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SYNTHESIS, CHARACTERIZATION AND ANALYTICAL STUDIES OF SOME NEW AZODYES DRIVEN FROM O-VANILLIN

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ABSTRACT

Two newo-vanillin-based Azodye ligands (Z1,Z2) were prepared by reaction of sulfadiazine and sulfaguandin and with o-vanilin **(**2-Hydroxy-3-methoxybenzaldehyde). The characterization of dyes have been described by C.H.N., I.R. N.M.R, mass spectra and visible. spectroscopic techniques, the electronic spectra of these azo dyes were studied in term of acid-base properties at different pH values (2- 12), which includes establishing isobestic point, mechanism and determination of protonation and ionization constants of dyes. The effect of solvents of different polarities on the electronic spectra were also investigated.

KEYWORDS: Azo-dyes, Sulfadiazine, Sulfonamide, o-vanilin, protonation and ionization constants.

1. INTRODUCTION

Azo compounds are mostly used as dyes due to its various applications in the fields such as textile fibres, colouring of different materials, biomedical studies and organic synthesis.[1-2] Azo compounds are mostly widely used in fields such as dyeing textile fibers, biomedical studies, advanced applications in organic synthesis and high technology areas like lasers[3], filters.[4] In addition to this, azo dyes were reported to have variety of biological applications like antineoplastics, antidiabetics, antiseptics, anti-inflammatory and other useful chemotherapeutic agents.[5-8] Scarlet red and diamazon are the most commonly used azo dyes which are antiseptics. Several azo compounds derived from thymol[9], aspirin[10], paracetamol][11], m-cresol[12], resorcinol[13] and vanillin[14] moieties have been frequently reported and exhibit excellent biological propertiesas an indicator of acid-base titration.[15] Vanillin’s are used as antioxidant activity, antitumor action, and its therapeutic potential in cancer treatment and prevention.[16] And its widly used as flavoring agent, antimutagen and anticarinogen.[17]

This work involves the synthesis and characterization of two new dyes, Z1 ((E)-4-((3-formyl-4-hydroxy-5-methoxyphenyl)diazenyl)-N-(pyrimidin-2-yl)benzenesulfonamide) And Z2(E)-N-carbamimidoyl-4-((3-formyl-4- hydroxymethoxyphenyl) diazenyl) benzenesulfonamide followed by the study of solvent effect of different polarity, acid–base properties of different pH values and the determination of protonation and ionization constants of those dyes.

EXPERIMENTAL

MATERIALS AND APPARATUS

All the reagents and solvents were of reagent-grad quality, The progress of reaction was monitored by TLC using silica gel coated plates (0.5mm thickness, Merck) and spots were visualized under UV radiation. Infrared spectra (as KBr pellets) were recorded on F.T.IR-8400S shimadzu. NMR spectra were recorded by Bruker ultra shield 300MHz spectrometer DMSO as solvent and TMS as internal reference. Elemental analysis (C.H.N.), were carried out by Perkin element 2400.UV/Vis. absorption spectra of the these compounds in different buffer solutions at room temperature were recorded using Perkin Elmer Lampda EZ 210 UV/ Vis. Spectrophotometer. The EI-MS of the studied dyes were obtained using Agilent spectrometer at ionizing energy value of 70 eV To calculate the ionization and protonation constants for hydroxyl and nitrogen groups, a series of acetate and universal buffer solutions were prepared with different pH values(2-12).[18]

Preparation of azodyes[19]

The azo ligand (Z1 and Z2) with the structure depicted in figure 1 was prepared as describedin the earlier methods for azo dyes. In short details 10mmol of sulfadiazineZ1 and sulfonamide Z2 was dissolved in 30 mL of water and 2.5 mL of concentrated hydrochloric acid to prepare 10 mmol solution. This solution was diazotized below 5 °C with 13 mL of aqueous sodium nitrite (1.0 mol. L–1). A drop of the reaction mixture was tested from time to time with starch-iodide paper until nitrous acid persists in the solution for 10 min. Theresulting diazonium chloride solution was added drop-wise with continuous stirring to o-vanillin solution of (10 mmol concentration in 150 ml alkaline ethanol). The reaction mixture was stirred for 1 hr at 0-5 °C, and left in the refrigerator for overnight. The mixture was acidified with 0.1 N hydrochloric acid until the pH becomes 6. The soiledproduct was filtered off, washed with cold water, air dried and recrystellized twice from hot ethanol and then dried in the oven at 80 °C for 6 hrs.

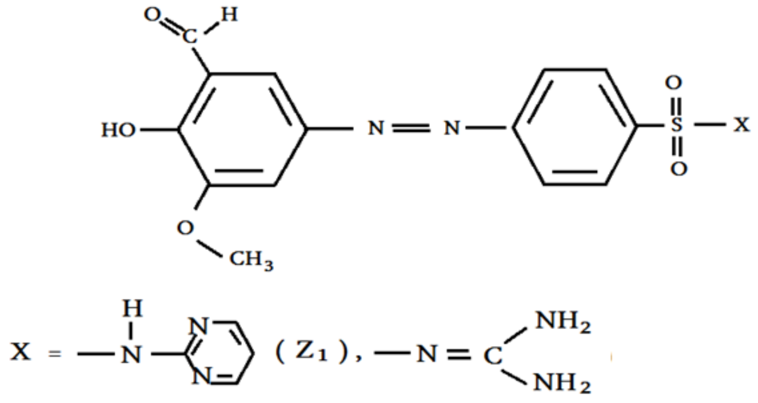

Figure. 1: Structures of azo dyes Z1 and Z2.

- For acid – base studies and determination of ionization and protonation constants of the dye, a series of buffer solutions were prepared with different pH values (0.65 – 12) for total dye concentration 6 x 10-^{5} M via using universal buffer, the absorbance of these solutions were recorded at range of (350 – 660 nm.) using cell of 1cm. length, by aid of half height method the protonation and ionization constants were calculated.
- For solvent effect studies, a series of solution of dye at total concentration 6 x 10-5 M were prepared with, Acetone, Methanol, DMF, DMSO, Ethanol and H2O, the absorbance of these solutions were recorded at range of (350 – 600 nm.) using cell of 1cm. length.

RESULTS AND DISCUSSION

The prepared azodyes are stable in air at room temperature and soluble in DMF, DMSO, methanol, ethanol and aceton.Table-1 shows the collects the physical properties and analytical data for the prepared azo-dyes (Z1 and Z2).

Table (1): Physical properties and elemental analysis for novel azodyes.

Comp.	Molecular formula	m.p °C	Yield (%)	Color	C % Cal. (found)	H % Cal (found)	N % Cal (found)
Z1	$C_{18}H_{15}N_5O_5S$	199-200	70%	orange	52.30 (52.69)	3.66 (3.44)	16.94 (16.76)
Z2	$C_{15}H_{15}N_5O_5S$	195-197	74%	brown	47.74 (47.49)	4.28 (4.01)	18.56 (17.89)

Infrared spectra of Z1 and Z2: The most important IR absorption bands corresponding to the azodyes (fig.2&3) are presented in table 2. The observed band in the range 1450 cm–1 is due to ν (N=N) group of the ligand. The sharp band in the range 1521-1587cm-1 are due to ν (C=C) respectively.[20]

Table 2: Selected infrared and uv.visible data of Z.

Comp.	ν(OH) cm^{-1}	ν(N=N) cm^{-1}	υ(C =C) cm^{-1}	ν(C=N) cm^{-1}	Y (C=O) cm^{-1}	υ (O=S=O) cm^{-1}
Z1	3417m	1581	1604	1126	1640	1166s
Z2	3417m	1581	1608	1130	1635	1356

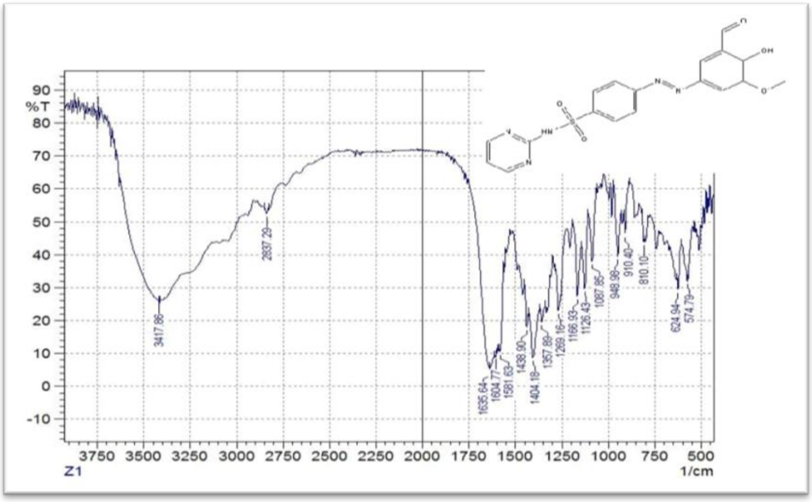

Figure. (2): IR spectrum ofZ1.

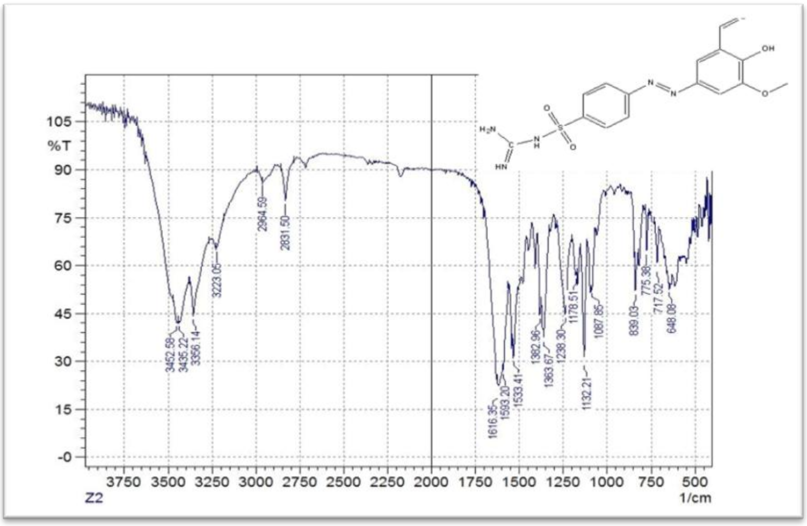

Figure. (3): IR spectrum ofZ2.

^{1}H-NMR spectrum of azoschiff base ligand

The^{1}H-NMRspectrum of the azoschiff base ligand figure(4 and 5) was measured using in DMSO as a solvent. Theazosdyes base spectral results show peaks at δ =7.27-7.28 ppm attributed to the phenyl ring. The single peakat δ = 10.38 ppm due to the OH groups in azodyes.[11] The singal peak at 10.5 ppm due to S,1H, CHO. The result shows in table.(3)

Table 3: ^{1}H -NMR data of the azodyes.

Comp.	δ (ppm)
Z_1	10.38(S, 1H, OH),7.4-8.6 (m, 9H, Ar-H), 10.5(S,1H, CHO), 3.8(S,3H,OCH_3)
Z_2	7.2 -8.5 (m, 6H,Ar-H), 10.2 (S,1H, - CHO),4.0 (S,3H,OCH_3)

(S) = Singlet, (m) = Multiplet

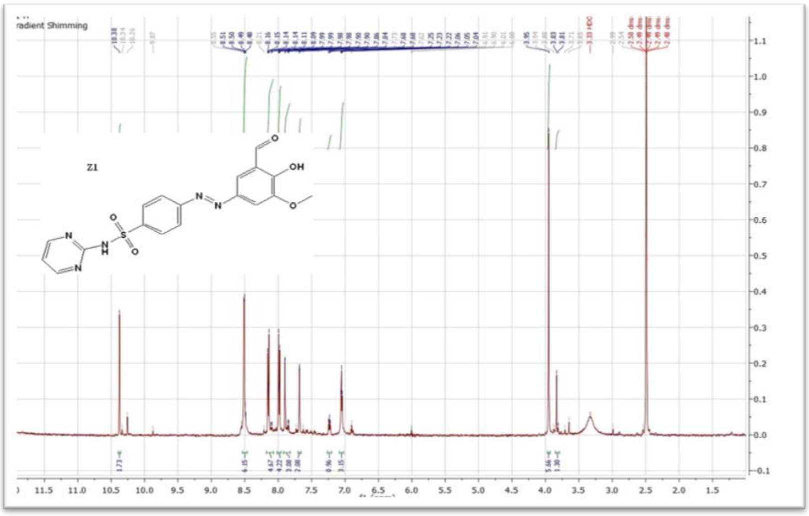

Fig. 4. Mass spectra of Z1.

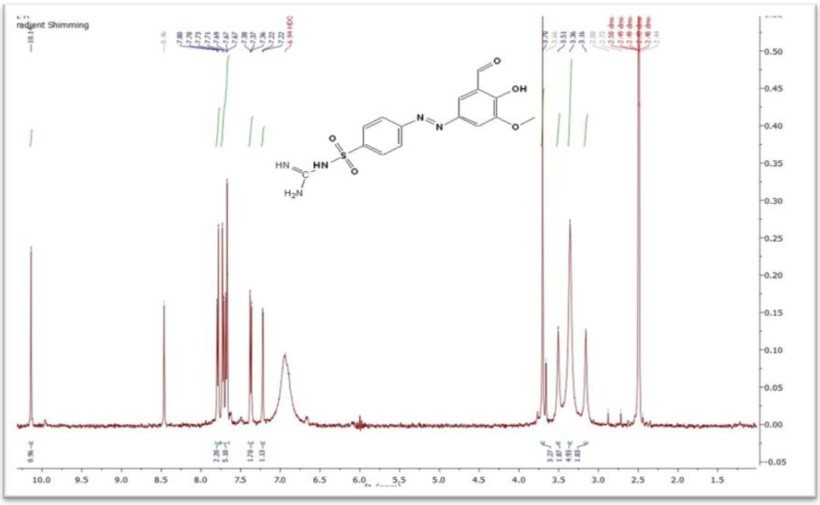

Fig. 5: Mass spectra of Z2.

Mass spectrometry plays pivotal role in the structural characterization of organic molecules.[21] The EI-MS of the azo dyes at 70 eV are represented in Figs(6,7). The signal appeared in the mass spectra of Z1and Z2 at m/z =413.1, 377.2 are due to the formation of molecular ions.

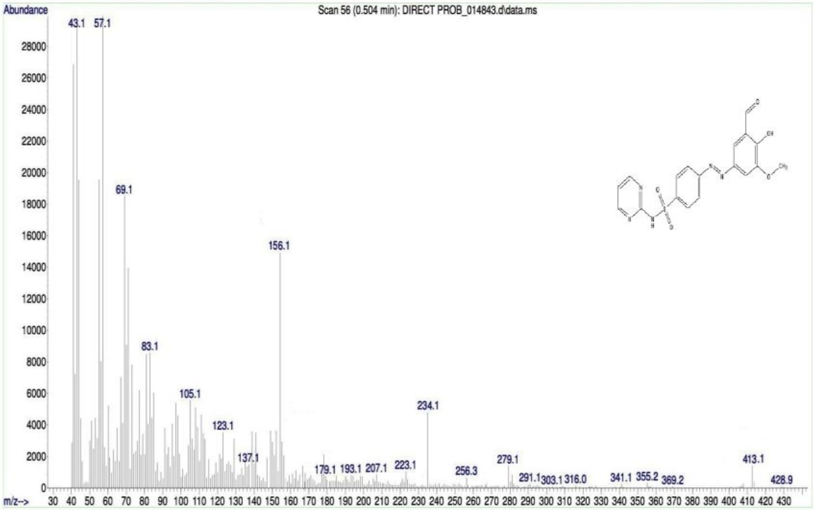

Fig. 6: Mass spectra of Z1.

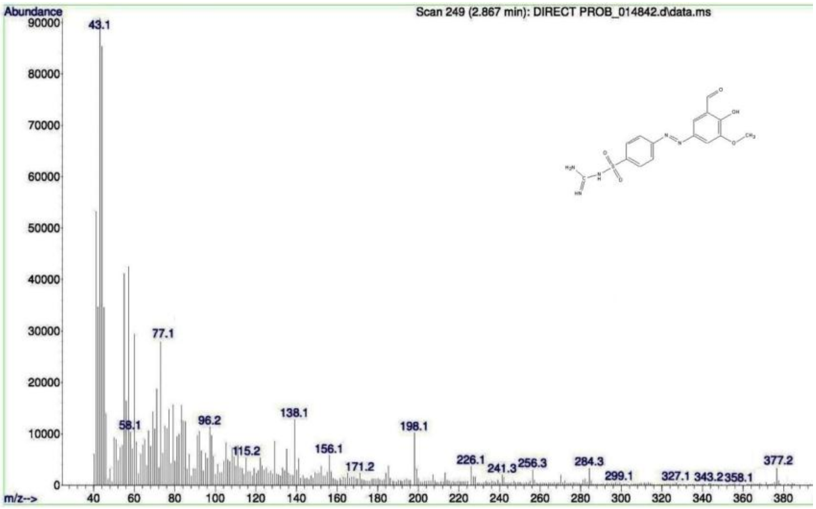

Fig. 7. Mass spectra of Z2.

Acid-Base properties

The absorption spectra of 6 x 10^{-5} M solution of each dye in the range of wavelength (360-550 nm) of varying pH values (0.65 – 12) were represented graphically (**Fig. 8**). The spectra characterized two bands, the first at (377- 385nm) and. in the acidic medium due to the protonation of dye (cationic form). The second high intense band at (435-458) the first ban at in range the alkaline medium due to ionization of dye (anionic form).

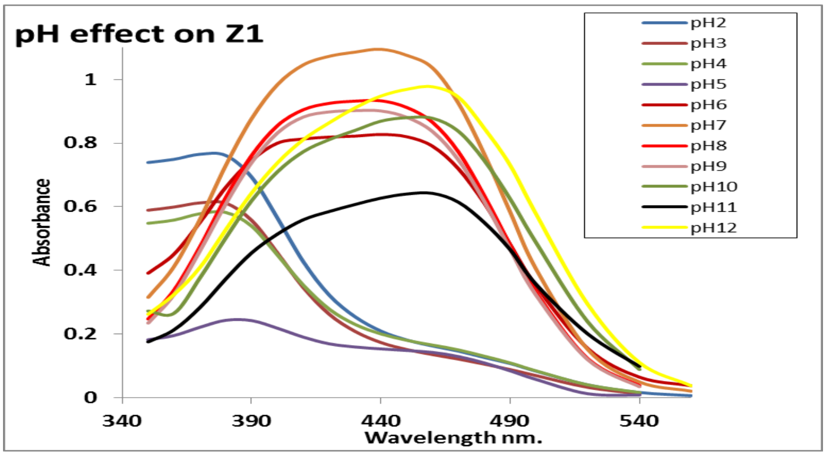

Fig. 8. PH effect on visible spectra of Z1.

From Absorbance – pH curve and by the aid of height method[22], the protonation (pKp) and ionization (pKa) constants were calculated (**Table 4**).

Table. 4: The Protonation And Ionization Constants Of Dyes.

Dye	λ nm	$A_{1/2}$	pK_a	$A_{1/2}$	pK_p	$A_{1/2}$	pK_{a1}
Z_1	440	0.620	5.70	0.190	3.40	-----	-
Z_2	440	0.115	5.80	0.035	3.45	0.18	9.5

pKp is protonation constant for nitrogen atom

pKais ionization constant for hydroxyl group

pKa1 is the ionization constant for NH group

Solvents effect

Figure 9 shows the spectra of dyes at different solvents with λmax in the range of (340-540nm.) for dyes Z1 and Z2. The absorption spectra in various solvents are influenced by salvation and / or dielectric effects of solvents. The result were show in table 5.

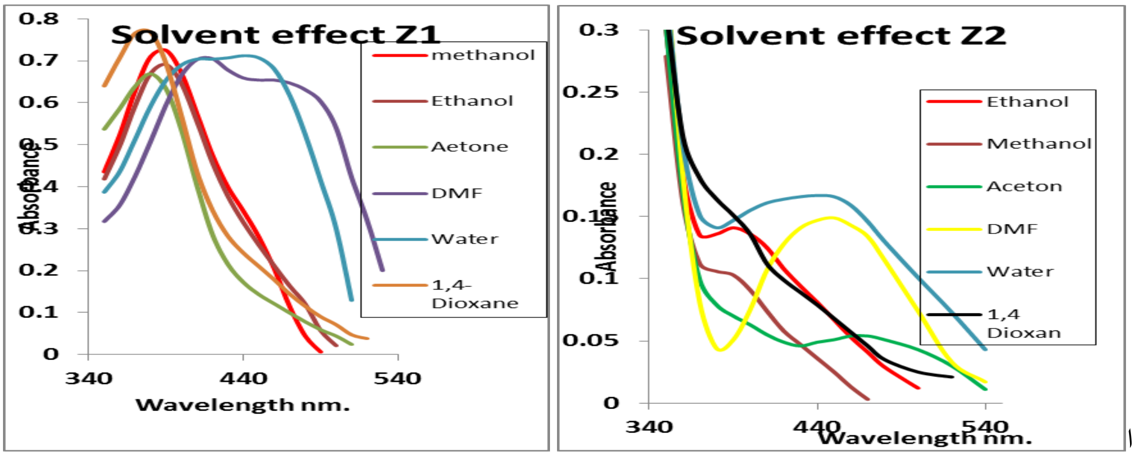

Fig. 9: Visible Spectra of Z1 and Z2 At Different Solvents.

Table 5: Solvent effect on spectra of Z1 and Z2.

Solvents	**(D – 1) / (D + 1)**	**λ_{max} nm.**	
		Z1	**Z2**
1,4-Dioxane	0.394	380	385
Acetone	0.909	380	370
Methanol	0.920	390	390
Ethanol	0.940	390	390
DMF	0.947	430	450
Water	0.975	405	450

It can be seen from **table 5 and from** the plot of λmax vs. dielectric function of solvents from Gati and Szalay equation[23], shows a linearity relationship that means the dielectric constant is the main factor covering the salvation.

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