



## Spectroscopic Investigation, HOMO-LUMO Analysis and Non Linear Optical Studies on Iso Vanillin Thiosemicarbazone

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### Abstract

The present investigation is aimed at the experimental and theoretical studies on molecular structure, vibration spectra of Ortho vanillin Thiosemicarbazone ( $C_9H_{11}N_3OS$ ) were studied. The FT-IR spectra was recorded. The molecular geometry and vibrational frequencies of the ground state were calculated by using Hartee-Fock and Density functional methods (B3LYP) with 6-311++G(d,p) basis sets. Comparison of the observed fundamental vibrational frequencies of Ortho Vanillin Thiosemicarbazone by HF and DFT method are reported. The electric dipole moment ( $\mu$ ) and the first hyperpolarizability ( $\beta$ ) values of the investigated molecule were also computed.

Key words: DFT, HF, and IVTS

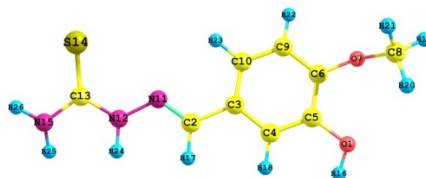
### Introduction

Semicarbazones and Thiosemicarbazone have been investigated due to interest in their coordination behaviour analytical applications [1] and biological properties such as antibacterial [2] Semicarbazones [3,4] and Thiosemicarbazone [5,6] are biologically important nitrogen and oxygen/sulphur donor ligands. Semicarbazones of aromatic and unsaturated carbonyl compounds have anticonvulsant properties and their advantage over the analogues thiosemicarbazones is their lower neurotoxicity [7] the alkylated sulphur atom remains uncoordinated on complexation. These characteristics and properties make these compounds attractive for the preparation of variety of new complexes. In recent years, among the computational methods calculating the electronic structure of molecular systems, DFT and HF have been a favourite one due to its great accuracy in reporting the experimental values. The success of quantum chemical methods in predicting a large number of important parts of their emergence as a legitimate tool for many chemical problems.

### Synthesis & Experimental details

Iso vanillin Thiosemicarbazone abbreviated as IVTS were synthesised in laboratory by refluxing acetone (0.05 mol) and Thiosemicarbazide (0.05 mol) in ethanol medium with constant string for 2 hrs. The solvent was evaporated under reduced pressure and un reacted Thiosemicarbazide was separated

from the mixture by washing with ethanol. The yellow precipitated compound was dried in vacuum in desiccators. The molecular structure of IVTS as shown in figure 1.



**Figure:1 Molecular Stretching of IVTS**

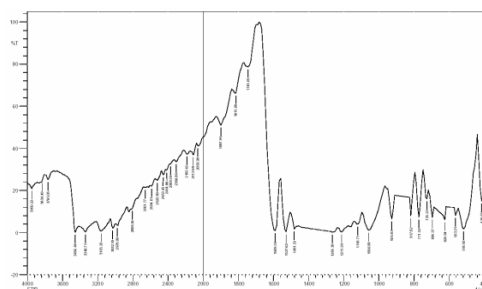
The FT-IR spectrum was recorded on a Perkin Elmer infrared spectrometer with KBr pellets. For excitation of the spectrum, the emission of ND:YAG laser was used (excitation wavelength 1064 nm, laser power of 100 mW, resolution 4cm<sup>-1</sup>, number of scans 50 and measurement on solid sample).

### Computational details

The molecules under investigation have been analysed with density functional theory (DFT) employing Beckle's three parameter hybrid exchange functional B3LYP and HF. All the calculations were performed using Gaussian 09 program[8]. The DFT was also used to calculate the dipole moment, and the first static hyperpolarizability ( $\beta$ ) of the title compound.

### Vibrational Analysis

The maximum number of potentially active observable fundamentals of a non-linear molecule which contains N atoms is equal to (3N-6), apart from three translational and three rotational degrees of freedom [9]. Hence, IVTS molecule, which was planar, has 26 atoms with 72 normal modes of vibrations. All vibrations are active in infrared absorptions. The detailed vibrational assignment of the experimental wavenumbers is based on normal mode analyses and a comparison with the experimental values. The observed IR and Raman bands and calculated wave numbers and assignments are given in Table1. The experimental FT-IR spectrums are shown in figure 2.



**Figure:2 Experimental FT-IR spectra of IVTS**

### C=N Stretching

The C=N stretching skeletal bonds are observed in the range 1650-1550 cm<sup>-1</sup>. According to Socrates [10] The C=N stretching for semicarbazones in the range 1655-1640 in IR spectrum. Ferraz et al[11] Reported C=N at 1618 for Thiosemicarbazone derivatives. For the title compound sharp band at



1743cm<sup>-1</sup> IR spectra coincides with the experimental values can be contributed to the characteristic C=N group.

**Table1:** Comparison of the experimental (FT-IR) and theoretical harmonic wave numbers (cm<sup>-1</sup>) of IsoVanillin Thiosemicarbazone calculated by HF, B3LYP with 6-311++G (d, p) basis set.

Mode No	Experimental IR	HF/ 6-311++G(d,p)	B3LYP 6-311++G(d,p)	Assignment
1	3834	3756.6	3713.1	OH Stretching
2	3765	3721.7	3658.8	NH <sub>2</sub> Asymmetric Stretching
3		3640.2	3558.5	NH Stretching
4	3456	3588.3	3525.3	NH <sub>2</sub> Symmetric Stretching
5	3163	3137.8	3054.1	CH Stretching
6		3121.7	3039.9	CH Asymmetric Stretching
7		3111.9	3031.7	CH Stretching
8		3088.5	2991.6	CH Stretching
9	3032	3031.3	2949.2	CH <sub>3</sub> Asymmetric Stretching
10	2978	3005.3	2932.1	CH <sub>3</sub> Asymmetric Stretching
11	1897	2933.9	2849.0	CH <sub>3</sub> Symmetric Stretching
12	1743	1854.7	1747.7	C=N Stretching
13		1782.4	1618.3	NH <sub>2</sub> Inplane bending
14		1702.1	1578.8	CH ring Stretching
15		1701.0	1562.3	CH ring bending
16		1680.0	1539.3	CH <sub>3</sub> Inplane bending
17		1670.2	1532.3	N <sub>12</sub> H <sub>24</sub> -bending (wagging)
18		1647.3	1520.6	CH <sub>3</sub> Inplane bending
19		1636.3	1504.9	CH <sub>3</sub> ring bending
20		1604.6	1477.0	CH <sub>3</sub> Inplane bending
21	1589	1551.3	1461.2	C=S Stretching
22	1527	1538.1	1417.0	C-H Stretching
23	1481	1491.6	1373.7	OH bending
24		1458.5	1334.0	OH, CH bending
25		1413.7	1315.5	NH bending
26		1403.8	1309.8	CH bending
27		1391.2	1302.1	CH <sub>3</sub> Outplane bending
28		1388.1	1278.3	CH <sub>3</sub> Outplane bending
29		1354.1	1260.9	CH <sub>3</sub> Outplane bending
30		1313.7	1220.0	CH ring bending
31		1302.8	1205.4	N-N Stretching
32	1265	1254.8	1193.8	CH Outplane bending
33	1211	1219.1	1140.4	CH bending
34		1206.8	1129.7	CH bending
35		1158.8	1097.8	NH <sub>2</sub> Inplane bending
36		1149.9	1093.6	O <sub>7</sub> -C <sub>8</sub> -struture
37	1118	1140.3	1014.7	CH, C9, C10 twisting
38	1056	1028.1	994.6	CH wagging
39		1014.2	954.0	CH bending
40		1009.2	899.5	CH Outplane bending
41		1002.7	884.4	NNH bending



42	925	924.5	875.2	CH bending
43		861.7	791.6	OCH <sub>3</sub> bending
44	817	835.0	772.0	CH ring bending
45	771	797.1	746.7	CH ring bending
46		756.9	681.5	CH ring bending
47	725	732.0	645.9	CH Outplane bending
48	694	699.3	604.8	CH ring bending
49		650.9	579.4	COH bending
50		637.6	545.5	C-S bending
51	624	628.7	535.3	OCH <sub>3</sub> bending (wagging)
52		599.8	498.8	OCH <sub>3</sub> twisting
53	563	567.7	484.3	OH bending
54		550.8	477.2	OCH <sub>3</sub> twisting
55	516	522.9	456.3	CH <sub>3</sub> twisting
56		485.6	431.9	CH ring bending
57		464.0	379.2	NH bending
58	416	420.5	331.0	OCH bending
59		382.1	287.0	COH bending
60		368.8	265.1	OC bending
61		336.8	251.4	NH bending
62		306.2	232.6	NH bending
63		272.2	205.0	NH <sub>2</sub> bending
64		177.2	99.7	OCH <sub>3</sub> bending
66		149.2	67.7	NH bending (wagging)
67		118.6	-45.3	NH bending (wagging)
68		86.6	-68.1	NH bending
69		30.2	-89.4	OCH <sub>3</sub> bending
70		-108.8	-138.9	OCH <sub>3</sub> bending
71		-147.8	-300.4	NH bending
72		-377.9	-495.2	NH <sub>2</sub> Outplane bending

### C-N Stretching

The C-N stretching vibration [12] coupled with NH active in this region  $1275 \pm \text{cm}^{-1}$  El- Shahawy et.al [10]. In present case the band at  $1265 \text{cm}^{-1}$   $1320 \text{cm}^{-1}$  in the IR spectrum as this C-N mode is assigned in this mode the DFT calculations gives the corresponding bands at  $1260 \text{cm}^{-1}$

### N-N Stretching

The N-N stretching has been reported at  $1151 \text{cm}^{-1}$  by crane et.al [13] In the present case the band is observed  $1302.8, 1205.4 \text{cm}^{-1}$  in IR spectra and  $1038.11 \text{cm}^{-1}$  DFT is assigned to the N-N is reported.

### OCH<sub>3</sub> Stretching

In the spectra of methyl group overlap of the region in which both asymmetric stretching CH<sub>3</sub> absorb with weak bond at  $(2985 \pm 25 \text{cm}^{-1}, 2970 \pm 30 \text{cm}^{-1})$  the computed wave numbers of modes corresponding to CH<sub>3</sub> groups are  $2962, 3003 \text{cm}^{-1}$ . The symmetrical stretching mode is expected in the range  $2920 \pm 80 \text{cm}^{-1}$  in which all the three C-H bonds extending and contracting in phase [14] The bands

present in experimental (IR) are assigned these particular modes. Two bending vibrations accrue in methyl group

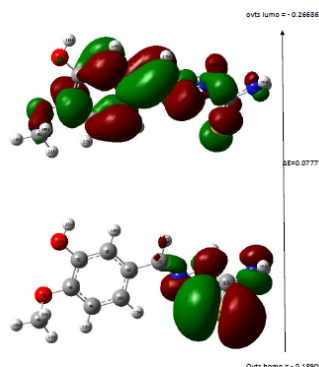


Figure 3 HOMO-LUMO Analysis of IVTS

### ***NH<sub>2</sub> Stretching***

The NH<sub>2</sub> asymmetric stretching vibrations [14] gives rise to a strong band in the region  $3390 \pm 60$  cm<sup>-1</sup> and the symmetric NH<sub>2</sub> stretching in the region  $2985 \pm 25$  cm<sup>-1</sup> with somewhat weaker intensity for this compound. The NH<sub>2</sub> bending is observed at 1361 in IR theoretically NH<sub>2</sub> is reported at 3588.3 in HF 3525.3 in DFT. The amide band absorbing in the region  $775 \pm 45$  cm<sup>-1</sup> is assigned to NH<sub>2</sub> out of plane twist and wagging mode NH<sub>2</sub> wag is expected in the region [15]  $670 \pm 60$  cm<sup>-1</sup>. In which all the three C-H bonds extend and contract in phase [17] The bands seen at 272.2 in HF 205.0 in DFT are assigned as these bending modes.

### ***N-H Stretching***

The NH stretching vibration [17] appears as strong and broad band in the region  $3390 \pm 60$  cm<sup>-1</sup>. In the present study the NH stretching band appeared as doublet at 3640.2, 3558.5 cm<sup>-1</sup> in the IR region owing to the Davydov coupling between the neighbouring units. The splitting in IR spectrum is due to Strong inter molecular hydrogen bonding. A similar type of splitting observed in acetanilide [16, 17] and N methyl acetamide [17] in the stretching band is attributed to the Davydov splitting.

### ***C=S Stretching***

The identification of C=S stretching vibration is assigned to 1589.3 cm<sup>-1</sup> in IR spectra. The calculated values are 1551.3 cm<sup>-1</sup> in HF and 1461.2 cm<sup>-1</sup> in DFT method. There bands appear consistently in the region of 1140.61 cm<sup>-1</sup> to 940.61 cm<sup>-1</sup> in the IR spectrum because of mixed vibrations of -N-C=S moiety [18]

Atoms	HF/ 6-311++G (d,p)	B3LYP/ 6-311++G (d,p)
O <sub>1</sub>	-0.334	-0.242
C <sub>2</sub>	-0.601	-0.546
C <sub>3</sub>	0.934	1.275
C <sub>4</sub>	-0.914	-0.556
C <sub>5</sub>	-0.036	-0.214
C <sub>6</sub>	-0.750	-0.622
O <sub>7</sub>	-0.214	-0.166
C <sub>8</sub>	-0.276	-0.324
C <sub>9</sub>	0.144	-0.015
C <sub>10</sub>	0.312	-0.136
N <sub>11</sub>	0.022	-0.016
N <sub>12</sub>	0.139	0.186
C <sub>13</sub>	-0.112	-0.214
S <sub>14</sub>	-0.407	-0.288
N <sub>15</sub>	-0.270	-0.171
H <sub>16</sub>	0.289	0.267
H <sub>17</sub>	0.130	0.060
H <sub>18</sub>	0.168	0.121
H <sub>19</sub>	0.161	0.185
H <sub>20</sub>	0.147	0.154
H <sub>21</sub>	0.113	0.154
H <sub>22</sub>	0.265	0.198
H <sub>23</sub>	0.247	0.176
H <sub>24</sub>	0.288	0.246
H <sub>25</sub>	0.246	0.219
H <sub>26</sub>	0.308	0.269

$\beta$ component	B3LYP/6-311++G
$\beta_{xxxx}$	4.5740
$\beta_{yyyy}$	2.8225
$\beta_{zzzz}$	2.2431
$\beta_{xxyy}$	1.6650
$\beta_{yyxx}$	1.3423
$\beta_{xyyx}$	-1.2568
$\beta_{yyxx}$	-2.3100
$\beta_{xxyy}$	1.2299
$\beta_{yyxx}$	-1.8576
$\beta_{xxyy}$	9.1126
<b>(a u)</b>	<b>11.7477</b>
<b>(esu x 10<sup>-33</sup>)</b>	<b>101.4919x10<sup>-33</sup></b>

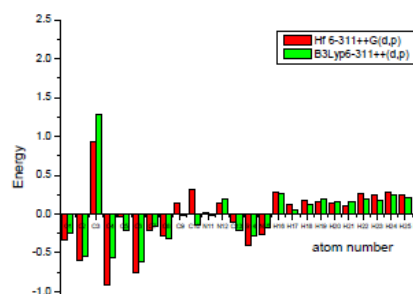


Figure-4 Mulliken atomic charges of IVTS

## 2.10 Mulliken atomic charges



Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because of atomic charge affects dipole moment electronic structure, molecular systems. The total atomic charges of Vanillin thiosemicarbazone are obtained by Mulliken population analysis is shown in Table 2. The results show that substitution of methyl group in the thiosemicarbazone leads to the redistribution of electron density. The charge distribution shows all the hydrogen atoms and carbon atoms in few sets are positively charged where as the magnitude of the carbon atomic charges were found to be both positive and negative values The charge of N positive and negative at the basis set, however the highest value 0.0277 in B3LYP method with 6-311++G(d,p) is observed. The charge of the nitrogen atom -0.5799 is lowest 6-311++G(d,p) basis set. The sulphur atom has negative values only in all basis sets due to electron withdrawing nature. The comparative graph for Mulliken charges is shown in figure 4.

### **Hyperpolarizability**

The Hyper polarizability is calculated using HF, B3LYP method on the basis of finite field approach. Calculated parameters are listed in Table-4, The polarizabilities and hyperpolarizability are reported in atomic units (a.u), the calculated values have been converted into electrostatic units (esu) (for  $\alpha$ ; 1 a.u =  $0.1482 \times 10^{-24}$  esu, for  $\beta$ ; 1 a.u =  $8.6393 \times 10^{-33}$  esu). The calculated value of dipole moment ( $\mu$ ) was found to be 5.0434 Debye. The highest value of dipole moment is observed for compound  $\mu_x$ . The calculated polarizability of IVTS is  $1.84913 \times 10^{-24}$  esu. The magnitude of the molecular hyperpolarizability  $\beta$ , is one of important key factors in a NLO system. The B3LYP/6-311++G(d,p) basis set calculated first hyperpolarizability values ( $\beta$ ) of VTS is  $101.491 \times 10^{-33}$  esu respectively. The dipole moment and first hyperpolarizability of title molecule is approximately 3.29 and 0.29 times than those of urea ( $\mu$  and  $\beta$  of urea are 1.5285 Debye and  $343.272 \times 10^{-33}$  esu obtained by B3LYP/6-311G(d,p) method). It is well known that the higher values of dipole moment, molecular polarizability, and hyperpolarizability are important for more active NLO properties.

### **Frontier molecular Orbital's (FMOs)**

The highest occupied molecular orbital's (HOMO) and the lowest lying unoccupied molecular orbital's (LUMO) are named as Frontier molecular orbital's (FMO) The FMO play an important role in the optical and electric properties [18] as well as in quantum chemistry and UV visible spectra. The HOMO-LUMO energy gap of ATS have been calculated by using ab-initio HF/6-31G levels is shown in Fig 3. It reveals that the energy gap reflect the chemical activity of the molecule are presented. LUMO as an electron acceptor represents in the electron ability to obtain an electron; HOMO represents to donate an electron. It is clear that the HOMO-LUMO gap is - 0.07777 it reveals that the molecule is soft and easily reactive.



## Conclusion

A complete vibrational analysis of OVTS are performed by HF and DFT(B3LYP) methods with 6-311++G (d , p) basis sets. Any discrepancy noted between and the observed and the calculated frequencies may be due to The fact that the calculations have been done on a single molecule in the gaseous state in contrary to the experimental vales recorded in solid state .The influence of methyl group, amino group and carbon sulphur bond to the vibrational frequencies of the title compound were discussed. The N and S atoms negative charge shows that electron withdrawing nature. The HOMO-LUMO gap is as small - 0.07777 it reveals that is a easily reactive compound. The first order hyper polarizability values are  $101.491 \times 10^{-33}$ esu.This indicates that the title compound is an attractive object for future studies of Non linear optical properties.

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