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Combined experimental and theoretical studies on the X-ray crystal structure, FT-IR, ^{1}H NMR, ^{13}C NMR, UV–Vis spectra, NLO behavior and antimicrobial activity of 2-hydroxyacetophenone benzoylhydrazone

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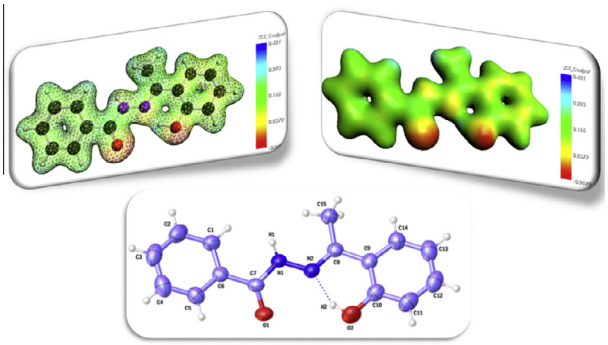
HIGHLIGHTS

- Vibrational spectra of 2-hydroxyacetophenone benzoylhydrazone were analyzed.
- Title compound can be a good applicant in the development of NLO materials.
- NBO, NMR and UV spectral analysis were carried out.
- Frontier molecular orbitals (FMOs) and chemical reactivity were performed.
- The experimental results were compared with computed values.

GRAPHICAL ABSTRACT



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ABSTRACT

A Schiff base ligand, 2-hydroxyacetophenone benzoylhydrazone (HL) was synthesized and fully characterized with FT-IR, elemental analyses, UV–Vis, ^{1}H NMR and ^{13}C NMR spectra. DFT calculations using B3LYP/6-31+G(d,p) and PW91/DZP are performed to optimize the molecular geometry. Optimized structures are used to calculate FT-IR, UV–Vis, ^{1}H NMR and ^{13}C NMR spectra of the compound. Also the energies of the frontier molecular orbitals (FMOs) have been determined. The results obtained from the optimization and spectral analyses are in good agreement with the experimental data. To investigate non-linear optical properties, the electric dipole moment (μ), polarizability (α) and molecular first hyperpolarizability (β) were computed. The linear polarizabilities and first hyperpolarizabilities of the studied molecule indicate that the compound can be a good candidate of nonlinear optical materials. In addition, the minimal inhibitory concentration (MIC) of this compound against *Staphylococcus aureus*, and *Candida albicans* was determined.

Introduction

In past decades, attention to hydrazone ligands has been increased because of various properties and wide applications

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[1,2]. They have a good potential for biochemical processes and are used as antimicrobial [3], anti-diabetic [4], antimalarial [5], anti-cancer and potentially DNA damaging and mutagenic agents [6,7]. Also presence of fragment such as azomethine and other structural properties of hydrazones have made them a good candidate for new drug development [8] and opto-electronic applications [9]. In addition the interest to these ligands are due to the fact that aromatic ring in them is a constituent of many biological system [10].

Furthermore, hydrazones react with transition metal ions in living systems that their mode of chelation had been of significant interest in last decades [11]. They can form wide variety of coordination compounds with different metal ions and many applications such as catalytic and biological activities have been reported for them [12,13].

Based upon, we have synthesized hydrazone derivative compound, 2-hydroxyacetophenone benzoylhydrazone (HL), and characterized using FT-IR, ^{1}H NMR, ^{13}C NMR and electronic spectra. DFT calculations have been performed to investigate detailed experimental spectroscopic data, NLO properties and chemical reactivity of synthesized compound. These calculations are valuable for providing insight into molecular properties of hydrazone derivative compounds. Also, the biological activity of the title compound as antimicrobial especially against Gram-positive and Gram-negative bacteria was investigated.

Experimental

Reagents and physical measurements

All the chemicals were purchased from Merck Co. and used without further purification. The UV–Vis spectrum of the HL was run in methanol solution on a Perkin Elmer Lambda25 in the range 200–800 nm. The FT-IR spectrum was recorded on a Nicolet-Impact 400D spectrometer (4000–400 cm^{-1}) in KBr pellets. NMR spectra were acquired on a Bruker DRX400 spectrometer operating at 400 MHz for ^{1}H NMR and ^{13}C NMR in DMSO-d_6 as a solvent. Carbon, hydrogen and nitrogen analyses were carried out using a Thermo Finnigan Flash Elemental Analyzer 1112EA instrument.

2-hydroxyacetophenone benzoylhydrazone (HL)

The HL have been prepared according to a previous report [14]. A mixture of benzohydrazide (0.14 g, 1 mmol) and 2-hydroxyacetophenone (0.12 mL, 1 mmol) was refluxed in 10 ml methanol. After 4 h, the precipitate was filtered, washed with cold ethanol and dried in vacuum over silica gel. Colorless Crystals suitable for crystallography were obtained in mother liquor after 3 days at room temperature.

Yield: 72%. m.p.: 183 °C. Anal. Calc. for $C_{15}H_{14}N_2O_2$ (254.28 g mol^{-1}): C, 70.85; H, 5.55; N, 11.02. Found: C, 69.93; H, 4.92; N, 11.95%. FT-IR (KBr), cm^{-1}: ν(NH) 3445, ν(OH) 3222, ν(C=O) 1652, ν(C=N) 1608, ν(N—N) 1131, ν(C—O) 1253. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 13.37 (s, 1H, OH); 11.34 (s, 1H, NH), 6.87–7.94 (m, 9H, rings), 2.48 (s, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 164.88, 159.24, 158.58, 133.43, 132.43, 131.73, 131.51, 128.97, 128.87, 128.75, 128.59, 127.41, 119.85, 118.97, 14.51.

Computational methods

The geometry of the synthesized compound was fully optimized without any symmetry constraints using density functional theory (DFT), B3LYP exchange correlation functional and 6-31+G(d,p) [15,16] with Gaussian 03 program package [17]. The starting atomic coordinated were taken from X-ray structure (Fig. 1). The optimized structures were characterized by frequency calculations as true minima. Vibrational frequencies were scaled by 0.963 [18]. The density functional theory has been used to calculate the dipole moment (μ), mean polarizability (α) and the total first static hyperpolarizability (β) for HL in terms of x, y, z components and are given by following equations [19].

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta_{tot} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zyy} + \beta_{zxx})^2\right]^{1/2}$$

The polarizability and hyperpolarizability tensors (α_{xx}, α_{xy}, α_{yy}, α_{xz}, α_{yz}, α_{zz} and β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{yzz}, β_{zzz}) can be obtained by a frequency job output file of Gaussian. However, α and β values of Gaussian output are in atomic units (a.u.) so they have been converted into electrostatic units (esu) (α; 1 a. u. = 0.1482×10^{-24} esu, β; 1 a.u. = 8.6393×10^{-33} esu).

The GIAO method was used for calculating ^{1}H NMR and ^{13}C NMR chemical shifts at the B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) levels. Solvent (DMSO) was considered as a uniform dielectric constant 46.7 and Polarized Continuum Model (PCM). In addition, electronic transitions were calculated at DFT level, as implemented in the Amsterdam density functional package (ADF2009.01) [20]. The tautomer structures were fully optimized via generalized-gradient approximation (GGA) employing the Perdew–Wang exchange and correlation functionals (PW91) with DZP basis set [21]. The excitation energies were estimated by Time Dependent Density Functional Theory (TDDFT) [22]. This methodology is based on the linear response formalism within the iterative Davison procedure implemented in the ADF2009.01 code. The calculations performed by first-principles method let to obtain accurate excitation energies and oscillator strengths for the

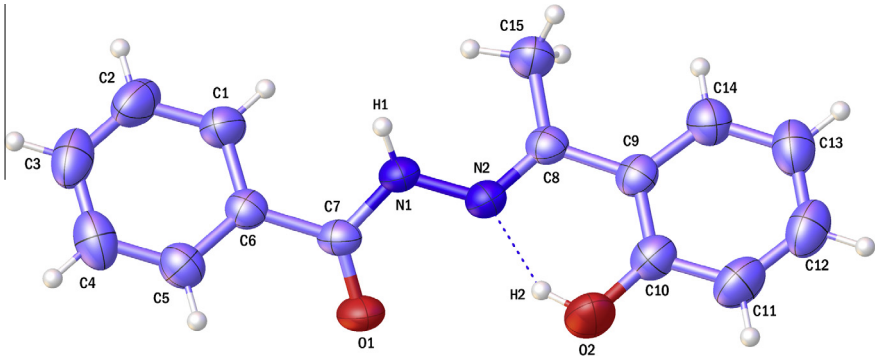

Fig. 1. ORTEP diagram of HL.