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Vibrational spectroscopic investigations of 4,4-dimethyl-2-oxazoline: A density functional theory approach



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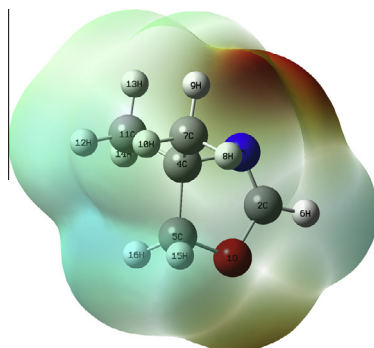
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HIGHLIGHTS

- Vibrational spectra were examined via FT-IR, FT-Raman and DFT calculations.
- Thermodynamic properties such as heat capacity, entropy and enthalpy were gauged against a range of temperature.
- The magnetic susceptibility for various temperatures are predicted.
- The electronic structure attributes were examined by means of NBO, HOMO, LUMO and MEP.

GRAPHICAL ABSTRACT

The FT-IR (4000–400 cm^{-1}) and FT-Raman (3500–100 cm^{-1}) spectra in the liquid phase were recorded for 4,4-dimethyl-2-oxazoline (abbreviated as DMOZ). The structure of the compound was optimized and quantum chemical calculations of energies, geometric parameters (bond lengths and bond angles) and vibrational wavenumbers of DMOZ were carried out using DFT/B3LYP method with 6-311++G(d,p) basis set. The molecular electrostatic potential (MEP) map showed the electrophilic and nucleophilic region of the molecule by means of various color representation.



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ABSTRACT

The spectroscopic properties were investigated by FT-IR, FT-Raman and ^1H and ^{13}C nuclear magnetic resonance (NMR) techniques. The FT-IR (4000–400 cm^{-1}) and FT-Raman (3500–100 cm^{-1}) spectra in the liquid phase were recorded for 4,4-dimethyl-2-oxazoline (abbreviated as DMOZ). The ^1H and ^{13}C NMR spectra were recorded and chemical shifts were calculated by using the gauge independent atomic orbital (GIAO) technique with DFT/B3LYP/6-311++G(d,p) basis set and compared with experimental results. The structure of the compound was optimized and quantum chemical calculations of energies, geometric parameters (bond lengths and bond angles) and vibrational wavenumbers of DMOZ were carried out using DFT/B3LYP method with 6-311++G(d,p) basis set. Temperature dependence thermodynamic parameters and magnetic properties of the title compound have been analyzed. The dipole moment (μ), polarizability ($\bar{\alpha}$), anisotropy polarizability (γ^2) and hyperpolarizability (β_{tot}) of the molecule have been reported. Stability of the molecule arising from hyper conjugative interactions and charge delocalization has been analyzed using natural bond orbital (NBO) analysis. The energy and oscillator strength were calculated using absorption spectra (UV–Vis spectrum), this spectral analysis confirms the charge transfer of the molecule. A study on the electronic properties, such as HOMO and LUMO energies, molecular electrostatic potential (MEP) were also performed.

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Introduction

Oxazolines are known as important heterocyclic compounds and have been found to have numerous applications in organic synthesis. The efficiency of oxazoline analogues as chemotherapeutic agent especially as analgesic and anti-inflammatory agent is well documented. Besides, additional functionalities can readily be introduced into 2-oxazolines via functional monomers units and these compounds fulfil fundamental requirements for an application as carrier molecules in radionuclide therapy. Recent studies have shown that highly active sugar oxazoline act as donor substrates for transglycosylation and exhibit potent anti-HIV activity [1–5]. Oxazoline analogues have also been shown to induce cell growth inhibition, apoptosis, and microtubule disruption without alkylating beta-tubulin [6]. Polyoxazoline based polymers have shown biological and biomedical application contexts which include nanoscale systems such as membranes and nanoparticles, drug and gene delivery application, as well as stimuli responsive systems [7].

The popularity of this ring system in organic synthesis has grown due to the well-understood chemical behavior. The use of oxazolines in directed metalation reactions to construct complex molecules or as protecting groups is ubiquitous throughout the literature. Oxazolines are found in many microbial metal chelators such as vibriobactin, mycobactin and parabactin [8–10]. Chiral oxazolines, readily accessible from a large pool of chiral amino alcohols, have been widely employed as auxiliaries in asymmetric syntheses [11–13]. For example, an important extension in the area of aromatic substitution of aryloxazolines is the development of symmetrical, unsymmetrical and axially chiral biaryl synthesis. Similarly, oxazoline-directed nucleophilic additions to naphthalenes as a synthetic method for the preparation of dihydronaphthalenes have also expanded to include asymmetric versions with excellent stereochemical controls. Another significant development in oxazoline chemistry is the application of oxazoline-containing ligands for asymmetric catalysis, such as palladium-catalyzed allylic substitutions, Heck reactions, hydrogenations, dialkylzinc additions to aldehydes, and Michael reactions. The discovery of diastereoselective metalation of chiral ferrocenyloxazolines has further expanded the availability of chiral ligands for metal-catalytic reactions [14].

Oxazoline compounds are well-known for their properties of corrosion inhibition. These compounds find wide application as additives in the formulation of lubricants, motor oil, hydraulic fluids, cutting fluids and numerous other oil products. They can also be utilized as secondary emulsifiers or particulate dispersants [15–25]. Further explorations in these areas of oxazoline chemistry will undoubtedly continue and the list of new applications will grow.

The main application of 4,4-dimethyl-2-oxazoline (DMOZ) of fatty acids as useful derivatives for mass spectrometric analysis. The properties of these derivatives that are the basis for their widespread use include stable chromatographic behavior, high volatility, intense ion current and formation of relatively simple mass spectra [26–28]. It is well known that vibrational spectroscopy is an efficient tool for the characterization of crystalline materials. It is effectively used to identify functional groups and determining the molecular structure of any material. It can also provide deeper knowledge about the relationships between molecular architecture, nonlinear response, hyperpolarizability and support the efforts toward discovery of new efficient materials of technological applications. The combination of Infrared Fourier transformation and Raman spectroscopy with quantum chemical computations have been used as effective tools in the vibrational analysis of complex molecular systems. The natural bond orbital (NBO) analysis

can be employed to identify and substantiate the possible intra and intermolecular interactions between the units that would form the H-bonded network. On the other hand, the literature survey reveals that to the best of our knowledge, no density functional theory (DFT) studies on the vibrational and electronic spectra of 4,4-dimethyl-2-oxazoline (DMOZ) have not been carried out. Thus, in the present investigation, owing to the industrial and biological importance of oxazoline, motivated us to do an experimental and theoretical studies of 4,4-dimethyl-2-oxazoline (DMOZ) have been undertaken by recording their FT-IR and FT-Raman spectra. For the proper assignment of the vibrational fundamentals and to understand the effect of dimethyl group on the characteristic frequencies of the oxazoline ring, normal coordinate analysis (NCA) were carried out.

Experimental methods

The compound 4,4-dimethyl-2-oxazoline (DMOZ) in liquid state with a stated purity of 99% were purchased and it was used as such without further purification. The Fourier transform infrared spectrum (FT-IR) of the title compound is recorded in the wavenumber region 4000–400 cm^{-1} on a NEXUS 670 spectrophotometer equipped with an MCT detector in a KBr pellet technique. The FT-Raman spectrum is recorded in the wavenumber region 3500–100 cm^{-1} on a NEXUS 670 spectrophotometer equipped with Raman module accessory operating at 1.5 W power with Nd:YAG laser of wavelength 1064 nm is used as an excitation source. The ^1H and ^{13}C nuclear magnetic resonance (NMR) (400 MHz; CDCl_3) spectra were recorded on a BRUKER HC400 instrument. The chemical shifts for protons are reported in parts per million (ppm) scales downfield from tetramethylsilane.

Computational details

Quantum chemical calculations were mainly carried out by using density functional method (DFT) [29], since they provide a very good overall description of medium-sized molecules. Moreover, for the wave number calculations [30–32] they appear more accurate than HF and MP2 [33] and at lower computational cost. Geometry optimization, an important issue in molecular mechanics, was performed as the first task of the computational work for the DMOZ molecule. It requires in particular the sensitivity of the interaction energy with respect to the change of the molecule's shape which is in general induced by the movement of the nuclei positions. The optimized ground state molecular structure is shown in Fig. 1. The molecular structure, vibrational frequencies and energies of the optimized geometries of DMOZ were computed by DFT using Gaussian 09W [34] software and the default fine integration grid was applied, the B3LYP method which is simply combinations of the correlation functional of Lee, Yang and Parr (LYP) [35] were employed using 6-311++G(d,p) basis set. This basis set 6-311++G(d,p) augmented by 'd' polarization functions on heavy atoms and 'p' polarization functions on hydrogen atoms as well as diffuse functions for both hydrogen and heavy atoms were used [36,37]. The absolute Raman intensities and IR absorption intensities were calculated in the harmonic approximation at the same level of theory as used for the optimized geometries associated with each normal mode, respectively. The normal mode analysis was performed and the potential energy distribution (PED) was calculated along the internal coordinates using localized symmetry.

The vibrational modes were assigned by means of visual inspection using GAUSSVIEW program [38]. The vibrational mode analysis of DMOZ is presented in some detail in order to better describe

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