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Synthesis and Application, their Dyeing Application and their Antimicrobial Activity, AZO Disperse Dyes based on Saccharin

Ibtihal Qahtan Abdullah, Olfat A. Nief

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Abstract: Dyes are chemical compounds that contain, within their chemical structure, chemical composition (nitrogen = nitrogen). This chemical group is known as the Azo group, which is responsible for absorbing light at different wavelengths to give different colors. There are many factors that affect the strength and stability of light absorption by compounds prepared as chemical dyes. One of the most important factors to determine the ability of compounds prepared to dye other materials and the survival of this dye for a longer period is the presence of active groups (carbonyl, sulfonate and cyano) adjacent to the Azo group increases the ability of these dyes to absorb the highest wavelength of light.In this research, we tried to collect more than one effective chemical group to produce distinct dyes with effective biological properties. For this purpose, biological material was used as raw material in the preparation plan of these dyes. To verify the chemical composition of the prepared compounds, the following chemical techniques (UV, IR and H NMR) were used, which were examined by thin layer chromatography. The dye efficiency of all synthesis compounds on (Nylon fibers and cotton fibers) was evaluated. It was found that the efficiency of pigmentation of textile nylon fibers is higher than that of cotton fibers. Biological activity (antibacterial) was also measured for all prepared compounds. Biological activity (antibacterial) was also measured for all prepared compounds. Antibacterial activity against E. coli was demonstrated and these compounds showed good biological activity.

Keywords: Saccharin, Benzoic Sulfimide, Azodyes, Bisazo, Heterocyclic Compounds.

INTRODUCTION

Benzoyl sulfimide is used to sweeten food and drink as an alternative to sugar. Saccharin is produced industrially and is called "artificial sweeteners" and does not contain calories. It is used for people with diabetes and those who follow a diet (low-calorie diet). It was first produced by the world "Vellberg" in 1879 (2). In 1989 year of the publication of an article on saccharin (3, 4) six years later this material was produced as an industrial material in a small suburb in Magdeburg, Germany. The importance of diazonium compounds lies that they contain two nitrogen atoms that are bonded in their carbon structure. This type of compounds (diazonium compounds) was therefore used as the intermediate products to preparation compounds organic and industrial compounds (6). Where they were used in the preparation of compounds with diverse biological activity (7). Also,used to prepare industrial materials such as commercial colorants for clothing, food and beverages, and in the manufacture of plastics and cosmetics (8).Condensation Aldol is very important in chemical reactions, because this type of chemical used as Initial materials to synthesize different types of chemical compounds through the formation of (C-C). [9] Condensation Aldol is the addition of nucleophile for ketone or alcohol to aldehydes to synthesize new chemical compounds containing the chemical form (β -hydroxy carbonyl). This type of compounds was found in many natural compounds and pharmaceuticals. [10] [11] [12].

Ibtihal Qahtan Abdullah, Chemistry Department, Science College, Tikrit University, Tikrit, Iraq.
Olfat A. Nief, Chemistry Department, Science College, AL-Mustansiraya University, Bagdad, Iraq.

Many of reactions that are similar to aldol condensation, for example, the Robinson annulation reaction, the Wieland–Miescher condensation[13[14] and Clauson-Schmidt reaction. The reaction of Clauson-Schmidt is a condensation reaction between aldehydes and carbonyl compounds to form chemical compounds containing the chemical formula β-hydroxy carbonyl. This type of chemical compounds, as previously mentioned, be of fundamental importance in organic chemistry, industrial chemistry and biochemistry [15,16]. These compounds suffer from the loss of a water molecule to synthesize compounds known as Schifes bases, which are known in the pathways of organic chemistry reactions as nuclei in the synthesis of a large number of biologically active compounds and industrial compounds through various reactions, for example; cyclic closure reactions to form hetercyclic compounds, addition reactions and other chemical reactions [19].reactions. In addition [19].

EXPERIMENTAL SECTION

Description of Materials and Products

Melting points were determined on FALC instrument (s.r.I) 50/60 HZ (Italy).FT-IR spectra of compounds were recorded on ((Shimadzu fourier transform infrared Spectrophoto meter FT-IR 8400 s (KBr) scale (4000 – 400)cm-1)). HNMR spectra (solvent DMSO-d6) were recorded on broker ultra shield 400 MHz spectro meter with TMS on internal slanders in Al-Bayt university – Jordan 1-Chromatography class thin TLC

This test is done for all the prepared compounds. It was performed at different periods of preparation. The checked using U.V Lights, sheets silkjel and moble phase (ethanol absolute)

Chemical Synthesis

Synthesis of azo dyeX(20)

For the synthesis of 1, (0.1 mol) p-aminobenzldehyd is dissolved into a solution of(0.06 mol) sodium carbonate into (250 ml)water, to which (0.1 mol) sodium nitrite as 30 % water solution are added. This solution is further poured slowly, upon continuous stirring, over a mixture of (22.6 ml, 30 %) hydrochloric acid and (100 g ice).

The temperature is kept (0 - 5ºC). After an hour the reaction of diazotization was finished. (0.1 mol) Saccharin was dissolved at room temperature into (35 ml water) to which (15 ml 30 %) hydrochloric acid were added. The solution of the coupling component is slowly poured with continuous stirring into the diazo derivative solution. The reaction was performed at(10 - 15ºC)and pH (4 - 4.5) (7 g of sodium acetate).

The process was monitored by TLC on silica gel plates using as an eluent system chloroform: acetone (2:1, v/v).

After 3 h when the process was completed, to the mixture 15.9 g sodium carbonate were added until reaching pH(8 - 8.5). Dye 1 was isolated using 15 % NaCl, filtered off and dried at 40ºC under vacuum.

The Characteristic Data of Dye X

Calculated for($C_{14}H_9O_4N_3S$) : M. wt.: 315, % yield: 54%, m. p.: 209-212C, Rf. value: 0.62; C, 53.333 %; H, 2.857%;; N, 13.333 %;. Found: C, 53.402 %; H, 2.862 %; N, 13.132 %. IR : 3072 cm-1 (=CH, aromatic);1711 cm -1 (C=O,aldy.),1669 cm-1 (C=O,ring amid); 1606 cm-1 (N=N); 1417 cm-1 (C=C, aromatic); 1400cm-1 (C-N);(1136-1344) cm-1 (for SO2). 1H-NMR: 7.2-7.4 δ (Ar-H, multiplet), 11.3 δ (COH,s.H).

Synthesis of AZO Dyes I,II (23)

A mixture of ethyl cyanoacetate or ethyl acetoacetate (15mmol), dye (I) (4.7 g, 15mmol) and ammonium acetate (6.93 g, 9mmol) in (40 ml) absolute ethanol was heated under reflux for ((10 hs)), where a crystalline yellow solid formed. The formed precipitate cooled, collected by filtration, washed with cold Benzene, dried and crystallized from ethanol to give crystals of :-

Dye (I)(60% yield), m.p= 266 -268 C^0.IR (ν/cm^{-1}): 2215 (CN).^{1}H-NMR (DMSO-d^6): δ/ppm= 3.85 (s,3H,OCH3), 4.06 (s, 1H, HC=C), 7.07-7.35(m, 8H Ar-H).Anal. calcd. for C18H12N4O5 S(396): C, 54.545; H, 3.03; N, 14.141, found%: C, 54.593; H, 3.062; N, 14.139.

. Dye (II) (52% yield), m.p= 258-260 C^0. IR (ν/cm^{-1}):;1761 cm -1 (C=O,estr),1723 cm $^{-1,}$ 1669 cm^{-1} (C=O,); 1626 cm^{-1} (C=C); 1417 cm^{-1} (C=C, aromatic); ^{1}H-NMR (DMSO-d^6): δ/ppm= 2.07(s,3H, CH3), 3.85 (s,3H,OCH3), 4.06 (s, 1H, HC=C), 7.07-8.35 (m,8H, Ar-H). Anal. calcd. for $C_{17}H_{12}N_4O_5$ S(396): C, 55.205; H, 3.631; N, 10.169, found%: C, 55.213; H, 3.762; N, 10.139.

Synthesis of azo dyes (IIa,b,c)(23)

A stirred mixture of dye I (0.3 mole) with (0.3 mole)of(*o*-aminoaniline for synthesis dye (I_a), *o*-aminophenol for synthesis dye (I_b),*o*-marcaptoaniline for synthesis dye(I_C) in chloroform (10 ml) was heated to (40-50)°C under stirring for (45 min.), then the mixture was refluxed for (5 hrs.).Dyes ($I_{a,b,c}$) are exposed to direct sunlight in open air for 2 days, washed by hot water and dried to give dyes with bright, fast and stable color.

The Characteristic Data of dyeII$_{a,b,c}$

Calculated for dye I_a($C_{24}H_{13}O_3N_5S_2$): M. wt.: 483, % yield: 41, m. p.: 238-240^{0}C, R_f. value: 0.82;C, 59.627 %; H, 2.691 %; N, 14.492. Found: C, 59.538 %; H, 2.652 %; N,14.461 %. IR : 3463 cm^{-1} (NH); 3072 cm^{-1} (=CH, aromatic);2236 cm^{-1} (CN); 1628 cm^{-1} (C=O,); 1521 cm^{-1} (N=N); 1481 cm^{-1} (C=C, aromatic); 1333 cm^{-1} (C-N); 1101 - 1330 cm^{-1}(for SO_2)1H-NMR (DMSO-d6): δ/ppm=6.2-8.4 δ (Ar-H, multiplet), 6.34(HC=C, singlet).

Calculated for dye I_b $C_{23}H_{13}O_4N_5S$: M. wt.: 467 % yield: 52, m. p.: 322-324 C^0, R_f. value: 0.78; C, 61.702%; H, 2.783 %; N, 14.892 %.

Found: C=61.71 %; H, 2.909 %; N, 14.737%. IR: 3082 cm^{-1} (=CH, aromatic); 1624 cm^{-1} (C=O); 1522 cm^1 (N=N); 1490 cm^{-1} (C=C, aromatic); 1345 cm^{-1} (C-N); (1101-1362) cm^{-1} (SO_2). 1H-NMR (DMSO-d6): δ/ppm= 6.2-8.4 δ (Ar-H, multiplet), 6.34 (HC=C, singlet).

Calculated for dye I_c $C_{23}H_{14}O_3N_6S$: M. wt.: 466, % yield: 42, m. p.: 341-346^{0}C, R_f. value: 0.85; C, 61.802%; H, 3.004 %; N, 18.025 %. Found: C, 61.924 %; H, 3.035 %; N,18.031 %. IR : 3481 cm^{-1}(NH); 3070 cm^{-1} (=CH, aromatic); 1632 cm^{-1} (C=O); 1542 cm^{-1} (N=N); ; 1483 cm^{-1} (C=C, aromatic); 1337 cm^{-1}(C-N); (1103-1362) cm^{-1} (SO_2) ^{1}H-NMR: 7.1-7.3 δ (Ar-H, multiplet), 9.35 δ (NH, singlet,1H)

Synthesis Dyes II a,b.c

A mixture of dye (II) (0.05 mole) in (20 ml) ethanol and mixing with (0.05 mole) (hydrazine hydrate) for synthesis (IIIa), and (hydroxylamine. HCl) for synthesis (IIIb), were put in around bottom flask and refluxed for (7 hrs.). The mixture was concentrated, cooled and the crystal was filtered, dried and purified by ethanol.

The Characteristic Data of Dye IIa,IIb,IIc

Calculated for $C_{18}H_{13}O_4N_5S$dye II$_a$: M. wt.: 395, % yield: 66, m. p.: 240-244C, Rf. value: 0.46; C 54.683%; H, 3.291 %; N, 17.721 %. Found: C, 54.932 %; H, 3.384 %; N, 17.706 %. IR : 3292 cm^{-1} (-NH, pyrazol); 3070 cm^{-1} (=CH, aromatic); 1631 cm^{-1} (C=O); 1598 cm^{-1} (N=N); 1511cm^{-1} (C=C, aromatic); 1464 cm^{-1} (C-N); (1172-1287) cm^{-1} (for SO_2). ^{1}H-NMR: 7.1-7.8 δ (Ar-H, multiplet), 9.3 δ(NH pyrazol, singlet), 3.2 δ (2CH_3 pyrazol, singlet, 6H).

Calculated for $C_{18}H_{12}O_5N_4S$ dye II$_b$: M. wt.: 396, % yield: 43, m.p.: 240-243°C, R_f.value: 0.73; C,54.545%; H, 3.03%; N, 14.141 %.Found: C, 54.602 %; H, 3.003 %; N, 14.15%. IR : 3063 cm^{-1} (=CH, aromatic); 1632 cm^{-1} (C=O); 1533cm^{-1} (N=N); 1471 cm^{-1} (C=C, aromatic); 1324 cm^{-1}(C-N); 1108-1367 cm^{-1} (for SO_2). ^{1}H-NMR: 7.1-7.8 δ (Ar-H, multiplet), 4.3 δ(CH_3, position 3,isooxazole,3H) 3.7 δ (CH3, position 5,isooxazole,3H),

Calculated for $C_{24}H_{16}O_4N_4S$ dye IIc: M. wt.: 470, % yield: 43, m.p.: 240-243°C, Rf. value: 0.73; C,61.276%; H, 2.162%; N, 14.893 %.Found: C, 61.304%; H, 2.203 %; N, 14.915%. 1632 cm^{-1} (C=O); 1533cm^{-1} (N=N); 1471 cm^{-1} (C=C, aromatic); 1324 cm^{-1}(C-N); 1108-1367 cm^{-1} (for SO2). ^{1}H-NMR: 7.1-7.8 δ (Ar-H, multiplet), 4.3 δ(CH3, position 3,isooxazole,3H).

Dyeing procedure(24)

Dyeing was achieved using ten synthesized dyes of 2.5 % on weight of material, excepting on the other hand in water with ethanol ratio ((50:1)).

The dyes solutions were formed bydissolving the dyes in water at t(45 – 40)ºC, 10 % ((Na_2SO_4)) and 4 % ((CH_3COOH)) concentration of 30 % were added.

Then the previously wetted material (1 g) was dipping in the solution dye and leave for 30 min at this t^{0}c. Then the temperature was raised to boilingpoint and leave it to boil for 30 min. After that, the material samples were outside and washedand dried with heat at 40ºC.

Measurements and Analyses

Dye Exhaustion

The wavelength of light absorbed by materials is measured before and after dyeing. A bath of pigments prepared at g/l concentration was prepared and the wavelength of absorbed light was measured with HP8452A, UV /. The pigment absorption ratio was calculated by (E%) using the equivalent. (1) [25]. Data are shown in Table 2.

$$\%E = \frac{C_{1-}\ C_2}{C_1} * 100\ (1)$$

where: E - degree of absorption of dye, %, C_1, C_2: concentration of the dye before and after dyeing, respectively.

Dye Fixation

The pigment deposition rate (% F) was measured by measuring the proportion of dye chemically consumed by the tissue of the selected material for the test by re-flowing the samples dyed in water for 30 minutes to extract the unstable dye. This procedure has been repeated three times. The residual dye concentration was determined on the texture of the material by λmax measurement and the percentage of the fixation percentage (% F) of the dye texture was calculated using an equivalent [26]. The obtained data is obtained in the table. (2)

$$\%F = \frac{C_{1-}\ C_2 - C_3}{C_1 - C_2} * 100\ (2)$$

From the dye bath exhaustion (E) and dye fixation ratio (F), the total dye fixation (T), which is the percent-age of dye chemically bound relative to the total amount of dye used, was calculated for dyeing material (% T) using eq. (3) The obtained data are given in Table 2.

$$\%T = \%E * \%F * 100\ (3)$$

Table 1: Absorption maxima (λ_{max}), intensities (log ε), exhaustion (E) and fixation (F) ofacid azo dyes on wool and silk.

Dyes	sorption maxima(λ_{max} /nm in DMF)	Intensities (log ε)	Acid azo dyeing			Acid azo dyeing		
No			on wool			on silk		
			%E	%F	T%	%E	%F	T%
x	465	4.60	80	89	5	72	90	80
I	495	4.36	75	94	6	75	87	75
I_I	521	4.45	72	90	9	80	92	72
$_{ia}$	435	4.27	-	-	-	32	52	45
Ib	430	4.20	74	86	4	82	91	74
II_a	420	4.18	71	88	8	75	89	71
IIb	422	4.21	85	92	6	78	90	85
IIc	455	4.52	71	87	3	73	81	71

Table 2: Results of acid azo dyeing and various fastness properties of dyes on wool

Dyes	Color shades	Fastness Properties		Fastness Properties	
No.	on wool	Wool		Silk	
		Light	Wash	light	Wash
x	yellowish orange	4	3	4	3
$_1$	Orange	5	4	4	2
I_a	Yellow	-	-	2	1
Ib	Yellowish whit	2	1	3	2
II	Orangish red	4	2	5	4
IIa	Orange	3	1	5	3
III_c	Yellowish red	5	5	4	4
IIIc	Red	5	5	5	4

Fastness: 1 - poor, 2 - fair, 3 - good, 4 - very good, 5 - excellent

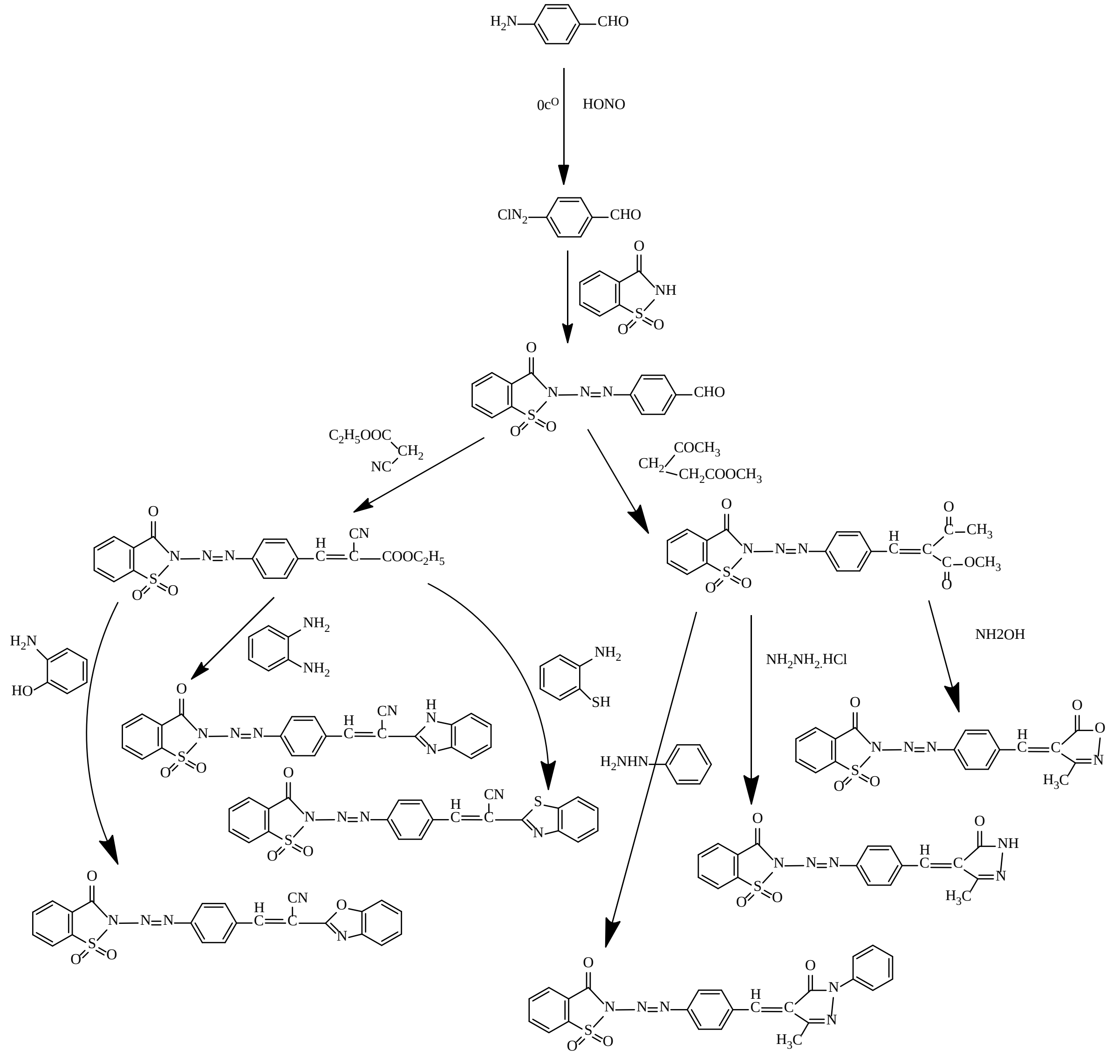
Determination of Antimicrobial Activity

All the synthesized dyes were tested against four different microorganisms: *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Candidaalbicans*. The a*gar well-diffusion* method was applied for the determination of inhibition zone andminimum inhibitory concentration (MIC).

Briefly, 0.75 mL of broth culture containing *ca.* 106 colon-forming units (CFU) per mL of the test strain was added to 75 mL of nutrient agar medium at 45 ºC, mixed well, and then poured into a 15 cm sterile metallic Petri plate. The medium was allowed to solidify, and 8 mm wells were dug with a sterile metallic borer. Then, a DMSO solution of the test sample (1 mL) at 1 mg/mL was added to the respective wells. DMSO served as negative control, and the standard antimicrobial drugs rifampicin (5 g/disc) and ampicillin (10 g/disc) were used as positive controls. Triplicate plates of each microorganism strain were prepared and were incubated aerobically at 37 ºC for 24 h. The activity was determined by measuring the diameter of zone showing complete inhibition (mm), thereby, the zones were precisely measured with the aid of a Vernier Caliper (precision 0.1 mm).The growth inhibition was calculated with reference to the positive control.

RESULTS AND DISCUSSION

The synthesis dyes derived from saccharin are represented in Scheme 1.Scheme 1: preparation of dyes derived from saccharin



The research showed the identification of the chemical structure according to the basic criteria, and then used important applications (dye quality applications for different materials, measuring their biological effectiveness) to explain the importance of the chemical compounds prepared in this research.

First, the Diaz onium salt was prepared from 4-amino benzaldehyde and then coupling with the biological compoundsaccharin. The success of this process has been evidence by measuring the melting point and spectroscopy methods(FTIR, UV-Vis and^{1}HNMR spectroscopy). FTIR spectrum for dye (X), is prove frequency disappearance for NH2, NH and the appearance of a new frequency in1635 cm -1 due to N = N stretching.

While the V-Vis spectrum showed a red shift for wavelength due to the introduction of new electronic transitions, and finally ^{1}HNMR spectrum (in DMSO) showed that the returning signals frequency for protons NH2, NH,were disappearedand showed a sharp signal at 11.3 ppm and integrated one proton attributable to CH = O.

The second reaction in the synthesis scheme is the reaction of the dye condensation (X) with the methylene group active in the compounds (acetyl ciano acetate, ethyl acetate) to give the synthetic dyes (I, II) respectively and confirm the chemical composition of the dyes (I, II)) Was from the values of the elemental analysis and values read from the spectrum of the FTIR, UV-Visand^{1}HNMR spectroscopy), where it was exactly identical to the chemical formula proposed for the dyes(I, II).

Final step in the synthesis scheme for this research is to prepare the heterocyclic compounds (Ia, Ib, Ic),(IIa, IIb, IIc) by the cyclic closure for dyes (I)and(II) previously synthesized.

For the success of the final step was accomplished by two paths of reaction:

The first is the synthesis of heterocyclic substituted (benzothiazoles (Ia), benzooxazoles (Ib), benzoimidazoles) by the dye(I) reaction with different o-anilne substituted

The second pathway was to synthesize heterocyclic substituted (diazole (IIa), phenyl diazole(IIb), oxazole (IIc)), was performed by dye(II) reaction with(a- hydrazine hydrate, b-hydroxyl amine hydrochloride and c- phenylhydrazine).

All dyes are obtained in the form of crystalline powder. Ranging in color from yellowish orange, red, orange and yellowish red. The purity of dyes AZO and other synthesized compounds was tested by TLC using a different 2 solvents system. The TLC results show only one spot for each Azo dye and for all other compounds.

For both the dyes and heterocyclic compounds prepared in this study, the results of the analysis of the elements and reading values of the spectra of (FTIR, UV-vis and 1HNMR spectroscopy) were fully consistent with the proposed chemical formula described in the synthesis scheme 1.

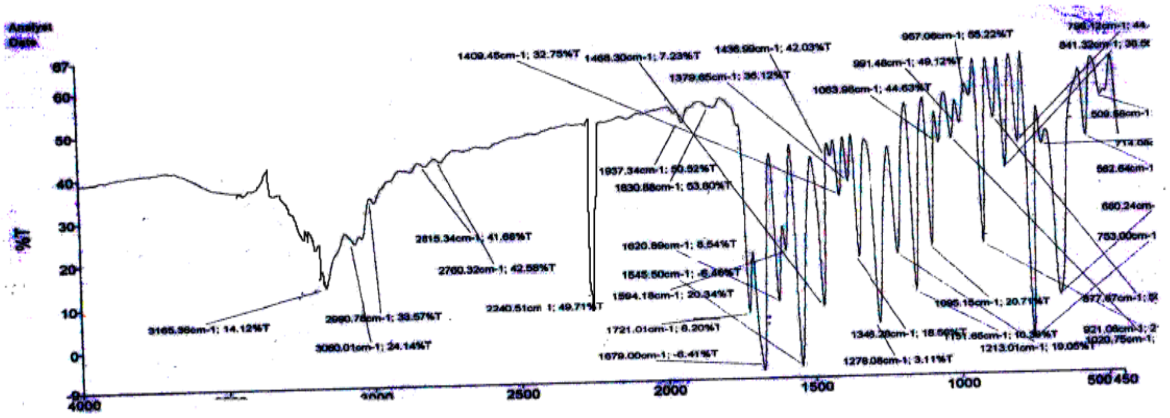


Figure 1: IR Spectrum for dye I

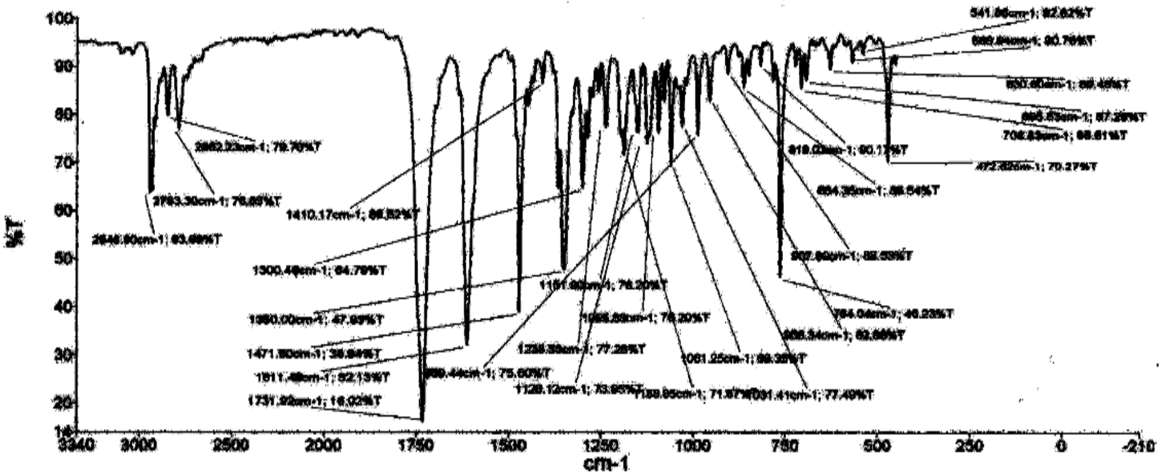


Figure 2: IR Spectrum for dye III

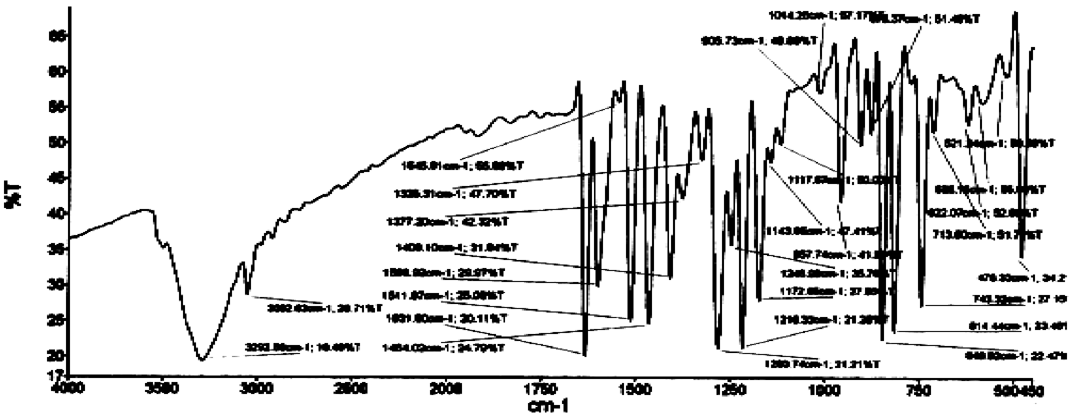


Figure 3: IR Spectrum for dye III$_a$

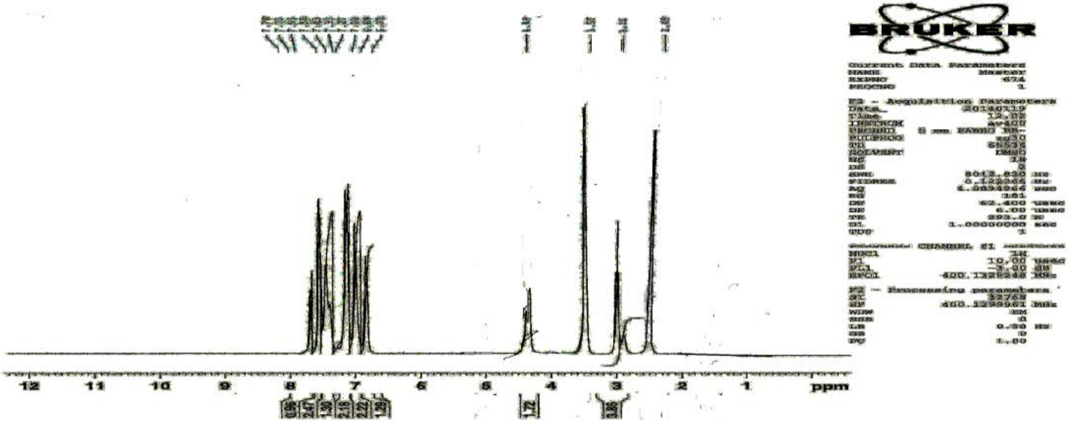


Figure 4: ^{1}H-NMR spectrum of compound (I)

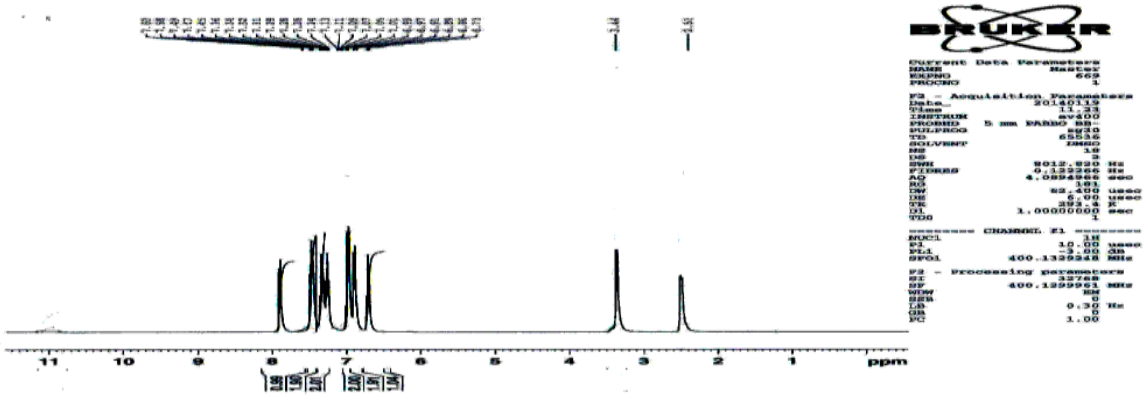


Figure 5: ^{1}H-NMR spectrum of compound (IIIc)

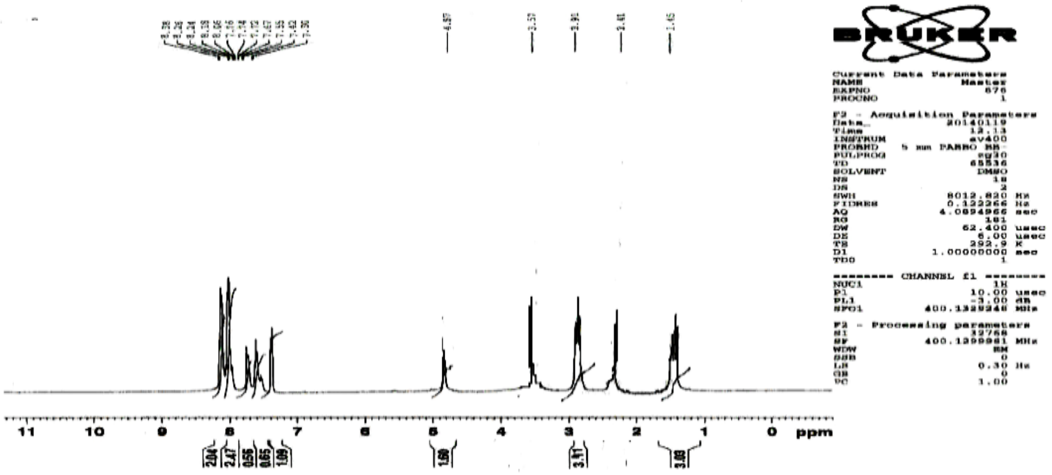


Figure 6: ^{1}H-NMR spectrum of compound (II)

Dying Properties of the Dyes

The acid azo dyes were applied at 2% depth on wool and silk fabric respectively. Their dyeing properties are given in Table 1to Table 2. These dyes gave a wide range of colours varying from yellowish orange to yellowish red shades with good levelness, brightness and depth on the fabrics. The variation in the shades of the dye fabric results from both the nature and position of the substituent present on the diazotized compound. The dyeing showed an excellent fastness to light, with very good to excellent fastness to washing, perspiration and sublimation.However, these dyes showed little efficiency for fiber dyeing rubbing fastness.

Moreover, the presence of electron donating groups,do not resulting any shift for λmax in the visible region and log ε remained nearly constant. However, substitutions such as CN and COOR increase the polarizability. This leads to a decrease energy between the highest occupied molecular orbital and lowest unoccupied molecular orbital and thus, the π→π electronic transition occurs with lower frequency photons, resulting in a bathochromic shift of the visible absorption*

Antimicrobial Activity

All the synthesized heterocyclic derivatives, (X-II), (Ia,b,c - II a,b,c), were assayed for their antimicrobial activity against four test organisms: *Staphylococcus aureus* ATCC6538P, *Escherichia coli* ATCC8739, *Pseudomonas aeruginosa* ATCC9027 and *Candidaalbicans* ATCC2091 using rifampicin (5 g/disc) and ampicillin (10 g/disc) as standard drugsfollowing agar well-diffusion method [21].

The tested heterocyclic azo compounds showed no significant effect against *Pseudomonas aeruginosa* and *Candida albicans,* whereas they showed a potent activity against *Staphylococcus aureus* and *Escherichia coli.* These results suggest that the electron-withdrawing nitro group plays a crucial rolein enhancing the observed activity.

Dyes	Organism			
No.	*E. coli*	*S. aureus*	*S. typhi*	*B. subtilis*
X	+++	++	++	++
I	+	+	+	+
II	+++	++	++	++
Ia	+	+	+	+
Ib	+	+	+	+
Ic	++	++	+	++
II$_a$	+++	+++	++	++
IIb	++	++	+	++
IIc	+++	+++	++	++

(Diameter of inhibition zone in mm; concentration 100 µg/mL), (-)=inactive (10 mm and less); (+)=weakly active (11-15 mm);(++)=moderately active (16-20 mm); (+++)=highly active (21 mm and above).

CONCLUSIONS

As a result of the present study, three new acid dyes, one mono and two bisazo dyes were obtained. All newly synthesized dyes exhibited good to very good fastness to washing, perspiration and rubbing. They can be used as dyes for wool.

In summary, this work demonstrates a rapid, efficient method for synthesis of new heterocyclic compounds of pharmacological interest.

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