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Molecular structure, vibrational and electronic properties of 4-Phenyl-3H-1,3-thiazol-2-ol using density functional theory and comparison of drug efficacy of keto and enol forms by QSAR analysis



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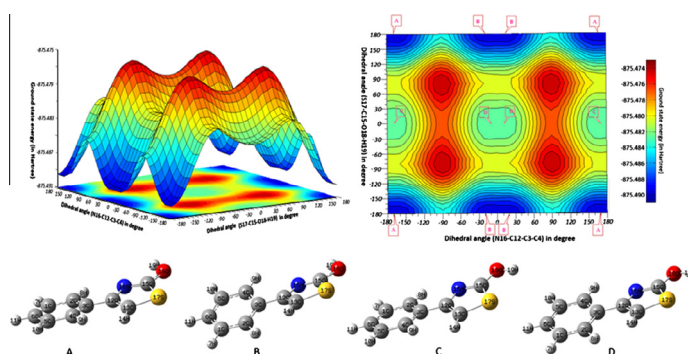
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HIGHLIGHTS

- FT-Raman, FT-IR and UV-Vis analysis of 4-Phenyl-3H-1,3-thiazol-2-ol has been done.
- DOS and PDOS plots drawn to show the make-up of the molecular orbitals.
- QSAR analysis of both the keto and enol form establishes the efficacy of enol form.

GRAPHICAL ABSTRACT



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ABSTRACT

4-Phenyl-3H-1,3-thiazol-2-ol can exist in two tautomeric forms – keto and enol. Comprehensive investigation of molecular geometry and electronic structure in ground as well as in the first excited state of 4-Phenyl-3H-1,3-thiazol-2-ol (enol) has been carried out. To determine lowest-energy molecular conformation of the title molecule, the selected torsion angles were varied in steps of 10° and molecular energy profile was calculated from −180° to +180°. Experimental FT-IR and FT-Raman spectra of title compound were compared with the spectral data obtained by DFT/B3LYP method. Dipole moment, polarizability, first static hyperpolarizability and molecular electrostatic potential surface map have been calculated to get a better insight of the properties of title molecule. Natural bond orbital (NBO) analysis has been done to study the stability of the molecule arising from charge delocalization. UV-Vis spectrum of the title compound was also recorded and electronic properties such as frontier orbitals and band gap energies were calculated by TD-DFT approach. To compare the drug efficacy of enolic and keto forms, QSAR properties of both forms have also been computed and discussed.

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Introduction

Thiazoles exhibit a variety of biological activity namely antibacterial, antifungal, anti-HIV, anti-hypertension, anti-inflammatory, anticancer, anticonvulsant and antidepressant [1–6], hence are

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valuable structural components in the field of medicinal chemistry. In fact thiazole moiety appears commonly in structures of various natural products and biologically active compounds, like thiamine (vitamin-B) and also is an integral part of most of the available antibiotics drugs such as penicillin, micrococin which have revolutionized the therapy of bacterial diseases [7]. Phenyl and substituted phenyl-thiazoles are also common structures of a wide range of biologically active natural products [8]. Recently it has been found that phenyl-thiazole ring system provides a template for the design and synthesis of antiviral agents which inhibit the flavi-viruses by targeting their E-protein [9]. Pharmaceutical importance of thiazoles and their derivatives drove us to investigate the molecular structural properties, vibrational and energetic data of 4-Phenyl-3H-1,3-thiazol-2-ol (4P3HT) with a long-term objective to achieve a better understanding of the properties of such derivatives. 4P3HT can exist in two tautomeric forms – keto and enol (Fig. 1). DFT/B3LYP/6-311++G(d,p) calculations show that the keto form (ground state energy –875.50601 a.u.) is more stable than enol form (ground state energy –875.48940 a.u.). Pihlaja et al. [10] have reported geometric and electronic properties of 4-Phenylthiazol-2(3H)-one (keto form), at the most elementary HF level of theory which does not take into account the electronic correlation effects. The work reported in the present communication deals with the comprehensive investigation of geometrical and electronic structure of enolic form of 4P3HT in ground as well as in the first excited state. The significance of enol form lies in the fact that this form ionizes into the enolate form under physiological conditions and increases the interaction of the drug with the vis-à-vis receptors, functional proteins or enzymes. To compare the drug efficacy of enolic and keto forms, QSAR properties of both forms have also been computed and discussed. Experimentally observed spectral data (FT-TR and FT-Raman) of the title compound is compared with the spectral data obtained by DFT/B3LYP method. The molecular properties like dipole moment, polarizability, first static hyperpolarizability and molecular electrostatic potential surface, contour map have been calculated to get a better understanding of the properties of the title molecule. Natural bond orbital (NBO) analysis has been applied to study the stability of the molecule arising from charge delocalization. UV-Vis spectrum of the title compound was also recorded and electronic properties, such as frontier orbitals and band gap energies were calculated by TD-DFT approach.

Experimental and computational methods

Sample and instrumentation

The pure 4-Phenyl-3H-1,3-thiazol-2-ol (4P3HT) of spectral grade was purchased from M/s Aldrich Chemical Co., as a white crystalline solid and was used as such without any further purification. The sample was used to record FT-Raman and FT-IR spectra. FT-IR and FT-Raman spectra were recorded on a Varian 7000 series spectrometer in the region 4000–400 cm^{-1} with a spectral

resolution of 0.5 cm^{-1} at AIRF, Jawaharlal Nehru University, New Delhi. For Raman spectra the 1064 nm laser line of Nd:YAG laser was used as the exciting wavelength with an output power of about 2 mW at the sample position. The spectrum was recorded in the range of 4000–100 cm^{-1} with a scanning speed of 10 $\text{cm}^{-1} \text{min}^{-1}$ and the spectral resolution of 4.0 cm^{-1} . UV absorption spectra of 4P3HT were recorded in methanol and chloroform using the Shimadzu 1800 UV-Vis recording spectrometer in the spectral region of 200–500 nm.

Computational details

Density functional theory [11] treated according to hybrid Becke's three parameter and the Lee-Yang-Parr functional (B3LYP) [12–14] supplemented with polarized triple-zeta 6-311++G(d,p) basis sets was used to study 4P3HT, as this quantum chemical method provides a very good overall description of medium-sized molecules. It has also been used to calculate the dipole moment, mean polarizability and first static hyperpolarizability based on the finite field approach. All calculations in this study have been performed with the Gaussian 09 program package [15] and results were analyzed with the Gaussview 5.0 molecular visualization program [16]. The most stable geometry of the molecule has been determined from the potential energy scan by varying the S17–C15–O18–H19 and N16–C12–C3–C4 dihedral angles at B3LYP/6-311++G(d,p) level of theory. 3-dimensional potential energy surface showing the variation of dihedral angles and their corresponding energies are given in Fig. 2(a) and (b) and thus obtained stable conformers of the title molecule are shown in Fig. 2(c). Geometrical structure corresponding to the lowest minima in the potential energy surface (represented as conformer A in Fig. 2(c)) has been used for the calculation of molecular properties and for the calculation of vibrational wavenumbers. Optimized parameters of the title molecule are very close to the experimental values reported by Garbarczyk et al. [17] for N-phenylthioamide thiazole-2. Positive value of all the calculated wavenumbers confirms the stability of optimized geometry. An empirical uniform scaling factor of 0.983 up to 1700 cm^{-1} and 0.958 for greater than 1700 cm^{-1} [18,19] was used to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity [20]. Theoretical vibrational assignment of the title compound using percentage potential energy distribution (PED) has been done with the MOLVIB program (version V7.0-G77) written by Sundius [21–23]. The theoretical UV-Vis spectrum has been computed by TD-DFT method with 6-311++G(d,p) basis set for gas phase and solvent effect also has been taken into consideration by implementing IEFPCM model at the same level of theory.

Natural bonding orbital (NBO) calculations [24] were performed using Gaussian 09 package 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 the intermolecular delocalization or hyper conjugation. The second

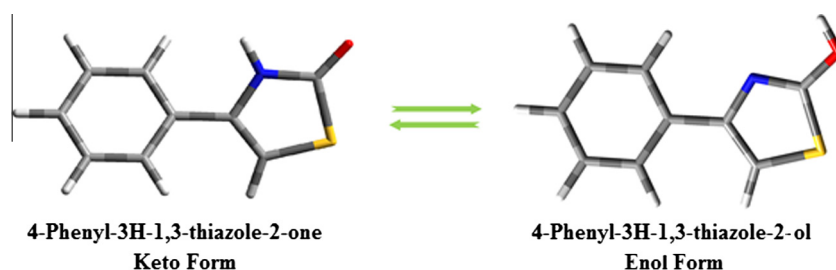


Fig. 1. Tautomeric forms (keto and enol) of 4P3HT.

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