From the Research Laboratories
В изследователските лаборатории

AB INITIO STUDY ON STRUCTURAL PROPERTIES AND VIBRATIONAL ANALYSIS OF Z-(1-PYRIDIN-2-YL-METHYLENE)-THIOSEMICARBAZONE COMPOUND

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Abstract. In this work, we will report a combined experimental and theoretical study on molecular structure, vibrational spectra and energies of Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone. The FTIR spectra of Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone (1) molecule have been recorded using Bruker Tensor 27 spectrometer in the range of 400–4000 cm^{-1}. The molecular geometry and vibrational frequencies and energies in the ground state are calculated by using the HF methods with 6-31G(d,p) basis sets. The calculated HOMO and LUMO energies also confirm that charge transfer occurs within the molecule. The geometries and normal modes of vibrations obtained from HF/6-31G(d,p) calculations are in good agreement with the experimentally observed data.

Keywords: thiosemicarbazone, HF, IR, HOMO, LUMO

Introduction

Heterocyclic nitrogen containing compounds, such as pyridine and its derivatives, are commonly present in synthetic and natural products (Gilchrist, 1988; Fallas et al., 2009). Pyridine heterocycles are a repeated moiety in many large molecules with interesting photo physical, electrochemical and catalytic applications (Lizarraga et al., 1997; Georgopoulou et al., 1999; Liaw et al., 2000; Trotter & White, 1978; Rajpure & Bhosale, 2000; Licht, 1995). They serve as good anesthetic agent and hence are used in the preparation of drugs for certain brain disease. These pharmaceutically acceptable salts and the pre-drugs are used for the treatment or prevention of diabetic neuropathy (Altenburger et al., 2004).

Heterocyclic thiosemicarbazones have aroused considerable interest in chemistry and biology due to their antibacterial, antimalarial, antineoplastic and antiviral activities and represent an important series of compounds because of potentially beneficial, biological activity (Gallego et al., 1979). Thiosemicarbazones display a broad spectrum of pharmacological properties, including antitumor, antifungal, antibacterial, antiviral and antimalarial activities (Beraldo & Gambino, 2004). Much effort has been devoted

to structural variations of the thiosemicarbazones for achieving the ultimate goal of medicinal applications (Hu et al., 2006; French et al., 1974; French & Blanz, Jr., 1966; Sartorelli et al., 1971; Liu et al., 1995; Agrawal & Sartorelli, 1969). However, the detailed HF/6-31G(d,p) comparative studies on the complete FTIR spectra of Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone have not been reported so far.

In this study, molecular geometry, optimized parameters and vibrational frequencies, energies are computed and the performance of the computational methods for ab initio at 6-31G(d,p) basis sets are compared.

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron the HOMO and LUMO energy calculated by HF at 6-31G(d,p) method.

Experimental

General

All chemicals were purchased from Merck chemicals and were used without further purification. Nuclear magnetic resonance spectra were recorded using a Bruker Avance 500 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^{1}H NMR spectra were referenced to external TMS. Melting points were determined in an Electrothermal 9200. Infrared spectra (400-4000 cm^{-1}), were recorded using FT-IR Bruker Tensor 27 spectrophotometer at room temperature. The samples were prepared as KBr pellets.

Preparations of Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone

Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone (1) was synthesized starting from of 2-Pyridinecarboxaldehyde (1 mmol) in EtOH (15 mL) was added stoichiometric amount (equimolar) of thiosemicarbazone (1 mmol). The mixture was refluxed for about 4 h. After removal of the ethanol the white solid that appeared was filtered off, and washed three times with dichloromethane and dried in vacuum at 80 °C for 24 h. m.p. 212 °C. IR (KBr) υ: 3857, 3743, 3421, 3265, 3134, 1617, 1582, 1489, 1299, 1159, 982, 877. Anal. calcd. (%) for $C_7H_8N_4S$: C, 46.65; H, 4.47; N, 31.09. Found. (%): C, 46.73; H, 4.48; N, 31.14.

Computational method

All calculations were performed using the Gaussian 98 package of program on a Windows-XP operating PC. The molecular structure of the title compound in the ground state is computed by performing HF with 6-31G(d,p) basis sets. Full optimization for the all molecule were carried out by the HF method using with the 6-31G(d,p) basis set.

Results and discussion

Molecular geometry

The optimized molecular structure of Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone molecule is obtained from Gaussian 03 package of program are shown in the (Fig. 1).

Fig. 1. Numbering system adopted in the study for compound (1) using HF/6-31(d,p)

Computational (theoretical) calculations energy differences for the compound (1) were determined by optimizing the geometry at various computational levels. Comparison of the energies at the HF/6-31G(d,p) levels listed in Table 1 shows the differences in the energies. The optimized structural parameters of compound (1) calculated by ab-initio/HF levels with the standard 6-31G(d,p) basis set are listed in Table 2.

Table 1. Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol^{-1} K^{-1}) for compound (1) at the HF/6-31G(d, p)

Total energy	Zero-point energy	Entropy total	Translational	Rotationa	Vibrationa
-885.02339	102.7803	103.830	41.471	31.405	30.955

Table 2. Theoretical and experimental IR spectral data (cm^{-1}) of compound (1) at the HF/6-31G(d, p)

Bond lengths	HF/6-31G(d, p)	Bond angles	HF/6-31G(d, p)
C1-C2	1.383	N20-C1-C2	123.218
C2-C3	1.385	N20-C5-C4	123.165
C3-C4	1.38	C1-C2-C3	118.256
C4-C5	1.389	C2-C3-C4	118.965
C5-N20	1.322	C3-C4-C5	118.071
C1-N20	1.319	N20-C5-C10	114.516
C5-C10	1.48	C5-C10-N12	120.48
C10-N12	1.255	C10-N12-N13	116.242
N12-N13	1.389	N12-N13-C15	125.314
N13-C15	1.355	N13-C15-S16	126.463
C15-S16	1.673	N13-C15-N17	112.579
C15-N17	1.345	S16-C15-N17	120.956

Vibrational spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, reaction kinetics, *etc.* The observed and calculated data of the vibrational spectrum of compound (1) are given in Table 3. The comparative graph of calculated vibrational frequencies by HF method at 6-31G(d,p) basis sets for the compound (1) are given in Fig. 2.

Table 3. Theoretical frequencies (in cm^{-1}) calculated by HF/6-31G(d,p) method for compound (1)

Exp. Frequencies FTIR	HF/6-31G(d, p)	Assignment
3857	3851	N-H symmetric stretching
3743	3827	NH_2 symmetric stretching
3421	3405	C-H stretching
3265	3381	C-H stretching
3134	3366	C-H stretching
1617	1923	C-N stretching
1582	1801	C-C stretching
1489	1781	C-C stretching
1299	1277	N-N stretching
1159	1192	C-H in-plane bending
982	1097	N-H out-of-plane bending
877	873	C-H out-of-plane bending

The suggested reason was that the result obtained by the calculation was harmonic oscillation frequency, while the experimental value contained the anharmonic oscillation frequency. Assignment of compound systems could be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamental modes.

The prominent peaks around 3857, 3743 and 1617 cm^{-1} in the FT-IR spectra are attributed to νN–H, νNH_2 and νC=N modes, respectively. The C=C stretching vibration of the aromatic ring appeared around 1582 and 1489 cm^{-1}. The peaks around 1299 and 982 cm^{-1} are due to νN–N and N–H out of plane bending vibrations, respectively. The in plane bending vibration and out of plane bending vibrations of aromatic C–H group are characterized by bands in the range of 1159 and 877 cm^{-1}, respectively (Fig. 3).

The highest occupied molecular orbitals (HOMOs) and lowest–lying unoccupied molecular orbitals (LUMOs) are named as Frontier molecular orbitals (FMOs). Frontier molecular orbitals (FMOs) i.e. the highest occupied molecular orbital (HOMO) and

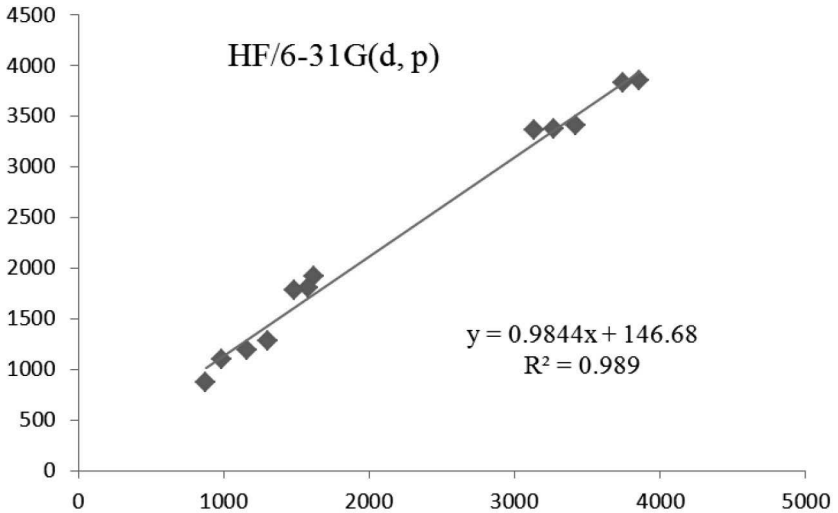


Fig. 2. Comparative graph of computed frequencies [HF] with experimental values for compound (1)

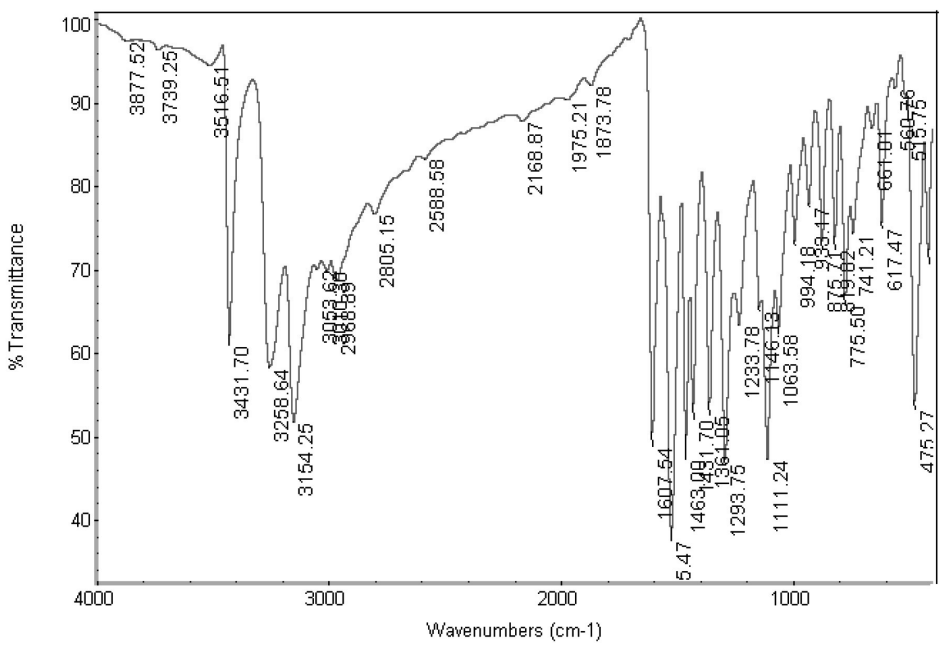
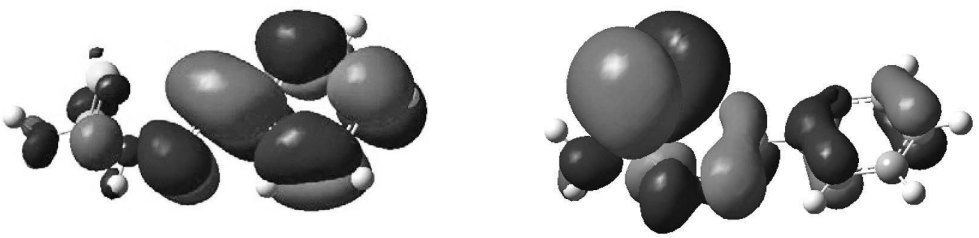


Fig. 3. The atomic orbital compositions of the frontier molecular orbital for compound (1) at the HF/6-31G(d, p)

the lowest unoccupied molecular orbital (LUMO) are shown in (Fig. 4). The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by the HF level with the 6-31G(d, p) basis set. The HOMO−LUMO energy gap is an important stability index. The HOMO–LUMO energies were also calculated at the HF level with the 6-31G(d, p) basis set and the values are listed in (Fig. 4).



E_{LUMO} = 0.21779 a.u
(First excited state)

E_{HUMO} = -0.31734 a.u
(First excited state)

ΔE = LOMO-HOMO = 0.53513 a.u
(Ground state)

Fig. 4. The atomic orbital compositions of the frontier molecular orbital for compound (1) at the HF/6-31G(d, p)

This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular or orbital (LUMO). The HOMO is located over the group, the HOMO→LUMO transition implies an electron density transfer to ring from chlorine and partially from ring.

Conclusion

The structure of Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone geometry was compared with optimized parameters obtained by means of ab initio calculations with the 6-31G(d,P) basis set. The geometries and normal modes of vibrations obtained from HF/6-31G(d,p) calculations are in good agreement with the experimentally observed data. The HOMO and LUMO levels of Z-(1-pyridin-2-yl-methylene)-thiosemicarbazone have been studied with HF/6-31G(d,p) level.

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