



Conformational search, spectral analysis and electronic properties of 5-(4-Pyridinyl)-1,3,4-thiadiazol-2-amine



Vikas K. Shukla ^a, Monirah A. Al-Alshaikh ^b, Ali A. El-Emam ^c, Alok K. Sachan ^a, Ruchi Srivastava ^a, Onkar Prasad ^a, Leena Sinha ^{a,*}

^a Department of Physics, University of Lucknow, 226007, Lucknow, India

^b Department of Chemistry, College of Sciences, King Saud University, Riyadh 11451, Saudi Arabia

^c Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, Riyadh 11451, Saudi Arabia

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ABSTRACT

Comprehensive investigation of molecular geometry and electronic structure of 5-(4-Pyridinyl)-1,3,4-thiadiazol-2-amine in ground as well as in the first excited state has been carried out. The stable conformers of the title compound have been determined from the 3D potential energy scan by varying selected dihedral angles, responsible for conformational flexibility. As the energy difference between the conformers was very small, the relative stability has been confirmed at potentially high-level G2MP2 method. The most stable structure was optimized with B3LYP and M06-2X functional using polarized triple-zeta 6-311++G(d,p), to obtain the ground state structure and calculation of vibrational wave-numbers. Experimental FT-IR and FT-Raman spectra were compared with theoretical spectral data. 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. Frequency-dependent first hyperpolarizability $\beta(-2\omega;\omega,\omega)$ has also been evaluated to gauge the non-linear optical behavior of the title compound. Natural bond orbital (NBO) analysis has been done to study the stability of the compound arising from charge delocalization. UV-Vis spectrum, possible solvent-solute interaction and electronic properties such as frontier orbitals, band gap energies have been calculated by TD-DFT approach. ¹H nuclear magnetic resonance chemical shifts of the title compound were calculated using the Gauge-Including Atomic Orbital (GIAO) method and compared with experimental data.

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1. Introduction

1,3,4-thiadiazoles, five-membered ring systems containing one sulfur and two nitrogen atoms are one of the most imperative and acclaimed heterocyclic nuclei, being a core structural constituent in a collection of drug classes namely antimicrobial, anti-inflammatory, analgesic, antiviral, antineoplastic, and anti-tubercular agents [1–8]. El-Gohary and Shaaban [9] have synthesized new series of fused 1,3,4 thiadiazoles and reported their antimicrobial, anti-quorum-sensing and antitumor activities. Very recently Patel et al. [10] have synthesized and reported 1,3,4 thiadiazole derivatives as inhibitors of transforming growth factor- β type-I receptor kinase (ALK5). Sulfamethazole, cefazoline, acetazolamide and methazolamide etc. are few drugs containing

thiadiazole nucleus. In addition to pharmaceutical zone, the thiadiazoles are also being used in industrial, agricultural and polymer area [11,12]. Synthesis of new thiadiazole derivatives and analysis of their chemical behavior as well as biological activities have achieved prominence in recent decades. Despite extensive spectroscopic studies on thiadiazole and its derivatives [13–19], literature survey reveals that neither Raman, IR and UV-Vis spectroscopic studies nor the quantum chemical calculations on 5-(4-Pyridinyl)-1,3,4-thiadiazol-2-amine (PTA) have been reported so far. To have a decent insight of the structural profile of the compound, a detailed conformational search using 3D potential energy scan at DFT/B3LYP has been obtained by varying selected dihedral angles and relative conformational stability has been confirmed at G2MP2 level. The most stable conformer has been optimized at B3LYP and M06-2X level and vibrational analysis has been performed. Electric moments like Dipole moment, polarizability, first static hyperpolarizability have been calculated at B3LYP and M06-2X

* Corresponding author.

E-mail address: sinhaleena27@gmail.com (L. Sinha).

functionals and compared. Molecular electrostatic potential surface have been drawn at DFT/B3LYP/6311++G(d,p) level of theory. Frequency-dependent first hyperpolarizability $\beta(-2\omega;\omega,\omega)$ has also been evaluated to gauge the non-linear optical behavior of the title compound. 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. The method has also been used to investigate hydrogen bonding interaction between PTA and methanol. Thermo-dynamical properties such as heat capacity, entropy and enthalpy change at various temperatures have been calculated to gain a deeper insight of the thermal characteristics of the title compound. ^1H NMR chemical shifts also have been assigned with the help of calculated and experimental findings.

2. Experimental and computational methods

2.1. Sample and instrumentation

Pure 5-(4-Pyridinyl)-1,3,4-thiadiazol-2-amine (PTA) 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 FT-IR spectrum of the title compound was recorded using Perkin Elmer spectrometer (version 10.03.06) in the region 4000–400 cm^{-1} using KBr pellet method. The FT-Raman spectrum in the region 4000–100 cm^{-1} with a spectral resolution of 0.9 cm^{-1} was recorded on Planer RAME model of Planer RAM micro Raman systems. A 532 nm laser line of single longitudinal mode diode-pumped solid state (SLM-DPSS) laser was used as the exciting wavelength. The UV absorption spectrum of PTA was examined in the range 500–200 nm using the JASCO UV V-670, UV-VIS recording spectrometer. The UV pattern was taken from a 10^{-5} M solution of PTA, dissolved in methanol. All the spectral measurements have been performed at the Indian Institute of Technology, Kanpur.

2.2. Computational details

Density functional theory [20] using B3LYP [21–23] and M06-2X [24] functionals with polarized triple-zeta 6-311++G(d,p) has been used for obtaining the ground state structure and calculation of vibrational wavenumbers. The exceedingly popular B3LYP (Becke, three-parameter, Lee-Yang-Parr) exchange-correlation functional, mixes a certain amount of the exact Hartree–Fock exchange energy into the exchange and correlation obtained from other functionals. The M06 suites of functional are meta-hybrid GGA DFT functional fabricated with empirical fitting of their parameters, but restraining to concept of the uniform electron gas. The suite has a very good response under dispersion forces, and thus fixing one of the biggest deficiencies in DFT methods. The M06-2X, functional is one of the best functional for the study of non-covalent interactions. All calculations in this study have been performed with the Gaussian 09 program package [25] and results are analyzed with the Gaussview 5.0 molecular visualization program [26]. Possible conformers of the title compound have been determined from the potential energy scan at DFT/B3LYP/6-311++G(d,p) level, by varying the N4–C5–C6–C11 and N3–C2–N12–H17 dihedral angles. 3-D Potential energy surface showing the variation of dihedral angles and their corresponding energies are given in Fig. 1(a) and thus obtained stable conformers of the title molecule are shown in Fig. 1(b). Calculated energies of four conformers (Table 1), indicates the conformer B is the most stable one. Due to small energy difference between the conformers, it was essential to confirm the

relative stability, which has been done at G2MP2 level. Geometrical structure corresponding to the lowest minima in the potential energy surface (conformer B in Fig. 1)(b) has been used as input for optimizing the structure at B3LYP and M06-2X functionals and for the calculation of vibrational wavenumbers. As X-ray crystallographic data of the compound is not available optimized parameters of the title compound are compared with experimental data of the compound with similar structure [15]. Positive value of all the calculated wavenumbers settles 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} [27,28] was used to offset the systematic errors caused by basis set incompleteness and vibrational anharmonicity [29]. 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 T. Sundius [30–32]. The Raman activities (S_i) provided with the Gaussian output were subsequently converted to relative Raman intensities (I_i) using the relationship derived from the basic theory of Raman scattering [33,34]. The calculated Raman and IR spectra were plotted using the pure Lorentzian band shape with a band width of FWHM of 5 cm^{-1} . The theoretical UV–Vis spectrum has been computed by TDDFT method, using 6-311++G(d,p) basis set for gas phase and the solvent effect also has been taken into consideration by implementing IEFPCM model at the same level of theory. IEFPCM is integral equation formalism (IEF) version of the polarizable continuum model (PCM). In this method solute cavity is created via a set of overlapping spheres. The optimized geometry has also been used to calculate dipole moment, mean polarizability and first static hyperpolarizability based on the finite field approach. Frequency-dependent first hyperpolarizability $\beta(-2\omega;\omega,\omega)$ for the second harmonic generation (SHG) were also calculated by couple-perturbed (CP) DFT method with B3LYP functional, at the same basis set, used to calculate static β_{tot} .

Natural bonding orbital (NBO) calculations [35] were performed 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 hyper conjugation or intramolecular delocalization. The second order perturbation theory analysis of Fock matrix in NBO basis, was carried out to evaluate the donor-acceptor interactions. For each donor (i) and acceptor (j), the stabilization energy E^2 associated with the delocalization $i \rightarrow j$ is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

Where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements and $F(i,j)$ is the off diagonal NBO Fock matrix element. NBO analysis provides a detailed insight into the electronic structure of a system namely–electronic density distribution on atoms, electronic conjugation between the bonds, hybridization as well as binding affinity towards a system.

3. Results and discussion

3.1. Molecular geometry and PES scan studies

Conformational search for the title compound has been performed through potential energy surface (PES) scan at DFT/B3LYP/6-311++G(d,p) level of theory by varying dihedral angles N4–C5–C6–C11 and N3–C2–N12–H17 in steps of 10° from -180° to 180° and all the geometrical parameters were simultaneously relaxed during the scan except the two selected dihedral angles. Dihedral angle N4–C5–C6–C11 and N3–C2–N12–H17 are the

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