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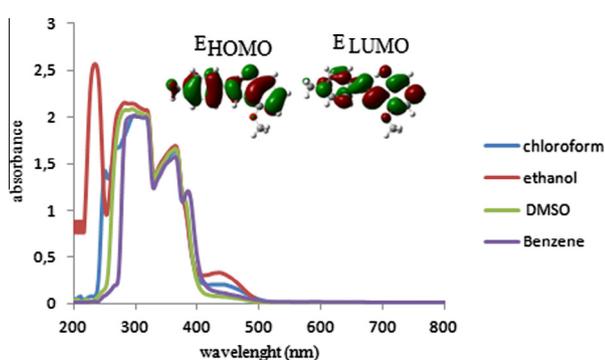
Experimental (X-ray, FT-IR and UV–vis spectra) and theoretical methods (DFT study) of (E)-3-methoxy-2-[(p-tolylimino)methyl]phenol

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HIGHLIGHTS

- Experimental (X-ray, FT-IR and UV–vis spectra) methods and theoretical methods (DFT study) were investigated.
- Nonlinear optical properties (NLO) and natural bond orbital (NBO) analysis were analyzed.
- Mulliken population method and natural population analysis (NPA) were calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

A suitable single crystal of (E)-3-methoxy-2-[(p-tolylimino)methyl]phenol, formulated as $C_{15}H_{15}N_1O_2$, reveals that the structure is adopted to its E configuration about the azomethine $C=N$ double bond. The compound adopts a enol–imine tautomeric form with a strong intramolecular $O-H\cdots N$ hydrogen bond. The single crystal X-ray diffraction analysis at 296 K crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.4791(11)$ Å, $b = 6.8251(3)$ Å, $c = 18.3561(15)$ Å, $\alpha = 90^\circ$, $\beta = 129.296(5)^\circ$, $\gamma = 90^\circ$ and $Z = 4$. Comprehensive theoretical and experimental structural studies on the molecule have been carried out by FT-IR and UV–vis spectrometry.

Optimized molecular structure and harmonic vibrational frequencies have been investigated by DFT/B3LYP method with 6-31G(d,p) basis set. Stability of the molecule, hyperconjugative interactions, charge delocalization and intramolecular hydrogen bond has been analyzed by using natural bond orbital (NBO) analysis.

Electronic structures were discussed by TD-DFT method and the relocation of the electron density were determined. The energetic behavior of the title compound has been examined in solvent media using polarizable continuum model (PCM). Molecular electrostatic potential (MEP), Mulliken population method and natural population analysis (NPA) have been studied. Nonlinear optical (NLO) properties were also investigated. In addition, frontier molecular orbitals analysis have been performed from the optimized geometry. An ionization potential (I), electron affinity (A), electrophilicity index (ω), chemical potential (μ), electronegativity (χ), hardness (η), and softness (S), have been investigated.

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Introduction

Schiff bases are important in diverse fields of chemistry and biochemistry owing to their biological activity [1,2] and can be classified according to their photochromic or thermochromic properties [3,4]. From observations on some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar [5,6]. *o*-hydroxy schiff base ligands are of interest mainly because of the existence of typical hydrogen bonds and tautomerism between the O—H···N in phenol-imine and N—H···O in keto-amine forms and N⁺—H···O⁻ in zwitterionic forms [7–9]. This compound undergoes tautomerism by proton transfer between the hydroxy O atom and the imine N atom, namely the enol-imine tautomer. In Schiff base compounds, the imine nitrogen can act as an inter- or intramolecular hydrogen-bond acceptor and the hydroxyl oxygen in salicylaldehyde derivatives can act as an intermolecular hydrogen-bond acceptor. Schiff bases non-linear properties have an importance for the design of various molecular electronic devices such as optical switches and optical data storage devices [10,11].

For Schiff bases, NLO studies provide the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections.

The title molecule was determined by single crystal X-ray diffraction technique. In the present study, it is planned to have a joint experimental and theoretical investigation of FT-IR and UV-vis spectra. Electronic absorption spectra of the title compound were predicted by using time-dependent density functional theory (TD-DFT) [12–14] in the calculation of electronic excitation energies for gas and solution phases (different solvent media). The excitation energies, wavelengths and oscillator strengths were obtained at TD-DFT level at the optimized geometry. In addition to, it is also planned to illuminate theoretical determination of the optimized molecular geometries, HOMO–LUMO energy gap, MEP, NLO, Mulliken charges, NPA and NBO analysis of the title compound by using density functional theory (DFT) with B3LYP/6-31G(d,p) basis set. In addition, the ionization potential, electron affinity, electrophilicity index, chemical potential, electronegativity, hardness and softness are determined.

Experimental and computational methods

Synthesis

For the preparation of (E)-3-methoxy-2-[(*p*-tolylimino)methyl]phenol compound the mixture of 2-hydroxy-6-methoxybenzaldehyde (0.5 g, 3.3 mmol) in ethanol (20 ml) and 4-methylaniline (0.35 g, 3.3 mmol) in ethanol (20 ml) was stirred for 2 h under reflux. The crystals suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield; %84, m.p.; 342–344 K).

Instrumentation

The FT-IR spectrum of the title compound was recorded in the 4000–400 cm⁻¹ region with a Bruker Vertex 80V FT-IR spectrometer using KBr pellets. Absorption spectra were determined on Unicam UV-vis spectrometer.

Crystal structure determination

The single-crystal X-ray data were collected on a STOE IPDS II image plate diffractometer at 296 K. Graphite-monochromated

Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and the ω -scan technique were used. The structure was solved by direct methods using SHELXS-97 [15] and refined through the full-matrix least-squares method using SHELXL-97 [16], implemented in the WinGX [17] program suite. Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located in a difference Fourier map and were refined isotropically. Data collection: Stoe X-AREA [17], cell refinement: Stoe X-AREA [17], data reduction: Stoe XRED [18]. The general-purpose crystallographic tool PLATON [19] and ORTEP-3 [17] was used for the structure analysis and presentation of the results. The structure was refined to $R_{\text{int}} = 0.030$ with 2132 observed reflections using $I > 2\sigma(I)$ threshold. Details of the data collection conditions and the parameters of the refinement process are given in Table 1.

Computational details

The entire calculations conducted in the present work were performed at B3LYP levels included in the Gaussian 03 W package [20] program together with 6-31G(d,p) basis set function of the density functional theory (DFT) utilizing gradient geometry optimization [21]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree–Fock level, adopting the standard 6-31G(d,p) basis set. We have utilized the gradient corrected density functional theory [22] with three parameter hybrid functional (B3) [23] for the exchange part and the Lee–Yang–Parr (LYP) correlation function [24], accepted as a cost effective approach for the computation of molecular structure, vibrational frequencies and energies of optimized structures. By combining the results of the Gaussview program [25] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy.

The significant values for energy, bond lengths, bond angles and torsions were obtained by using B3LYP/6-31G(d,p) basis set. The optimized structural parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima. At the optimized structure of the examined species, no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. We have scaled the vibration frequency numbers with standard scaling factor 0.9627 to neglect of vibrational anharmonicity.

Table 1

Crystal data and structure refinement parameters for the title compound.

Chemical formula	C ₁₅ H ₁₅ N ₁ O ₂
Color/shape	Orange/plate
Formula weight	241.28
Temperature	296 K
Crystal system	Monoclinic
Space group	P21/c
Unit cell parameters	$a = 13.4791(11) \text{ \AA}$ $b = 6.8251(3) \text{ \AA}$ $c = 18.3561(15) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 129.296(5)^\circ$ $\gamma = 90^\circ$
Volume	1306.85(16) \AA^3
Z	4
Density	1.226 Mgm^{-3}
Absorption coefficient	0.086 mm^{-1}
Diffractometer/meas. meth.	STOE IPDS 2/ ω -scan
θ range for data collection	2.83–26.50°
Unique reflections measured	14,753
Total reflection/observed reflections	2704/2132
Goodness of fit on F ²	1.15
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.165$, $wR_1 = 0.155$
R indices (all data)	$R_2 = 0.058$, $wR_2 = 0.073$

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