



Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

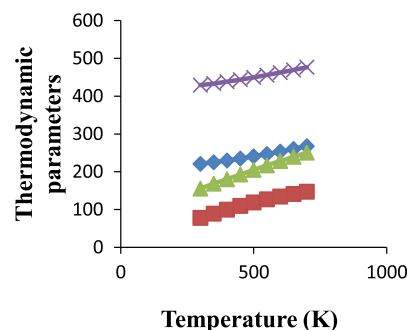
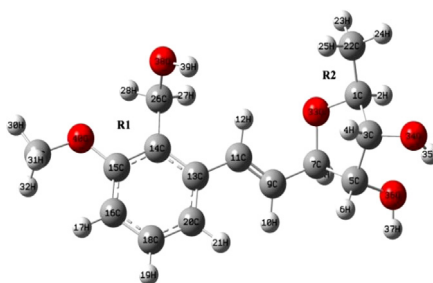
Determination of geometrical, spectroscopic, thermal and nonlinear optical parameters of (+)-Varitriol by DFT/*ab initio* calculations

V. Vasantha Kumar^a, M. Nagabhushanam^{a,*}, J. Laxmikanth Rao^{b,*}^a Department of Physics, University College of Science, Osmania University, Hyderabad 500 007, Andhra Pradesh, India^b I&PC Division, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, Andhra Pradesh, India

HIGHLIGHTS

- Computational studies on (+)-Varitriol have been carried out using *ab initio* and DFT methods.
- Vibrational frequencies obtained from B3LYP method are in good agreement with the experiment.
- The complete assignments are performed on the basis of the potential energy distribution (PED).
- Thermodynamic and nonlinear optical properties have been calculated and reported.
- Effect of temperature on various thermodynamic properties have been calculated and reported.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 February 2013

Received in revised form 10 June 2013

Accepted 17 June 2013

Available online 11 July 2013

Keywords:

(+)-Varitriol

FT-IR spectra

Micro-Raman spectra

DFT calculations

Hyperpolarizability

Thermodynamic properties

ABSTRACT

Theoretical studies have been carried out on (+)-Varitriol using both the B3LYP/6-311+G and HF/6-311+G methods. The vibrational spectra of the title molecule have been recorded in solid state with FT-IR and Micro-Raman spectrometry. The calculated geometrical parameters of the title molecule, like bond length, bond angle and dihedral angles have been compared with the experimental data. The spectral frequencies have been calculated theoretically using both the above mentioned methods and are compared with the observed spectra. The complete vibrational assignments of wavenumbers have been made on the basis of potential energy distribution (PED). From this analysis, it is seen that the vibrational frequencies obtained from B3LYP method are in good agreement with the experiment, when compared to HF method. Nonlinear optical properties like dipole moment, hyperpolarizabilities and thermal properties like rotational constants, zero point vibrational energies are calculated. The effect of temperature on various thermodynamic properties have been calculated and reported.

© 2013 Elsevier B.V. All rights reserved.

Introduction

Fungi isolated from the marine environment plays an important role in large number of biological properties. During their lifespan, fungi metabolize and produce a broad range of organic compounds, from simple to very complex in nature. Among them, (+)-Varitriol (**1**) a tetrahydrofuran derivative, isolated from the marine derive

strain of the fungus *Emericella varicolor* and is a potent cytotoxic in nature [1]. Barrero et al reported the isolation and structure elucidation of (+)-Varitriol [2]. The cytotoxic activity showed by **1** is more than 100-fold increased in potency towards the renal, breast and CNS cancer where it is lower in potency against leukemia, prostate, ovarian and colon cancer cell lines [2]. Due to its fascinating biological activity towards cancer, it is very interesting to study the geometrical, vibrational, thermal and nonlinear optical properties of the title molecule. Density functional theory (DFT) is becoming more useful to experimentalists in computing the geometrical

* Corresponding authors.

E-mail address: lkjoshiji@yahoo.com (J. Laxmikanth Rao).

parameters and other properties like vibrational, thermal, nonlinear, optical etc. of polyatomic molecules [3]. In the present study the geometrical parameters and spectral investigations (like FT-IR and Micro-Raman) of **1**, have been carried theoretically using DFT and *ab initio* methods for the first time. The spectral investigation have been carried out using the standard techniques. The calculated geometrical parameters and vibrational spectra have been compared with the experimentally observed geometrical parameters and spectra respectively. The nonlinear optical (NLO) properties (like dipole moment, polarizability, mean polarizability, first hyperpolarizability and total polarizability) and thermodynamic properties (like total energy (E_{tot}), heat capacities (C_v) entropy (S) and total thermal energy (C_{tot}), rotational constants (r_c) and rotational temperatures (r_T)) have been calculated and reported. The calculated geometrical parameters have been compared with the existing crystal data. The effect of temperature on some thermodynamic properties at various temperatures have been calculated and reported.

Experimental details

The title molecule has been synthesized previously [4,5] and the crystal structure determination has been carried out by Palík et al. [5]. The FT-IR spectrum of **1** was recorded on Nicolet Nexus 670 FT-IR spectrometer with resolution 4 cm^{-1} . The Micro-Raman spectrum of **1** was recorded using HORBIA Jobin Yvon LabRAM HR spectrometer with 17 mW internal He–Ne laser source.

Computational details

The geometry optimization of the molecule plays an important role in the predicting the geometrical, thermal, spectral and NLO properties, since these are controlled by the geometry of the molecule. The spatial coordinates of **1** are considered from the literature [5] and are used as the initial coordinates for geometrical optimization. In order to arrive at the minimum energy conformer of the title molecule, we have scanned the total energy by varying both the dihedral angles namely 20C–13C–11C–9C (R1 moiety) and 33O–7C–9C–11C (R2 moiety) simultaneously by constraining in 30° increments (from 0° to 180°), followed by re-optimizing all remaining parameters using B3LYP method. The energies of all the conformers are compared and a minimum energy conformer, is chosen for carrying out further studies. To select a suitable basis set for **1**, the geometry optimization and vibrational frequency analysis have been carried out using different basis sets (like 6-31G, 6-311G, 6-31G* and 6-311+G) with both the B3LYP and HF methods with Gaussian 03W software [6]. Among all these basis sets, the geometrical parameters (like bond lengths, bond angles and dihedral angles) and the vibrational frequencies calculated using the 6-311+G basis set is in good agreement with the experiment [5]. In addition to this, the mean absolute deviation (MAD) values for the vibrational frequencies [7,8] have been calculated using same methodology using different basis sets. Here also it has been observed that the MAD values calculated by using the 6-311+G basis set have shown less deviation when compared to the other basis sets. Hence, the 6-311+G basis set has been chosen for carrying out further studies. The optimized geometry of the title molecule is shown in Fig. 1. Frequency calculations have been carried out to ensure that the optimized geometry has all positive frequencies and thus is a minimum on the potential energy surface. The vibrational frequencies for **1** have been calculated using both the methods namely B3LYP/6-311+G and HF/6-311+G and are compared with the experimentally observed IR and Raman spectra. The assignments of the calculated vibrational frequencies have been made by considering the corresponding PEDs. The PEDs are

computed from quantum chemically calculated vibrational frequencies using VEDA program [9]. Gauss View 3.0 program [10] have been used to get visual animation and also for the verification of the vibrational frequency assignments. Thermodynamic and NLO properties have been calculated and reported. The effect of temperature on some thermodynamic parameters have been calculated and reported.

Results and discussions

Geometrical properties

The experimental geometrical parameters of title molecule has been characterized by Palík et al. [5] and the title compound crystallizes in the triclinic space group *P*-1 with the unit cell dimensions: $a = 4.6531\text{ \AA}$, $b = 7.2128\text{ \AA}$, $c = 10.156\text{ \AA}$, $\alpha = 94.2^\circ$, $\beta = 95.1^\circ$, $\gamma = 90.2^\circ$, $Z = 1$ and V (volume) = $338.5\text{ (\AA}^3)$. The geometry optimization has been carried out on the title molecule using B3LYP/6-311+G and HF/6-311+G methods. The calculated geometrical parameters like bond lengths, bond angles and dihedral angles of **1**, using both the methods are shown in Table 1, along with the experimental parameters for the sake of comparison. The molecular geometry of **1** have been described in two parts namely R1 (2-methoxy benzyl alcohol moiety) and R2 (ribose moiety) (Fig. 1). The R1 moiety is linked to R2 moiety via a carbon–carbon double bond and adopts *trans* configuration. All the geometrical parameters calculated from B3LYP and HF methods are in good agreement with the experiment (Table 1). It can be seen from Table 1, that The calculated $\text{C}=\text{C}$ bond length (R(9-11)) in both the B3LYP (1.34 \AA) and HF (1.33 \AA) methods is similar to the experiment (1.34 \AA) [5]. Furthermore it can be seen that the calculated $\text{C}-\text{C}$ bond lengths namely R(1-22), R(1-3) and R(3-5) and $\text{C}-\text{O}$ bond lengths namely R(3-34) and R(3-36) associated with the R2 (ribose) moiety using both the methods are comparable to the observed bond lengths [5,11]. The calculated value of dihedral angle which exist in between the R1 and R2 rings (D(7-9-11-13)) using both the B3LYP (-177.9°) and HF (-179.6°) methods are in good agreement with the experiment (177.3°). It can be seen that there exists a strong intramolecular hydrogen bond in between $35\text{H}\cdots 36\text{O}$ of R2 moiety. The calculated hydrogen bond length using both the B3LYP (2.07 \AA) and HF (2.34 \AA) are comparable to the reported value (1.88 \AA) [5]. In case of calculated dihedral angles, there is a variation in between the B3LYP and HF methods. This may be due to the change in the structural conformers affected by the entropy effect. The entropy effect which arises from the rotational and vibrational contributions to the entropy, which is associated with the molecular conformer which inturn affects the structure of the molecule. Here in case of the **1**, the vibrational contributions are predominant when compared to the rotational contributions. Due to this entropy effect, there may be differences in few dihedral angles of **1**, when compared to the bond angles [7].

Vibrational analysis

The vibrational frequencies of **1** have been calculated using both the methods namely B3LYP and HF using 6-311+G basis set and the results are tabulated in Table 2, along with the experimentally observed IR and Raman frequencies. From these results, it can be observed that the vibrational frequencies calculated using the HF method tends to overestimate the experimentally reported values. In order to improve the calculated values in agreement with the experimental values, a spectral uniform scaling factor is used to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity. Hence, all the vibrational frequencies calculated at HF level are scaled with

Download English Version:

<https://daneshyari.com/en/article/7672504>

Download Persian Version:

<https://daneshyari.com/article/7672504>

[Daneshyari.com](https://daneshyari.com)