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SYNTHESIS AND SPECTROSCOPIC STUDIES OF BISAZO REACTIVE DYES BASED ON 3,3'-DIMETHOXY[1,1'-BIPHENYL]-4,4'-DIAMINE AND BENZENE-1,3-DIAMINE

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Abstract: *Five cold brand bis-dichlorotriazinyl (Bisazo) reactive dyes have been synthesized by coupling tetrazotized substituted phenylenediamines and Dianisidine using various cyanurated coupling components and their physical properties were examined. The spectroscopic properties of the synthesized dyes ($D_1 – D_5$) were carried out using Fourier Transform Infra-red (FT – IR) and UV – visible spectroscopy. The FT – IR Spectra cover infrared region of 400 – 650 cm^{-1} which shows band stretching vibrations of an azo (-N = N-) group in the region between 1587 – 1356 cm^{-1}, C – H aromatic stretching from 2880 – 2117 cm^{-1} C = C vibration appeared in the region 1709 – 1740 cm^{-1}, OH and NH vibrations in the region 3600 – 2900 cm^{-1}. Furthermore, C – N vibration of the triazine appeared in the region 1507 – 1403 cm^{-1}, S = O vibration between 1161 – 993 cm^{-1} and finally C – Cl substituted benzene ring appeared in the region of 780 – 766 cm^{-1}. The UV – visible absorption spectra of a solution of the synthesized reactive dyes ($D_1 – D_5$) with a concentration of 0.999 g/l were measured. The maximum absorption wavelength of D_1 appeared at 440 nm with absorbance of 0.361. D_2 at 540 nm with absorbance of 0.338 and other D_3, D_4, D_5, showed a strong absorption band at 500, 540, and 580 nm respectively. The λmax values are directly based on the nature, position of substituent used and presence of auxochromes like OH, SO_3H produces the bathochromic effect which give rise to the change in values of the λmax. The molar extinction coefficient of the synthesized dyes showed higher values due to the oscillation of electrons which indicates the dyes have higher intensity of absorption. The FT – IR and UV – visible results depicts the behavior of the synthesized bis –bifunctionalbisazo reactive dyes.*

Keywords: *Auxochromes, Dyes, Spectroscopy, Substituted phenylenediamines, Fourier Transform Infra-red and Ultraviolet –Visible.*

Introduction

Various literatures vindicate that reactive dyes are colored compounds which contains one or two groups capable of forming a covalent bond between the dye molecule and a given substrate (the fiber). The covalent bond is being formed between a carbon atom of the dye molecule and oxygen, nitrogen, or sulfur atom of the substrates, corresponding to hydroxyl, amino, or mercapto group of the substrate (fiber). According to Zhang *et al.,* (2005); Lewis, (2014) Patel *et al.,* (2015) and Benkhaya *et al.,* (2020), Hongjuan *et al.,* (2020), Dyes (2020), Adedeji *et al.,* (2023), Manoj *et al.,* (2023). Reactive dyes have many parts: a color part, a solubilizing part, and a reactive part.

Polya *et al.,* (2016) described reactive dyes as an anionic compound soluble in water due to the existence of a sulfonic group in the molecule. The presence of a reactive group in reactive dye, are able to fix covalently to the textile fibers macromolecules forming etheric, thioetheric, aminic or amidic bonds.

Bis- (Bifunctional Reactive Systems) as the main concern and product of this research work, various attempt has been made to explain the reactive system. Manoj *et al.,* (2023) and Adedeji *et al.,* (2023); explained vividly, and Kangqin Chen (2006) in his un-published thesis work mentioned the work of Renfrew and Taylor, (1990), and Kanetkar *et al.,* (2000), Omer (2011), Zahid Maqbool (2015), Tawfik and Mohamed, (2018) and Suhail *et al.,*(2021) which clearly explained that inadequate degree of fixation has been regarded one of the problems of dyeing. Introducing two or more reactive systems into a dye molecular system was viewed as a logical to enhance the percentage fixation of reaction between dye and fiber. According to them, bifunctional reactive dyes contain two separate reactive centers capable of reacting with hydroxyl groups in the cellulose chain. However, the work of Betrabet *et al.,* (1977) reported by Kangqin Chen, (2006) vindicate clearly that, Analytical techniques, such as electron microscopy, surface area determination, and swelling in cadoxen solvent, have been used to provide evidences for the formation of crosslinks between adjacent cellulose chains in cotton dyed with either bi or poly-functional reactive dyes. They also added that bifunctional reactive dyes can be divided into two classes viz: homobifunctional dyes containing two of the same reactive groups and heterobif unctional dyes with two different reactive groups in the reactive dye structure.

Experimental

The mass of the dyes synthesized D_1 to D_5 was weighed using a digital weighing balance and the percentage yield was calculated, the molecular weight of the dye obtained was calculated from the str ucture of the synthesized dyes as adopted from Divyesh *et al.,* (2010) and Dharmishtha *et al.,* (2015). Also the melting point of the synthesized dyes was examined using the melting point apparatus. The wavelength of maximum absorption (λmax) of the synthesized dyes was determined in ethanol, toluene, acetone and in water (distilled), using the UV spectrophotometer (JENWAY 6305/752N) in the wavelength range of 400 –700 nm. The molar extinction coefficient of each of the dyes was calculated using the maximum absorbance value of a known concentration of the dyes ε = A/CL. UV- Visible analyses of synthesized dyes were carried out on (752N and JENWAY 6305) spectrophotometre (Mousa, 2006, Aamer and Ghulam, 2014, Mondal *et al.,* 2019 and Iyun *et al.,* 2020). FT-IR analysis of each synthesized dyes were carried out on (CARY 630 AGILLENT) Agilent Technology Micro-Laboratory from Department of Chemical Engineering A.T.B.U Bauchi, Bauchi State, Nigeria.

Synthesis of Dyes

The method described by Divyesh *et al.,* (2011) and Dharmishtha *et al.,* (2015) was adopted throughout the synthesis.

Cyanuration of acids

The method described by Divyesh *et al.,* (2011) and Dharmishtha *et al.,* (2015) was adopted throughout the synthesis in which, Cyanuric Chloride (3.69 g, 0.02 mole) was stirred in acetone (20 ml) at a temperature below 5 °C for a period of an hour. A neutral solution of C1 to C2 acids (i.e. H-acid, J-acid, Gamma acid and Napthionic acid) (6.38 g, 0.02 mole) in aqueous sodium carbonate solution (10 % w/v) was then added in small lots in about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1 % w/v). The solution will be used for subsequent coupling reaction.

Tetrazotization

Two different starting materials which includes O-Dianisidine, and 1,2-Phenylenediamine was used. The method described by Divyesh *et al*., (2010) and Dharmishtha *et al*., (2015) was adopted in which

(1.68 g, 0.01 mole) was suspended in H_2O (20 ml). Concentrated hydrochloric acid (150 ml) was added drop wise to this well stirred suspension. The mixture was gradually heat up to 70 °C, till clear solution obtained. The solution was cooled to 0 - 5 °C in an ice bath. To this solution, $NaNO_2$ (1.68 g, 0.02 mole) in water (5 ml) was added to the above solution at 0 °C temperature, over a period of five minutes with continuous stirring. The stirring continued for an hour, maintaining the same temperature. The clear tetrazotized solution at 0 - 5 °C was obtained and used for subsequent reactions.

Formation of Dye

The above mentioned freshly prepared tetrazotized solution S_1 and S_2 acids (where S1-2 are the starting materials) was added to an ice cooled and well stirred solution of cyanurated acids **(**i.e. H-acid, J-acid, and Napthionic acid) over a period of 10-15 minutes. The pH was maintained at 8.0 to 8.5 by simultaneous addition of sodium carbonate solution (10 % w/v) and stirring continued for 4 hours. So dium chloride (10 g) was then added and the mixture stirred for an hour. The dye solution was filtered , washed with minimum amount of acetone and dried at room temperature. As adopted from Divyesh *et al*., (2010), (2011) and Dharmishtha *et al*., (2015).

Results and discussion

Physical Properties of the dyes:

Physical properties of the dyes synthesized was carried out viz: Percentage yield, melting point, extinction coefficient and molecular weight. Table 1.1 shows the results obtained.

Table 1.1: Physical properties of bisazo reactive dyes

Dyes	Color	Melting point (°C)	Weight (g)	Percentage yield (%)	Molecular weight g/mol
D_1	Burgundy	299	8.41	71	904
D_2	Purple	289	10.79	92	1064
D_3	Black	290	7.37	63	872
D_4	Mauve	300	10.78	92	1040
D_5	Olive	300	6.081	52	1008

All the dyes show different colours ranges from burgundry, purple, black, mauve and olive colouration respectively. The dyes show excellent yield ranging from (52 - 92 %). All the melting point were determined in open capillary tube apparatus which gives temperature values between 289 to 300 °C, the same values ranges of melting temperature may be attributed to the similarity in their chemical structures. And lastly molecular weight was determined from the molecular formular of the dyes, different values may be attributed due to the differences in their molecular structures and attachment such as solubilizing groups and the coupling components presence in them, which were similar to the results obtained from various literatures.

Spectral properties

The UV-Visible absorption spectra of the synthesized five (5) reactive dyes were recorded in the wavelength range of 400 – 600 nm using distilled water. The UV-Visible absorption spectra results of the synthesized dyes are shown in Table 1.2. Wavelength of maximum absorption (λ_{max}) appeared in the visible region of spectrum which is attributed to the electronic transition of azo (N=N) chromophoric group of the reactive dyes. The differences in the λ_{max} of the $D_1 – D_5$ was due to the extended conjugation present in the dyes. UV-Visible absorption spectra of solution of the synthesized reactive dyes D_1-D_5 with a concentration of 0.99 g/l were measured. The maximum absorption wavelength of D_1 appears at 440 nm with absorbance of 0.361. This agrees with the work done by Lili yang *et al.,* (2021) in synthesis, characterization, and dyeing assessment of reactive dyes containing a benzsulfonamide moiety. D_2 appears at 540 nm with the absorbance of 0.338 and others D_3,D_4 and D_5 showed a strong absorption

band at 500, 540 and 580 nm respectively. The maximum absorption wavelength of dyes depends on the types of chromophores and the coupling components used for the synthesis. The synthesized dyes showed a higher molar extinction coefficient values ranges from $3.25x10^2$ - $10.47x10^2$ due to the oscillation of electrons and presence of substituents like electron attracting and donating group which indicate the dyes synthesized have higher intensity of absorption. The introduction of auxochromes like hydroxyl groups, sulfonic acid groups in some coupling components produces a bathochromic effect. Hence the presence of electron donating and electron attracting groups at different position in the synthesized dye ring affect the absorption of the dyes. The result obtained from the determination of λ_{max} for all the dyes synthesized are shown in Table 1.2. The values are very close to the λ_{max} figures obtained from other literature sources (Divyesh *et al.,* 2011, Patel *et al.,* 2015, Hongjuan *et al.,* 2020, Iyun *et al.,* 2020, Juliana *et al.*, 2023 and Adedeji *et al.,* 2023). It is apparent, that the value of the λmax depends on the coupling component used during the synthesis.

Table 1.2: UV-visible spectroscopic properties of the dyes

Dyes No.	λ_{max} in water	Absorbance (optical density)	Extinction coefficient(ε) $Lmol^{-1}cm^{-1}$	Concentration $moldm^{-3}$
D_1	440	0.361	$3.25x10^2$	$1.11x10^{-3}$
D_2	540	0.338	$3.59x10^2$	$9.39x10^{-4}$
D_3	500	0. 882	$7.73x10^2$	$1.14x10^{-3}$
D_4	540	0. 493	$5.13x10^2$	$9.61\ x10^{-4}$
D_5	580	0. 751	$7.57x10^2$	$9.91x10^{-4}$

The figure 1 shows the uv-visible absorption spectra of dyes D_1 to D_5. D_1 shows λ_{max}at 440 nm with the absorbance of 0.361 and D_2 shows λ_{max}540 nm with the absorbance of 0.338. Thus there is bathochromic shift of 100 nm in the λ_{max} of D_1 (moving towards higher wavelength λ_{max}= 440 nm). This is due to the introduction of phenyl group, D_1 also shows hyperchromic compare to D_2 to D_3 in the figure 1. However, D_3 show a hypochromic shift from the intensity against wavelength plot. All the results are in line with the findings of Divyesh *et al.,* 2011 and Patel *et al.,* 2015 in Synthesis of monoazo reactive dyes and their dyeing performances on various fibers.

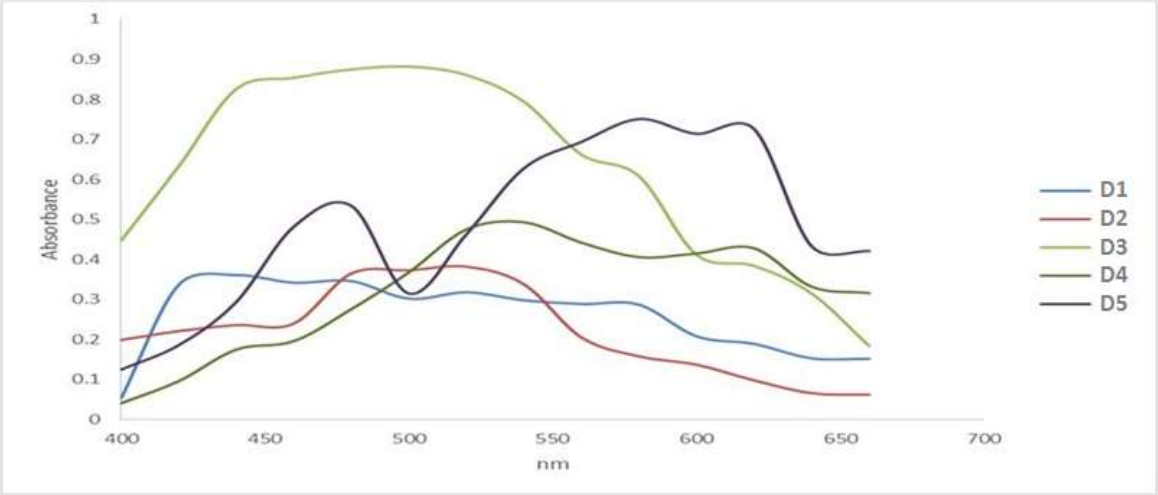
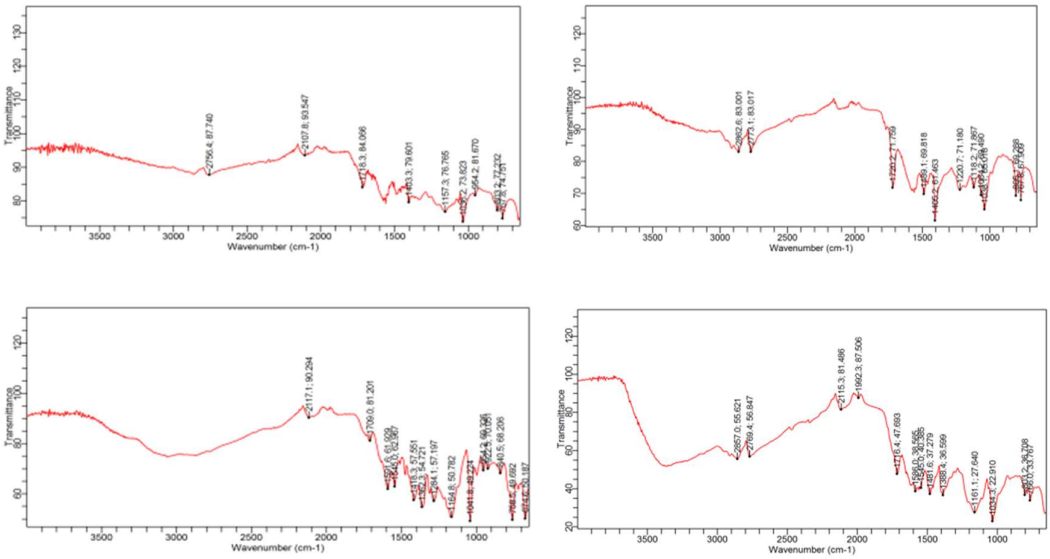


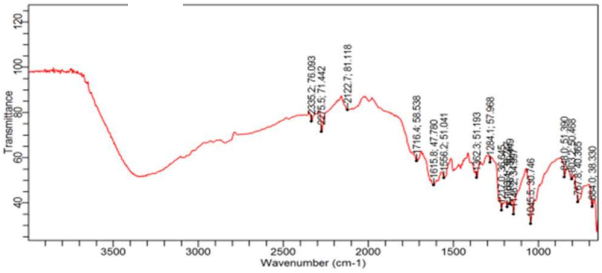
Figure1: UV-visible absorption of the synthesized D_1 to D_5

Similarly, D_4 and D_5 shows a very good absorbance values, with D_5 moving toward a higher wavelength compared to others D_1, D_2, D_3 and D_4 respectively. However, D_3 shows a hyperchromic shift, being the highest dyes among D_1, D_2, D_4, and D_5 with the highest value of absorbance, and D_5 with the highest λ_{max}value of 580 nm. This might be as a result of different substituents attached to D_5 and the nature of the coupling component present in the dye. All these results are in conformity with the studies of various literature sources (Umme Habibah, 2016, Divyesh *et al.,* 2011, Juliana *et al.,* 2023 and Adedeji *et al.,* 2023) in synthesis, characterization and application of novel reactive dyes on various fibers. All the dyes showed very broad absorption curves leading to a large tinctorial strength. This attributed to the presences of many benzene rings and auxochromes leading to highly conjugated aromatic dye structures.

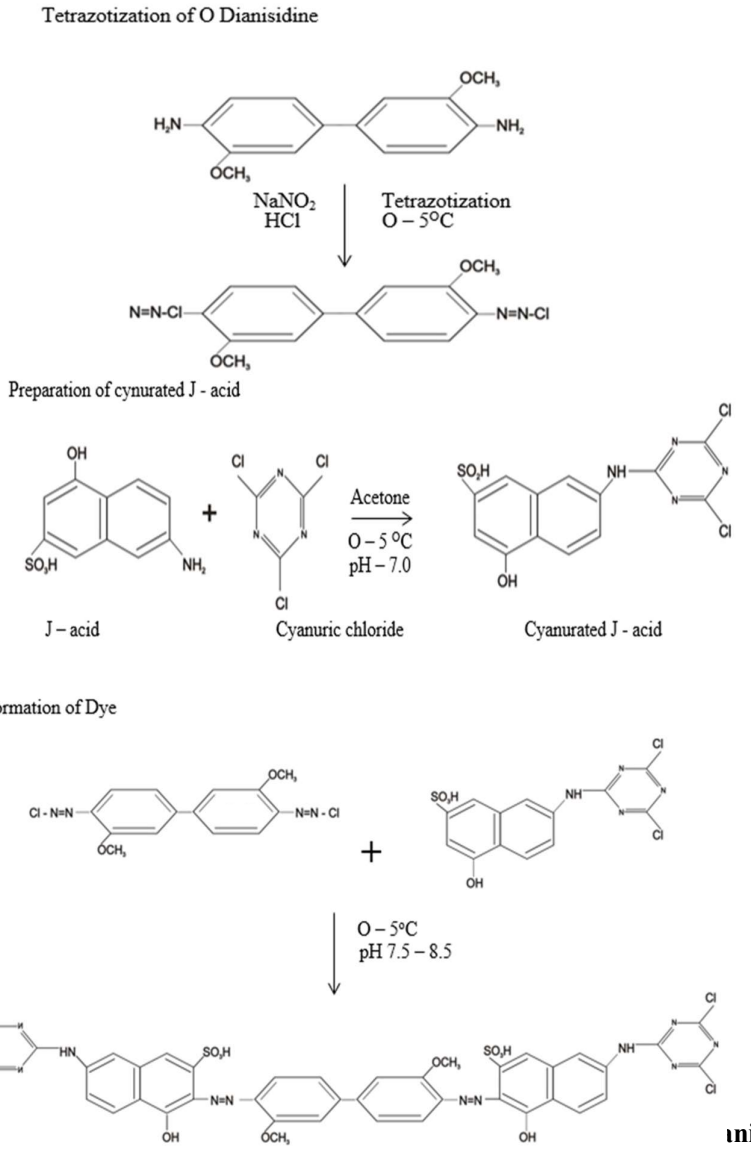
Infra-red Spectra

The absorption of infra-red radiation resulting from atom containing in the molecules showed the functional group present in the molecules of the compound synthesized, each dyes synthesized gave characteristics absorption peaks in the finger print region and in the functional groups regions. As can be deduced from infra-red spectrum results in the figure below. Almost all the dyes synthesized gave absorption peak due to azo functional group, -N=N - stretching vibration from 1587 - 1356 cm^{-1}, C-H aromatic stretching vibration bands appeared from the region 2880 - 2117 cm^{-1} which agrees with the work reported by Diveyesh *et al.,* 2010, 2011, Juliana *et al.,* 2023 and Adedeji *et al.,* 2023 in synthesis, characterization and application of novel reactive dyes on various fibers. C=C stretching vibration band of the aromatic ring appeared in the region 1709 - 1740 cm^{-1}, OH and NH stretching vibration in the region between 3600 - 2900 cm^{-1}. However, C-N stretching vibration of the triazine appeared in the region between 1507 - 1403 cm^{-1} of all the synthesized dyes. S=O symmetric and asymmetric vibration in the range between 1161 - 993 cm^{-1}, C-Cl vibration of substituted benzene ring appeared in the visible region of 780 - 766 cm^{-1}. All the FT-IR values obtained are similar to the functional groups values reported by Juliana *et al.,* 2023 in the synthesis, spectroscopic studies and fastness properties of monoazo dyes derived from substituted arylamines and Adedeji *et al.,* 2023 in spectrophotometric and infra-red analysis of azo reactive dyes derived from 2-methyl-3-(2-methylphenyl) -6-arylazo -4-oxoquinazoline.





Reaction scheme



Reaction S **unisidine**

Conclusion

The results of the FT – IR and UV – visible spectroscopy depicts the behavious of an azo dye, which showed the stretching vibration of all the functional groups present for a typical azo reactive dye like the presence of chromophores (N = N) and auxochromes like OH, NH, C – N, S=O and Cl groups. The considerable change in the values of maximum absorption wave length was due to the nature, position of the coupling components used which results in bathochromic shift effects. However, the bifunctional reactive dyes showed higher values of molar extinction coefficient which vindicates the hue of the dye due to extended conjugation of their double bonds.

Competing Interest

The authors declares that there are no competing interests

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