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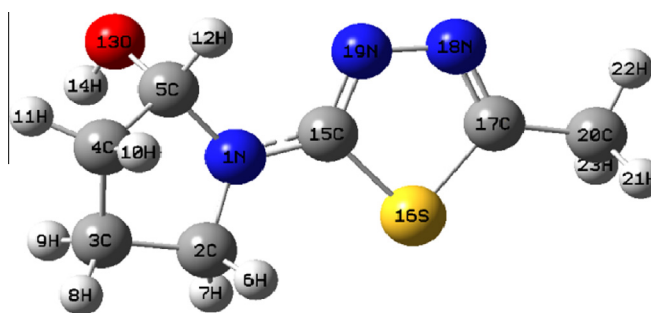
Structural and vibrational studies on 1-(5-methyl-[1,3,4]thiadiazol-2-yl)-pyrrolidin-2-ol

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HIGHLIGHTS

- FT-IR and FT-Raman spectral studies.
- Total energy distribution analysis.
- Prediction of hyperpolarizability.
- Determination of band gap energy.
- Molecular electrostatic potential.

GRAPHICAL ABSTRACT



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ABSTRACT

FT-Raman and FT-IR spectra were recorded for 1-(5-methyl-[1,3,4]thiadiazol-2-yl)-pyrrolidin-2-ol (MTPN) sample in solid state. The equilibrium geometries, harmonic vibrational frequencies, IR and the Raman scattering intensities were computed using DFT/6-311++G (d,p) level. Results obtained at this level of theory were used for a detailed interpretation of the IR and Raman spectra, based on the TED of the normal modes. Molecular parameters such as bond lengths, bond angles and dihedral angles were calculated. The intra-molecular charge transfer was calculated by means of NBO. Hyperconjugative interaction energy was more during the $\pi-\pi^*$ transition. Energy gap of the molecule has been found using HOMO and LUMO calculation, hence the less band gap, which seems to be more stable.

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1. Introduction

In the last few decades, there is tremendous growth in the development of antimicrobial drugs. However, investigation and development of the resistance against the antimicrobials is at an alarming stage. Thiadiazole is a five membered heterocyclic compound that shows various types of biological activities. It contains

two nitrogen atoms and one sulfur atom as hetero atoms. Heterocyclic nucleus 1,3,4-thiadiazole constitutes an important class of compounds for the development of new drugs. The synthesis of novel thiadiazole derivatives and investigation of their chemical and biological behavior have gained more importance in recent decades. During recent years, an intense investigation of different classes of thiadiazole compounds in many of which are known to possess vast biological properties such as antimicrobial [1], anti-tuberculosis [2,3], anti-inflammatory [4,5], analgesic [6], anticonvulsant [7], antihypertensive [8], antioxidant [9] anticancer [10,11],

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antifungal [12,13], antiviral [14], antidepressant [15], antibacterial [16–18] and antitumour [19]. Thiadiazole become very important compound in medicine, agriculture, and many fields of technology. A larger number of 1,3,4-thiadiazole have been patent in the fields of agriculture as herbicides and bactericides [20].

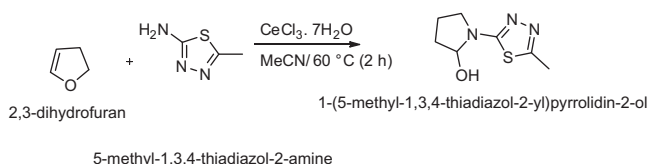
Pyrrolidine and its derivatives are widely used in agrochemicals, photographic chemicals, corrosion inhibitors and used as curing agent for epoxyresins and acted as a catalyst in the manufacture of polyurethane [21–24]. Literature survey shows that, many biologically active alkaloids are possessing pyrrolidine ring system [25,26]. Procyclidine is a drug, which is derivative of pyrrolidine, used for the treatment of dystonia and also used as anti-cholinergic drug [27]. Bepridil is an another derivative of pyrrolidine, used as calcium channel Blocker (CCB) drug [28,29]. The hydroxy substituted pyrrolidines have been reported as anti-cancer drugs [30–32]. Further, Pyrrolidine derivatives employed as organo-catalysts for many chemical reactions [33–35].

Literature survey reveals that, the study on thiadiazole fusing with pyrrolidin has been carried out vastly in the field of biological studies. In view of the remarkable considerations, an attempt has been made to synthesis 1-(5-methyl-1,3,4-thiadiazol-2-yl)pyrrolidine-2-ol (MTPN). Suresh et al. [36] have reported the synthesize and characterization of 2-hydroxy pyrrolidine and 2-hydroxy piperidine derivatives using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst. In the present study, we have synthesized the title compound (MTPN) using $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ as catalyst and our focus is to study the geometry, vibrational behavior and intra-molecular charge transfer analysis.

2. Experimental details

2.1. Synthesis

The 10 ml solution of 5-methyl-1,3,4-thiadiazol-2-amine (1.84 g, 0.0159 mol) in acetonitrile was taken in a round bottom flask and 2,3-dihydrofuran (0.75 ml, 0.0142 mol) was added with ceriumchloride heptahydrate (1.86 g, 0.5 mol). The reaction mixture was taken in an oil bath with continuous stirring and kept at 60 °C for 2 h. The crude mass obtained was purified by column Chromatography using ethyl acetate. The purified sample was dried over in a vaccum and recrystallized from ethanol. (Yield 95%, melting point 167–169 °C.)



2.2. FT-IR, FT-Raman and UV-Visible details

The FT-IR spectrum of MTPN was recorded in the region of 400–4000 cm^{-1} on an IFS 66V spectrophotometer using the KBr pellet technique. The spectrum was recorded in room temperature with a scanning speed of 10 cm^{-1} per minute at the spectral resolution of 2.0 cm^{-1} in the SAIF Laboratory, IIT(M), Tamilnadu, India. The FT-Raman spectrum of the title compound was recorded by using the 1064 nm line of a Nd:YAG laser as an excitation wavelength in the region of 50–3500 cm^{-1} on Bruker model IFS 66V spectrophotometer equipped with an FRA 106 FT-Raman module accessory at the spectral resolution of 4 cm^{-1} . The FT-Raman spectrum was recorded from the SAIF Laboratory, IIT(M), Tamilnadu, India. The ultraviolet absorption spectrum of MTPN was recorded in the range of 200–500 nm by using a Perkin

Elmer Lambda-35 spectrometer and UV pattern was taken from a 10^{-5} molar solution of MTPN dissolved in methanol.

3. Computational details

In order to establish the stable possible conformers, the conformational space of MTPN compound was scanned with molecular mechanic simulations. For meeting the requirements of accuracy and computing economy, theoretical methods and basis sets were considered. The Density Functional Theory (DFT) has been proved to be extremely useful in treating electronic structure of molecules. The entire calculations were performed at B3LYP/6-311++G (d,p) level of basis set using Gaussian 03W [37] program package, invoking gradient geometry optimization [37,38]. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all the stationary points as minima. The vibrationally averaged nuclear positions of MTPN were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The vibrational modes were assigned on the basis of TED analysis using the Scaled quantum mechanical program [39].

The Raman activity was calculated by using Gaussian 03W package and the activity was transformed into Raman intensity using Raint program [40] by the expression:

$$I_i = 10^{-12} \times (v_0 - v_i)^4 \times \frac{1}{v_i} \times RA_i \quad (1)$$

where I_i is the Raman intensity, RA_i is the Raman scattering activity, v_i is the wavenumber of the normal modes and v_0 denotes the wavenumber of the excitation laser [41].

4. Results and discussion

4.1. Molecular geometry

The optimized geometrical parameters of MTPN calculated by B3LYP level with 6-311++G (d,p) basis set are listed in Table 1, which are in accordance with the atom numbering scheme is shown in Fig. 1. The molecular structure is non-planar with the dihedral angle between the planes of the thiadiazol and pyrrolidin ring. The dihedral angles of $\text{C}_5\text{—N}_1\text{—C}_{15}\text{—S}_{16}$ and $\text{C}_2\text{—N}_1\text{—C}_{15}\text{—N}_{19}$ are 174.69° and –166.39° respectively. So the difference between the two dihedral angles of the adjacent rings is ~8° and hence two rings are non-planar. Kohata et al. [42] reported the N–N bond length of hydrazine at 1.449 Å and for tetramethyl hydrazine reported by Naumo et al. [43] at 1.401 Å. In this study, the $\text{N}_{18}\text{—N}_{19}$ bond length is 1.369 Å, which is nearly in agreement with above literature.

The C–N bonds of MTPN have different bond lengths: viz. $\text{C}_{15}\text{—N}_1$ (1.365 Å), $\text{C}_5\text{—N}_1$ (1.470 Å), $\text{C}_2\text{—N}_1$ (1.467 Å). Similarly the C=N bond distances are also differ by ~0.013 Å ($\text{C}_{17}\text{=N}_{18}$: 1.296 Å and $\text{C}_{15}\text{=N}_{19}$: 1.309 Å). These deviations may be due to the conjugation occurring in the ring. The bond distances of $\text{S}_{16}\text{—C}_{17}$ and $\text{S}_{16}\text{—C}_{15}$ are calculated as 1.776 and 1.772 Å, respectively. The C–C bond distance usually observed as ~1.400 Å. In the present investigation, the C–C bond lengths are $\text{C}_2\text{—C}_3$ (1.536 Å), $\text{C}_3\text{—C}_4$ (1.537 Å), $\text{C}_4\text{—C}_5$ (1.540 Å) and $\text{C}_{17}\text{—C}_{20}$ (1.495 Å), which was slightly higher than the normal C–C bond length, due to ring strain and may be hetero atom present in the ring. It is evident from the Table 1, that the $\text{C}_{17}\text{C}_{20}\text{H}_{22}$ bond angle (108.05°) is negatively deviated (3.64°) from $\text{C}_{17}\text{C}_{20}\text{H}_{21}/\text{H}_{22}$ bond angles. This may be due to presence of N_{18} atom as the nearest neighbour for H_{22} atom. The bond angles are found to be within the expected range. The difference of dihedral angles may be

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