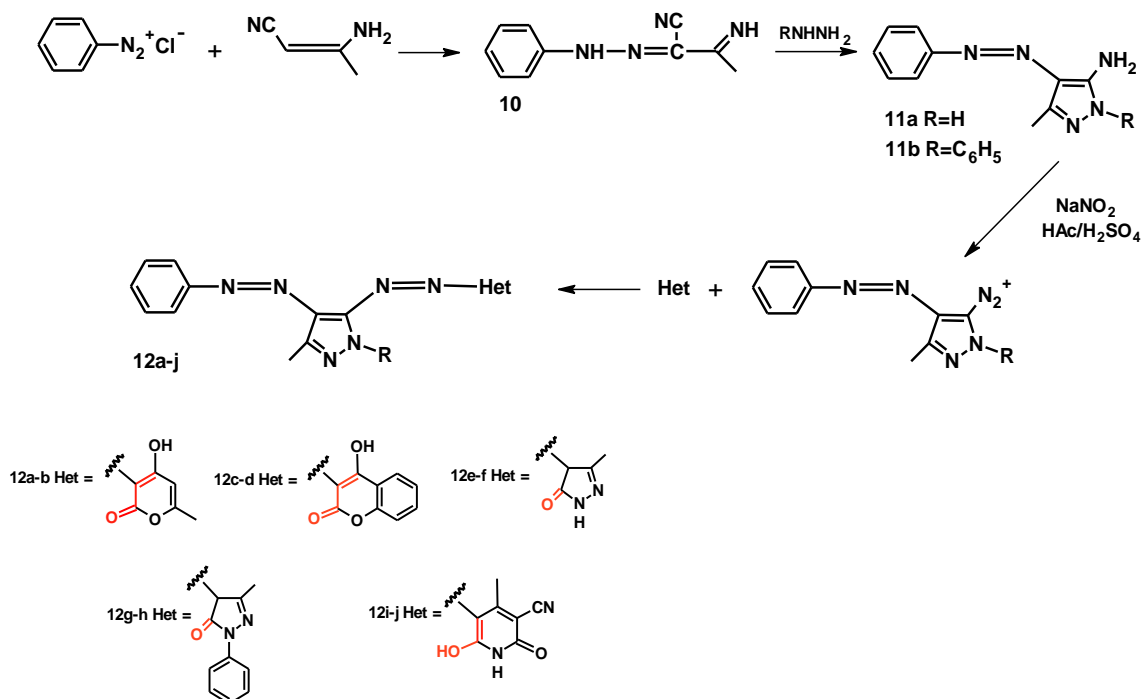


Figure 12. Synthesis process of diazo dyes 12a–j.

All diazo compounds **12a–j** may exhibit keto–enol tautomerism due to the functional groups highlighted in red in Figure 12. The tautomeric forms for compounds **12a–b** are shown in Figure 13 as an example. In the particular case of dyes, tautomerism is important not only because the two tautomeric forms can have different colors but also different tinctorial strengths and properties [28–30]. From the data of the infrared spectra of compounds **12a–j**, it appears that some of them are predominantly in the hydrazone–keto form in the solid state, while other in the azo–enol form.

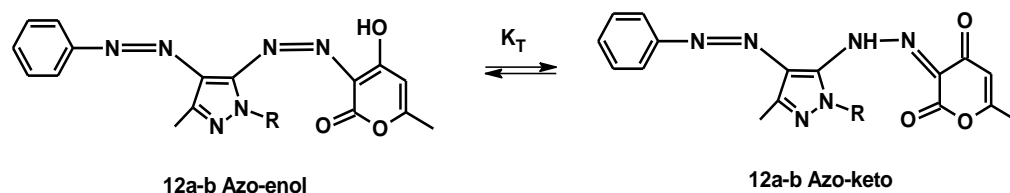


Figure 13. Tautomeric forms ketone–enol for diazo compounds **12a–b**.

Instead, the ^1H NMR spectra in dimethyl sulfoxide (DMSO) show that compounds **12a–d** are present as a mixture of tautomeric forms, whereas in **12e–j** the single tautomeric form predominates.

The effect of solvent and acid or base on the wavelength of the absorption maximum (λ_{max}) was also investigated. It was found that the absorption spectra of dyes **12i–j** show a maximum at a longer wavelength than those of dyes **12a–h** in all the solvents used. In addition, a bathochromic shift was observed for dyes **12c** and **12e** compared to the analogous dyes **12d** and **12f** in all the solvents tested, while the other analogs showed very similar λ_{max} but only in DMSO and dimethylformamide (DMF). These results led us to conclude that for the dyes **12a**, **12c**, **12e**, **12g**, and **12i**, there could be a tautomeric equilibrium between the pyrazole ring and the phenylazo group at 1-H (Figure 14).

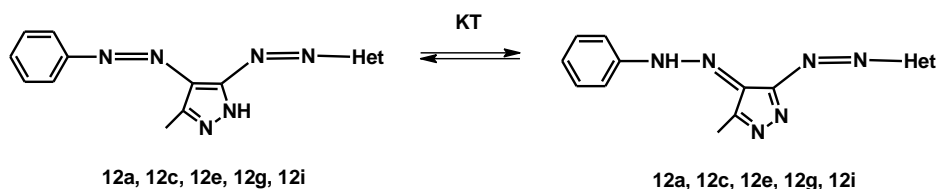


Figure 14. Tautomeric forms enamine–imine for diazo compounds **12a**, **12c**, **12e**, **12g**, and **12i**.

In conclusion, the authors report that all dyes **12a–j** can be applied to polyester and/or polyamide fibers as disperse dyes.

Another important aspect studied over the years is the color yields obtainable by modifying the position of the substituents on the heteroatomic rings. In particular, for example, in a 2016 article, a study on six novel pyrazole diazo disperse dyes (**13a–c**, **14a–c**, Figure 15), substituted with methyl ($-\text{CH}_3$) group at their *o*-, *m*-, *p*-position, was reported [31]. Their synthesis was carried out according to the literature procedures [27,32,33] (Figures 12 and 15), and the studies of their application to three different synthetic fibers at certain dyeing conditions are described.

All synthesized dyes were characterized by elemental analysis and spectral methods and then tested on different fibers. The fibers used for the evaluation were polylactic acid (PLA), polyethylene terephthalate (PET) and polyamide 6.6 (PA 6.6) fibers.

The colorimetric properties, yield, and fastness parameters of all fiber samples dyed with the novel synthesized disperse dyes were described and compared. Yellow and orange shades were obtained on PLA, PET, and PA 6.6 fibers by applying 2% of all dyes. With the dyes **13a–c** ($K/S > 10$), predominantly darker shades were achieved, and with the dyes **14a–c** ($K/S < 10$), medium-dark shades were obtained. In addition, due to the different molecular weights, the exhaustion and color yield of the **13a–c** dyes (lower molecular weight) were higher than those of the **14a–c** dyes. The following differences between the

dyes resulting from the position of the methyl group were also observed: The color yield of all tissues dyed with **13b** and **14b** dyes (meta-methyl auxochrome) had the darkest hue compared to the other dyes (ortho- and para-methyl auxochrome). The darkest shade was observed in the PLA tissue dyed with **14a** (p-CH₃). The yield of all dyes was over 76%, with the exception of the PET fiber fabric dyed with **14c**, where the yield was 67%.

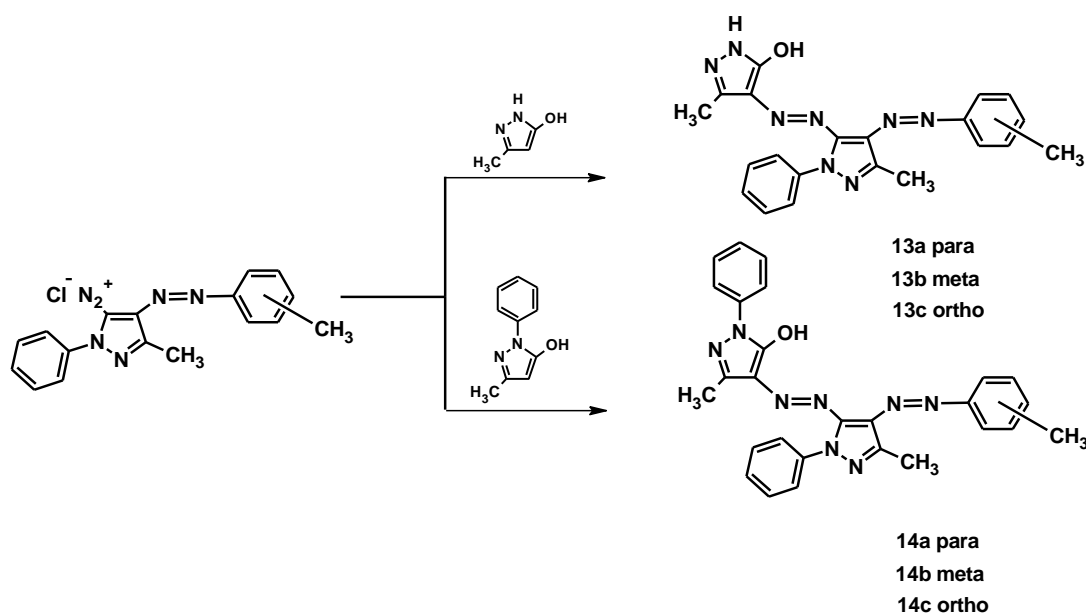


Figure 15. Synthesis and molecular structures of pyrazole disperse dyes **13a–c** and **14a–c**.

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The fastness values (wash fastness, acid and alkaline perspiration fastness, wet and dry rubbing fastness, sublimation fastness, light fastness, water fastness, and seawater fastness) were in the commercially acceptable range, which means that the dyeing of PLA, PET, and PA 6.6 with the dyes **13a–c** and **14a–c** is suitable for the textile industry.

3.3. Heterocyclic Polyazo Dyes

Polyazo dyes are complex dyes characterized by the fact that the azo group is repeated three or more times in the same molecule. They are intended for dyeing leather in the colors red, brown, and dark black [23]. The presence of multiple -N=N- groups increases conjugation and enhances the delocalization of electrons. They also appear to be more stable, as the more azo groups present in the dye, the less likely it is to degrade; in general, monoazo or diazo dyes are more degradable than polyazo dyes [34].

There are few studies in the literature on the use of heterocyclic polyazo dyes in general but especially with regard to their use for dyeing textiles.

In 2022, a paper was published on the synthesis and characterization of a novel heterocyclic polyazo dye, but the authors referred to its application as a universal acid–

base indicator [35]. The authors also reported that the polyazo dyes could find numerous practical applications, but there was no mention of their use as dyes for tissues [35–38].

In any case, an article published in 2011 [39] reported on the synthesis of various natural trisazo dyes. Arylazopyridone dyes have been intensively synthesized as disperse dyes since the 1970s (the 20th century). One of them, the trisazo pyridone dye shown in Figure 16, is used to dye polyamide materials such as nylon 6.

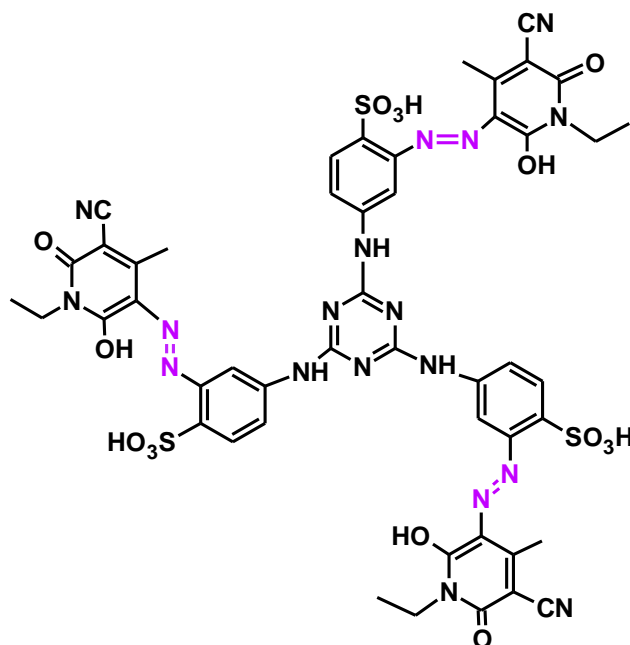


Figure 16. Structure of a trisazo pyridone dye.

4. Ecological Impacts and Sustainable Solutions for Heterocyclic Azo Dyes

Approximately 70% of the dyes used in the textile industry are azo dyes. During the dyeing process, 15–20% of these dyes are not absorbed and end up in wastewater, causing environmental pollution due to their toxicity. The industry is trying to mitigate these effects by improving dye binding or promoting degradation through biological or physico-chemical methods [40]. Wastewater also contains toxic substances such as heavy metals, which pose health risks such as cancer and chronic diseases [41] and damage ecosystems by interfering with aquatic life and plant growth [17]. Conventional treatment methods (filtration, adsorption, coagulation/flocculation) [42] have disadvantages such as secondary sludge formation, limited effectiveness, and high costs [40]. Therefore, environmentally friendly approaches and methods are being researched not only for azo dyes in general but also for those containing heterocycles.

In an article published in 2021 [43], for example, the authors reported on an environmentally friendly approach for the synthesis of an azocoumarin dye using cation exchange resins. The azo dye with coumarin moieties **17** was prepared by diazotization of 4-nitroaniline **15** and the subsequent coupling of the resulting diazonium salt with coumarin **16** (Figure 17). Amberlyst-15 was used as the acidic catalyst for the diazotization (Figure 18). Amberlyst-15, which consists of brown-gray granules, is a reticulated polystyrene-based ion exchange resin with strong acidic sulfonic groups. It is an effective heterogeneous acid catalyst for reactions in acidic media. It is safe to use and can be easily separated from the reaction mixture after completion of the reaction. Amberlyst-15 is also environmentally friendly as it can be renewed and reused up to four times.

The described synthesis has shown that it is an effective method for organic synthesis and that it could be suitable and economical for industrial and applied fields, possibly including textile dyeing as the applications of some coumarin-based azo dyes on polyester fibers [44] are already known.

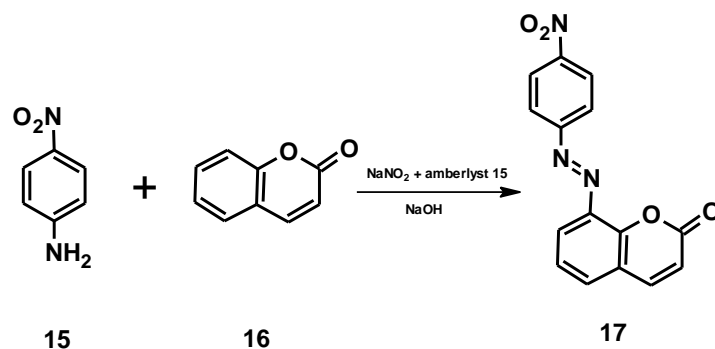


Figure 17. Synthesis of the azocoumarin 17.

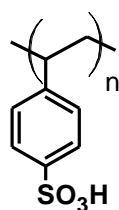


Figure 18. Structure of amberlyst-15.

Research into the removal of azo dyes from factory wastewater is constantly evolving. The activated carbon method has been extensively studied [45]. Unfortunately, the activated carbon currently available comes from non-renewable sources and is therefore not cheap. Research into the possibility of producing activated carbon from renewable, environmentally friendly and economically advantageous sources has shown that biomass is a very effective alternative. The effectiveness of activated carbon for the adsorption of azo dyes depends on several factors as follows: Type of biomass, activating agent, pH value, activation temperature, contact time, initial concentration of the dye and dosage of the adsorbent. Future research could focus on optimizing the absorptive capacity of activated carbon for specific types of azo dyes [46].

Another research group has developed a bioprocess that utilizes the complementary catalytic properties of azoreductases and laccases to convert various azo dyes into valuable aromatic compounds that are precursors of biologically active molecules. The enzymes in question, azoreductases and laccases, are supplied by free and immobilized *E. coli* cells. The reaction mixtures produced in this way are less contaminated and have a final yield of up to 90%. The result is that these optimized biocatalytic systems are not only an effective method for purifying wastewater but are also a source of valuable chemicals for various applications in the chemical industry [47].

Another alternative method recently reported consists in the biosorption of some azo dyes using activated biochar sewage sludge adsorbent, demonstrating high absorption percentages of the tested colors [48].

5. Conclusions

The field of heterocyclic azo dyes continues to be dynamic, driven by the need for brighter, more durable, and environmentally friendly dyes. The synthesis and application of heterocyclic azo dyes, especially in textiles, offers significant advantages in terms of color brilliance, fastness, and versatility. The development of novel dyes, including those with antimicrobial properties, is evidence of the constant innovation in this field. However, the impact of azo dyes on the environment, particularly in terms of wastewater pollution, remains a critical issue. Innovative and sustainable methods such as enzyme-based biocatalysis and biosorption using renewable materials are promising approaches to mitigate these effects. Future research should continue to focus on improving the environmental

footprint of dye synthesis and application to ensure that advances in dye technology serve both industry needs and environmental sustainability.

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Conflicts of Interest: The authors declare no conflicts of interest.

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