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Synthesis, Structural Characterization And Theoretical Investigations of New Azo-Azomethine Compounds Bearing Acryloyl Moiety

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ABSTRACT

In this study six new azo-azomethine dyes containing acryloyl group, 4-[[[4-[4′-methyl phenyl azo) phenyl] imino] methyl] phenyl-2-propenoat, 4-[[[4-[4′- hydroxy phenyl-azo) phenyl] imino] methyl] phenyl-2-propenoat, 4-[[[4-(phenyl azo) phenyl] imino] methyl]- phenyl-2-propenoat, 4-[[[4-[4′-chloro phenyl azo) phenyl] imino] methyl] phenyl-2-propenoat, 4-[[[4-[4′- nitro phenyl azo) phenyl] imino] methyl] phenyl-2-propenoat were synthesized. The acryloyl derivatives of the azo-azomethine dyes were prepared with metallic sodium and acryloyl chloride in 1:1 Molar ratio and characterized using elemental analysis, IR, UV-Vis, 1H-NMR and 13C-NMR spectroscopy. The molecular geometry was also optimized using density functional theory (DFT/B3LYP) method with the 6-311G(2d,2p) and cc-pvtz basis sets in ground state. From the optimized geometry of the compounds, vibrational frequencies, UV-Vis, molecular electrostatic potential distribution and frontier molecular orbitals were performed using same method and basis stets, and the results were compared with the experimental data.

Keywords:
Azo-Azomethine, Schiff bases, Imine group, DFT, Acryloyl chloride

INTRODUCTION

Azo dyes which are characterized by the presence of the azo chromophore [-N=N-] have attracted much attention not only for their easy preparation and lower cost but also for their wide application in industry as textile dyeing [1-3], coloring of plastic and polimers [1,4], colorimetric indicators [5-6], high-technology applications [3,7], cosmetics [8] and photostorage units [4,9]. In addition azo dyes and its derivatives exhibit photoactive properties with potential application as lasers [9], organic solar cells [10], organic NLO materials [6] and liquid crystals [9].

Azomethines, generally known as Schiff bases, are one of the most widely used organic compounds in various areas including photoluminescence materials [11], organic light emitting diodes [11],polymer stabilisers [12] and dyes and pigments [12]. Schiff bases also show a variety of the biological activities containing anti-fungal [12, 13], anti-bacterial [14], anti-malarial [14], anti-proliferative [12,14] and anti-viral [14] properties.

With the advancement in technology, one of the most important scientific problems is how to correlate between chemical and physical properties of the compound [2,15]. The density functional theory (DFT) method is widely used for structural determination of organic compounds, determining the mechanisms of chemical reactions, calculation of the ground state geometries and prediction of spectroscopic data such as UV-Vis, IR and NMR peaks [2,16].

In this study we have synthesized new azo-azomethine dyes containing acryloyl groups and the compounds were characterized by Uv-Vis, IR and NMR spectroscopy. Also in this research we report the results of DFT calculations to investigate UV-Vis absorption spectrum and FT-IR regions as well as HOMO-LUMO orbital energies, electostatic potential (ESP) maps, chemical hardness and electronegativity of the compounds. Theoretical UV-Vis calculations were carried out in EtOH (polar protic), CH_2Cl_2 (apolar aprotic) and DMF (polar aprotic) phases in accordance with the experiments and the solvent effect was also investigated.

Experimental Process

All reagents were analytical grade and purchased from commercial suppliers (Merck and Aldrich). All melting points were determined using Melting point apparatus (Stuart Melting Point 30) without any corrections. Ultra-Visible (UV-Vis) spectra were taken in CH_2Cl_2 (apolar aprotic), EtOH (polar protic) and DMF (polar aprotic) in the range of 600-190 nm using a quartz glass cell with a path length of 10 mm at room temperature. Infrared spectra's were obtained using ATR in the range of 4000-650 cm^{-1} Class 1 Laser product FTIR (Thermo Scientific, US) FT-IR spectrophotometer. NMR spectrums were recorded on a Bruker ^{1}H-NMR 400 MHz/^{13}C-NMR 100 MHz spectrometer in a d_6-DMSO solvent with a internal standart TMS.

Theoretical Processes

Kohn-Sham density functional theory (DFT) [17-18] was used in the quantum-chemical calculations. Geometric restrictions were not placed on the optimization processes. Molecular structures of the compounds were optimized by using Becke3-Lee-Yang-Parr hybrid functional (B3LYP) with 6-311++g(2d,2p) and cc-pvtz basis set. Furthermore, mentioned methods were used to obtain ground state energies, molecular conformations, UV-Vis and IR spectra of the compounds. Time-dependent DFT (TDDFT) were employed to calculate vertical excitation energies. The Self-Consistent Reaction Field (SCRF) method and the Conductor-Polarizable Continuum Model (CPCM) were used for the geometry optimizations of compounds in different solvent environments such as EtOH, CH_2Cl_2 and DMF phases. IR calculations were also carried out in gas phase. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies were calculated with the titled methods and basis sets. Furthermore, molecular electrostatic potential (MEP) surfaces were also obtained. FMO energy eigenvalues were used to calculate the chemical hardness (η) and electronegativity (χ) of the compounds. All calculations were performed using the GAUSSIAN 09 software package program [19].

Initial conformations to be used for optimization calculations of the compounds were obtained by dihedral-scanning of unsubstituted compound 4 with a step size of 18° for a total of 400 steps (Figure 1), by using M06/3-21g method in order to predict the minimum energy conformations of the compounds.

6-311++g(2d,2p) and cc-pvtz basis sets used in the calculations gave very consistent results. As seen from Table 1, the functional groups CH_3, OH, Cl and NO_2 have a great influence in determining the minimum molecular energy of the optimized compounds. The molecular energies of the compounds decreased as the electronegativity of the substituents increases. The minimum molecular energy of compound **4**, which does not contain any substituent, was calculated to be around -1163 au, and of NO_2 substituted compound **6** was -1368 au with the lowest molecular energy. The dipole moments of the compounds **5** and **6** bearing higher electronegative substituent were calculated to be significantly higher than those of the other compounds because the higher electronegative substitue groups, attracting electron density on themselves, made the molecule more polarized. Substituent NO_2 greatly affected the HOMO and LUMO energies (Table 1 and Figure 2), and also increased the electronegativity of the compound while decreased the chemical hardness. The chemical hardness

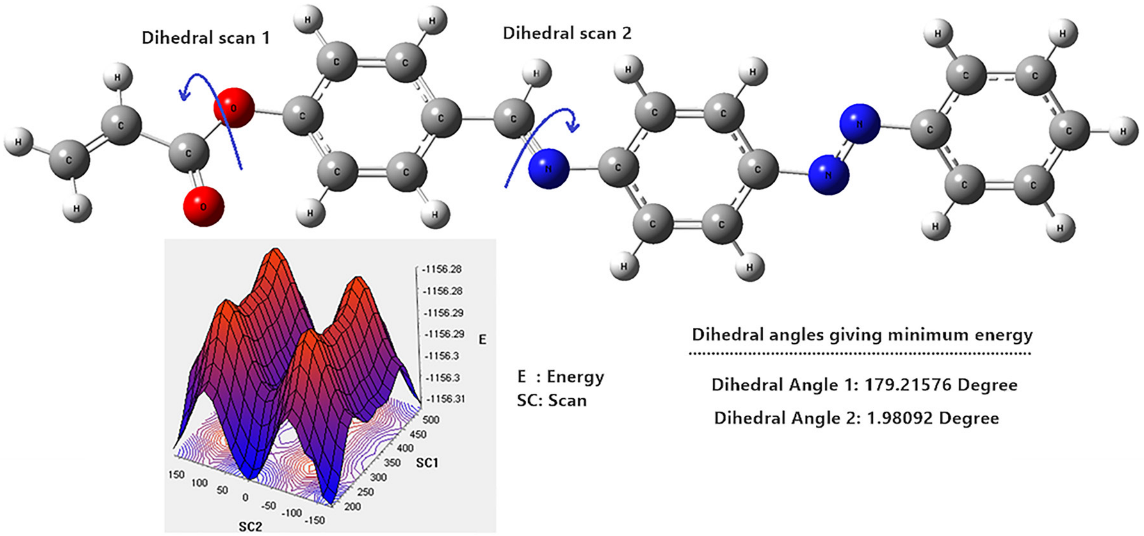


Figure 1. Dihedral scanning of unsubtituted compound **4**.

Table 1. Theoretical calculations: Electronic and chemical parameters

Comp.	Method	E (au)	(eV)	(eV)		(eV)	(eV)	m (Debye)
2	6-311++g (2d,2p)	-1202.895	-5.968	-2.544	3.424	1.712	4.256	2.762
3		-1238.817	-5.857	-2.523	3.333	1.667	4.190	2.474
4		-1163.565	-6.074	-2.624	3.449	1.725	4.349	2.893
5		-1623.190	-6.138	-2.755	3.383	1.691	4.447	4.958
6		-1368.135	-6.459	-3.330	3.129	1.565	4.895	9.926
2	cc-pvtz	-1202.959	-5.911	-2.470	3.441	1.721	4.190	2.9101
3		-1238.882	-5.782	-2.435	3.346	1.673	4.109	2.3077
4		-1163.628	-6.013	-2.547	3.466	1.733	4.280	2.8431
5		-1623.259	-6.075	-2.675	3.399	1.700	4.375	4.9028
6		-1368.206	-6.381	-3.203	3.178	1.589	4.792	9.5686

E: Energy, : , : Chemical Hardness, Electronegativity, ***m***: Dipole moment

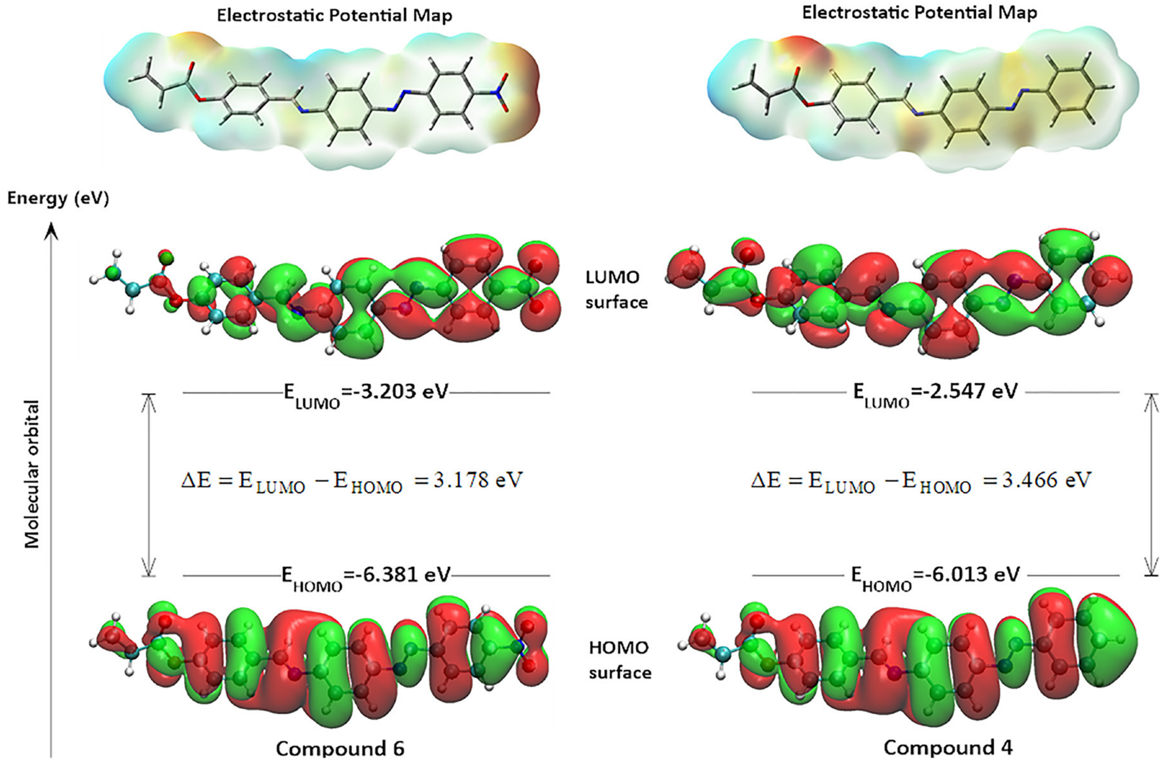


Figure 2. HOMO-LUMO energy gab and ESP maps of compound **4** and **6**.

of unsubstituted compound **4** was also calculated to be the highest (1.725 eV by 6-311++g(2d,2p) and 1.733 eV by cc-pvtz basis sets).

General procedure for the synthesis of azo-azomethine dyes

Azo-Azomethine compounds containing acryloyl group were synthesized by a two step procedure as shown in Figure 3. In the first step sodium salts of the azo-azomethine were synthesized by using metallic sodium in 1:1 molar ratio at room temperature for 24 h [9-11]. In the second step novel acryloyl derivatives of azo-azomethine compounds were synthesized using acryloyl chloride under an inert atmosphere by our previous methods [20-24].

Synthesis of Azo-Azomethine Compounds, 1

Azo-azomethine derivatives (**1**) were synthesized by the coupling reaction with *E*-4-((phenylimino)methyl)phenol [25,26] and diazonium salts as described in the literature method [8,9,22,26].

Synthesized of 4-[[[4-[4′-methyl)phenylazo)phenyl]imino]methyl]phenyl-2-propenoat, 2

A solution of 4-[[[4-[(4-methylphenyl)azo]phenyl]imino]methyl]-Phenol (1.0 g; 3.04 mmol) and metallic sodium

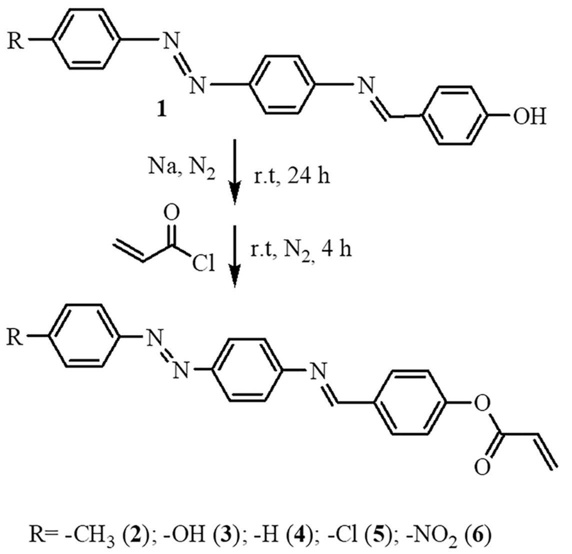


Figure 3. Synthetic route of azo-azomethine compounds bearing an acryloyl group.

(69 mg; 3.04 mmol) in dry THF (40 mL) was stirred at room temperature under N$_2$ atmosphere for 24 h. Then acryloyl chloride (0.245 mL; 3.04 mmol) was added to this solution at room temperature and stirred for 4 h under N$_2$ atmosphere. Dark red product was evaporated and purified with THF/water. Yield: %43 mp: Oily product IR (cm^{-1}): ν=3053 (C-H arom.), 2972, 2883 (aliph. C-H), 1749 (>C=O), 1671 (-C=C-), 1594 (-CH=N-), 1540, 1411 (-N=N-), 1249, 1045 (-C-O). ^{1}H-NMR (d$_6$-DMSO, ppm): δ= 1.23 (s, H1), 7.98 (m, H4), 7.95 (s, H6), 7.88 (m, H3), 7.78 (m, H7), 7.40 (m, H5), 7.05 (m, H2), 6.68 (m, H8), 6.33 (d, J=17.3 Hz, H11), 5.80 (d, J=10.9 Hz, H9), 5.72 (m, H10) ^{13}C NMR (101 MHz, d$_{6-}$DMSO, ppm) δ 21.3 (C1), 141.7 (C2), 130.4 (C3), 123.9 (C4), 148.0 (C5), 150.5 (C6), 124.1 (C7), 122.8 (C8), 150.8 (C9), 162.8 (C10), 129.8 (C11), 129.06 (C12), 120.1 (C13), 162.8 (C14), 164.1 (C15), 129.4 (C16), 132.3 (C17). Elemental Analysis calc. (%) for $C_{23}H_{19}N_3O_2$: C 74.78, H 5.18, N 11.37; found: C 74.23, H 5.09, N 10.87

1.4 Synthesis of 4-[[[4-[4′-hydroxyphenyl-azo) phenyl]imino]methyl]phenyl-2-propenoat, 3

This compound was prepared with a method similar to that described in Section 1.3. Yield: %52 mp: oily product, IR (cm^{-1}): ν=3584-3180 (br, O-H), 3046 (C-H arom.), 2921, 2875 (Aliph. C-H), 1749 (>C=O), 1662 (-C=C-), 1572 (-CH=N-), 1513, 1442 (-N=N-), 1284, 1163 cm^{-1} (-C-O). ^{1}H-NMR (d$_6$-DMSO, ppm): δ= 9.71 (s, H1), 8.13 (s, H6), 7.89 (s, H4), 7.89 (m, H3), 7.69 (m, H7), 7.69 (m, H5), 6.94 (m, H2), 6.94 (m, H8), 6.51 (m, H11), 5.97 (m, H9), 5.44 (m, H10) ^{13}C NMR (101 MHz, d$_{6-}$DMSO, ppm) δ 163.1 (C2), 112.3 (C3), 128.3 (C4), 148.5 (C5), 149.0 (C6), 128.3 (C7), 116.3 (C8), 152.0 (C9), 164.4 (C10), 130.0 (C11), 132.3 (C12), 128.5 (C13), 160.4 (C14), 164.4 (C15), 129.1 (C16), 132.1 (C17). Elemental Analysis calc. (%) for $C_{22}H_{17}N_3O_3$: C 71.15, H 4.61, N 11.31; found: C 70.96, H 4.35, N 10.54

Synthesis of 4-[[[4-(phenylazo)phenyl]imino] methyl]-phenyl-2-propenoat, 4

This compound was prepared with a method similar to that described in Section 1.3. Yield: %56 mp: oily product, IR (cm^{-1}): ν=3134 (C-H arom.), 2924 cm^{-1}, 2850 (Aliph. C-H), 1740 (>C=O), 1668 (-C=C-), 1598 (-CH=N-), 1541, 1411 (-N=N-), 1248 (-C-O). ^{1}H-NMR (d$_6$-DMSO, ppm): δ= 7.92 (s, H6), 7.92 (s, H4), 7.92 (s, H3), 7.86 (d, *J*=7.87 Hz, H7), 7.59 (m, H1), 7.59 (m, H5), 7.59 (m, H2), 7.59 (m, H8), 6.48 (*dd*, *J*=6.50 Hz, H11), 6.35 (d, *J*=6.33 Hz, H9), 5.84 (d, *J*=5.83 Hz, H10) ^{13}C NMR (101 MHz, d$_{6-}$DMSO, ppm) δ 131.6 (C2), 129.9 (C3), 122.8 (C4), 152.5 (C5), 142.6 (C6), 124.2 (C7), 119.7 (C8), 149.0 (C9)163.9 (C10), 128.1 (C11), 132.1 (C12), 119.7 (C13), 163.9 (C14), 163.9 (C15), 127.5 (C16), 131.5 (C17). Elemental Analysis calc. (%) for $C_{22}H_{17}N_3O_2$: C 74.35, H 4.82, N 11.82; found: C 73.67, H 4.54, N 10.96

Synthesis of 4-[[[4-[4′-chlorophenylazo)phenyl] imino]methyl]phenyl-2-propenoat, 5

This compound was prepared with a method similar to that described in Section 1.3. Yield: %47 mp: oily product IR (cm^{-1}): ν= 3132 (C-H arom.), 2965, 2933 (Aliph. C-H), 1705 (>C=O), 1672 (-C=C-), 1594 (-CH=N-), 1537, 1407 (-N=N-), 1250, 1088 (-C-O), 830 (-C-Cl). ^{1}H-NMR (d$_6$-DMSO, ppm): δ= 7.95 (s, H6), 7.87 (m, H4), 7.87 (m, H3), 7.60 (m, H7), 7.60 (m, H5), 7.32 (m, H2), 7.32 (m, H8), 6.55 (m, H11), 6.32 (m, H9), 5.83 (m, H10). ^{13}C NMR (101 MHz, d$_{6-}$DMSO, ppm) δ 138.4 (C2), 129.3 (C3), 124.5 (C4), 150.8 (C5), 142.8 (C6), 124.3 (C7), 119.6 (C8), 148.1 (C9), 162.7 (C10), 132.0 (C11), 129.9 (C12), 122.8 (C13), 152.4 (C14), 164.0 (C15), 128.1 (C16), 135.9 (C17). Elemental Analysis calc. (%) for $C_{22}H_{16}ClN_3O_2$: C 67.78, H 4.14, N 10.78; found: C 67.42, H 4.01, N 10.23

Synthesis of 4-[[[4-[4′-nitrophenylazo)phenyl] imino]methyl]phenyl-2-propenoat, 6

This compound was prepared with a method similar to that described in Section 1.3. Yield: %62 mp: oily product IR (cm-1): ν=3071 (C-H arom.), 2968, 2921 (Aliph. C-H), 1702 (>C=O), 1595 (-C=C-), 1504 (-CH=N-), 1548, 1407 (-N=N-), 1173, 1016 (-C-O), 1504, 1323 (-NO2). 1H-NMR (d6-DMSO, ppm): δ= 8.31 (s, H6),), 8.22 (m, H2), 7.84 (m, H4), 7.84 (m, H3), 7.52 (m, H7), 7.48 (m, H5), 7.28 (m, H8), 6.71 (m, H11), 6.71 (m, H9), 6.60 (m, H10). 13C NMR (101 MHz, d6-DMSO, ppm) δ 154.8 (C2), 122.1 (C3), 125.5 (C4), 156.4 (C5), 143.5 (C6), 126.8 (C7), 119.1 (C8), 149.1 (C9), 162.8 (C10), 129.26 (C11), 129.9 (C12), 112.8 (C13), 156.9 (C14), 170.4 (C15), 129.3 (C16), 136.2 (C17) Elemental Analysis calc. (%) for C22H16N4O4: C 66.00, H 4.03, N 13.99; found: C 65.86, H 3.94, N 13.38

RESULTS AND DISCUSSION

The UV-Vis spectrum of the compounds were recorded in EtOH, CH_2Cl_2, DMF, pH=2 and pH=12 (in DMF) at the range of 190-600 nm. The UV-Vis spectra of the compounds 2-6 in all solvents, two bands were dedected at 297-342 nm and 355-510 nm which are attributed to π→π* and n→π* transitions respectively as seen in the Table 2. The UV-Vis spectra of the compound 4 are given in Figure 4. In EtOH the introduction of electron-withdrawing substituents ($-NO_2$, -Cl) into the phenyl ring (compound 5 and 6) has caused a bathochromic shift compared with the compound 2 and 3 having electron-donating groups ($-CH_3$ and -OH). In addition, bathochromic shift in λ_{max} of all compounds in DMF (polar aprotic) and pH=12 (in DMF) were observed compared with EtOH (polar protic) and CH_2Cl_2 (apolar aprotic) due to the increasing of the polarity of the solvent.

In EtOH and CH_2Cl_2 the UV-Vis spectrum of the compounds 2-6 display two peaks at 355-396 nm and 380-431 nm as a shoulder peak and 343-380 nm and 442 nm as a shoulder peak which were attributed to π→π* and n→π* transitions, respectively. Furthermore, the calculated value of maximum wavelenghts in EtOH are 350- 469 nm (according to 6-311++g(2d,2p) basis set) and 343-457 nm (according to cc-pvtz basis set) and in CH_2Cl_2 349-469 nm (according to 6-311++g(2d,2p) basis set) and 343-458 nm (according to cc-pvtz basis set). In DMF π→π* and n→π* transitions were observed at 327-383 nm and 359-467 nm experimentally whereas the theoretical value is calculated as 351-472 nm (according to 6-311++g(2d,2p) basis set) and 343-459 nm (according to cc-pvtz basis set). The theoretical $\lambda_{max.}$ of all compounds are given in Table 3.

The theoretical and experimental IR spectral data are given in Table 4. The aromatic =C-H stretching peaks appear in the range of 3000-3100 cm^{-1} [2,26,27]. The aromatic =C-H streching peaks were observed at 3046- 3134 cm^{-1} which are in good agreement with the calculated frequencies such as 3148-3201 cm^{-1} (according to cc-pvtz basis set) and 3154-3199 cm^{-1} (according to 6-311++g(2d,2p basis set). The >C=O streching peaks of the compounds were assigned at 1702-1749 cm^{-1} and the corresponding theoretical value is 1799-1802 cm^{-1} (according to cc-pvtz basis set) and 1788-1790 cm^{-1} (according to 6-311++g(2d,2p) basis set). This peak indicated the presence of acrylyol group. The –OH streching peak of the compounds **3** were observed at 3584-3180 cm^{-1} as a broad peak in agreement with the literature [6,22,26] and the theoretical value which appeared in the range of 3812 cm^{-1} (according to cc-pvtz basis set) and 3832 cm^{-1} (according to 6-311++g(2d,2p) basis set). The characteristic streching peaks of the azo group –N=N-are observed in the range of 1400-1550 cm^{-1} as a medium band in the literature [2,4,26,27]. In our study –N=N- streching peaks of the compounds (**2**-**6**) are observed at 1407-1442 cm^{-1} and 1513 -1548 cm^{-1} experimentally and calculated as 1496-1547cm^{-1} (according to cc-pvtz basis set) and 1478-1543 cm^{-1} (according to 6-311++g(2d,2p) basis set.

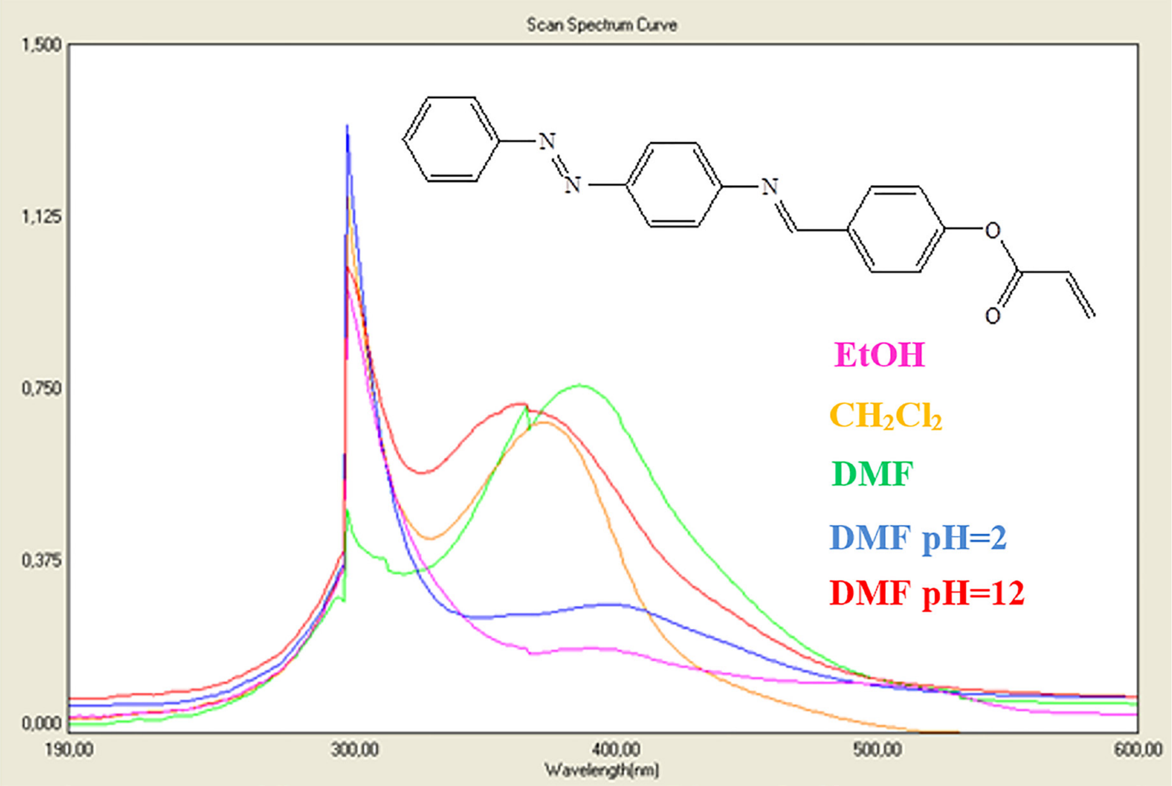


Figure 4. UV-Vis spectrum of the compound **4**

Table 2. UV-Vis data of the compounds

Compound	λ max. EtOH	Log ε (l/mol.cm)	λ max CH_2Cl_2	Log ε (l/mol.cm)	λ max DMF	Log ε (l/mol.cm)	λ max DMF (pH=2)	Log ε (l/mol.cm)	λ max DMF (pH= 12)	Log ε (l/mol.cm)
2	355 380° 431°	3.94 3.92 3.51	380 442°	3.89 3.49	372 430°	3.98 3.76	297 390° 445°	3.96 3.59 3.46	360 510°	3.58 3.09
3	352	3.74	365	3.14	352 396	3.71 3.44	354	3.73	342 460°	3.74 3.03
4	382	3.86	362	3.55	382 467	3.86 3.26	358 437°	3.67 3.25	376	3.54
5	374	3.88	343	3.67	327 359	3.73 3.81	372	3.08	383 414°	3.69 3.56
6	396	3.68	367	3.39	383 398	3.41 3.28	368 405°	3.54 3.21	356 408 498	3.43 3.27 3.17

Table 3. Theoretical UV-Vis data of the compounds 2-6 (nm)

	B3LYP					
Comp	6-311++g(2d,2p)			cc-pvtz		
	CH_2Cl_2	DMF	Ethanol	CH_2Cl_2	DMF	Ethanol
2	417.48	418.13	416.30	414.37	414.67	412.99
3	426.13	426.85	424.87	423.46	423.53	421.67
4	412.55	413.12	411.31	410.06	409.50	407.84
5	420.53	421.00	419.16	411.81	411.23	409.59
6	469.07 349.40	472.55 351.30	469.99 350.67	458.20 343.74	459.18 343.48	457.49 343.47

Experimentally the imine >C=N- strecthing peak was observed at 1504-1598 cm^{-1}. The calculated values for the same peak were 1687-1688 cm^{-1} (according to cc-pvtz basis set) and 1680-1681 cm^{-1} (according to 6-311++g(2d,2p) basis set). The bands at 2968-2850 cm^{-1} corresponds to the asymmetric and symmetric C-H strecthing bands due to the imine and acryloyl group whereas theoretical calculations predicts these peaks at 3005-3009 cm^{-1} (according to cc-pvtz basis set) and 3014-3017 cm^{-1} (according to 6-311++g(2d,2p) basis set). The bands observed at 1672-1595 cm^{-1} are assigned to the >C=C< strecthing peaks which are in good agreement with the calculated peaks such as 1543-1651 cm^{-1} (according to cc-pvtz basis set) and 1542-1645 cm^{-1} (according to 6-311++g(2d,2p) basis set). NO_2 strecthing peaks in the compound **6** are observed at 1504 cm^{-1} and 1323 cm^{-1} (Figure 6) as a strong band and calculated at 1582 cm^{-1} and 1367 cm^{-1} (according to cc-pvtz basis set) and 1561 cm^{-1} and 1360 cm^{-1} (according to 6-311++g(2d,2p) basis set). The correlation coefficient between experimental and theoretical values was calculated around R = 0.99 (Table 4), and the linear regression curve was given at Figure 5.

The ^1H-NMR and ^{13}C-NMR spectra of compounds are obtained in d_6-DMSO and TMS was used as an internal standard. The obtained data are given in Table 5 and Table 6, respectively. Theoretical data are in good aggreement whit the data given in Table 5. The imine protons were observed in the range of 7.92-8.31 ppm as a singlet peak. The aromatic protons of all compounds (**2**-**6**) were observed at 8.22-6.68 ppm as multiplet peaks. In the ^1H-NMR spectra of the compound **6** H2 protons are most deshielded due to the nitro group compared with compound **2** and **3**. The ^1H-NMR spectra of compound **4** (Figure 7) consist of aromatic and viniyl protons which appear in the range of multiplet peaks 7.59-7.92 ppm and dublet peaks in the range of 5.84-6.35 ppm and double-doublet at 6.48 ppm. Compared with the other compounds (**2**,**3**,**5**,**6**) these peaks are shifted to high and low fields due to the substituted groups. These results are in agreement with the calculated values.

^{13}C-NMR spectra of the compounds consist of seventeen carbon atoms which is given in Table 6. Aromatic and viniyl carbon atoms are appear in the same region. Carbonyl carbon atoms of the acryloyl group are obseved in the range of 163.9 -170.4 ppm in accordance with the literature [13,22]. The ^{13}C-NMR spectra of compound **4** (Figure 8) aromatic and viniyl carbon atoms were dedected at 119.7-163.9 ppm in accordance with the literature. [13,22]

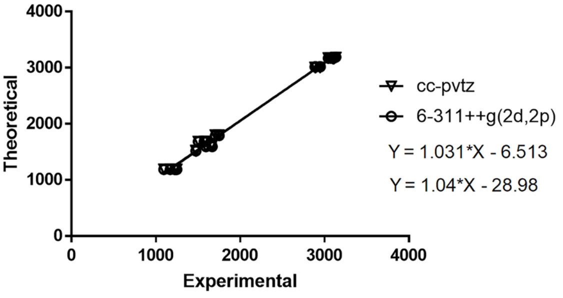


Figure 5. Linear regression analysis of experimental and theoretical IR data.

Table 4. Experimental and theoretical IR spectral data of compounds

Comp.		ν_{C-H} Arom	$\nu_{=C-H}$ Aliph	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{C=N}$	$\nu_{N=N}$	ν_{Ar-O}	Other functional groups
2	Experimental	3053	2972 2883	1749	1671	1594	1540 1411	1249 1045	2921-2883 (-CH_3)
3		3046	2921 2875	1749	1662	1572	1513 1442	1284 1163	3584-3180 (-OH)
4		3134	2924 2850	1740	1668	1598	1541 1411	1248	-
5		3112	2965 2933	1705	1672	1594	1537 1407	1250 1088	830 (-C-Cl)
6		3071	2968 2921	1702	1595	1504	1548 1407	1173 1016	1504 (-NO_2) 1323
2	B3lyp/cc-pvtz	3165.08 3156.82	3005.98	1802.13	1651-1601	1688.44	1547.70 1505.87	1228.84 1152.53	3103-3024 (-CH_3)
3		3201.65 3148.76	3008.44	1799.37	1650-1601	1687.41	1547.33 1502.80	1228.32 1154.79	3812 (-OH)
4		3195.81 3186.18 3175.05	3008.64	1800.02	1647-1600	1687.90	1544.96 1505.99	1228.76 1153.21	-
5		3175.48 3149.08	3008.46	1800.13	1648-1601	1687.81	1546.51 1504.18	1229.01 1153.61	784 (-C-Cl)
6		3178.12 3168.98	3009.71	1800.97	1648-1543	1688.24	1533.93 1496.82	1230.77 1149.75	1582 (-NO_2) 1367
2	B3lyp/6-311g++(2d,2p)	3169.96 3161.54	3014.21	1790.40	1645-1597	1681.54	1543.29 1489.97	1223.23 1148.17	3109-3031 (-CH_3)
3		3180.11 3154.68	3016.14	1788.75	1644-1597	1680.82	1543.17 1496.77	1222.99 1149.42	3832 (-OH)
4		3199.53 3190.01 3179.17	3016.30	1789.38	1642-1543	1681.45	1534.54 1478.73	1223.48 1148.58	-
5		3179.47 3173.55	3016.19	1789.59	1643-1542	1681.35	1537.58 1497.38	1223.77 1148.22	780 (-C-Cl)
6		3181.94 3173.79	3017.61	1790.54	1642-1542	1681.68	1529.27 1489.82	1225.53 1145.04	1561 (-NO_2) 1360
	R	0.9941 obtained from Experimental versus cc-pvtz, 0.9938 obtained from Experimental versus 6-311++g(2d,2p)							

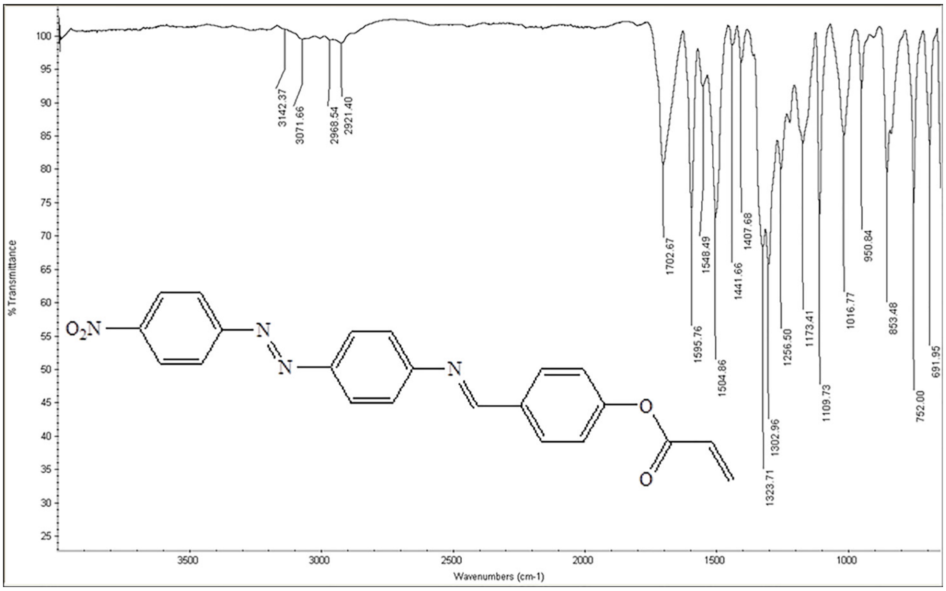
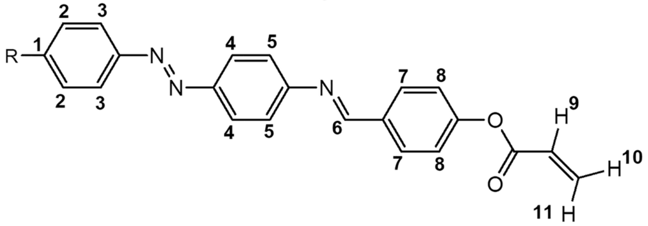


Figure 6. IR spectrum of the compound **6**

Table 5. ^{1}H-NMR data of the compounds

R= CH_3 (2), -OH (3), -H (4), -Cl (5), NO_2 (6)



Comp.		H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11
2	Experimental	1.23	7.05	7.88	7.98	7.40	7.95	7.78	6.68	5.80	5.72	6.33
3		9.71	6.94	7.89	7.89	7.69	8.13	7.69	6.94	5.97	5.44	6.51
4		7.59	7.59	7.92	7.92	7.59	7.92	7.86	7.59	6.35	5.84	6.48
5		-	7.32	7.87	7.87	7.60	7.95	7.60	7.32	6.32	5.83	6.55
6		-	8.22	7.84	7.84	7.48	8.31	7.52	7.28	6.71	6.60	6.71
2	cc-pvtz	2,71	7.94	8.45	8.58	7.67	8.99	8.25	7.66	6.95	6.64	7.24
3		5.55	7.27	8.45	8.53	7.94	9.01	8.22	7.66	6.94	6.63	7.24
4		8.04	8.01	8.51	8.64	7.98	9.02	8.25	7.66	6.94	6.64	7.23
5		-	7.62	8.55	8.61	7.97	9.01	8.25	7.66	6.94	6.64	7.23
6		-	8.95	8.56	8.75	8.00	9.00	8.26	7.68	6.94	6.64	7.24

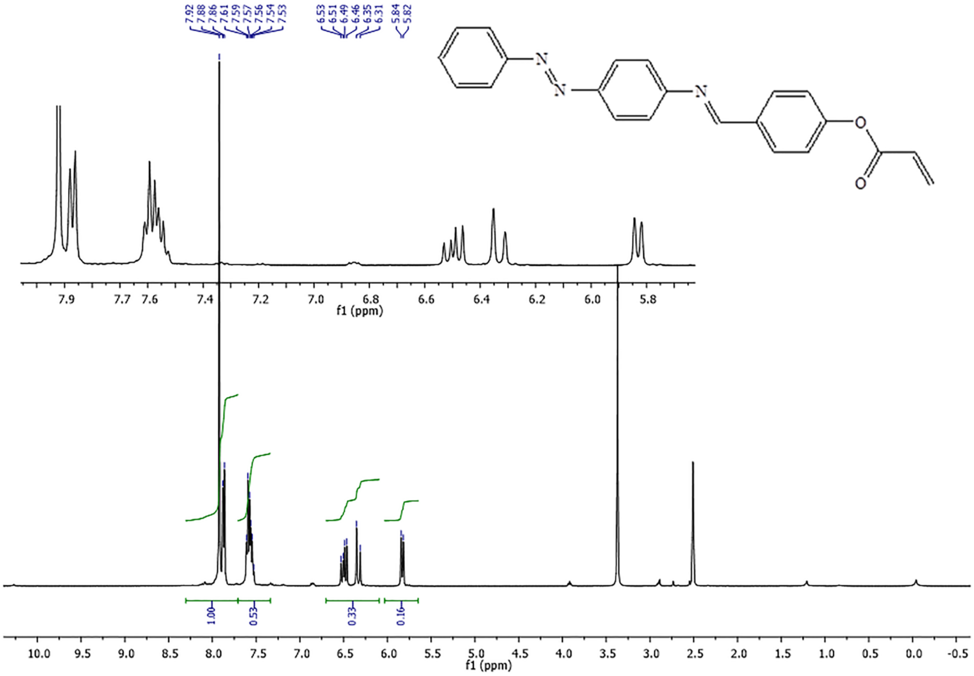


Figure 7. ^{1}H-NMR spectrum of the compound **4**

C5, C6, C9 and C14 carbon atoms were deshielded to low-field compared with the other aromatic carbon atoms due to the electronegativity effect of nitrogen and oxygen atoms.

CONCLUSION

In this study novel azo-azomethine dyes bearing an acryloyl moiety have been successfully synthesized through a reaction between azo-azomethine dyes and acryloyl chloride in 1:1 M ratio at room temperature. The characterisation of these compounds were made by IR, UV-Vis, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques.

After esterification of azo-azomethine dyes in IR spectrum of acryloyl derivatives the –OH stretching peaks were disappeared. Also in ^{1}H-NMR spectrums of compounds (**2**-**6**) evidence of viniyl protons at 5.44-7.24 ppm and in ^{13}C-NMR spectrums the evidence of

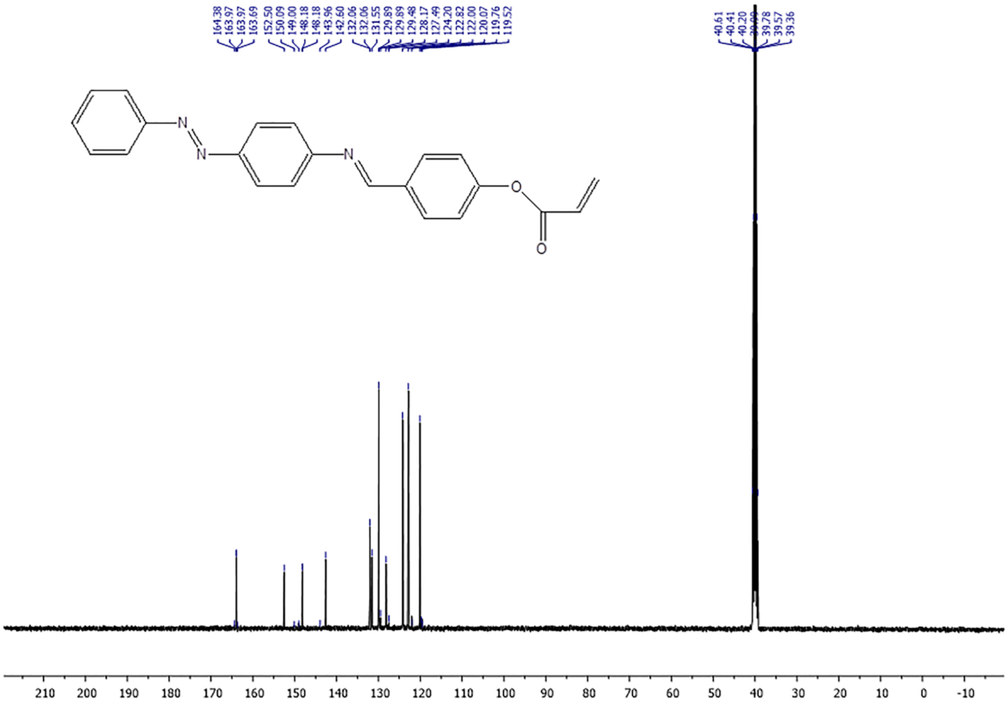
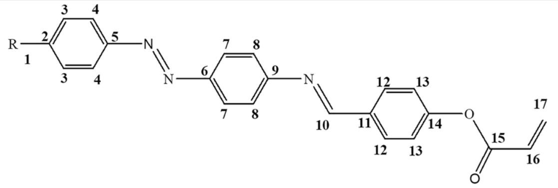


Figure 8. ^{13}C-NMR spectrum of the compound **4**

Table 6. ^{13}C-NMR data of the compounds

R= CH_3 (7), -OH (8), -H (9), -Cl (10), NO_2 (11)



	R	*Substituted Phenyl*	*Azo Phenyl*	*Imine Phenyl*	*Acryloyl Group*
	C1	*C2, C3, C4, C5*	*C6, C7, C8, C9*	*C10, C11, C12, C13, C14*	*C15, C16, C17*
2	*21.3*	*141.7 (C2), 130.4 (C3), 123.9 (C4), 148.0 (C5)*	*150.5 (C6), 124.1 (C7), 122.8 (C8), 150.8 (C9)*	*162.8 (C10),129.8 (C11), 129.06 (C12), 120.1 (C13), 162.8 (C14)*	*164.1 (C15), 129.4 (C16), 132.3 (C17)*
3	-	*163.1 (C2), 112.3 (C3), 128.3 (C4), 148.5 (C5)*	*149.0 (C6), 128.3 (C7), 116.3 (C8), 152.0 (C9)*	*164.4 (C10), 130.0 (C11), 132.3 (C12), 128.5 (C13), 160.4 (C14)*	*164.4 (C15), 129.1 (C16), 132.1 (C17)*
4	-	*131.6 (C2), 129.9 (C3), 122.8 (C4), 152.5 (C5)*	*142.6 (C6), 124.2 (C7), 119.7 (C8), 149.0 (C9)*	*163.9 (C10), 128.1 (C11), 132.1 (C12), 119.7 (C13), 163.9 (C14)*	*163.9 (C15), 127.5 (C16), 131.5 (C17)*
5	-	*138.4 (C2), 129.3 (C3), 124.5 (C4), 150.8 (C5)*	*142.8 (C6), 124.3 (C7), 119.6 (C8), 148.1 (C9)*	*162.7 (C10), 132.0 (C11), 129.9 (C12), 122.8 (C13), 152.4 (C14)*	*164.0 (C15), 128.1 (C16), 135.9 (C17)*
6	-	*154.8 (C2), 122.1 (C3), 125.5 (C4), 156.4 (C5)*	*143.5 (C6), 126.8 (C7), 119.1 (C8), 149.1 (C9)*	*162.8 (C10), 129.26 (C11), 129.9 (C12), 112.8 (C13), 156.9 (C14)*	*170.4 (C15), 129.3 (C16), 136.2 (C17)*

>C=O peaks at 163.9-170.4 ppm demonstrated that of the acrylyol group are bonded to azo-azomethine dyes. Good agreement was observed between theoretical calculations and experimental results. The results of UV-Vis calculations using the cc-PVTz basis set were observed at lower wavelengths than those of 6-311++g(2d,2p) basis

set. In the IR calculations, 6-311++g(2d,2p) basis set calculated the aromatic and aliphatic -C-H vibrations at higher frequencies while >C=O, -C=C-, >C=N-, -N=N- and Ar-O peaks at lower frequencies. The cc-pvtz basis set calculated the oscillation frequencies of the -NO_2 and -Cl substitute groups higher, while the -O-H vibration was lower. It can be said that the cc-pvtz basis set, in general, gave higher frequency in the calculation of the vibration frequencies of the double bounded structures. Furthermore, in calculations performed with 6-311++g(2d,2p), the ΔE was found to be lower, but the molecular energy, electronegativity and dipole moment were calculated to be larger. The correlation between the experimental data and theoretical calculations showed that the cc-pvtz basis set was more compatible with the experimental results.

To best of our knowledge, this report is the first example to compare theoretical and experimental spectroscopic results of new azo-azomethine dyes bearing acryloyl group. These compounds also have potential applications in textile industry and also may show anti-microbial properties.

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