Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 143 (2015) 230–241

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Vibrational spectroscopy investigation and density functional theory calculations on (E)-N′-(4-methoxybenzylidene) benzohydrazide

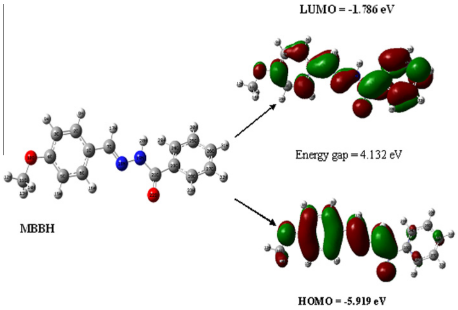
H. Saleem [a], S. Subashchandrabose [b,*], N. Ramesh Babu [c], M. Syed Ali Padusha [d]

[a] Dept. of Physics, Annamalai University, Annamalainagar 608002, Tamil Nadu, India
[b] Centre for Research and Development, PRIST University, Thanjavur 613403, India
[c] Dept. of Physics, M.I.E.T. Engineering College, Trichy 620007, Tamil Nadu, India
[d] PG and Research Dept. of Chemistry, Jamal Mohamad College (Autonomous), Tirchy 620020, Tamil Nadu, India

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



ARTICLE INFO

Article history:
Received 15 October 2014
Received in revised form 9 December 2014
Accepted 4 February 2015
Available online 13 February 2015

Keywords:
FT-IR
FT-Raman
TED
NBO
MBBH

ABSTRACT

The FT-IR, FT-Raman and UV–Vis spectra of the Schiff base compound (E)-N′-(4-methoxybenzylidene) benzohydrazide (MBBH) have been recorded and analyzed. The optimized geometrical parameters were calculated. The complete vibrational assignments were performed on the basis of TED of the vibrational modes, calculated with the help of SQM method. NBO analysis has been carried out to explore the hyperconjugative interactions and their second order stabilization energy within the molecule. The molecular orbitals (MO's) and its energy gap were studied. The first order hyperpolarizability (β_0) and related properties (β, α_0, Δ_α) of MBBH are also calculated. All theoretical calculations were performed on the basis of B3LYP/6-311++G(d,p) level of theory.

Introduction

Hydrazides, the acylated derivatives [1] of hydrazine are being useful for number of biological properties. Hydrazides are important starting materials for a wide range of derivatives utilizable in pharmaceutical products and as surfactants. Hydrazides have been known to be associated with antibacterial [2], antifungal [3], anthelmintic [4] and anticonvulsant [5] activities. Biological assessment of fatty hydrazide and their derivatives have been the focus of earlier investigative studies [6,7]. The fatty hydrazides are further derivatised to obtain new antibacterial and antifungal agents. Acyl hydrazones, as an example of Schiff bases and their metal complexes have been widely studied due to their versatile applications in the fields of analytical and medicinal chemistry and biotechnology [8–11].

P-Hydroxybenzohydrazide moiety and its analogs seemed to be suitable parent compounds upon which variety of biological

---

* Corresponding author. Mobile: +91 9976853476.
E-mail address: sscbphysics@gmail.com (S. Subashchandrabose).

http://dx.doi.org/10.1016/j.saa.2015.02.016
1386-1425/© 2015 Elsevier B.V. All rights reserved.

activities were reported such as antitumor [12], antianginal [13], antitubercular [14], antihypertensive [15] and antibacterial [16]. Hydrazides have recently become attractive to theoreticians as well as experimentalists due to the biological significance particularly in medicinal and enzyme chemistry. Harmonic force fields of polyatomic molecules play a vital role in the interpretation of vibrational spectra and in the prediction of other vibrational properties. IR spectra of N-benzoylhydrazine (BHZ) phCONHNH2 and its uranyl complex have been [17] studied in the 4000–50 cm^{-1} frequency range. Complete equilibrium geometry of the ligand molecule has been determined by DFT and BLYP/6-31G force field calculations. A complete vibrational assignment of the solid state IR and Raman spectra of BHZ was performed on the basis of NCA of a single molecule. In this present study, MBBH molecule was synthesized and the spectral characterizations were made by FT-IR, FT-Raman and UV–Visible spectra and the corresponding theoretical predictions were carried out by using B3LYP/6-311++G(d,p) level of calculation.

Experimental details

Synthesis

The 3.0 ml (0.025 mol) ethanolic solution of anisaldehyde was added to (0.025 mol) 3.4 g of benzohydrazide. The reaction mixture was taken in a round bottom flask and kept over a magnetic stirrer and stirred well in ice cold condition for 2 h. The white precipitate obtained was filtered and dried over vacuum.

FT-IR, FT-Raman and UV–Visible details

The FT-IR spectrum of MBBH 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 MBBH 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 MBBH dissolved in methanol.

Computational details

In order to establish the stable possible conformers, the conformational space of MBBH 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 03 W [18] program package, invoking gradient geometry optimization [18,19]. 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 MBBH 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 [20].

The Raman activity was calculated by using Gaussian 03 W package and the activity was transformed into Raman intensity using Raint program [21] by the expression:

$$I_i = 10^{-12} \times (\nu_0 - \nu_i)^4 \times \frac{1}{\nu_i} \times \mathrm{RA}_i \qquad (1)$$

where I_i is the Raman intensity, RA_i is the Raman scattering activity, ν_i is the wavenumber of the normal modes and ν_0 denotes the wavenumber of the excitation laser [22].

Results and discussion

Molecular geometry

The optimized geometrical parameters namely bond lengths, bond angles and dihedral angles calculated by B3LYP/6-311++G(d,p) level are listed in Table 1. The optimized molecular structure of MBBH and the atom numbering scheme is shown in Fig. 1. The optimized structural parameters are compared with the experimental X-ray data for MBBH [23]. In the ring part (both ring 1, 2), the optimized geometries of the molecule show good agreement with X-ray data. The bond lengths (ring 1) of $C_1–C_2$, $C_2–C_3$, $C_3–C_4$, $C_4–C_5$, $C_5–C_6$ and $C_1–C_6$ are calculated as 1.407, 1.387, 1.403, 1.404, 1.391 and 1.404 Å and their corresponding recorded values (XRD) are 1.389, 1.387, 1.383, 1.383, 1.373 and 1.384 Å [23], respectively. Similarly for ring 2, the bond lengths of $C_{23}–C_{24}$, $C_{24}–C_{25}$, $C_{25}–C_{26}$, $C_{26}–C_{27}$, $C_{27}–C_{28}$ and $C_{23}–C_{28}$ are calculated as 1.403, 1.395, 1.395, 1.397, 1.392 and 1.401 and their corresponding recorded values are as 1.382, 1.393, 1.363, 1.370, 1.376 and 1.383 Å. The CH bond lengths of ring 1 and ring 2 are almost equal. In this study, the most significant difference was seen in bond lengths of $C_1–C_7$ (1.460 Å) and $C_{21}–C_{23}$ (1.503 Å). In MBBH, the hydrazone linkage plays an important role. For the carbonyl ($C_{21}{=}O_{22}$) group bond length in hydrazone link was observed at 1.224 Å which is exactly matches with the literature [24], whereas the calculated bond length was about 1.219 Å. The bond length of $>N_{19}–C_{21}<$ group was observed at 1.350 Å whereas the computed value is 1.388 Å. The bond $N_{18}–N_{19}$ behaves as a bridge between the two rings and its observed value is about 1.388 Å, whereas the calculated value is about 1.356 Å, it found support from the literature [24]. Similarly the bond length of $C_{17}{=}N_{18}$ is about 1.269 and 1.284 Å as observed and calculated values respectively and which are coincided well with the literature [25].

The bond angle of $N_{18}–N_{19}–C_{21}$ was calculated about 120.8° whereas the observed value is 121.29°. The $N_{19}—C_{21}{=}O_{22}$ (123.2°) bond angle is (3°) positively deviated from [25] ($N_{19}—C_{21}{=}O_{22}$). This may be due to the attachment of ring 2 with C_{21} atom. Similarly the dihedral angle $H_{20}–N_{19}–C_{21}–O_{22}$: 167.8° is positively (167.3°) deviated from our earlier study [25] ($H_{20}–N_{19}–C_{21}–O_{22}$: −0.5°) which shows that the hydrazone linkage is in chair form rather than boat form. The asymmetries of the benzene rings are also evident from the positive and negative deviation from the normal value of 120°. The bond angles $C_6–C_1–C_7$: 122.0° (ring 1), $C_{21}–C_{23}–C_{24}$: 123.8° (ring 2) are greater than $C_2–C_1–C_7$: 119.7° (ring 1), $C_{21}–C_{23}–C_{28}$: 117.0° (ring 2) because of interaction between hydrazone group and hydrogen atom (ring 1)/oxygen atom (ring 2). The $C_4–O_{10}–C_{11}$ bond angle is 118.4°, which is in excellent agreement with X-ray value (118.0°).

Vibrational assignments

The molecule under study possesses C_1 point group symmetry. The title compound MBBH consists of 33 atoms, which makes 93