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The Triazine-based Azo-azomethine Dyes; Synthesis, Characterization, Spectroscopy, Solvatochromism and Biological Properties of 2,2'-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene)bis (methanylylidene))bis(4-(phenyldiazenyl)phenol

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The Triazine-based Azo-azomethine Dyes; Synthesis, Characterization, Spectroscopy, Solvatochromism and Biological Properties of 2,2'-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene)bis (methanylylidene))bis(4-(phenyldiazenyl)phenol

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Abstract

The macrocyclic azo-azomethine dyes 2,2'-((((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene)bis(methanylylidene))bis(4-(phenyldiazenyl)phenol) and its derivatives were synthesized and characterized by elemental analysis, mass, FT-IR, UV-vis and NMR spectroscopy. The solvatochromism as well as effects of substitutions on the electronic absorption of these compounds have been studied in the DMSO, DMF, THF, CH_3CN, CH_3OH and CH_3COOH as solvents. Also they positive solvatochromism behaviors are explained on the basis of intramolecular hydrogen bonding, enol–keto tautomeric and dipole moment changes. Compounds having electron donating substituent on the phenyl ring showed good antioxidant activity. However, none of them has a considerable antibacterial activity.

Keywords: Azo-azomethine, Schiff base, Triazine, Solvatochromism, Enol–keto tautomeric, Antibacterial activity, Antioxidant activity.

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1. Introduction

The azo dyes are one of the major groups of synthetic organic dyes; which their applications of high technology have been attracting much attention. They are used in various fields such as paper printing, electronic photography, color formers, dyeing, bleaching, polymers, liquid crystal displays, laser technology, data storage and solar energy conversion [1-10]. Recently, there is a rapidly growing interest in the potential of their biological-medical applications. They are known to have a broad range of biological activities such as antibacterial, antifungal, antitumor and antioxidant activities [11-14]. In addition, azo dyes also have an adverse impact in terms of total organic carbon (TOC), biological oxygen demand (BOD) and chemical oxygen demand (COD) [15]. It is worth to mention that many synthetic azo dyes and their metabolites are toxic, carcinogenic, and mutagenic [16]. The azo-azomethine compounds provide the possibility of forming different type of intra- and intermolecular hydrogen bond and allow the formation of an intramolecular proton transfer with the nitrogen atoms. This tautomerization can be induced either by light, heat or the solvent [17-22]. We are now interested on the tautomerization and solvatochromism of azo-azomethine compounds. On the other hand, s-triazines have found widespread applications in the pharmaceutical, textile, plastic, and rubber industries, and are used as pesticides, dyestuffs, optical bleaches, explosives, and surface active agents [23–29]. The azo dyes including s-triazines ring (i.e., Reactive Red 141 (RR141), Reactive Blue 171 (RB 171), Reactive Green 19 (RG19) have appropriate chemical behavior [30-33]. Therefore, the ultimate scope of our investigation is preparation of azo-azomethine dyes of **3a-d** with three objectives: (i) Synthesis of 1,3,5-triazine-based azo-azomethine dyes, (ii) Study of solvatochromic behavior and substituent effects of the prepared dyes in various solvents, (iii) Study of antibacterial and antioxidant properties of synthesized compounds and comparison with similar known compounds.

2. Experimental

2.1. Materials and Measurements

All chemical reagents were obtained from the Merck and used without further purification. For UV–vis measurements solvents with spectroscopic grade (>99.9%) were used, without any further purification. 2,4-Dichloro-6-methoxy-1,3,5-triazine,2-hydroxy-5-[(aryldiazenyl)]benzaldehydes (**1a-d**) and 2-((2-mercaptophenyl imino)methyl)-4-(aryldiazenyl)phenols (**2a-d**) have been prepared and purified according to the methods reported in the literature [34, 17-22]. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Mass spectra were recorded on a Agilent MS Model 5973. Melting points were measured with Electrothermal 9300 apparatus. FT-IR spectra were recorded on Shimadzu 8400S spectrometer with samples investigated as KBr discs. The electronic absorption spectra were recorded with a Shimadzu 1650 spectrophotometer. The structure of all synthesized compounds were confirmed by ^{1}H and ^{13}C NMR spectra, in DMSO-d_6 as solvent recorded on a Bruker AV 300 MHz spectrometer.

2.2. General procedure for synthesis of 2,2'-((((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl) bis(2,1-phenylene))bis(azanylylidene)bis(methanylylidene))bis(4-(phenyldiazenyl)phenol) (3a-d):

2,4-Dichloro-6-methoxy-1,3,5-triazine [34] (10 mmol) was dissolved in THF (20 ml). K_2CO_3 (20 mmol) was added and the suspension mixture was cooled to 0-5 °C. Then 2-((2-mercaptophenylimino) methyl)-4-(aryldiazenyl)phenols (**2a-d,** 20 mmol) [21] in 30 ml THF was added portionwise to the mixture. The suspension mixture was allowed to increase to 25 °C and kept for 1 h then heated at 60-70 °C for 6 h. The mixture was filtered and the solvent of the filtrate was removed to give the crude product. Products are air stable and soluble in DMSO, DMF, CH_3OH, CH_3COOH and THF. They were

purified by recrystallization and their structures were characterized by elemental analysis, mass, FT-IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy.

2.2.1. Compound **3a**

The orange product crystallized from CH_3CN. Yield, 4.49 g (58%), m.p.239 ºC. Anal. Calcd. for $C_{42}H_{31}N_9O_3S_2$: C, 65.18; H, 4.04; N, 16.29; S, 8.29.Found:C, 65.14; H, 3.96; N, 16.12; S, 8.16. The EI-MS: m/z; 775$(M+1)^+$, 774$(M)^+$, 669, 578, 558, 474, 442, 333, 301, 225, 198, 106. FT-IR (KBr, cm^{-1}): 3300-3500 *v*(bs, OH), 3056 *v*(Ar-H), 2943, 2848 *v*(CH=N),1612 *v*(C=N),1581 *v*(N=N), 1490 *v*(C=C), 1277, 1153 *v*(C-N), 1217, *v*(C-S), 1070 *v*(C-O). ^{1}H NMR ppm:11.11 (1H, OH, D_2O exchangeable),9.92(s, 1H, C<u>H</u>=N),8.84-6.83(m, 11H, Ar-H), 3.91(s,3H).^{13}C NMR ppm: 190.98, 178.24,163.63, 161.66, 161.58, 160.75, 152.89, 149.92, 144.99, 134.87, 132.99, 131.84, 128.99,119.59, 119.52, 119.49, 118.94,116.84, 116.78 , 54.12.

2.2.2. Compound **3b**

The yellow product crystallized from CH_3CN. Yield, 4.88 g (61%). m.p. 256 ºC. Anal. Calcd. for $C_{44}H_{35}N_9O_3S_2$: C, 65.90; H, 4.40; N, 15.72; S, 8.00. Found: C, 65.78; H, 4.36; N, 15.66; S, 7.92. The EI-MS: 804$(M+2)^+$, 802$(M)^+$, 746, 685, 652, 626, 582, 559, 399, 239, 196, 92. FT-IR (KBr, cm^{-1}): 3300-3500 *v*(bs, OH), 3070 *v*(Ar-H),2972, 2869 *v*(CH=N),1618*v*(C=N), 1575 *v*(N=N),1479 *v*(C=C), 1286, *v*(C-N), 1205(C-S), 1174, 1089 *v*(C-O). ^{1}H NMR ppm: 11.21 (1H, OH, D_2O exchangeable), 9.95 (s, 1H, C<u>H</u>=N), 8.64-6.42 (m, 11H, Ar-H), 3.95 (s,3H), 2.28 (s,3H). ^{13}C NMR ppm: 191.42, 175.98, 165.59, 154.92, 152.58, 142.26, 135.68, 131.86, 130.73, 128.84, 127.16, 123.09, 123.03, 122.53, 119.52, 119.46 , 119.17, 116.89, 116.62, 53.49, 21.48.

2.2.3. Compound **3c**

The yellow product crystallized from a mixture of THF/C_2H_5OH (1:1). Yield, 4.96 g (59%). m.p. 271-273 ºC. Anal. Calcd. For $C_{42}H_{29}Cl_2N_9O_3S_2$: C, 59.86; H, 3.47; N, 14.96; S, 7.61. Found: C,

59.78; H, 3.40; N, 14.84; S, 7.52. The EI-MS: m/z 845$(M+2)^+$, 843$(M)^+$, 732, 704, 612, 585, 509, 367, 232, 102. FT-IR (KBr, cm^{-1}): 3300-3500 *v*(bs, OH), 3058 *v*(Ar-H), 2954, 2864 *v*(CH=N), 1616 *v*(C=N), 1583 *v*(N=N), 1490 *v*(C=C), 1274, 1217 *v*(C-N), 1217 *v*(C-S), 1108, 1066 *v*(C-O), 831(C-Cl). ^{1}H NMR ppm: 11.19(1H, OH, D_2O exchangeable), 9.83 (s, 1H, C<u>H</u>=N), 8.85-7.30 (m, 11H, Ar-H), 3.90 (s, 3H) . ^{13}C NMR ppm: 191.87, 178.38, 164.22, 161.83, 161.66, 160.75, 151.21,149.93,144.99,134.87, 132.79, 132.27, 127.99, 119.59, 119.52, 119.49 , 118.82, 116.69, 116.58, 54.46.

2.2.4. Compound **3d**

The brown product crystallized from a mixture of THF/CH_3CN (1:1). Yield, 4.85 g (56%). m.p.292-293 ºC. FT-IR (KBr, cm^{-1}): 3300-3500 *v*(bs, OH), 3068 *v*(Ar-H), 2966, 2874 *v*(CH=N), 1610 *v*(C=N), 1581 *v*(N=N), 1532 *v*(N=O, Unsym. Stretching), 1488 *v*(C=C), 1336 *v*(N=O, Sym. Stretching), 1263, 1211*v*(C-N), 1205 *v*(C-S), 1112 *v*(C-O), 1076,921*v*(N-O). ^{1}H NMR ppm:11.18(1H, OH, D_2O exchangeable), 10.43 (s, 1H, C<u>H</u>=N), 8.87(m, 2H), 8.72(m, 2H), 8.34, 8.18(dd, 8H, J=5.82 Hz), 7.39(m, 2H), 7.35-7.23(m, 8H), 3.93 (s, 3H). Anal. Calcd. For $C_{42}H_{29}N_{11}O_7S_2$.: C, 58.39; H, 3.38; N, 17.84; S, 7.42. Found: C, 58.31; H, 3.34; N, 17.78; S, 7.38.The EI-MS: m/z 865$(M+1)^+$, 864$(M)^+$, 863$(M-1)^+$, 818, 742,714, 622, 595, 519, 487, 378, 346, 270, 243, 151, 123.

2.2.4. Antioxidant activity

Antioxidant activity of compounds was investigated using DPPH method [35]. Briefly, 50 µl of test samples at a concentration of 100 µg/ ml in DMSO was added to 5 ml of a 0.004 % solution of diphenyl picryl-hydrazyl (DPPH) in methanol. After incubation for 30 min at room temperature in the dark, the absorbance at 517nm was measured and the inhibition percentage was calculated using the following equation:

$$\% \text{ Inhibition} = [(A_{Control} - A_{Sample}) / A_{Control}] \times 100$$

Where $A_{Control}$ is the absorbance of DPPH without sample and A_{Sample} is the absorbance of DPPH in the presence of sample.

2.2.5. Antibacterial activity

The synthesized compounds were evaluated for their antibacterial activity against gram positive (*Bacillus cereus PTCC* 1556 and *Staphylococcus aureus* PTCC 1112) and gram negative (*Escherichia coli* PTCC 1330 and *Klebsella pneumonia* PTCC 1053) bacteria using disc diffusion method [36]. Nutrient agar plates were inoculated with the test strains. The compounds were dissolved in DMSO and at different concentrations were placed on the surface of the inoculated plates. The petri plates were incubated at 37°C for 24 h and then the antibacterial activity was determined by measuring the diameter of the zone of growth inhibition.

3. Results and discussion

The condensation reaction of 2-hydroxy-5-(aryldiazenyl)benzaldehydes **(1a-d)** with 2-aminothiophenole afforded Schiff base compounds 2-((2-mercaptophenylimino)methyl)-4-(phenyldiazenyl)phenols (**2a-d**) in good yields [17, 21]. Then, the azo-azomethine triazine-based dyes 2,2'-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene)bis (methanylylidene))bis(4-(phenyldiazenyl)phenols (**3a-d**) were synthesized using **2a-d** and 2,4-dichloro-6-methoxy-1,3,5-triazine (**4**) in THF (Fig.1).

Fig. 1:

3.2. Infrared spectra

In order to clarify the mode of bonding, the IR spectra of prepared compounds **1a-d, 2a-d** and **3a-d** were studied on careful comparison of the latter with the former [17-22, 37, 38]. Strong bands observed in the IR spectra of **1a–d** in the region of 1665–1668 cm^{-1} and 1286-1288 cm^{-1} can be assigned to the *ν*(C=O) and *ν*(C-O) functions. The total absence of *ν*(C=O) absorption in the IR spectra of the prepared dyes together with the appearance of new *ν*(C=N) absorption in the range of 1610–1614 cm^{-1} clearly indicated that new Schiff base compounds (**2a-d**) had been formed. In the IR spectra of **2a-d**, appearance of absorption bands at 3413-3444 *ν*(OH), 2944-2868 *ν*(CH=N), 1610-1614 *ν*(C=N), 1457-1490 *ν*(N=N) are in agreement with the structures proposed of **2a-d** [19-22, 38]. The N···O-H bands are located the range of 3300-3600 cm^{-1} in compounds **3a-d**. The bands ν(CH=N), ν(C=N) and *ν*(N=N) vibrations are in the range of 2869-2948, 1612-1618 , 1575-1583 and 2966-1610 cm^{-1}, respectively. The *ν*(C-N), *ν*(C-S) and *ν*(C-O) bands were observed in the range of 1274-1286, 1205-1217, 1070-1108 and 1263-1112 cm^{-1}, respectively. Also, the IR spectrum of **3d** showed strong bands at 1336 and 1532 cm^{-1} which could be assigned for ν_s and ν_{as} of the NO_2 groups and it is in agreement with results obtained for similar azo-azomethine dyes [17-22, 39].

3.3. The ^{1}H and ^{13}C NMR spectra

The NMR spectral results obtained from compounds **3a-d** at ambient temperature in DMSO-d_6, with the hydrogen assignments are presented in experimental section. The NMR analysis appeared to support the synthesis of all compounds. The ^{1}H NMR spectrum of **3a-d** exhibited D_2O exchangeable signals for the OH protons in the range of 11.11-11.21 ppm. The C<u>H</u>=N and Ar-H protons signals appeared in the range of 9.83-10.43 and 6.42-8.87ppm, respectively [17-20]. The ^{13}C NMR spectra of **3a-c** consisted of nineteen carbon peaks; two peak for triazine rings carbons (190.98-191.87 and 175.98-178.38 ppm), one peak for CH=N, two peak for C-O, C-N and thirteen peak for benzene

aromatic region. The C-OH carbon peak was appearing at 163.63-165.59 ppm, which indicated more character of C=O, suggesting compounds (**3a-c**) exists as a keto-amine tautomer. These chemical shifts are supported by IR and ^{1}H NMR spectra, as well as it is in agreement with results obtained for similar Schiff bases dyes [17-22, 38--44].

3.3. The electronic absorption spectra

Electronic spectroscopy is one of the most applicable and successful techniques for investigating the tautomerism of azo-azomethine compounds. Therefore, the tautomers can be detected from the absorption spectra in the visible region. The electronic spectra of compounds (**1a-d, 2a-d** and **3a-d**) were measured (in the range of 300–600 nm) in six solvents DMSO, DMF, THF, CH_3CN, CH_3OH and CH_3COOH at room temperature (Table 1). The absorption curves of **3c** are shown in Fig. 2.

Table 1 and Fig. 2

The UV–vis absorption spectra of **2a–d** and **3a-d** in CH_3OH, CH_3CN, CH_3COOH and THF solvents show main band at 339-387 nm which can be assigned to the moderate energy transition of the aromatic ring. However, in the DMSO and DMF solvents mainly two bands are displayed arising from the $\pi\rightarrow\pi^*$ transitions in the backbone. The first band that located at 342-375 nm, similar to other solvents, is because of transition of the aromatic ring, while the second one which appeared at 440-585 nm can be assigned to an intramolecular charge transfer $n\rightarrow\pi^*$ transition of azo-aromatic chromophore [17-22, 38-44].

In all studied solvents, the absorption bands of **2a-c** and **3a-c** at 342-375 nm and 440-585nm generally shows bathochromic shift (positive solvatochromism) with polarity change of solvent (Table

1). Our study indicates that solvatochromism exhibited by the dyes may be due to the effect of proton transfer or dipole moment changes in various solvents [19-22].

Absorption spectra of compounds **3a-d** in DMF solvent are shown in Fig. 3. It clearly show that the 310-360 nm bands are in the order, 3b>3d>3a>3c and 410-490 nm bands are in the order, 3d>3c>3a>3b (Table 1). Results are indicating those bands appeared at 410-490 nm ($n\rightarrow\pi^*$ absorption) are influenced by the nature of substitutions (Table 1). It shows that solvatochromism is influenced by the substituents [17-22, 38-44].

Fig. 3

Furthermore, the absorption spectra of **3c** at different volume ratios of the applied pair of solvents DMF/H_2O were also recorded (Fig. 4). It was observed that with increasing the volume content of water the intensity of absorption of the band about 343 nm (probably azo-enol-imine form) decreased and shifted to 363 nm. Also band at 453 nm for other form (hydrazo-keto-imine or azo-keto-enamine) shifted to 470 nm. This implies presence of enol–keto equilibrium that its direction depends on the polarity of solvent. In general, the nature of substitutions, solvent environment, hydrogen bonds, temperature, pH and changes in the dipole moment of the molecules are the key factors in deciding the solvatochromism of azo-azomethine dyes [17-22, 38-44].

Fig. 4

3.4. Biological results

DPPH is a stable free radical, which has been widely accepted as a tool for evaluation of antioxidant activity [45]. In the DPPH assay, compounds **3a-d** with ascorbic acid as standard were evaluated. As are shown in Table 2, compounds **3a** and **3b** showed good antioxidant activity, while compounds **3c** and **3d** did not display remarkable activity. The minimum activity observed in

compound **3c** containing Cl group on the phenyl ring. In the disc diffusion antimicrobial sensitivity testing, none of the compounds showed inhibitory effects against all the tested pathogens.

Table 2

4. Conclusion

The synthesized compounds were obtained from condensation reactions of 2-((2-mercaptophenylimino)methyl)-4-(phenyldiazenyl)phenol and with 2,4-dichloro-6-methoxy-1,3,5-triazine. The nature of substitutions, solvent environment, hydrogen bonds and dipole moment of the molecules are the key factors in deciding the solvatochromism of azo-azomethine dyes. The present results, compared to previous studies (20-22, 40, 46) showed that 2,2'-(((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfanediyl)bis(2,1-phenylene))bis(azanylylidene)bis(methanylylidene))bis(4-(phenyldiazenyl) phenol and its substituted derivatives (**3a-d)** have greater antioxidant activity than 2,2′-((2,2′-(6-methoxy-1,3,5-triazine-2,4-diyl)bis(oxy)bis(2,1-phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene))bis(4-phenyldiazenyl)phenol and its substituted derivatives (**3e-h)**. In addition to, the compounds **3a-d** compared to **2a-d** exhibited relatively higher antioxidant property, while the compounds **3e-h** showed less activity than **2e-h**.

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Tables and Figures Captions

Table 1: Summary of the UV-Vis absorption bands for synthesized compounds **1a-d**, **2a-d** and **3a-d**

Table 2: Comparison of antioxidant activity of compounds **2a-d**, **3a-d, 2e-h** and **3e-f** at a concentration of 100 μg/mL

Fig. 1: The synthesized **3** with azo precursors

Fig. 2: Absorption spectra of **3c** in; 1) DMSO, 2) DMF, 3) THF, 4) CH_3OH, 5) CH_3CN and 6) CH_3COOH solvents.

Fig. 3: Effects of substituent on absorption spectra of the compounds **3a-d** in DMF at room temperature

Fig. 4: Absorption spectra of **3c** in DMF (C= 4.3×10^{-5} M) and H_2O: (a) 0%; (b) 10% (c) 20% and (d) 30% water.

Table 1.

Compound	DMSO	DMF	CH_3OH	THF	CH_3CN	CH_3CO_2H
1a	340, 441(sh)	340, 450	343	341	341	343
1b	350, 441(sh)	349, 444	345	343	342	344
1c	349, 455(sh)	347, 454	341	342	341	345
1d	377,526(sh)	365,535	361,456(sh)	361,454(sh)	360,454(sh)	364,458(sh)
2a	355, 470(sh)	343, 480	346	346	345	346
2b	356, 468(sh)	355, 450	347	345	342	347
2c	357, 463(sh)	355, 497	348	347	343	346
2d	375,467(sh)	350,585	386,508(sh)	386,506(sh)	385,506(sh)	387,510(sh)
3a	342, 451(sh)	347, 449(sh)	341,452(sh)	341	340	340
3b	357, 455(sh)	357, 440(sh)	356,458(sh)	340	339	340
3c	345, 456	343, 453	346,435(sh)	339	335	338,431(sh)
3d	370,461	348,583	381,503(sh)	384,504	381,503(sh)	386,508(sh)

Table 2.

Compounds	DPPH Scavenging (%)	Compounds	DPPH Scavenging (%)
(X=S)		**(X=O)**	
2a	10.4[g]	**2e**	41.4[h]

2b	48.7[g]	**2f**	45.3[h]
2c	16[g]	**2g**	11.8[h]
2d	9.6[g]	**2h**	31.1[h]
3a	28	**3e**	14.4[m]
3b	48.9	**3f**	19.0[m]
3c	11	**3g**	1.0
3d	6.9	**3h**	-
Ascorbic acid	92.1	*g:ref 21 , h; ref 22, m:ref 40*	

Fig. 1

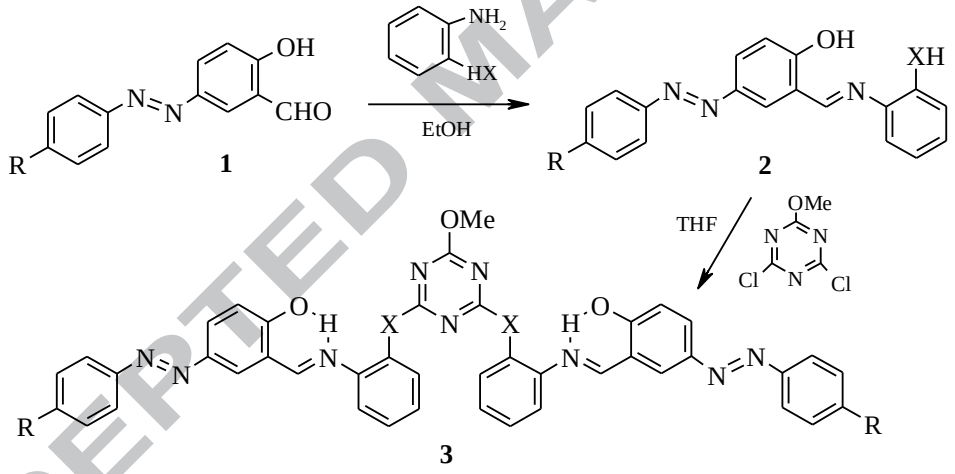


Fig. 2

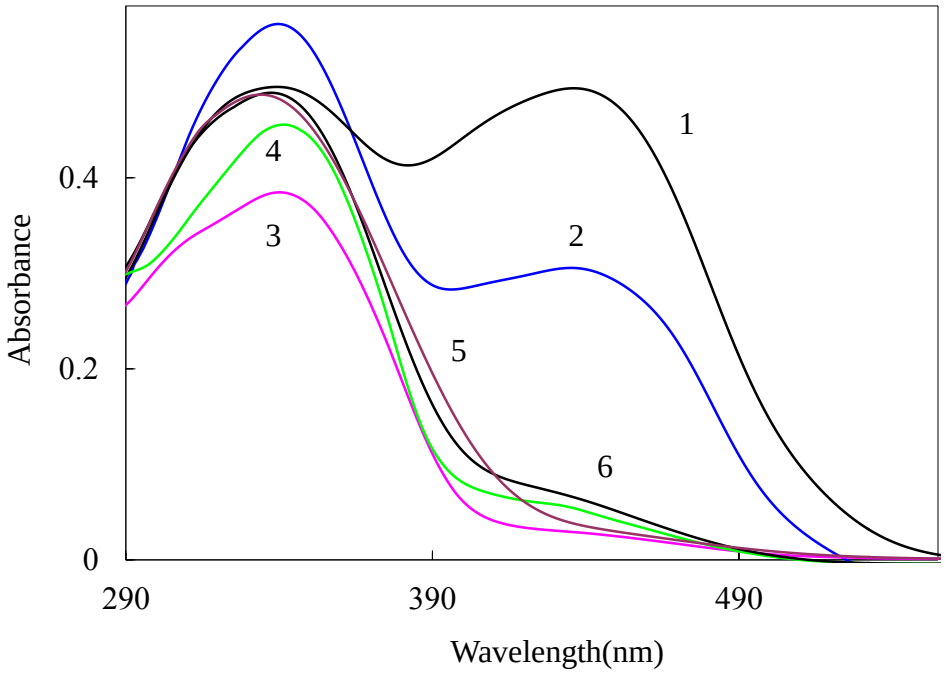


Fig. 3

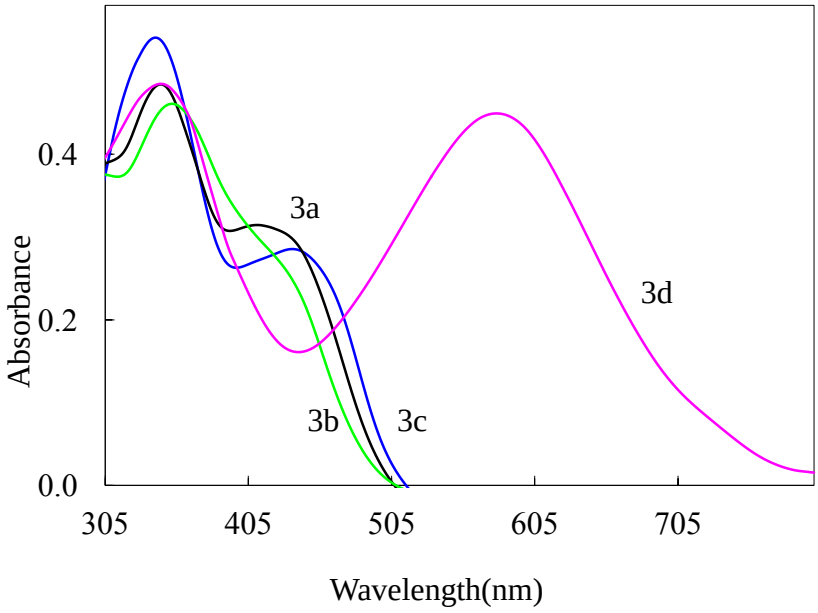
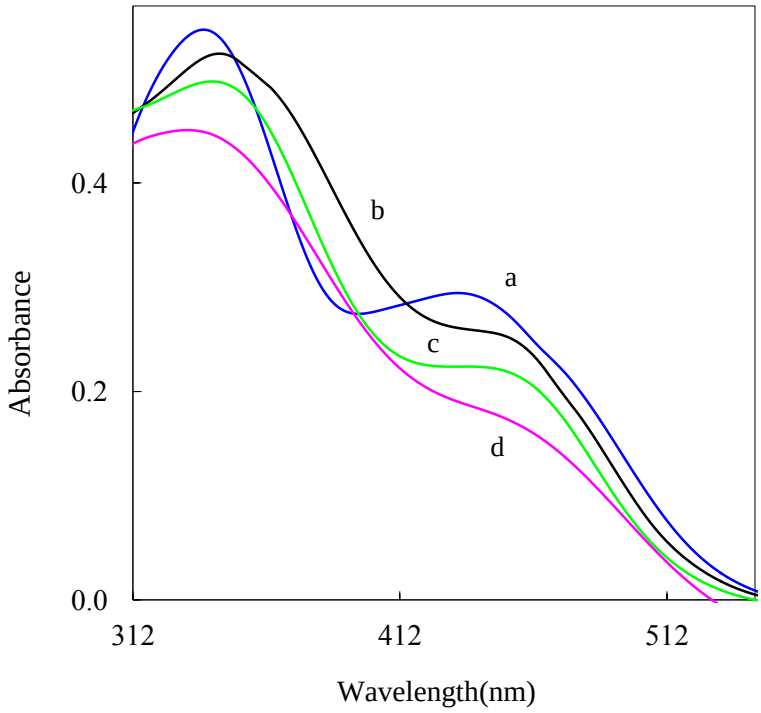


Fig. 4



Highlights

► azo-azomethine dyes with triazine based. ► the tautomerism between enol-amine, enaminone and hydrazone forms in organic solvent was studied. ► the solvatochromism is dependent on the substitution, solvent, pH and temperature. ►the azo-azomethine dyes has antioxidant activity, which are dependent on electron releasing of substituents.

The azo-azomethone dyes were prepared via condensation reaction of 2,4-dichloro-6-methoxy -1,3,5-triazine with azo couled 2-(2-mercaptophenylimino)methyl)-4-(aryldiazenyl)phenol. The UV-vis spectra indicated positive solvatochromism in synthesized compound are dependent on the substitution, solvent, pH and temperature. Some compounds exhibited antibacterial, antioxidant activities.