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# COMPUTATIONAL STUDY ON VIBRATIONAL SPECTRAL AND THERMAL CHARACTERIZATION USING ORGANIC DERIVATIVE OF 3-FORMLNITROBENZEN

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**ABSTRACT**
*In this work, the vibrational spectral analysis was carried out by using FT-IR and FT-Raman spectroscopy in the range 400-4000 cm-1 and 100-1900 cm-1 respectively, for Thiosemicarbazone of m-nitrobenzaldehyde molecule. The potential energy curve shows that molecule molecule has one stable structure. The molecular structure, fundamental vibrational frequencies and loudness of the vibrations bands were interpreted with the aid of structure optimizations and normal coordinate force field calculations-based density functional theory (DFT) and ab initio HF methods and different basis set combination. The outcomes of the computation were put on to simulated spectra of the title compound, which show excellent agreement with observed spectra. The scaled B3LYP/6-311++G (d -p) results show the best agreement with the experimental values over the other method. The energy and oscillator strength calculated by Time-Dependent Density Functional Theory (TD-DFT) complements with the experimental findings. In addition, molecular electrostatic potential and thermodynamic properties of the title compound were performed. Mulligan and natural charges of the title molecule were also calculated and interpreted.*
**KEYWORDS**: *FT-IR; FT-RAMAN; Chlorobenzene; DFT; HF and B3LYP.*

## 1. INTRODUCTION

Thiosemicarbazone of m-nitrobenzaldehyde is an organic crystal plays an important function in application in optical computing and optical communication devices. In recent year, an intense research study has been taken out to identify a limited form of thermally stable optical material. Organic compounds are frequently shaped by very weak Vander walls and hydrogen bonds and possess a high degree of delocalization. Hence, they are optically more nonlinear than inorganic crystals. Recent researches have brought up that organic crystals are bulk in size, hardness, stable, and large nonlinear optical susceptibilities compared to the inorganic crystals. The slow evaporation solution growth Technique (SESGT) is an important technique because large size, stability, optical crystals are being produced by this technique [1-6]. Hence, these crystals are employed in the field of optical communication and optical computing and information process. The harvested crystals were characterized by FT-IR spectral analysis, UV, $^{1}H$ and $^{13}C$ Nuclear magnetic resonance spectra, TGA-DSC studies, X-ray diffraction (XRD), Microhardness analysis, and SHG efficiency studied [7-12].

## 2. EXPERIMENTAL DETAILS

The compound under investigation, namely thiosemicarbazone m-nitrobenzaldehyde is purchased from M/S Aldrich chemicals, U.S.A with spectroscopic grade and it is used as such without any further refinement. The FT-IR spectrum of the compound has been entered in a Perkin-Elmer 180 Spectrometer in the range of 4000–400 $cm^{-1}$. The spectra are recorded with scanning speed of 30 $cm^{-1}$ $min^{-1}$ of spectral width 2 $cm^{-1}$. The frequencies of all sharp bands are accurate to ± 1 $cm^{-1}$. The frequencies of all sharp bands are accurate within ±1 $cm^{-1}$.The Bruker NMR spectrometer was used to record NMR spectra of the title compound at 500 MHz for 1H and 125.76 MHz for $^{13}C$ at the Research Center, College of Pharmacy, King Saud University, Saudi Arabia.

## 3. QUANTUM CHEMICAL CALCULATIONS

The quantum chemical computations have been performed at HF and DFT (B3LYP) methods with 6-311++G (d-p) basis sets using

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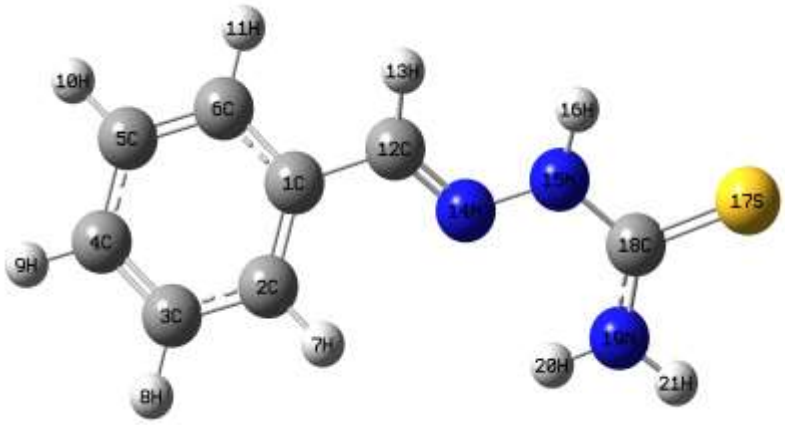
the Gaussian 09 W program [8]. The optimized structural parameters have been measured for the calculations of vibrational frequencies at different level of theories and a variety of basis sets by assuming $C_1$ point group symmetry. At the optimized geometry for the thiosemicarbazone of m-nitrobenzaldehyde imaginary wavenumbers modes were obtained, Hence there is a true minimum on the potential energy surface was found. As an event, the unscaled calculated frequencies, reduced masses, force constants, infrared intensities, Raman activities, Raman intensities, and depolarization ratios are held. In society to better the calculated values in arrangement with the experimental values, it is necessary to scale down the calculated harmonic wavenumbers. Hence, the vibrational wavenumbers calculated at the HF level are scaled by 0.9067 and the range of wave numbers above 1700 $cm^{-1}$ are scaled by 0.958 and below 1700 $cm^{-1}$ scaled by 0.983 for B3LYP [9, 10]. After scaling with the scaling elements, the difference from the experiments is less than 10 $cm^{-1}$ with a few exceptions. The PEDs are computed from quantum chemically calculated vibrational frequencies using VEDA program [11]. Gaussview program [12] has been counted to make a visual animation and also for the substitution of the normal mode assignment. The electronic absorption spectra for optimized molecule calculated with the time dependent density functional theory (TD-DFT) at B3LYP/6-311++G(d,p) level.

## 4. RESULTS AND DISCUSSION

### *4.1. Molecular Geometry*

The molecule with CH, S and N is the substitute in a planar six-member ring in the lower limit of the potential energy surface, the substituents being co-planar with the ring the disubstituted derivative. The optimized geometry by B3LYP/6-311++G(d,p) of the thiosemicarbazone of m-nitrobenzaldehyde with atom numbering is shown in Fig.1. By reserving the rest of all parameters, the calculations converge to optimized geometries, which equate to true energy minima, as exposed by the lack of imaginary frequencies in the vibration mode calculation [13, 14]. The optimized geometry thiosemicarbazone of m-nitrobenzaldehyde value is presented in the Fig 1. The global minimum energy is obtained for structure optimization of thiosemicarbazone of m-nitrobenzaldehyde is -872.86170 a.u. For B3LYP/6-311++G (d - p) and -869.16900 a.u HF/6-311++G (d- p). All the above observations are made without any symmetric constrains.

The optimized bond lengths and bond angles of thiosemicarbazone of m-nitrobenzaldehyde are calculated by various methods listed in Table 1. It is well known that HF methods underestimate and DFT method overestimate bond lengths, particularly the CH bond lengths. The aromatic C-C bond distances of thiosemicarbazone of m-nitrobenzaldehyde are found to have higher measures in case of B3LYP calculation with respect to HF computation. Merely knowing that electronegative substituent on aromatic rings course to shorten the C-C bonds adjacent to the substituent, we took for granted that the bond lengths C1-C2, C1-C6 and C3-C4 are higher values than C2-C3, C4-C5 and C5-C6. The highest value of C-C is obtained in the C1-C2 (1.405 Å) near to the substitution. The C-H aromatic bond distances are also in same trend, with relatively large distances in B3LYP/6-311++G (d-p). The C12-H13 bond length is higher in all B3LYP/6-311++G (d-p) basis sets. There are three N-H bond lengths with various values in B3LYP and HF. In this, N15-H16 is having the 1.016 and 0.997 a.u highest value. Similarly, C-N also is having the same values like this in N-H and N15-C18 is having the highest value. The bond angles are calculated using various methods show the same trends as significant variation in bond lengths. The remaining CCC angles are close to 120°. The remaining CCC angles are close to 120°. The B3LYP/6-311++G(d,p) calculations also gives shortening of the angle C1-C2-C6, C3-C4-C5 and C4-C5-C6 and increase of the angle C1-C2-C3, C2-C3-C4 and C1-C5-C6 and this asymmetry of exocyclic angles reveals the repulsion between the substitutions and the phenyl ring. The largest angle is obtained in S17-C18-N19 as 124.7° and 123.4°.



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Table 1. Optimized parameters of the thiosemicarbazone of m-nitrobenzaldehyde

| Bond length | B3LYP | HF | Bond angle | B3LYP | HF |
|---|---|---|---|---|---|
| C1-C2 | 1.405 | 1.392 | C1-C2-C6 | 118.8 | 119.2 |
| C1-C6 | 1.402 | 1.380 | C2-C1-C12 | 122.4 | 122.2 |
| C1-C12 | 1.461 | 1.398 | C6-C1-C12 | 118.7 | 118.6 |
| C2-C3 | 1.388 | 1.379 | C1-C2-C3 | 120.3 | 120.1 |
| C2-H7 | 1.082 | 1.073 | C1-C2-H7 | 119.2 | 119.5 |
| C3-C4 | 1.397 | 1.390 | C3-C2-H7 | 120.4 | 120.2 |
| C3-H8 | 1.084 | 1.075 | C2-C3-C4 | 120.4 | 120.3 |
| C4-C5 | 1.392 | 1.382 | C2-C3-H8 | 119.7 | 119.7 |
| C4-H9 | 1.084 | 1.075 | C4-C3-H8 | 119.8 | 119.9 |
| C5-C6 | 1.392 | 1.387 | C3-C4-C5 | 119.7 | 119.8 |
| C5-H10 | 1.084 | 1.075 | C3-C4-H9 | 120.1 | 120.1 |
| C6-H11 | 1.085 | 1.076 | C5-C4-H9 | 120.2 | 120.1 |
| C12-H13 | 1.095 | 1.084 | C4-C5-C6 | 119.9 | 119.8 |
| C12-N14 | 1.283 | 1.254 | C4-C5-H10 | 120.2 | 120.3 |
| N14-N15 | 1.355 | 1.355 | C5-C6-H10 | 119.8 | 119.8 |
| N15-H16 | 1.016 | 0.997 | C1-C6-C5 | 120.7 | 120.6 |
| N15-C18 | 1.372 | 1.345 | C1-C6-H11 | 119.5 | 119.8 |
| S17-C18 | 1.674 | 1.681 | C5-C6-H11 | 119.7 | 119.5 |
| C18-N19 | 1.346 | 1.328 | C1-C12-H13 | 116.5 | 116.2 |
| N19-H20 | 1.009 | 0.992 | C1-C12-N14 | 122.9 | 122.9 |
| N19-H21 | 1.005 | 0.991 | H13-C12-N14 | 120.5 | 120.9 |
| | | | C12-N14-N15 | 117.6 | 117.5 |
| | | | N14-N15-H16 | 121.7 | 121.2 |
| | | | N14-N15-C18 | 122.1 | 121.9 |
| | | | H16-N15-C18 | 116.1 | 116.8 |
| | | | N15-C18-S17 | 120.1 | 120.1 |
| | | | N15-C18-N19 | 115.1559 | 116.4 |
| | | | S17-C18-N19 | 124.7411 | 123.4 |
| | | | C18-N19-H20 | 120.397 | 121.1 |
| | | | C18-N19-H21 | 118.2909 | 118.1 |
| | | | H20-N19-H21 | 121.3109 | 120.9 |

***4.2. Thermodynamic properties***

On the basis of vibration analysis at B3LYP/6-311++G(d,p) level, the standard statistical thermodynamic functions: heat capacity ($C^0_{p,m}$), entropy ($S^0_m$), and enthalpy changes ($\Delta H^0_m$) for the title compound were obtained from the theoretical harmonic frequencies and listed in Table 2 and are shown in the Fig 2. From Table 2, it can be noted that these thermodynamic functions are increasing with temperature ranging from 100 to 500 K due to the fact that the molecular vibrational intensities increase with temperature [15, 16]. The correlation equations between heat capacities, entropies, enthalpy changes and temperatures were fitted by quadratic, linear and quadratic formulas and the corresponding fitting factors ($R^2$) for these thermodynamic properties are 0.99975,

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0.99970 and 0.9964, respectively. The corresponding fitting equations are as follows and the correlation graphics from those shows in Figs. 2.

$$C_{p,m}^{0} = 1.199956 + 0.15474T - 5.88904.x10^{-5}\,T^{2} \qquad (R^{2} = 0.99975)$$

$$S_{m}^{0} = 50.90793 + 0.22124\,T - 1.21877 \times 10^{-4}\,T^{2} \qquad (R^{2} = 0.99970)$$

$$\Delta H_{m}^{0} = -1.33596 + 0.02399\,T + 3.194\,x10^{-5}\,T^{2} \qquad (R^{2} = 0.9964)$$

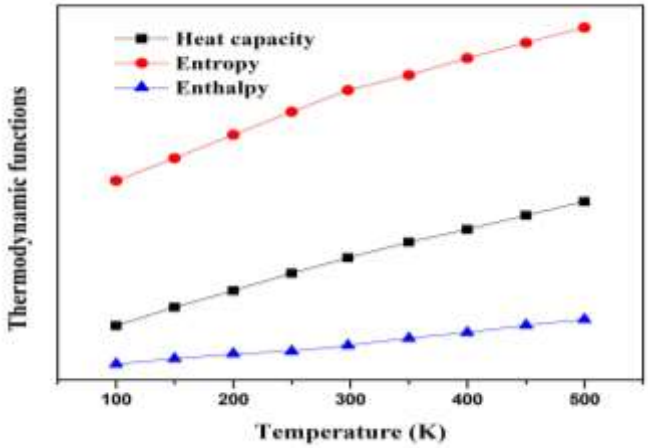



Table 2. Thermo dynamical distribution of thiosemicarbazone of m-Nitrobenzaldehyde

| Temperature | $C_{p,m}^{0}$ | $S_{m}^{0}$ | $\Delta H_{m}^{0}$ |
|---|---|---|---|
| 100 | 16.035 | 72.151 | 1.1769 |
| 150 | 23.191 | 80.832 | 3.260 |
| 200 | 29.566 | 89.900 | 5.145 |
| 250 | 36.300 | 98.789 | 6.133 |
| 298.13 | 42.327 | 107.164 | 8.404 |
| 350 | 48.331 | 112.975 | 11.160 |
| 400 | 53.269 | 119.529 | 13.405 |
| 450 | 58.746 | 125.544 | 16.188 |
| 500 | 64.066 | 131.352 | 18.456 |

All the thermodynamic data supply helpful information for the further written report on the thiosemicarbazone of m-nitrobenzaldehyde. They tin be applied to calculatite the other thermodynamic energies according to the relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in Thermochemical field [17]. Notice: all thermodynamic calculations were executed in gas phase and they could not be applied in solution. Dipole moment reflects the molecular charge distribution and is passed as a vector in three dimensions. Thus, it can be applied as a form to describe to depict the charge movement across the molecule.The focal point of the dipole moment vector in a particle depends on the centers of positive and minus accusations. Dipole moments are strictly set for neutral atom. For charged systems, its value depends on the choice of origin and molecular orientation.

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### *4.3. Mulliken Atomic Charge*

Mulliken atomic charge computation has an important in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular systems. The calculated Mulliken charge values are listed in Table 3 and in Fig 3. The direction of carbon atoms C1, C2 and C18 are positive and remaining carbon care are negative. This suggests, the carbon atoms near to the situational group are positive due to the electron are withdrawing group like N atoms and NH2. The hydrogen atoms are nearer to the subtntituional group also possesses low positive charge and the same in NH2 group hydrogen atoms are having high positive charge. Among the charges, N14 is having positive of 0.213824 and 0.292005 e in B3LYP and HF basis sets The root mean square deviation is very small in B3LYP/6-311++G (d, p) method.

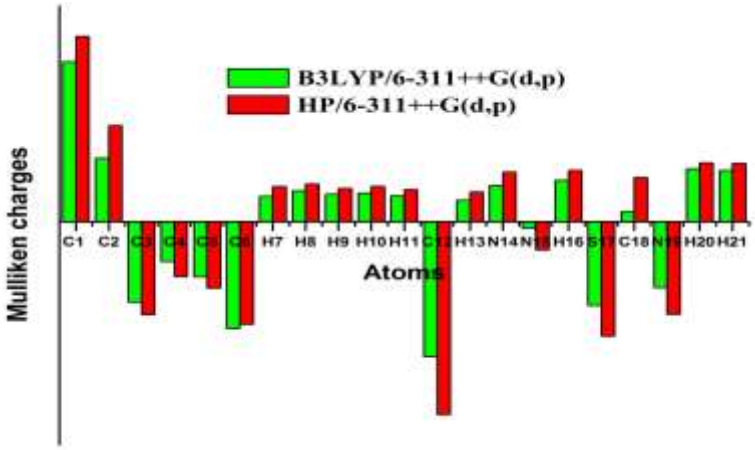



Table 3. Mulliken charge distribution of thiosemicarbazone of m-nitrobenzaldehyde

| ATOM | B3LYP | HF |
|---|---|---|
| C1 | 0.944372 | 1.094805 |
| C2 | 0.373656 | 0.566330 |
| C3 | -0.474751 | -0.550264 |
| C4 | -0.235913 | -0.325735 |
| C5 | -0.325897 | -0.391344 |
| C6 | -0.631320 | -0.606815 |
| H7 | 0.149691 | 0.206972 |
| H8 | 0.182606 | 0.221457 |
| H9 | 0.161155 | 0.196034 |
| H10 | 0.168122 | 0.208676 |
| H11 | 0.152672 | 0.187999 |
| C12 | -0.798078 | -1.140048 |
| H13 | 0.125594 | 0.175085 |
| N14 | 0.213824 | 0.292005 |
| N15 | -0.038749 | -0.166259 |
| H16 | 0.243890 | 0.302426 |
| S17 | -0.494547 | -0.675350 |
| C18 | 0.059889 | 0.259917 |
| N19 | -0.388393 | -0.546423 |
| H20 | 0.311711 | 0.346318 |
| H21 | 0.300466 | 0.344213 |

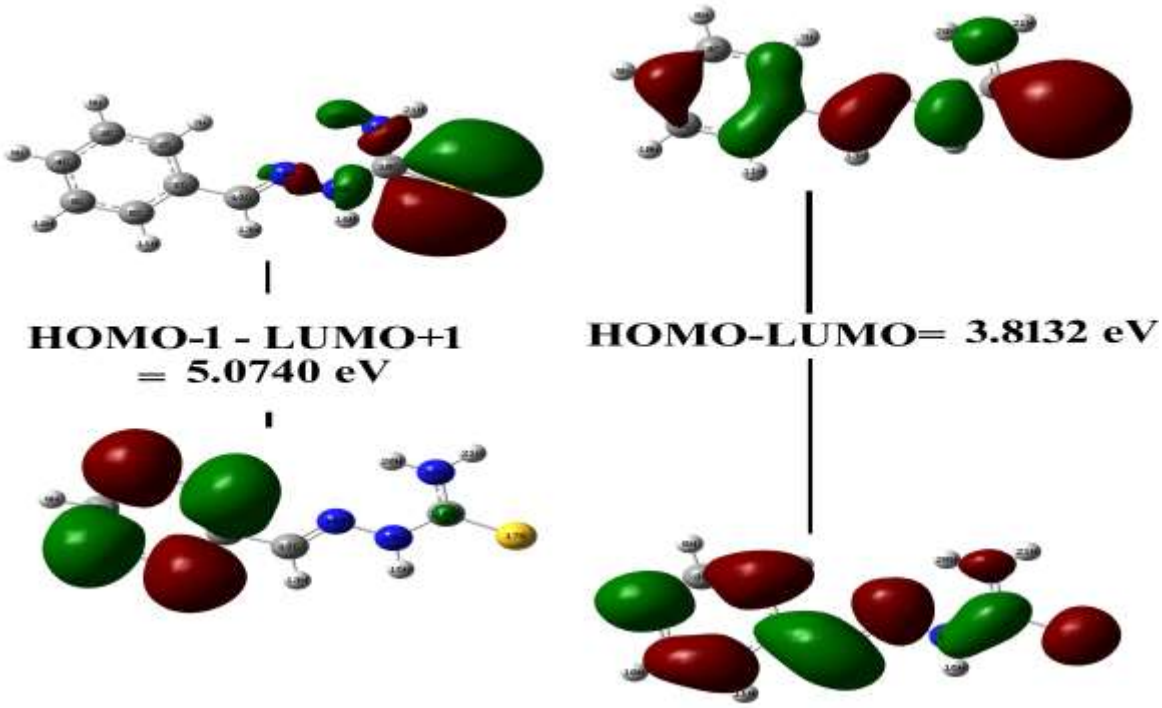
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### *4.4. Frontier Molecular Orbitals (FMOs)*

The highest occupied molecular orbital (HOMOs) and the lowest-lying unoccupied molecular orbital (LUMOs) are named as frontier molecular orbital (FMOs). The FMOs play a significant part in the optical and electrical attributes, as considerably as in quantum chemistry and UV–Vis spectra [18]. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity and, optical polarizability and chemical hardness–softness of a molecule [19, 20].

The energies of four important molecular orbital of thiosemicarbazone: the second highest and highest occupied MO's (HOMO, HOMO−1 and HOMO-2 ), the lowest and the second lowest unoccupied MO's (LUMO, LUMO+ 1 and LUMO+2) were calculated using B3LYP/6-311++G (d, p) and are presented in Table 4. 3D plots of the HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 orbits computed at the B3LYP/6-311G++ (d, p) level for thiosemicarbazone are illustrated in Fig. 4. But, while the HOMO-1 is localized on the benzene ring, LUMO+1 is localized on almost the whole molecule. Both the HOMOs and the LUMOs are, mostly π-anti-bonding type orbits.

The calculated energy values of HOMO are -6.2215, -6.2245, -6.2161 and -6.2204 a.u. In acetonitrile, DMSO, Ethanol and Methanol, respectively. LUMO are -1.9473, -1.9473, -1.9470 and -1.9473 a.u. In acetonitrile, DMSO, Ethanol and Methanol, respectively. The value of energy separation between the HOMO and LUMO is 4.2742, -4.2772, -4.2690 and -4.2731 a.u. In acetonitrile, DMSO, Ethanol and Methanol, respectively. The energy gap of HOMO–LUMO explains the eventual charge transfer interaction within the atom, which influences the biological activity of the speck. Furthermore, in proceeding from the gas phase to the solvent phase, the increasing value of the energy gap and the atom becomes more static. The HOMO is located over the group, the HOMO→LUMO transition implies an electron density transfer to ring from chlorine and partially from the pack. Consequently, the lowering of the HOMO–LUMO band gap is essentially a result of the large stabilization of the LUMO due to the strong electron-acceptor ability of the electron-acceptor group.



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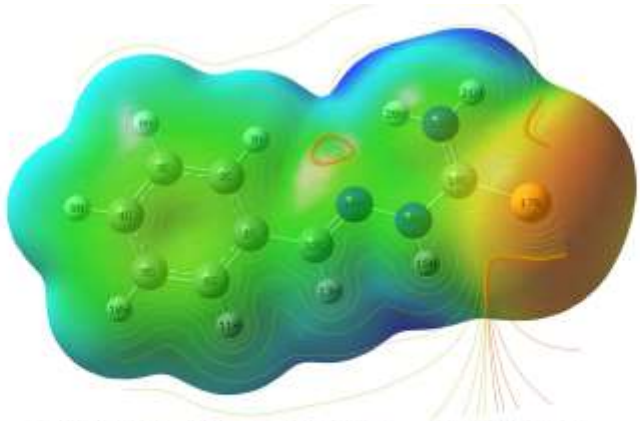
**Table 4.** Calculated energy values, chemical hardness, electronegativity and dipole moment of in Acetontrilie, DMSO, Ethanol and Methanol

| TD–DFT/B3LYP/ 6–311++G(d,p) | Acetontrilie | DMSO | Ethanol | Methanol |
|---|---|---|---|---|
| $E_{total}$ (Hartree) | -872.8670 | -872.8672 | -872.8667 | -872.8669 |
| $E_{HOMO}$ (eV) | -6.2215 | -6.2245 | -6.2161 | -6.2204 |
| $E_{LUMO}$ (eV) | -1.9473 | -1.9473 | -1.9470 | -1.9473 |
| $\Delta E_{HOMO–LUMO\ gap}$ (eV) | 4.2742 | 4.2772 | 4.2690 | 4.2731 |
| $E_{HOMO–1}$ (eV) | -6.4219 | -6.4278 | -6.4110 | -6.4194 |
| $E_{LUMO+1}$ (eV) | -0.7575 | -0.7567 | -0.7589 | -0.7578 |
| $\Delta E_{HOMO–1–LUMO+1\ gap}$ (eV) | 5.6643 | 5.6711 | 5.6521 | 5.6616 |
| $E_{HOMO–2}$ (eV) | -7.0067 | -7.0086 | -7.0032 | -7.0059 |
| $E_{LUMO+2}$ (eV) | -0.5536 | -0.5552 | -0.5504 | -0.5528 |
| $\Delta E_{HOMO–2–LUMO+2\ gap}$ (eV) | 6.4531 | 6.45337 | 6.4528 | 6.4531 |
| Electronegativity $\chi$ (eV) | -4.0844 | -4.0859 | -4.0815 | -4.0838 |
| Chemical hardness $\eta$ (eV ) | 2.1371 | 2.1386 | 2.1345 | 2.1365 |
| Softness $\zeta$ (eV )$^{-1}$ | 0.2339 | 0.2337 | 0.2342 | 0.2340 |
| Dipole moment (Debye) | 6.9963 | 7.0173 | 6.9581 | 6.9880 |

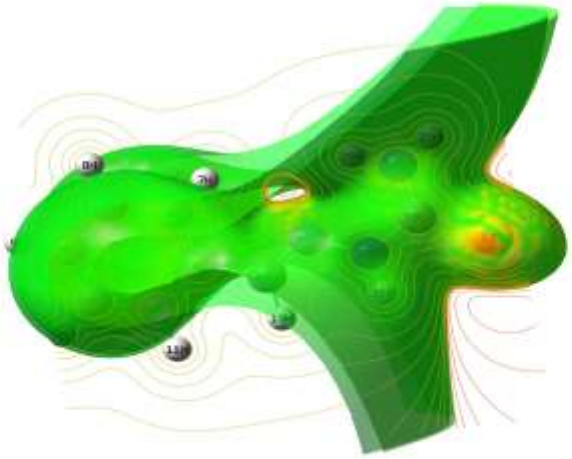
***4.5. Electrostatic potential, total electron density and Molecular electrostatic potential***

In the present study, the electrostatic potential (ESP) and molecular electrostatic potential (MESP) of thiosemicarbazone of m-nitrobenzaldehyde are illustrated in Fig. 5. Nevertheless, it can be viewed from the ESP figures, that while the negative ESP is localized to a greater extent over the particles and is chewed over as a greenish gloss. The MESP is a useful place to study the reactivity given that a nearing electrophile will be attracted to negative regions (where the electron distribution effect is dominant). The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading (Fig. 5) And is very useful in research of molecular structure with its physiochemical property relationship [21-25]. The resulting surface simultaneously displays molecular size and shape and electrostatic potential value.

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MSEP=+0.04884 to -0.04884



ESP=+0.006649 to -0.006649

The different values of the electrostatic potential at the show up are represented by different colors. Electric potential gains in the order red < orange < yellow < green < blue. The color code of these maps is in the range between -0.04884 a.u. (Deepest red) to 0.04884 (deep blue) in the compound, where blue indicates the strongest attraction and red indicates the strongest repulsion. The ESP color is in the range between -0.006649 to 0.006649 a.u. Regions of negative V (r) are usually associated with the lone pair of electronegative atoms.

***4.7 NMR Analysis***

The experiment and calculated $^{1}H$ and $^{13}C$ NMR chemical shift values of the thiosemicarbazone of m-nitrobenzaldehyde molecule is shown in Table 5 and in Fig.6 and have been compared with the experimental data. $^{1}H$ and $^{13}C$ NMR chemical shifts are reported in ppm relative to TMS. Firstly, full geometry optimization of the thiosemicarbazone molecule was carried out at the gradient corrected density functional level of theory using the hybrid B3LYP method based on Becke's three parameters functional of DFT. Thereafter, gauge-including atomic orbital (GIAO) $^{1}H$ and $^{13}C$ chemical shift calculations of the title compound was performed by the same method using 6-311++G (d,p) basis set. Aromatic carbons gave calculated signals in the overlapped regions of the $^{13}C$ spectrum of the title molecule with chemical shift values experimentally in the orbit of 131.5 to 142.3 ppm. Their corresponding theoretical chemical shift values occurred in the range of 135.5-143.5 ppm. Moreover, the highest $^{13}C$ chemical shift values were observed for C12 and C18 is 167.1 and 178.4 ppm. The hydrogen atoms are calculated values from 8.2 to 7.6 ppm.

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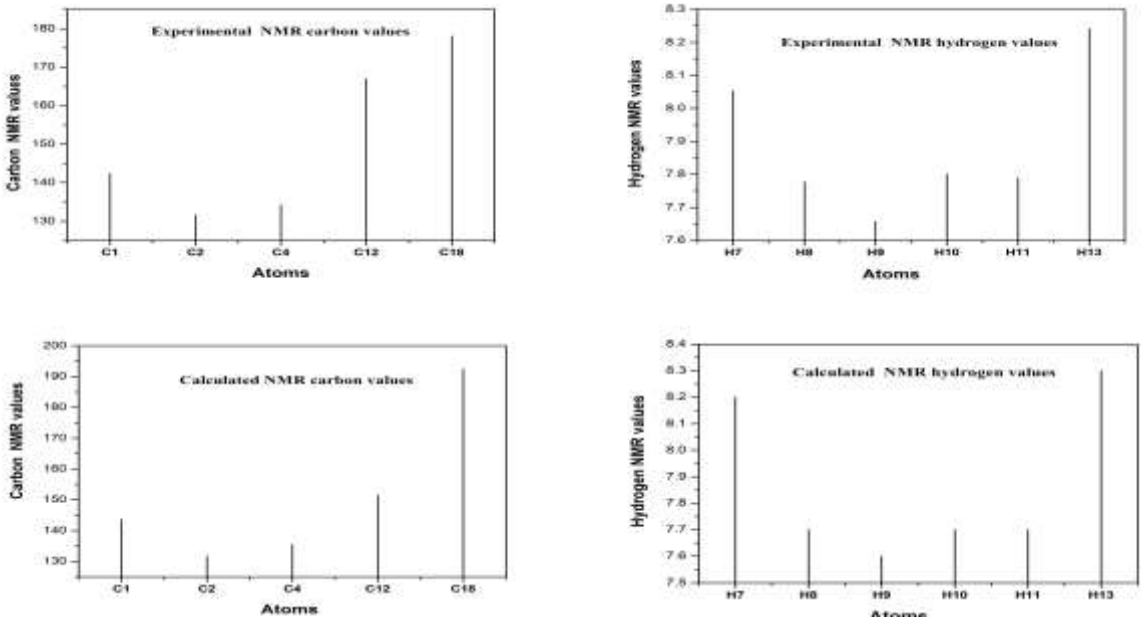


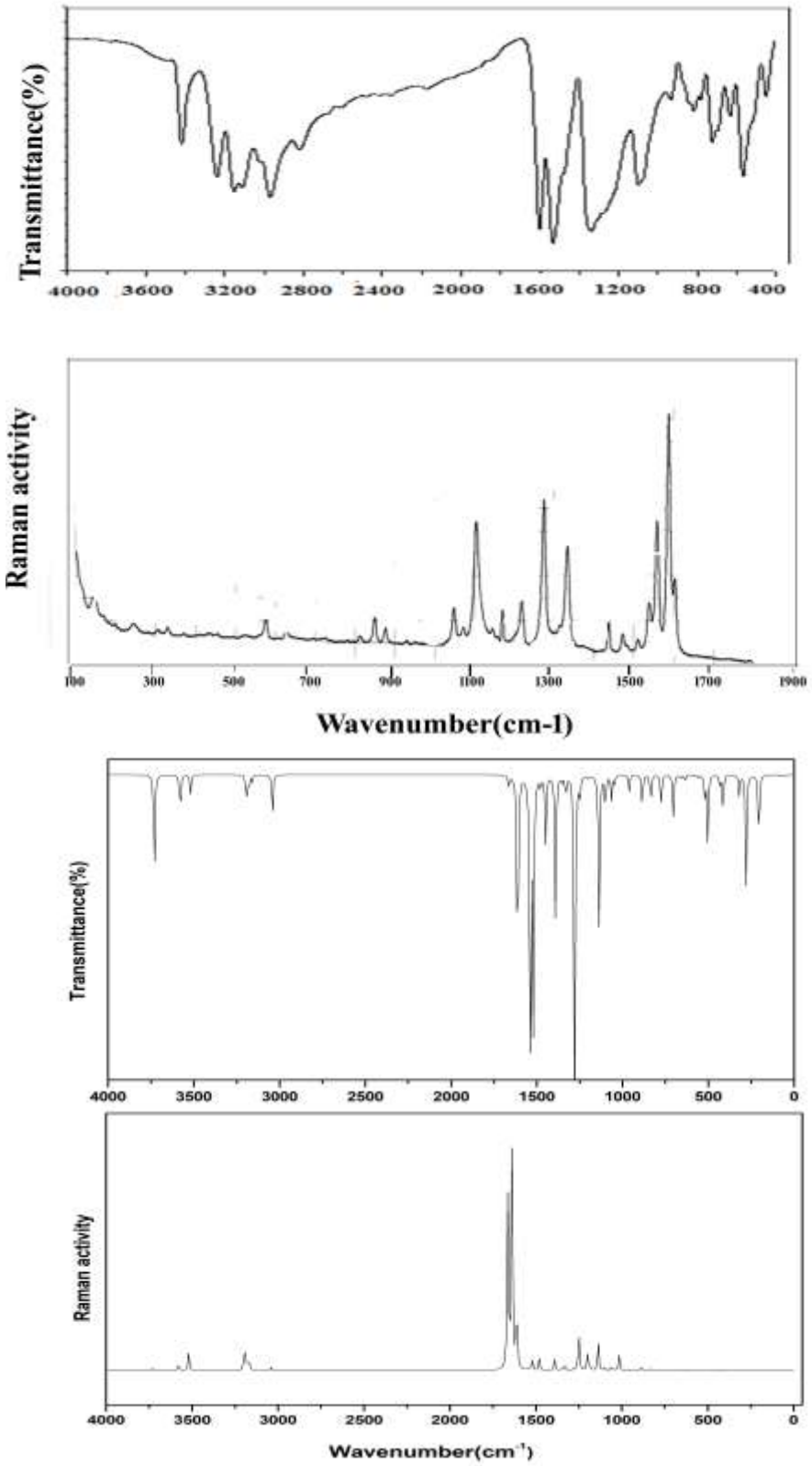

**Table .5:** Experimental and theoretical probable $^{13}C$ and $^{1}H$ NMR isotropic chemical shifts of compound (atom positions are numbered as in Fig. 1)

| Atom | Experimental | Theoretical | Atom | Experimental | Theoretical |
|---|---|---|---|---|---|
| C18 | 178.04 | 192.4 | H16 | | 9.4 |
| C12 | 167.01 | 151.5 | H13 | 8.242 | 8.3 |
| C1 | 142.38 | 143.5 | H7 | 8.053 | 8.2 |
| C4 | 134.22 | 135.5 | H10 | 7.801 | 7.7 |
| C6 | | 135.4 | H11 | 7.789 | 7.7 |
| C3 | | 135.4 | H8 | 7.777 | 7.7 |
| C5 | | 135.2 | H9 | 7.657 | 7.6 |
| C2 | 131.56 | 131.6 | H20 | | 6.3 |
| | | | H21 | | 6.3 |

### *4.8. Vibration analysis*

The upper limit form 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 exemption. Hence, thiosemicarbazone of m-nitrobenzaldehyde molecule, that was planar, has 21 atoms with 57 normal modes of oscillation. The fundamental modes are distributed species as: $\Gamma_{vib}=\Sigma$ (39A′+18A″). All vibrations are active both in infrared absorption. The detailed vibrational assignment of the experimental wavenumbers is based on normal mode analyses and a comparison with theoretical scaled wavenumbers by B3LYP method. Since the scaled wavenumbers following B3LYP/6-311++G (d-p) method are found closest to experimental data. The observed and simulated FT-IR of thiosemicarbazone is shown in Fig. 7 and 8.

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Table 6. Detailed assignments of theoretical wavenumbers of Thiosemicarbazone of m-nitrobenzaldehyde

| Number | Species | FTIR | FTRaman | B3LYP Unscaled | B3LYP scaled | $I_{IR}$ | SRaman | Mode description |
|---|---|---|---|---|---|---|---|---|
| 1. | A′ | 3419 | | 3730 | 3574 | 106.26 | 48.43 | γNH |
| 2. | A′ | | | 3579 | 3429 | 42.83 | 131.63 | γNH |
| 3. | A′ | 3350 | | 3519 | 3371 | 19.67 | 312.58 | γNH |
| 4. | A′ | | | 3200 | 3065 | 6.23 | 129.22 | γCH |
| 5. | A′ | | | 3191 | 3057 | 19.95 | 262.04 | γCH |
| 6. | A′ | 3040 | | 3179 | 3045 | 14.88 | 119.13 | γCH |
| 7. | A′ | | | 3168 | 3035 | 0.00 | 92.68 | γCH |
| 8. | A′ | 3025 | | 3159 | 3027 | 6.56 | 32.66 | γCH |
| 9. | A′ | 2920 | | 3042 | 2914 | 39.19 | 55.20 | γCH |
| 10. | A′ | 1630 | | 1663 | 1635 | 9.92 | 1910.25 | βNH |
| 11. | A′ | | 1610 | 1638 | 1610 | 1.07 | 2518.1 | βNH |
| 12. | A′ | | 1590 | 1613 | 1586 | 98.86 | 73.96 | βNH |
| 13. | A′ | | 1580 | 1611 | 1584 | 134.98 | 693.61 | γCC |
| 14. | A′ | | 1515 | 1539 | 1513 | 360.50 | 20.26 | γCC |
| 15. | A′ | | 1488 | 1521 | 1495 | 238.39 | 99.13 | γCC |
| 16. | A′ | | | 1479 | 1454 | 8.74 | 129.99 | γCC |
| 17. | A′ | | 1420 | 1449 | 1424 | 65.80 | 2.12 | γCC |
| 18. | A′ | 1365 | | 1391 | 1367 | 146.89 | 119.93 | γCC |
| 19. | A′ | | 1335 | 1354 | 1331 | 6.11 | 18.51 | γCC |
| 20. | A′ | | 1310 | 1331 | 1309 | 22.42 | 74.39 | γNN |
| 21. | A′ | | 1260 | 1279 | 1257 | 352.22 | 15.72 | γCN |
| 22. | A′ | | 1230 | 1250 | 1229 | 22.31 | 407.22 | γCN |

***4.8.1 C-H Vibrations***

Aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 $cm^{-1}$ [26, 27] due to aromatic C-H stretching vibrations. They are not appreciably affected by the nature of the substituent [28-30]. In the present study, the thiosemicarbazone is one substituted aromatic system; it has five C-H adjacent moieties. Hither, the C–H vibrations of the title compound are observed at 3040 and 3025 $cm^{-1}$ in FT-IR spectrum and one substituted C-H vibration in the range 2920 $cm^{-1}$. The bands due to C-H in-plane bending vibrations are observed in the region 1000–1300 $cm^{-1}$ [52, 53]. In this compound, the above vibrations are observed at 1025 and 950 $cm^{-1}$ in FT-IR. One band is slightly beyond the range. The theoretically scaled vibrations by B3LYP/6-311++G (d-p) level method also show good agreement with experiment recorded data. The C-H out-of-plane bending vibrations are appearing within the region 900-675 $cm^{-1}$ [52]. The vibrations obtained at 640 and 570 $cm^{-1}$ in FT-IR and 820 $cm^{-1}$ in FT-Raman is assigned to C-H out-of-plane bending for thiosemicarbazone of m-nitrobenzaldehyde. The C-H out-of-plane bending vibrations are also lie within the characteristic region.

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### *4.8.2 Ring Vibrations*

The ring stretching vibrations is expected within the region 1620-1390 $cm^{-1}$ [31]. Generally, the C-C stretching vibrations in aromatic compounds from the strong bonds. In the present study, the bands are of different intensity and are observed at 1580, 1515, 1488, 1420 and 1335 $cm^{-1}$ in FT- Raman and 1365 in FTIR have been assigned to C-C stretching vibrations. The experimental values are well coincide with calculated by B3LYP/6-311++G (d-p) method. The in-plane bending and out-of-plane bending modes are also good agreeing with experimental data. Only one infrared band at 430 $cm^{-1}$ is assigned to C–C-C in-plane bending vibrations of thiosemicarbazone of m-nitrobenzaldehyde. The bands are assigned to C-C-C out-of-plane bending vibrations 310 $cm^{-1}$ in FT-Raman spectrum of thiosemicarbazone.

### *4.4.6. C-N Vibrations*

Because of the mixing of several bands, the identification of C–N vibrations is a very difficult task. Silverstein [32] assigned C–N stretching absorption in the region 1382–1266 $cm^{-1}$. In the present work, the band observed in 1260, 1230 and 1170 $cm^{-1}$ in FT-Raman spectrum have been assigned to C-N stretching vibration. The mode calculated at 1257, 1229 and 1178 $cm^{-1}$ to 6-311++G (d-p) basis set is in agreement with experimental values. The experimental in-plane and out-of-plane bending vibrations well coincided with calculated values.

### *4.8.3. N-H and N-N vibrations*

Normally, the N–H stretching vibrations occur in the region 3500–3300 $cm^{-1}$. The asymmetric $–NH_2$ stretching, vibration appears from 3500 to 3420 $cm^{-1}$ and the symmetric $–NH_2$ stretching is observed in the range 3420–3340 $cm^{-1}$. In this work, the two $NH_2$ asymmetric stretches at 3419 and 3350 $cm^{-1}$ in FT-IR $cm^{-1}$ FT-Raman is in agreement with B3LYP/6-311++G (d-p) calculated values. The $NH_2$ in-plane deformation vibrations occur in the short range 1650–1580 $cm^{-1}$ region of the spectrum. Thus, a very strong band is observed at 1630 in FTIR $cm^{-1}$ and 1610 $cm^{-1}$ in FT-Raman is assigned in-plane deformation mode of the amino group. The amino out-of-plane bending normally appears in the range 1150–900 $cm^{-1}$. The out-of-plane bending modes are experimentally found at 1110, 1180 and 1150 $cm^{-1}$ and they are well assigned to the calculated values. These amino vibrations are also in good agreement with literature values of aniline [33-36]. The experimental values of N-N values are assigned well with calculated vibrations.

## 5. CONCLUSION

A complete vibration analysis of thiosemicarbazone of m-nitrobenzaldehyde is performed by HF and DFT-B3LYP methods in 6-311++G (d-p) basis sets. The influences of carbon-nitrogen bonds and phenyl ring to the vibrational frequencies of the title compound were discussed. The observed and simulated spectra are agreed for the good frequency fit in DFT/B3LYP/6-311++G (d-p) method. The conflict between theoretical and experimental wave numbers within 10 $cm^{-1}$ is supported by the qualitative agreement between the computed and observed frequencies. The same style is also contemplated in the optimized parameters. Various quantum chemical calculations help us to distinguish the structure and symmetry properties of the title molecule. The excellent agreement of the computed and observed vibrational spectra reveals the advantages of higher basis set for quantum chemical calculations. Furthermore, the thermodynamic and electronic absorption properties of the compound have been counted. The correlations between the statistical thermodynamics and temperature are also held. It was realized that the heat capacities, entropies and enthalpies increase with the increasing temperature owing to the intensities of the molecular vibrations increase with increasing temperature. The Milliken charge distribution is calculated and well in coincides with electronic distribution.

**Figure Captions**

Figure 1: The theoretical optimized possible geometric structure with atoms numbering of thiosemicarbazone of m-nitrobenzaldehyde
Figure 2: Thermodynamic functions and temperature for the thiosemicarbazone of m-nitrobenzaldehyde.
Figure 3: The Mulliken charge distribution for the thiosemicarbazone of m-nitrobenzaldehyde.
Figure 4: The molecular orbitals and energies for the HOMO-1, HOMO, LUMO and LUMO+1 of the thiosemicarbazone of m-nitrobenzaldehyde.
Figure 5: Electrostatic potential (ESP) and the molecular electrostatic potential map (MEP) for the thiosemicarbazone of m-nitrobenzaldehyde.
Figure 6: NMR experimental and calculated values of the thiosemicarbazone of m-nitrobenzaldehyde.
Figure 7: Experimental FT-IR and FT-Raman and spectra of thiosemicarbazone of m-nitrobenzaldehyde.
Figure 8: Calculated FT-IR and FT-Raman and spectra of thiosemicarbazone of m-nitrobenzaldehyde

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