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## A study of the molecular, vibrational, electronic and quantum chemical investigation of 2-methyl-1-vinylimidazole



R. John Xavier\*, P. Dinesh

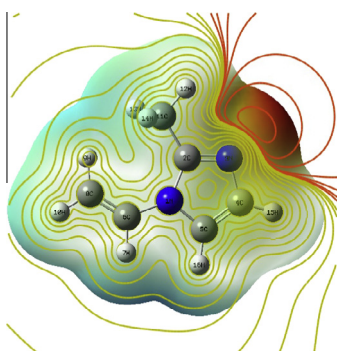
Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli 620 023, India

### HIGHLIGHTS

- The FT-IR and FT-Raman spectra of 1-methyl-2-imidazolethiol have been recorded.
- The temperature dependence of the thermodynamic properties was investigated.
- The atomic charges and charge delocalization of the molecule have been analysed.
- The reactivity sites have been identified by MESP analysis.
- NMR spectra have been investigated.

### GRAPHICAL ABSTRACT

The spectroscopic properties of the title compound 2-methyl-1-vinylimidazole (2M1VIM) led to the complete FT-IR and FT-Raman vibrational studies, calculation of HOMO–LUMO, NBO analysis and molecular electrostatic potential (2M1VIM). The temperature dependence of thermodynamic properties has been analysed. The values of the total dipole moment ( $\mu$ ) and the first order hyperpolarizability ( $\beta$ ) of the investigated compound were computed using B3LYP/6-311++G(d,p) calculations. The  $^{13}\text{C}$  and  $^1\text{H}$  nuclear magnetic resonance (NMR) chemical shifts of the molecule have been recorded.



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### ABSTRACT

The spectroscopic properties of 2-methyl-1-vinylimidazole (abbreviated as 2M1VIM) were examined by FT-IR, FT-Raman and NMR techniques. FT-IR and FT-Raman spectra were recorded in the region 4000–400  $\text{cm}^{-1}$  and 3500–50  $\text{cm}^{-1}$ , respectively. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$ . The structural and spectroscopic data of the molecule in the ground state were calculated by using density functional theory (DFT) employing B3LYP and LSDA methods with 6-311++G(d,p) basis set. The geometry of the molecule was fully optimized, vibrational spectra were calculated and fundamental vibration were assigned on the basis of potential energy distribution (PED) of the vibrational modes calculated with scaled quantum mechanical (SQM) method. The optimized structure of the compound was interpreted and compared with the reported experimental values. The observed vibrational wave numbers, absorption wavelengths and chemical shifts were compared with calculated values. The calculated HOMO and LUMO energies show that charge transfer occur within the molecule. As a result, the optimized geometry, and calculated spectroscopic data show a good agreement with the experimental results.

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\* Corresponding author. Tel.: +91 431 2780286.

E-mail address: [rj\\_xavier@yahoo.com](mailto:rj_xavier@yahoo.com) (R. John Xavier).

## Introduction

Vinylimidazoles are an important class of heterocyclic compounds and their biological activities have been investigated extensively [1–3]. Imidazole containing macromolecules have been suggested as carrying an active moiety of several electrolytic enzymes. Imidazole is an excellent electron donor (D), imidazoles also act as building block of many biologically relevant molecules and present in histidine, which plays a vital part in the structure and binding functions of hemoglobin. In nature, the imidazole ring of histidine is reversibly protonated and deprotonated on alteration of the tyrosine redox state. It can strongly interact with a variety of electron acceptors and a form charge transfer complexes with them. Imidazole and its derivatives are widely used as intermediates in synthesis of organic compounds including pharmaceuticals, agrochemicals, dyes, photographic chemicals, corrosion inhibitors, epoxy curing agents, adhesives and plastic modifiers [4,5]. The imidazole ring is present in most proteins (i.e. histamine, histidine, etc.,) and is responsible for their catalytic activity. Consequently, extensive studies of the catalytic behaviours of monomeric [6] and polymeric [7] imidazole have been reported. Poly N-vinylimidazole copolymer coatings has been shown to have good corrosion protection and adhesion promotion capabilities for copper substrate in severe environments [8,9]. Several theoretical investigations have been devoted to imidazoles covering their geometry, energetics, tautomer equilibrium and protonation enthalpies [10–20] involving *ab initio* [10,11,13,15–18], DFT [11,13] and semi empirical methods [10,12,13,15,20,21]. However, the structure and vibrational assignments using *ab initio*/DFT calculations have not been investigated for 2-methyl-1-vinylimidazole (2M1VIM). Therefore, in the present study FT-IR spectral measurement and DFT electronic structure calculations of 2M1VIM have been undertaken to provide a detailed spectroscopic and electronic structure properties.

## Experimental details

The compound 2-methyl-1-vinylimidazole in liquid state with a stated purity of 99% was purchased and it was used as such without further purification. The mid infrared spectrum of the compound was recorded between 4000 and 400  $\text{cm}^{-1}$  on a BRUKER IFS 66V model FT-IR Spectrophotometer. A KBr beam splitter and liquid nitrogen cooled MCT detector were used to collect the mid-infrared spectra. The FT-Raman spectra of 2M1VIM were recorded on a computer interfaced BRUKER IFS 66V model interferometer equipped with FRA-106 FT-Raman accessories. The spectra were recorded in Stokes region 3500–50  $\text{cm}^{-1}$  using ND:YAG laser operating at 200 mW power continuously with 1064 nm excitation. The reported wavenumbers are expected to be accurate within  $\pm 1 \text{ cm}^{-1}$ . The spectral resolution is 2  $\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) (400 MHz;  $\text{CDCl}_3$ ) spectra were recorded on a BRUKER HC400 instrument. The chemical shifts for protons are reported in parts per million (ppm) scales (scale) downfield from tetramethylsilane.

## Computational details

The combination of spectroscopic methods with DFT calculations are powerful tools for understanding the fundamental vibrations and the electronic structure of the compound. The density functional theory (DFT) algorithm was used in the calculation and all the calculations in this work were performed by using GAUSSIAN 09W software package [22]. The structural characteristics, stability, thermodynamic properties and energy of 2M1VIM are determined by DFT [23,24] with the Becke's three-parameter

hybrid functional (B3) [25,26] for the exchange part and the Lee–Yang–Parr (LYP) correlational functional [27], using basis set 6-311++G(d,p) augmented by “d” polarization functions on heavy atoms and “p” polarization function on hydrogen atoms were used [28,29]. Entire thermodynamic properties namely the SCF energy, total thermal energy, heat capacity at constant volume and entropy of 2M1VIM were calculated by B3LYP method using 6-311++G(d,p) basis set.

The isotropic chemical shifts are frequently used as aid in identification of organic compounds and accurate predictions molecular geometrics are essential for reliable studies of magnetic properties. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR isotropic shielding were calculated with the Gauge invariant atomic orbital (GIAO) method using the optimized parameters obtained from B3LYP/6-311++G(d,p) method. The effect of  $\text{CDCl}_3$  on the theoretical NMR parameters was included using integral equation formalism polarizable continuum model (IEFPCM) method. In IEFPCM, one divides the problem into a solute part lying inside a cavity, and a solvent part represented as structure less material, characterized by its dielectric constant as well as other macroscopic parameters.

Additionally, the electronic properties such as HOMO and LUMO energy values and energy gap for 2M1VIM were calculated by using B3LYP method 6-311++G(d,p) basis set. Furthermore, molecular electrostatic potentials (MEPs) of 2M1VIM were plotted in 3D by using optimized structures at B3LYP/6-311++G(d,p) level. Natural charges were determined by NBO analysis of with B3LYP/6-311++G(d,p) method.

## Results and discussion

### Structural parameters

Before computing the frequencies and electronic properties, it is necessary to analyses the molecular structure of the studied molecule. So that the structure is optimized at DFT level of theory and atomic numbering scheme of the title compound is given in Fig. 1. The calculated structural parameters containing bond lengths and bond angles using B3LYP and LSDA methods with 6-311++G(d,p) basis set are listed in Table 1 along with the available XRD for 2M1VIM.

As shown in Table 1, the theoretical values of optimized parameters, it is found that most of the optimized bond lengths are slightly larger than the experimental values and the bond angles are also slightly different from the experimental one. Taking into account that the molecular geometry in the vapour phase may be different from in the solid phase, owing to extended hydrogen bonding and stacking interactions there is responsible agreement between the calculated and experimental geometric parameters. It is observed that the C–N (ring) bond distances calculated for 2M1VIM are well agreed with experimental values as 1.344, 1.379, 1.326, and 1.347 Å respectively.

The C–C bonds for the title molecules are about equal to the experimental values. These bond lengths C4–C5 and C6–C8 were calculated 1.362, 1.364 and 1.331, 1.330 Å respectively at B3LYP and LSDA with 6-311++G(d,p) basis set respectively. Experimental values of C–C are 1.361 Å.

The optimized C–H bond lengths were calculated at 1.08 Å and 1.09 Å, respectively, using B3LYP and LSDA methods respectively. This calculated bond lengths show very good correlation with structurally similar molecule [30]. The C–N–C, N–C–N, and N–C–C bond angles are slightly higher than the experimental value. The determined structural parameters of the title compound well correlated with the X-ray data of imidazole derivative [30].

Although the theoretical configuration are not exactly close to the XRD values for the studied compound, they are generally

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