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New 1,2,4-triazole-based azo–azomethine dye. Part III: Synthesis, characterization, thermal property, spectrophotometric and computational studies



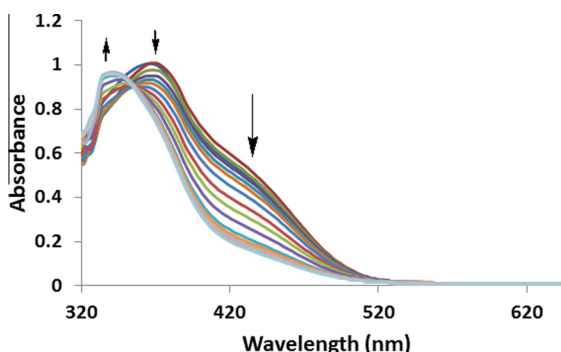
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HIGHLIGHTS

- New azo–azomethine dyes based on 1,2,4-triazole have been synthesized.
- TD-DFT and NBO studies on azo–azomethine dyes have been reported.
- ^1H NMR chemical shifts of the dyes studied by GIAO/DFT and CSGT/DFT methods.

GRAPHICAL ABSTRACT



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ABSTRACT

A new 1,2,4-triazole-based azo–azomethine compound, **H₂L**, has been prepared by condensation reaction of 1-(3-formyl-4-hydroxyphenylazo)-4-ethylbenzene with prepared triazole-based diamine. The structure of **H₂L** was characterized by using FT-IR, UV-Vis and ^1H NMR spectroscopic methods as well as elemental analysis. Hard model chemometrics method has been used to determine the formation constants of zinc(II), copper(II), nickel(II) and cobalt(II) complexes of **H₂L** in DMSO by UV-Vis spectrophotometric method. Solvatochromic behavior of the dye has been also investigated in some organic solvents with different polarities. Thermal properties of the prepared dye was examined by thermogravimetric analysis. Results indicated that the framework of the dye was stable up to 245 °C. Furthermore, ^1H chemical shifts and UV-Vis of **H₂L** were studied by the gauge independent atomic orbital (GIAO), continuous set of gauge transformations (CSGT) and time-dependent density functional theory (TD-DFT) methods respectively at the level of density functional theory using B3LYP/6-311+G(d) basis sets in DMSO. The computational data are in reasonably good agreement with the experimental data.

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Introduction

Azo dyes are well-known class of organic photoactive materials due to their excellent optical switching properties, good chemical

stabilities and high solution process abilities [1,2]. These materials are widely used in heat transfer printing and textile industries [3,4], optical data storage [5], switching technologies [6], photo-refractive polymer industries [7] and have been widely used in many biological reactions [8–10] and in analytical chemistry [11]. Recently, azo–azomethine dyes have also attracted increasing attention due to their interesting electronic and geometrical

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features in connection with their application for molecular memory storages [12], nonlinear optical elements [13], printing system [14] and biological–medical studies [15,16]. Therefore, several studies have been published on the synthesis and spectral properties of azo–azomethine dyes, as well as their transition metal complexes [17–22]. Among the plethora of new synthetic azo–azomethine dyes those containing 1,2,4-triazoles are of particular interest for several reasons. 1,2,4-Triazoles are stable compounds with rich and well-known chemistry [23–26]. The incorporation of 1,2,4-triazole into acyclic and/or macrocyclic ligands has facilitated the isolation of a wide range of transition metal complexes with interesting electrochemical and magnetic properties [27–29]. Also, their electronic properties make them suitable for surface enhanced resonance Raman scattering (SERRS) studies [30,31]. These diversified applications are at least in part a consequence of the numerous approaches that are available for the insertion of specific functionalities into the triazole nucleus.

As part of our ongoing interest in the synthesis and spectral studies of 1,2,4-triazole-based azo–azomethine dyes [25,26], we report the newly prepared azo–azomethine compounds on 1,2,4-triazole-based moiety (Fig. 1) and computationally investigated their intense electric absorption band in visible region, which is decisively responsible for their color appearance. The prepared dye has been characterized by spectroscopic methods (^1H NMR, UV–Vis and IR) as well as elemental analysis data. ^1H NMR spectrum of more stable tautomer, azo tautomer, was successfully simulated using Continuous Gauge Independent Atomic Orbitals/Density Functional Theory (GIAO/DFT) [32,33] and Continuous Set of Gauge Transformations/Density Functional Theory (CSGT/DFT) [34,35] with the B3LYP functional. Also, in order to theoretically establish the more stable tautomer in DMSO solution, we tried to assign the UV–Vis spectrum of dye by time-dependent density functional theory (TD-DFT) [36]. The thermal property of the prepared azo dye was examined by thermogravimetric analysis which indicated that H_2L was stable up to 245 °C.

Experimental

Materials

All of the reagents and solvents involved in synthesis were of analytically grade and used as received without further purification. Salicylaldehyde, 4-ethylaniline, 1,3-bis(bromomethyl)benzene and hydrazine (80%) were obtained from Aldrich and Merck.

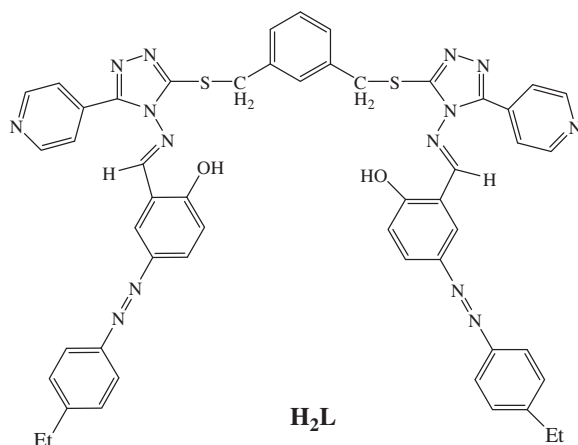


Fig. 1. The synthesized 1,2,4-triazole-based azo–azomethine dye (H_2L).

Instrumentation

The structure of all synthesized compounds was confirmed by ^1H NMR spectra, recorded on a Bruker AV 300 MHz spectrometer. FT-IR spectra were recorded as pressed KBr discs, using Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region of 400–4000 cm^{-1} . Melting points were determined on Electrothermal 9200 apparatus. Thermal analysis was performed on a TGA V5.1A DuPont 2000 and Perkin–Elmer Thermogravimetric Analyzer TG/DTA 6300 instruments. C.H.N. analyses were performed on a Vario EL III elemental analyzer. Electronic spectral measurements were carried out using Agilent hp 8453 spectrophotometer in the range 300–800 nm using 1 cm path quartz cells. The measurements were performed at 25 (± 0.5) °C. The pH measurements were made using a Metrohm 691 pH meter equipped with a glass calomel combined electrode. All calculations were performed in MATLAB 7.8 (R2009a) and Microsoft Excel 2007. Electrochemical measurements were recorded on an Autolab 30 V potentiostat/galvanostat for Eco Chemicompany. All readings were taken using three electrode potentiostatic systems in DMSO with 0.1 mol cm^{-3} tetrabutylammonium perchlorate (TBAP, electrochemical grade) as supporting electrolyte. A three-electrode assembly composed of a platinum working electrode, a platinum auxiliary electrode, and Calomel reference electrode was used with sample concentrations of 1×10^{-3} M.

Theoretical calculations

The structure data, ^1H chemical shifts of H_2L and TD-DFT calculation in DMSO were calculated using Gaussian-03 [37] series of programs. A starting molecular mechanics structure for the DFT calculations was obtained using the Hyper Chem 5.02 program [38]. The geometry of the prepared compound was fully optimized at the B3LYP/6-31G* level. Vibrational frequency analyzes, calculated at the same level of theory, indicate that the optimized structure is at the stationary points corresponding to global minima without any imaginary frequency. The calculations of the computed magnetic isotropic shielding tensors were performed using GIAO/DFT [32,33] and CSGT/DFT [34,35] methods at the B3LYP/6-311++G(d) basis set. In both step of DFT and TD-DFT calculations, solvent effects of ethanol and DMSO were included using the Polarizable Continuum Model (PCM) [39]. The default Gaussian03 PCM implementation (non-equilibrium formulation) is suitably designed to predict UV/Vis spectrum described within the vertical transition scheme, where solvent polarization responds to the change of electronic distribution of the excited state molecules with the molecular orientation fixed during electronic transition. The NBO calculations [40] were performed using NBO 3.1 program as implemented in the Gaussian 03W package at the DFT/B3LYP level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of delocalization or hyper conjugation. The second-order fock matrix was used to evaluate the donor–acceptor interactions in the NBO basis [41]. For each donor NBO(i) and acceptor NBO (j), the stabilization energy $E(2)$ associated with the i to j delocalization is estimated as

$$E(2) = \Delta E_{ij} = [q_i(F_{ij})^2]/[e_i - e_j] \quad (1)$$

where q_i is the donor orbital occupancy, e_i , e_j are diagonal elements (orbital energies) and F_{ij} is the off diagonal element associated with NBO matrix.

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