Spectrochimica Acta Part A 91 (2012) 248–255

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Density functional theory study on characterization of 3-chloro-1,2-benzisothiazole

R. John Xavier[a,*], E. Gobinath[b]

[a] PG and Research Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli 620 023, India
[b] Department of Physics, Jayaram College of Engineering and Technology, Tiruchirappalli 621 014, India

ARTICLE INFO

Article history:
Received 30 November 2011
Received in revised form 22 January 2012
Accepted 30 January 2012

Keywords:
FT-IR
FT-Raman
HOMO–LUMO
NBO
NLMO
3-Chloro-1,2-benzisothiazole

ABSTRACT

The FT-IR and FT-Raman spectra of 3-chloro-1,2-benzisothiazole (CBT) have been recorded and analyzed. Theoretical information on the optimized geometry, harmonic vibrational frequencies, infrared and Raman intensities were obtained by means of density functional theory (DFT) gradient calculations, using 6-311++G(d,p) basis set. Mulliken population analysis shows charge distribution on the molecule. Thermodynamic properties like entropy, heat capacity, zero point energy have been calculated for the molecule. The calculated HOMO and LUMO energies show the charge transfer occurs within the molecule. Stability of the molecule has been analyzed using Natural Bond Orbital (NBO) and Natural Localized Molecular Orbital (NLMO) analysis. The results of the calculations were applied to simulated spectra of the title compound, which show the excellent agreement with the observed spectra.

1. Introduction

Thiazole and their derivatives are some of the most important heterocyclic compounds. The thiazole ring is notable as a component of the Vitamin Thiamine (B1). Many authors have studied these compounds and their properties, such as antitubercular [1–4] and anti-microbial [5–8] activities. Thiazoles have been known to exhibit biological activities such as bacteriostatic, fungistatic, anti-thrombotic, anti-inflammatory, anesthetic, antihypertensive and sedative. Thiazoles are parent material for numerous of chemical compounds including sulfur drugs, biocides, fungicides and dyes. Thiazole dyes contain the color radicals of =C=N− and −S−C= which decide colors to a compound, and are useful in dying cottons. Mossini et al. [9] have studied the reaction of the title compound 3-chloro-1,2-benzisothiazole (CBT) with diethyl malonate and Carrington et al. [10] have studied the chemical reaction of the title compound with carbanions.

Harmonic force fields of polyatomic molecules play a vital role in the interpretation of vibrational spectra and in the prediction of other vibrational properties. The understanding of their structure, molecular properties as well as the nature of reaction mechanism they undergo have great importance and have been the subject of many experimental and theoretical studies.

The advent of fast computers along with sophisticated computational methods performs the task of solving various structural and chemical problems simple. Ab initio DFT computations have become an efficient tool in the prediction of molecular structure, harmonic force fields, vibrational wavenumbers, IR intensities and Raman activities of biological compounds [11,12]. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. Density functional theory (DFT) approaches, using hybrid functional have evolved into a powerful and very reliable tool, being routinely used for the determination of various molecular properties. B3LYP functional had been previously shown to provide an excellent compromise between accuracy and computational efficiency of vibrational spectra for large and medium size molecules [13–16]. It is well known that vibrational frequencies obtained by quantum chemical calculations are typically larger than their experimental counterparts, and thus, empirical scaling factors are generally used to obtain better experimental frequencies [17]. These scaling factors depend both on the method and basis sets used in calculations and they are determined from the mean deviation between the calculated and experimental frequencies [18,19].

Literature survey reveals that to the best of our knowledge, no ab initio DFT frequency calculations of the title compound CBT have been reported so far. Therefore, the present investigation has been undertaken to study the molecular structure, geometrical parameters, vibrational wavenumbers, modes of vibrations and various thermodynamic properties, and the Natural Bond Orbital (NBO)/Natural Localized Molecular Orbital (NLMO) analysis which

* Corresponding author. Tel.: +91 431 2705674.
E-mail address: rj_xavier@yahoo.com (R.J. Xavier).

1386-1425/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2012.01.083

explains the most important orbital interactions in order to classify general structural features. The Mulliken population analysis and the HOMO–LUMO energies have also been calculated.

2. Experimental details

The fine polycrystalline sample of 3-chloro-1,2-benzisothiazole was purchased from Alfa Aesar Chemical company, UK with a stated purity of 98% and it was used as such without further purification. The room temperature Fourier transform infrared spectra of the title compound was measured in the region 4000–400 cm^{-1} at a resolution of ±1 cm^{-1} using a JASCO FT/IR-6300 spectrometer. KBr pellets were used in the spectral measurements. Boxcar apodization was used for 250 averaged interferograms collector for both the sample and background.

The FT-Raman spectrum of the title compound was recorded on a BRUKER RFS 100/S model interferometer equipped with an FRA-106 FT-Raman accessory in the 3500–500 cm^{-1} stokes region using the 1064 nm line of Nd:YAG laser for excitation, operating at 150 mW power. The reported wave numbers are believed to be accurate within ±4 cm^{-1}.

3. Computational details

The molecular geometry optimizations, calculations of energy, vibrational frequencies, IR intensities and Raman activities were carried out for 3-chlroro-1,2-benzisothiazole (CBT) with the GAUSSIAN 09 software package [20] using DFT/B3LYP functional [21,22] combined with the standard 6-311++G(d,p) basis set. Initial geometry generated from the standard geometrical parameters was minimized without any constraint on the potential energy surface at Hartree-Fock level adopting the standard 6-311++G(d,p) basis set. This geometry was then re-optimized again at DFT level employing the Becke 3LYP keyword, which invokes Becke's three parameter hybrid method [21] using the correlation function of Lee et al. [22] implemented with the same basis set for better description of the bonding properties. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum; as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry. The multiple scaling of the force constants were performed according to SQM procedure [18,23] using relative scaling in the natural internal coordinate representation [24,25]. Transformations of the force field; and the subsequent normal coordinate analysis including the least square refinement of the scaling factors; calculation of the total energy distribution (TED) and the prediction of IR and Raman intensities were done on a PC with the MOLVIB Program (Version V7.0-G77) written by Sundius [26–28].

The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumbers.

3.1. Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN program were subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [29,30],

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 S_i}{[1 - \exp(hc\upsilon_i/k_b T)]\upsilon_i} \quad (1)$$

where υ_0 is the existing frequency in cm^{-1}, υ_i the vibrational wave number of the ith normal mode, h, c and k_b are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities.

4. Results and discussion

4.1. Molecular geometry and structural properties

The first task for the computational work is to determine the optimized geometry of the studied molecule. The molecular structure and numbering of the atoms of CBT are shown in Fig. 1. The global minimum energy obtained by DFT/B3LYP with 6-311++G(d,p) basis set for CBT is calculated as −1182.41957051 Hartrees. The optimized geometrical parameters of CBT obtained by DFT/B3LYP with 6-311++G(d,p) basis set are presented in Table 1 by comparing with the experimental XRD bond lengths and angles [31]. In the present work, geometry optimization parameters for CBT have been employed without symmetry constrain. The experimental and calculated geometric parameters agree well almost with all values. The small deviations are probably due to the intermolecular interactions in the crystalline state of the molecule. It must be noted that the experimental values belong to solid phase while the theoretical calculations belong to gases phase.

The thermodynamic properties like heat capacity, entropy, rotational constants, dipole moment and zero point vibrational energy (ZPVE) of the title compound have also been computed at DFT-B3LYP level using 6-311++G(d,p) basis set and they are presented in Table 2. The thermodynamic data provides helpful information for the further study on the title compound, when these are used as reactant to take part in a new reaction. These standard thermodynamic functions can be used as reference thermodynamic values to calculate changes in entropies (ΔS_T), changes in enthalpies (ΔH_T) and changes in Gibbs free energies (ΔG_T) of the reaction. The variation in ZPVEs seems to be significant. The ZPVE obtained by the DFT-B3LYP method is found to be 57.95335 kJ/mol. The knowledge of permanent dipole moment of a molecule provides wealth of information since the dipole moment and its principal inertial axes are strongly depending upon the conformation of molecule. Further, dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as a descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipoles are strictly determined for neutral molecules. For charged systems, its value depends on the choice of the origin and molecular orientations.

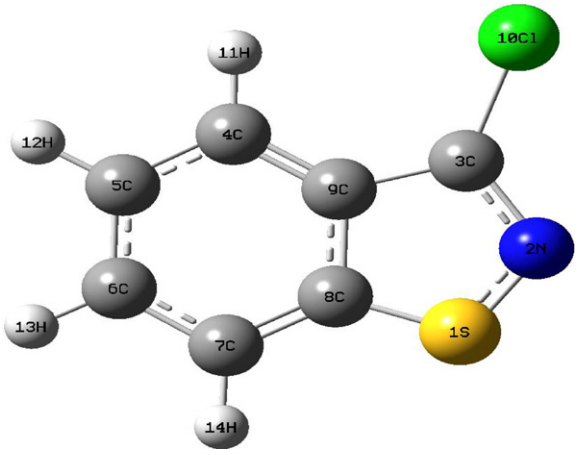

Fig. 1. Molecular structure of 3-chloro-1,2-benzisothiazole along with numbering of atoms.