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Synthesis of two new azo-azomethines; spectral characterization, crystal structures, computational and fluorescence studies





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HIGHLIGHTS

- Two novel azo-azometine dyes were synthesized.
- The dyes were characterized by
- analytical and spectroscopic methods.The structures of the dyes were
- determined by X-ray diffraction.Computational calculations have
- been performed using DFT methods.The photoluminescence properties of
- The photolumnescence properties of the azo-azomethines were also evaluated.

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ABSTRACT

This study describes the preparation, characterization and the photoluminescence properties of novel azo-azomethines $(2-{(E)-[(4-ethylphenyl)imino]methyl}-4-{(E)-phenyldiazenyl]phenol, HL¹ and 2-{(E)-[(3-ethylphenyl)methyl}-4-{(E)-phenyldiazenyl]phenol, HL¹ and 2-{(E)-[(3-ethylphenyldiazenyl]phenol, HL¹ and 2-{(E)-[(3-ethylphenyldiazenyl]phenol, HL¹ and 2-{(E)-[(3-ethylphenyldiazenyldia$ ethylphenyl)imino]methyl]-4-[(E)-phenyldiazenyl]phenol, HL² dyes). The dyes were characterized byelemental analysis, spectroscopic studies such as IR, ¹H and ¹³C NMR, mass and fluorescence spectra. Molecular structures of the dyes were examined by X-ray diffraction analysis. The molecular structures are mostly similar, differing mainly in the position of the ethyl group and dihedral angles between aromatic rings. X-ray data revealed that both HL^1 and HL^2 favor phenol-imine tautomer in the solid state. An intramolecular phenol-imine hydrogen bond (O1...N1) were observed in both compounds resulting in a S(6) hydrogen bonding motif. Molecular packing of both compounds are determined by $\pi \cdots \pi$ interactions. Quantum chemical investigation of mentioned molecules were performed by using DFT hybrid function (B3LYP) with 6-31+G(d) basis set. The compounds HL^1 and HL^1 gave intense light emissions upon irradiation by Ultra-Violet light. The photoluminescence quantum yields and long excited-state lifetimes of the compounds HL^1 and HL^2 were measured. The azo-azomethine dyes HL^1 and HL^2 have photoluminescence quantum yields of 34% and 32% and excited-state lifetimes of 3.21 and 2.98 ns, respectively. The photoluminescence intensities and quantum yields of these dyes were dependent on the position of alkyl group on the phenyl ring.

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Introduction

Azo-azomethines are known to be interesting because of the existence of both hard nitrogen and/or oxygen donor atoms in the backbones of these compounds, some of which have interesting physical and chemical properties [1] and potentially useful biological activities [2]. Further, azo dyes are a versatile class of colored organic dyes which continue to receive a great deal of attention, as noted in the literature, due to their biological properties and applications in various fields, such as textiles, papers, leathers, additives, and organic synthesis [3–7]. Recent studies show some azo compounds used in a wide variety of applications, such as medicines, cosmetics, food, paints, plastics, shipbuilding and automobile and cable manufacturing [8–15]. Also the applications of azo dyes has been applied in the electronics field as a storage components in digital versatile disc-recordable devices due to them being stable metal azo dyes [16,17].

Interest in new organic materials continues to grow owing to their photophysical properties and usefulness in light emitting devices [18–20]. In fact, some organic polymers have been noted as showing strong luminescence, allowing them to be considered for flat panel display technologies [21,22]. A number of studies on organic ligands and their metal complexes have found use in electroluminescent devices [23,24] and laser systems [25]. Further, various aromatic amines and polymeric arylamines have also been recognized as active layers in organic electroluminescent displays [26,27].

Recently, azo-azomethines and their metal complexes were reported by our group [28–33]. Here we report on the synthesis and characterization of the azo-azomethine dyes HL^1 and HL^2 . The compounds HL^1 and HL^2 were found to exhibit photoluminescence, emitting an intense light upon UV irradiation. Compounds HL^1 and HL² were characterized using ultraviolet-visible spectrophotometer (UV-Vis), photoluminescence spectrophotometer (PL) and Fourier transform infrared spectroscopy (FT-IR). The structures of compounds HL¹ and HL² were analyzed by IR, ¹H and ¹³C NMR, elemental analysis and single crystal X-ray studies. Computational studies of HL¹ and HL² are performed by using restricted B3LYP/6-31+G(d) level of theory in vacuo. Optimized structural parameters, vibration frequencies, frontier molecular orbitals (FMOs), molecular electrostatic potential (MEP) maps, MEP contours and non-linear optical (NLO) properties of relevant molecules are investigated by Gaussian09 package program. The optical behavior of the compounds in solution was also investigated.

Experimental

Reagents

9,10-Diphenylantracene, 3-ethylaniline, 4-ethylaniline and 2-hydroxybenzaldehyde were purchased from Aldrich Chem. Co. and Merck and used as received. All solvents for synthesis and analysis from commercial sources and used as received unless otherwise noted. The azo-aldehyde compound, 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde was prepared according to the published paper [29,34].

Instrumentation

NMR spectra were collected using a Bruker Advance 400 MHz. spectrometer. Mass spectrum of HL¹ was recorded on a Thermo Fisher Exactive + Triversa Nanomate spectrometer. IR spectra were obtained (4000–400 cm⁻¹) using a Perkin Elmer Spectrum 100 FTIR spectrophotometer. Carbon, hydrogen and nitrogen elemental analyses were performed with a Model CE-440 elemental analyzer.

X-ray crystallographic results were collected using a Bruker APEX2 CCD diffractometer and data reduction was carried out using Bruker SAINT [35]. Bruker (1998) *APEX2* and *SAINT* Bruker AXS Inc. SHELXTL was used for solving and refining the structures [36].

Preparation of azo-containing azomethines (HL¹ and HL²)

Azo-azomethines (HL^1 and HL^2) were synthesized by addition of 4-ethylaniline or 3-ethylaniline compounds (1 mmol) in methanol (10 mL) to a methanolic solution of 2-hydroxy-5-[(E)-phenyl-diazenyl]benzaldehyde (1 mmol). The mixtures were stirred for about 30 min and allowed to react at room temperature for about 24 h. The colored powders were recrystallized from chloroform/ methanol (1:1) v/v solution.

*HL*¹; Yield: 0.27 g (86%), color: orange yellow. M.p.: 212–213 °C. *Analysis* Calc. for C₂₁H₁₉N₃O: C, 76.57; H, 5.81; N, 12.76. Found: C, 76.45; H, 5.74; N, 12.76%. ESI-MS (*m*/*z* (rel. intensity)): 316(7%) [C₂₀H₁₈N₃O]⁺, 289(9%) [C₁₈H₁₄N₃O]⁺, 213(100%) [C₁₂H₁₂N₃O]⁺, 200(48%) [C₁₁H₁₀N₃O]⁺, 185(2%) [C₁₁H₁₁N₃]⁺. NMR (CDCl₃ as solvent, δppm); ¹H: 14.06 (s, 1H, phenolic OH), 8.77 (s, 1H, CH=N), 7.15–8.07 (m, 11H, aromatic-H), 2.75–2.70 (q, 2H, CH₂ of ethyl), 1.32–1.28 (t, 3H, CH₃— of ethyl group). ¹³C: 164.18 (C=N), 161.15 (C−OH), 118.17–152.64 (C, aromatic), 29.52 (C, CH₂ of ethyl), 15.62 (C, CH₃ of ethyl group). IR (KBr, cm⁻¹): 3431, 2957, 1618, 1569, 1508, 1432, 1280, 1102.

*HL*²; Yield: 0.20 g (82%), color: orange. M.p.: 124–125 °C. *Analysis* Calc. for C₂₁H₁₉N₃O: C, 76.57; H, 5.81; N, 12.76. Found: C, 76.53; H, 5.88; N, 12.74%. NMR (DMSO-d₆ as solvent, δppm): ¹H: 13.94 (s, 1H, phenolic OH), 9.17 (s, 1H, CH=N), 7.14–8.30 (m, 11H, aromatic-H), 2.69–2.66 (q, 2H, –CH₂ of ethyl group), 1.25– 1.22 (t, 3H, –CH₃ of ethyl group). ¹³C: 164.41 (C=N), 163.12 (C–OH), 118.51–152.44 (C, aromatic), 28.57 (C, CH₂ of ethyl), 15.97 (C, CH₃ of ethyl group). IR (KBr, cm⁻¹): 3415, 2961, 1620, 1569, 1436, 1305, 1277, 1105.

X-ray crystallography

Data for HL^1 and HL^2 were collected at 150(2) K with a Bruker Apex II CCD diffractometer using Mo K α radiation (λ = 0.71073 Å). Structures were determined by direct methods and the refinements were based on F^2 , using all reflections [36]. Non-hydrogen atoms were refined anisotropically by atomic displacement parameters. Hydrogen atoms bonded to carbons were placed at calculated positions by applying a riding model, where those hydrogens bonded to oxygen and nitrogen atoms were positioned on difference maps and refinement with temperature factors riding on the carrier atom was carried out. Crystal data and refinement are given in Table 1. Hydrogen bond parameters are given in Table 2 and bond lengths and angles are given in Table 3.

Computational method

All computational progresses were done by using GaussView 5.0.8 [37] and Gaussian 09 IA32W-G09RevA.02 package program [38]. Additionally, preparation of figures was done by using ChemBioDraw Ultra Version (13.0.0.3015) [39]. Becke, 3-parameter, Lee–Yang–Parr (B3LYP) hybrid function [40,41] which is one of the hybrid density functional theory functions was selected as computational method for investigated molecules. In calculations, 6-31+G(d) was selected as basis set. All calculations were made in vacuo. In the IR spectra, all frequencies were scaled by 0.975 [42].

Photoluminescence studies

The fluorescence spectra of the synthesized azo-azomethine dyes HL^1 and HL^2 were obtained using a Perkin Elmer LS55

Table 1	
Crystallographic data for	or the dyes HL^1 and HL^2 .

Identification code	HL^1	HL ²
Empirical formula	$C_{21}H_{19}N_3O$	$C_{21}H_{19}N_3O$
Formula weight	329.39	329.39
Crystal size (mm ³)	$0.57 \times 0.25 \times 0.09$	$0.67 \times 0.28 \times 0.09$
Crystal color	Yellow	Orange
Crystal system	Monoclinic	Monoclinic
Space group	P2/c	P2(1)/n
Unit cell a (Å)	12.4546(17)	7.1885(7)
b (Å)	6.5006(9)	6.4536(7)
<i>c</i> (Å)	21.408(3)	36.892(4)
α (°)	90	90
β (°)	100.482(2)	90.306(2)
γ (°)	90	90
Volume (Å3)	1704.4(4)	1711.5(3)
Ζ	4	4
Abs. coeff. (mm^{-1})	0.081	0.081
Refl. collected	14,486	14,430
Completeness to θ = 28.02°	99.6%	99.5%
Ind. Refl. [R _{int}]	3506 [0.0347]	3493 [0.0206]
R1, wR2 $[l > 2\sigma (l)]$	0.0396, 0.0961	0.0362, 0.0938
R1, wR2 (all data)	0.0587, 0.1064	0.0439, 0.0986
CCDC number	1034612	1034613

Table 2

Hydrogen-bond parameters (Å, °) for the dyes HL^1 and HL^2 .

	<i>D</i> −−H··· <i>A</i>	D—H	H···A	D····A	D—H···A
HL ¹	$O(1) - H(1A) \cdots N(1)$	0.933(17)	1.749(18)	2.5957(15)	149.4(15)
HL ²	$O(1) - H(1A) \cdots N(1)$	0.930(18)	1.755(18)	2.6035(14)	150.2(16)

Table 3 Selected bond lengths and angles (Å, $^\circ)$ for the dves.

	0 ()	, ,		
	HL^1	Calc. (HL ¹)	HL^2	Calc. (HL^2)
N(1)-C(9)	1.2860(16)	1.292	1.2864(16)	1.292
C(11) - O(1)	1.3456(16)	1.340	1.3451(15)	1.340
N(2)-N(3)	1.2558(15)	1.260	1.2574(14)	1.260
C(6)—N(1)	1.4185(16)	1.410	1.4191(15)	1.411
C(14) - N(2)	1.4292(18)	1.419	1.4196(16)	1.419
N(3)-C(16)	1.4294(18)	1.001	1.4260(17)	1.001
C(6) - N(1) - C(9)	121.43(12)	121.45	120.18(11)	121.33
N(3) - N(2) - C(14)	114.41(12)	115.41	114.05(11)	115.39
N(2)—N(3)—C(16)	112.71(12)	115.24	113.90(11)	115.24

spectrometer, where samples were prepared in spectrophotometric grade acetonitrile and analyzed using 1 cm optical cells. Solution concentrations of HL^1 and HL^2 in acetonitrile were 1.0×10^{-5} mol/L with excitations at 328 nm wavelength. The quantum yields of HL^1 and HL^2 were calculated using the standard 9,10-diphenylantracene [43–45].

Results and discussion

Synthesis

Treatment of the azo-aldehyde with two different aromatic amines, in refluxing MeOH yielded the novel azo-azomethine dyes (Scheme 1). The air-stable azo-azomethine dyes (HL^1 and HL^2) are soluble in DMSO, DMF, MeOH, EtOH, MeCN, and CHCl₃, and insoluble in H₂O. Elemental analysis data are provided in the experimental section and were found to be good agreement with the calculated values. The infrared, ¹H and ¹³C NMR and mass spectra of azo-azomethine dye HL^1 in CDCl₃ is shown in Figs. 1–3, respectively. The data are in good agreement with single crystal X-ray structures.

IR spectra

The positions of some prominent bands in the IR spectra of HL^1 and HL^2 and their assignments based on extensive data available for related compounds are given in the experimental section. The IR spectra of dyes HL^1 and HL^2 are given in Fig. 1. In the IR spectra of dyes HL^1 and HL^2 , broad peaks at 3431 and 3415 cm⁻¹ were attributed to the v(O-H) vibrations, respectively [32]. A band observed at 1618 cm^{-1} for HL^1 and 1620 cm^{-1} for HL^2 can be assigned to the v(C=N) group. Absence of v(C=O) absorption in the IR spectra of the prepared dyes, together with the appearance of new v(C=N) absorption in the range of 1618–1620 cm⁻¹ clearly indicated that the new azo-azomethine compounds had formed in each case. Aliphatic (C-H) vibration bands were observed in the range of 2850–2960 cm⁻¹. The symmetric N=N stretching mode, leads to a medium band at 1569 cm⁻¹ for both the synthesised dves and while the (C–N) stretching mode gives an intense band at 1280 and 1277 cm⁻¹, for HL^1 and HL^2 , respectively.

NMR spectra

¹H and ¹³C NMR spectra of the synthesized azo-azomethine dyes were recorded. The resonance of protons has been assigned on the basis of their integration and multiplicity pattern. The ¹H and ¹³C NMR spectra of HL^1 are shown in Figs. 2 and 3. Singlets in HL^1 and HL^2 dyes at 8.77 (HL^1) and 9.17 ppm (HL^2) are assignable to the azomethine protons. The multisignals within the 8.07-7.15 (HL^{1}) ppm and 8.30–7.14 (HL^{2}) ppm range are assigned to the aromatic protons of the three rings in the synthesized dyes. The peak observed at 14.06 and 13.94 ppm in the compounds is attributable to the -OH signal of salicylaldehyde derivatives molecule in HL^1 and HL^2 , respectively. NMR spectra for HL^1 and HL^2 were recorded in two different solvents (HL^1 in CDCl₃ and HL^2 in DMSO-d₆). By examining the chemical shifts of the phenolic (PhOH) and azomethine (-C=N-) proton signals, there was no significant change in the spectra. In addition to these, the proton NMR spectra of the azo-azomethines display two signals at 2.75-2.70 ppm (for HL^{1}) and 2.69–2.66 ppm (for HL^2) as triplet and 1.32–1.28 (HL^1) and 1.25–1.22 ppm (HL^2) as quartet with an integration equivalent to five hydrogens corresponding to the Ar-CH2- and Ar-C-CH3 groups, respectively.

¹³C NMR spectra further supported the structural characterization of the azo-azomethines. The number of signals found corresponds with the presence of magnetically nonequivalent carbon atoms, which were assigned by comparison with literature values. In the ¹³C NMR spectra of dyes (HL^1 and HL^2), a signal for carbon of CH=N groups of each compounds appears at 164.18 and 164.41 ppm for HL^1 and HL^2 , respectively. The carbon atom of C—OH groups was observed at 161.15 and 163.12 ppm for HL^1 and HL^2 , respectively. All the other aromatic carbon atoms were observed in the range of 152–118 ppm. Two aliphatic signals (29.52 and 15.62 ppm for HL^1 and 28.57 and 15.97 ppm for HL^2) were assigned to the ethyl group carbon atoms (Ar—CH₂CH₃). Both ¹H and ¹³C NMR spectra indicated that the compounds did not contain significant impurity.

Mass spectra

ESI mass spectrum of the azo-azomethine dye HL^1 was recorded in MeOH. The molecular ion signal was not observed. The ESI mass spectrum of the dye showed fragmentation signals at m/z 316(7%) $[C_{20}H_{18}N_3O]^+$, 289(9%) $[C_{18}H_{14}N_3O]^+$, 213(100%) $[C_{12}H_{12}N_3O]^+$, 200(48%) $[C_{11}H_{10}N_3O]^+$ and 185(2%) $[C_{11}H_{11}N_3]^+$. Mass spectrum and fragmentation pattern of the azo-azomethine dye HL^1 is shown in Figs. S1 and S2, respectively.



Scheme 1. Preparation of azo-azomethine dyes (HL^1 , $R_1 = -CH_2CH_3$, $R_2 = -H$ and HL^2 , $R_1 = -H$, $R_2 = -CH_2CH_3$) and possible tautomeric equilibriums [(*i*): (1) NaNO₂, HCl, 0 °C, (2) salicylaldehyde; (*ii*): 4-ethylanilineor 3-ethylaniline, MeOH and reflux].



Fig. 1. IR spectra of the dyes HL^1 and HL^2 .

X-ray structures

Molecular structures of HL^1 and HL^2 azo-azomethine dyes with atom numbering are shown in Fig. 4. The molecular structures are similar by large, differing mainly in the position ethyl group and dihedral angles between aromatic rings. For both structures, all bond lengths and angles are within the normal ranges. All bond lengths and angles in the phenyl rings have normal Csp2-Csp2 values with small distortions. X-ray analysis indicated that the azoazomethine dyes HL^1 and HL^2 favor the phenol-imine tautomer in the solid state. The harmonic oscillator model of aromaticity (HOMA) index for the ring C10–C15 are calculated for both compounds so as to evaluate the aromaticity of the phenol ring in the solid state [46,47]. HOMA indexes were in the range of 0.900–0.990 or 0.500–0.800 this showing that the rings were either aromatic or non-aromatic, respectively. HOMA index values for the ring C10–C15 were found to be 0.939 and 0.944 for HL^1 and HL^2 , respectively. These results revealed that the ring C10–C15 shows aromatic character for both compounds in the solid state. The azomethine (–C9=N1–) linkages are 1.2860(16) and 1.2864(16) Å for HL^1 and HL^2 , respectively; similar to those observed for related azo-azomethine compounds [48,49]. The diazenyl (–N2=N3–) bond distances are 1.2558(15) and 1.2574(14) Å for HL^1 and HL^2 , respectively. Aromatic rings (C10–C15) and (C16–C21) adopt the *trans*





Fig. 4. Molecular structures of azo-azomethine dyes HL¹ and HL² with atom numbering. Intra-molecular hydrogen bonding is shown as dashed lines.

configuration with regard to the azo double bond (-N=N-) with the torsion angle C(14)-N(2)-N(3)-C(16) of 178.99(10) and $-179.89(9)^{\circ}$ for HL^1 and HL^2 , respectively.

An intramolecular phenol-imine hydrogen bond (O1...N1) exists in both compounds resulting in a S(6) hydrogen bonding motif. In the structures of HL^1 and HL^2 , both outer rings twisted with respect to the central benzene ring. The mean planes of C1-C6 and C16-C21 to the central (C10-C15) ring are at 26.60(5) and 2.67(7)° for HL^1 and at 34.91(3) and 16.98(4)° for HL^2 , respectively. These differences reflect the different intermolecular interactions in the lattice. In *HL*¹, there are two sets of π - π stacking interactions in the structure (Fig. 5). First, C1–C11 section is stacked with the same section of an adjacent molecule under symmetry operation of 2 - x, -y, 1/2 - z; C1 and C11 are separated by 3.441 Å; C5 and C9 are separated by 3.406 Å. Second, C9-C17 section is stacked with the same section of the neighboring molecule under symmetry operation of 1 - x, y, 1/2 - z; C9 and C17 are separated by 3.388 Å. In HL^2 , there are face to face and edge to edge phenyl-phenyl stacking interactions were observed. The C9-C14 section is stacked with the same section of a neighboring molecule; C9 and C13 are separated by 3.393 Å (symmetry code: -x, 2 - y, -z). The C14–C15 edge is stacked with the same section of a neighboring molecule; C14 and C15 are separated by 3.477 Å, (symmetry code: 1 - x, 2 - y, -z) (Fig. 6). Unit

cell packing of both compounds are determined by π - π stacking interactions (Figs. 7 and 8).

Thermodynamic parameters and optimized structures

Molecules HL^1 and HL^2 are optimized at RB3LYP/6-31+G(d) level and thermodynamic parameters of the three possible isomers are listed in Table 4. Thermodynamic parameters are total energy (E_{Total}) , enthalpy energy (H), Gibbs free energy (G) and entropy (S). According to Table 4, the lower energy and the higher entropy values mean that molecule is more stable. Azo form more stable than other forms in each molecule. Additionally, the total energy, enthalpy and Gibbs free energy of HL^2 are lower than in HL^1 . Therefore, HL^2 is more stable than *HL*¹. These molecules are structural isomers of each other. Optimized structures of mentioned molecules are represented in Fig. S3. Some optimized structural parameters of molecules HL^1 and HL^2 are given in Table 3. According to Table 3, structural parameters are very close to each other and these results mean that optimized structures of mentioned molecules are similar to each other. These calculated results and their experimental values are used to plot the distribution graph and correlation coefficient of this graph is calculated as 0.9997. This value implies that there is a well agreement between experimental and calculated results.



Fig. 5. π - π stacking interactions in *HL*¹. Hydrogen atoms are omitted for clarity.



Fig. 6. π - π stacking interactions in *HL*². Hydrogen atoms are omitted for clarity.



Fig. 7. Packing diagram of HL^1 viewing down the *b* axis, $\pi - \pi$ interactions are shown as dashed.



Fig. 8. Packing diagram of HL^2 viewing down the b axis, π - π interactions are shown as dashed lines and hydrogen atoms are removed for clarity.

Calculated IR spectra

Functional groups in molecules can be easily determined by using vibration frequencies. Investigated vibration frequencies are scaled by 0.975 to obtain anharmonic frequencies. Some anharmonic frequencies are examined in detail and given in Table 5. There are 44 atoms in each molecule and there must be 126 vibration modes which is calculated with (3N–6). In calculated results, 126 vibration modes are observed and some vibration modes are examined in detail. In Table 5, intensity of vibration frequencies

is bigger than 25 D. Intensities of asymmetric C—H frequencies is less than 25 D. Therefore, there are mainly symmetric C—H frequencies in Table 5. There is a good agreement between experimental and calculated frequencies except O—H frequency.

Some molecular orbitals and contour diagrams

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) play an important roles in chemical processes and reactions. LUMO, HOMO, HOMO–1 and

Table 4

Thermodynamic parameters of investigated molecules at RB3LYP/6-31+G(d) in vacuo.

Structures	Isomer	E _{Total} (a.u.)	H (a.u.)	G (a.u.)	$S (J \text{ mol}^{-1} \text{ K}^{-1})$
HL ¹	Azo form	-1051.168419	-1050.791824	-1050.867941	670.285170
	Enamine form	-1050.790199	-1050.789255	-1050.865865	673.987380
	Hydrazone form	-1050.760853	-1050.759909	-1050.838323	689.850480
HL ²	Azo form	-1051.168529	-1050.791958	-1050.868141	670.858380
	Enamine form	-1050.790463	-1050.789519	-1050.865990	672.762640
	Hydrazone form	-1050.761080	-1050.760136	-1050.838311	687.747940

Table 5

Vibration modes, calculated frequencies and their assignments for each molecule at B3LYP/6-31+(d) level in vacuo.

HL^1	HL ¹			HL ²			
Mode	Frequency ^a	Intensity ^b	Assignment	Mode	Frequency ^a	Intensity ^b	Assignment
38	677.6	35.5600	ω CH _{aro.}	37	676.8	38.1762	ω CH _{aro.}
42	762.5	37.9463	ω C-H _{aro.}	42	761.5	37.5733	ω C-H _{aro.}
47	828.8	26.5903	ω CH _{aro.} , ω OH	45	791.2	25.0943	ω C—H _{aro.} , v C=C
48	830.7	86.7409	ω C-H _{aro.}	47	828.5	84.5103	ω CH _{aro.} , ω OH
50	857.0	29.4914	ω CH _{aro.} , ω OH	54	910.6	36.6279	ω C—H _{aro.} , ν C=N
69	1107.6	104.5261	α C—H _{aro.}	70	1107.2	102.4422	α C—H _{aro.}
72	1156.4	77.04073	γ C—H _{aro.}	71	1143.1	37.3202	ω C—H _{aro.} , $α$ C—H _{aro.} ν C=N
75	1194.4	34.4862	ν C=N, γ C-H _{aro.} γ Ο-Η	72	1150.2	35.3132	ω C-H _{aro.} , α C-H _{aro.} ν C=N
77	1214.9	47.0413	ν C—N, γ C—H _{aro}	74	1163.1	30.5264	ν C=N, ω C-H _{aro}
80	1254.8	25.1170	ν C=N, γ C-H _{aro.}	76	1200.3	28.1855	ω ΟΗ, ω CΗ _{aro.} ν CC, ν C=-N
81	1292.9	72.0548	ν C==0, γ CH _{aro.}	77	1215.2	53.4042	ω ΟΗ, ω CΗ _{aro.} ν C=-C, ν CN
88	1361.1	84.1590	γ C—H _{aliph.} , v C=C	81	1293.0	80.1526	ν CΟ, ω CH _{aro.} ν C=-C
90	1415.7	43.1273	ν C=C, γ C-H _{aro.} ν Ο-Η	88	1360.4	82.2848	ω C—H _{aliph.}
94	1472.3	30.6050	γ O H ν N=N, γ C-H _{aro.}	90	1415.4	59.1197	ω 0Η, ν C=-C
97	1488.8	51.7085	γ C H ν C=C, γ C-H _{aro.}	94	1471.7	28.6087	$v C = C, \omega C - H_{aro.}$
99	1509.3	65.4677	γ C=C, γ C-H _{aro.}	97	1487.2	29.8704	$v C = C, \alpha C = H_{aro.}$
100	1515.2	90.3296	ν N=N, ν C=C	98	1488.4	47.9597	ω ΟΗ ω ΟΗ, ω CΗ _{aro.}
102	1580.5	83.5044	γ C=H _{aro} , γ O=H γ O=H, ν C=C ν C=N	100	1514.8	73.7771	ν C=C ν N=N, ω Ο-H ω C-Haro, ν C=C
103	1592.2	10.8366	v C=C, γ C–H _{aro.}	101	1577.5	144.6035	$\omega O - H, v C = C$ v C = N, $\omega C - H_{are}$
104	1606.8	79.1341	γ C—H _{aro.} , γ O—H ν C=C ν C=N	104	1605.9	243.7911	v C = C, v C = N $w C = H_{uu}$
105	1609.7	114.6744	γ C-H _{aro} , γ O-H ν C=C, ν C=N ν N=N	105	1608.1	30.7644	$v C = C, \alpha C - H_{aro.}$ v N = N
106	1628.3	60.3676	γ C—H _{aro} , γ O—H ν C=C	106	1628.6	42.5376	ν C=C, ω C-H _{aro.} ν C=N
107	1637.0	395.1317	v C = N, v C = C $\gamma C = H_{arc}$	107	1636.3	384.4145	v C=N, v C=C $\gamma C=H_{arc}, \omega O=H$
108	2964.0	47.9279	$v_s C - H_{alinh}$	108	2965.1	39.3719	$v_s C - H_{alinh}$
109	2965.0	49.4335	$v_s C - H_{aliph}$	109	2966.0	41.7539	$v_s C - H_{aliph}$
110	2988.4	67.0623	$v_s C - H_{aliph}$	110	2989.1	62.5699	$v_s C - H_{aliph}$
112	3030.0	69.0246	$v_{\rm s}$ C—H _{aliph}	112	3030.8	60.3878	$v_{as} C - H_{aliph}$
113	3035.2	35.6848	Vas C—Haliph	113	3036.1	37,1072	Vas C—Haro
114	3059.6	765.4599	v O—H	114	3061.0	757.8592	v 0—H
121	3123.0	29.8244	v_s C—H _{aro.}	121	3122.6	29.2336	v _s C—H _{aro.}
124	3132.0	25.1931	v _{as} C—H _{aro.} v _s C—H _{aro.}	124	3131.8	25.0559	v _{as} C—H _{aro.} v _s C—H _{aro.}

Vibration modes: v, stretching; α , scissoring; γ , rocking; ω , wagging; δ , twisting. Abbreviations: s, symmetric; as, asymmetric; aro., aromatic; aliph., aliphatic. ^a In cm⁻¹.

^b In D (10^{-40} esu² cm²).

HOMO-2 are important to determine the reactivity of molecules. Contour diagrams of mentioned molecular orbitals and their energies are represented in Fig. 9.

According to Fig. 9, electrons which are belong to HOMO are mainly localized on N=N bond; HOMO-1 and HOMO-2 electrons

are mainly localized on molecule for each molecule. As for the LUMO, if molecules accept electrons, these electrons will be mainly localized on left side of molecules which is according to Fig. 9. In chemical reactions, electron can be transferred from HOMO or HOMO–1 or HOMO–2 to appropriate molecular orbitals. The



Fig. 9. Contour diagrams and energies of mentioned molecular orbitals of HL^1 and HL^2 at B3LYP/6-31+G(d) level in vacuo.

energy differences are important to determine the molecular orbitals which contain the transferred electrons. The energy differences between "LUMO and HOMO", "HOMO and HOMO–1" and "HOMO–1 and HOMO–2" are calculated as 343.26, 42.14, 6.80 kJ mol⁻¹, respectively for HL^1 ; 345.33, 40.09 and 14.34 kJ mol⁻¹, respectively for HL^2 . These results imply that electrons can easily be transferred from HOMO or HOMO–1 or HOMO–2 to appropriate molecular orbitals.

Molecular electrostatic potential (MEP) maps and contours

Molecular electrostatic potential (MEP) maps are related to electron density on molecule surface. These maps can be used to predict the active sites on molecules. Additionally, MEP contours are related to electron density on molecular plane. Steric effects and active sites can be easily determined by using of these contours. MEP maps and contours of investigated molecules are calculated at the B3LYP/6-31+G(d) level and represented in Fig. 10.

Different values of electrostatic potential at MEP maps are shown by different colors¹ which are mainly red, yellow, green, light blue and blue. The colors between red and green in MEP maps are related to electrophilic reactivity while the colors between green and blue in MEP maps is related to nucleophilic reactivity.

 $^{1}\,$ For interpretation of color in Fig. 10, the reader is referred to the web version of this article.

According to MEP maps in Fig. 10, electrophilic active regions are around the oxygen atom and nitrogen atoms which are connected to each other with double bonds in each molecule. Additionally, π -electrons in benzene ring on left side of molecule are slightly active in HL^2 . These results are supported with MEP contours and the last result are seen better with MEP contours.

Non-linear optical (NLO) properties

NLO is important property in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the technologies in areas such as telecommunications, signal processing and optical interactions [33]. Therefore, NLO is located on the foreground in current research. Some quantum chemical descriptors which are total static dipole moment (μ), the average linear polarizability (α), the anisotropy of the polarizability ($\Delta \alpha$) and first hyperpolarizability (β) have been used for explaining the NLO properties in many computational studies. The total static dipole moment, the average linear polarizability, the anisotropy of the polarizability and first hyperpolarizability are calculated by using the Eqs. (1)–(4), respectively and given in Table 6.

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \tag{1}$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$



Fig. 10. MEP maps and contours of studied molecules at B3LYP/6-31+G(d) level in vacuo.

Table 6

The calculated dipole moment (μ), average linear polarizability (α), the anisotropy of the polarizability ($\Delta \alpha$) and hyperpolarizability (β) for urea and investigated molecules.

Parameters	Urea	HL^1	HL^2
μ_x^a	0.0000	-0.9291	-0.77351
μ_{v}^{a}	0.0000	-0.5715	-0.44968
μ_z^a	-1.8058	-0.1945	0.296679
α_{xx}^{b}	23.6560	535.1930	508.4758
α_{vv}^{b}	0.0000	-146.8840	-154.703
α_{zz}^{b}	36.1116	374.9131	380.9196
α_{xy}^{b}	0.0000	2.9888	-0.90323
α_{xz}^{b}	0.0000	18.8451	-19.6799
α_{yz}^{b}	37.7298	157.5689	165.7135
β_{xxx}^{b}	0.0000	1247.6970	567.623091
β_{yyy}^{b}	0.0000	-1562.9124	-1406.7708
β_{zzz}^{b}	0.0000	1677.0764	1599.13189
β_{xyy}^{b}	0.0000	-1,646.3768	-1604.1212
β_{xxy}^{b}	-34.3289	-276.5585	357.70877
β_{xxz}^{b}	0.0000	-231.9426	-292.43902
β_{xzz}^{b}	36.2531	-197.3607	243.764081
β_{yzz}^{b}	0.0000	58.2370	62.5269691
β_{yyz}^{b}	0.0000	-88.6901	-108.3215
μ^{a}	1.8058	1.107993	0.942624
α ^c	2.9522	37.69924	36.2900
$\Delta \alpha^{c}$	10.7676	100.1942	99.9594
β^{d}	$4.31 imes 10^{-28}$	$2.00 imes 10^{-26}$	1.51×10^{-26}

^a In Debye.

^b In atomic unit (a.u.).

^c In Å³.

^d In cm⁵/esu.

$$\Delta a = \frac{1}{\sqrt{2}} \Big[(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{zz} - a_{xx})^2 + 6a_{xz}^2 + 6a_{xy}^2 + 6a_{yz}^2 \Big]^{1/2}$$
(3)

$$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz} \right)^2 + \left(\beta_{zzz} + \beta_{xzz} + \beta_{yzz} \right)^2 \right]^{1/2}$$
(4)

In Table 6, mentioned parameters of studied molecules and urea are calculated at B3LYP/6-31+G(d) level. NLO properties can be affected from polarizability, anisotropy of the polarizability and hyperpolarizability. NLO properties increase with increasing the linear polarizability, anisotropy of the polarizability and first hyperpolarizability. According to Table 6, all values of each mentioned molecules are greater than their urea values. Therefore, NLO properties of HL^1 and HL^2 are better than urea. According to Table 6, the general ranking of NLO properties should be as follows:

$HL^1 > HL^2 > Urea$

According to this ranking, molecule *HL*¹ is the best candidate for NLO properties.

Fluorescence measurements

The photophysical properties of the azo-azomethine dyes HL^1 and HL² were explored. Excitation and emission spectra were studied for solutions of the dyes which were excited at 328 nm. Dyes HL^1 and HL^2 gave intense light emission upon irradiation by UV light and their photoluminescence spectra in MeCN is shown in Fig. 11. Maximum luminescent intensity was observed at 402 nm and the full width at half maximum was 74 nm for compound HL¹. The dye HL¹exhibited a photoluminescence quantum yield of 34% and a long excited-state lifetime of 3.21 ns. Maximum luminescent intensity was observed at 397 nm and the full width at half maximum was 57 nm for compound HL^2 . Dye HL^2 exhibited a photoluminescence quantum vield of 32% and a long excited-state lifetime of 2.98 ns. The photoluminescence intensity and quantum yield of dye HL^1 were higher than that of the dye HL^2 due to the position of alkyl group on the phenyl ring. An explanation for the high quantum yields is that the phenyl ring alkyl group parasubstitution led to greater π -electron delocalization forming large conjugated system in the dye *HL*¹ structure.

Fig. 11 also shows the comparison of excitation and emission spectra of the dyes HL^1 and HL^2 in the solvent MeCN. The



Fig. 11. Photoluminescence spectra of dyes HL^1 and HL^2 in acetonitrile; samples were excited at 328 nm.

Table 7 Photoluminescence data for the dyes HL^1 and HL^2 .

Entity	λ_{\max} Ex (nm)	In Ex	λ_{\max} Em (nm)	In Em	ϕ_f (%)	τ_f (ns)
HL^1	333 (286;324;342)	704	402 (386;445;476;513)	695	34	3.21
HL ²	331 (284;321;339)	639	397 (383;436;475;512)	633	32	2.98

 λ_{\max} Ex: maximum excitation wavelength; In Ex: maximum excitation intensity; λ_{\max} Em: maximum emission wavelength; In Em: maximum emission intensity; ϕ_{f} : quantum yield; τ_{f} : excited-state lifetime.

photoluminescence intensity and quantum yield of compound HL² decreased with respect to that of the compound HL^1 due to the ortho-position of alkyl group on the phenyl ring. Compound HL² exhibited an excitation maximum wavelength at 331 nm, slightly shifting to 333 nm for compound HL¹. Decreases in excitation intensity of HL^2 was observed being dependent on the orthosubstitution of alkyl group on the phenyl ring. With excitation at 328 nm, the compound HL^1 showed an emission maximum at 402 nm, which also shifted to 397 nm upon changing from paraposition of alkyl group on the phenyl ring to ortho-position. Thus, the fluorescence emission intensity of the compound HL^{1} increased as compared to that of compound HL^2 . This increase of emission intensities is due to the better electron donating group effect of para-substitution of alkyl group on the phenyl ring. Compound *HL*¹ allows for energy transfer from the excited state of the dye *HL*¹ to ground state, hence decreasing the non-radiated transition of the compound *HL*¹ excited state and increasing the fluorescence emission. Also, upon changing from ortho-position of alkyl group on the phenyl ring to para-position, the maximum photoluminescence peak shifted from 397 to 402 nm, and shoulder peaks become more noticeable. The photoluminescence data for the compounds HL^1 and HL^2 are given in Table 7. The photoluminescent properties of these dyes may provide promising optical and electronic applications.

Conclusion

Two novel azo-azomethine dyes HL^1 and HL^2 were synthesized and characterized by spectroscopic and analytic methods. Molecular structures of the dyes were determined by single crystal X-ray diffraction study. X-ray data showed that both compounds adopt phenol-imine tautomer in the solid state. Optimized structures of HL^1 and HL^2 were obtained by using B3LYP/6-31+G(d) level in vacuo. HL^2 is more stable than HL^1 . There is a well agreement between experimental structural parameters and theoretical. IR spectra of each molecule were calculated and good agreement is obtained between experimental and calculated frequencies except O—H vibration. Some vibration modes which have higher intensity than 25D are examined in detail. NLO properties of HL^1 are better than HL^2 . The azo-azomethine dyes HL^1 and HL^2 were found to display an intense photoluminescence at 402 and 397 nm, respectively. The photoluminescence intensities and quantum yields of these compounds are affected by the position of alkyl group on the phenyl ring. The *para*-substituted alkyl group on the phenyl ring revealed better electron donating effect and thus higher fluorescence emission. These compounds are attractive materials which can be used in fabrication of electroluminescent devices.

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Appendix A. Supplementary material

CCDC 1034612 and 1034613 contain the supplementary crystallographic data for *HL*¹ and *HL*², respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre 12 Union Road Cambridge CB2 1EZ, UK. Fax: +44 (0)1223 336033. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2015.03.043.

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