

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



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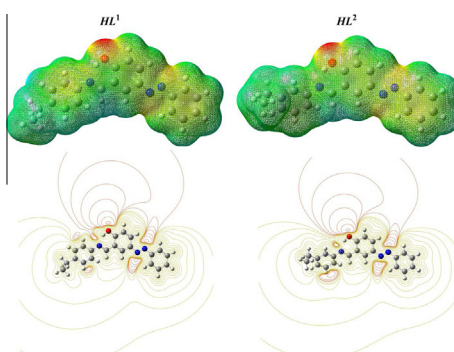
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HIGHLIGHTS

- Two novel azo-azomethine 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 azo-azomethines were also evaluated.

GRAPHICAL ABSTRACT



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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, *HL*¹ and 2-[(E)-[(3-ethylphenyl)imino]methyl]-4-[(E)-phenyldiazenyl]phenol, *HL*² dyes). The dyes were characterized by elemental 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 π ··· π 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*² 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 HL^2 were characterized using ultraviolet-visible spectrophotometer (UV-Vis), photoluminescence spectrophotometer (PL) and Fourier transform infrared spectroscopy (FT-IR). The structures of compounds HL^1 and HL^2 were analyzed by IR, 1H and ^{13}C NMR, elemental analysis and single crystal X-ray studies. Computational studies of HL^1 and HL^2 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-Diphenylanthracene, 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 HL^1 was recorded on a Thermo Fisher Exactive + Triversa Nanomate spectrometer. IR spectra were obtained ($4000\text{--}400\text{ cm}^{-1}$) 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 (HL^1 and HL^2)

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*)-phenyldiazenyl]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 $C_{21}H_{19}N_3O$: 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%) [$C_{20}H_{18}N_3O$] $^+$, 289(9%) [$C_{18}H_{14}N_3O$] $^+$, 213(100%) [$C_{12}H_{12}N_3O$] $^+$, 200(48%) [$C_{11}H_{10}N_3O$] $^+$, 185(2%) [$C_{11}H_{11}N_3$] $^+$. NMR ($CDCl_3$ as solvent, δ ppm): 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, CH_2 of ethyl), 1.32–1.28 (t, 3H, CH_3 of ethyl group). ^{13}C : 164.18 (C=N), 161.15 (C–OH), 118.17–152.64 (C, aromatic), 29.52 (C, CH_2 of ethyl), 15.62 (C, CH_3 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 $C_{21}H_{19}N_3O$: C, 76.57; H, 5.81; N, 12.76. Found: C, 76.53; H, 5.88; N, 12.74%. NMR (DMSO- d_6 as solvent, δ ppm): 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, CH_2 of ethyl group), 1.25–1.22 (t, 3H, CH_3 of ethyl group). ^{13}C : 164.41 (C=N), 163.12 (C–OH), 118.51–152.44 (C, aromatic), 28.57 (C, CH_2 of ethyl), 15.97 (C, CH_3 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 $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). 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

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