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# Molecular Structure and HOMO-LUMO Studies of β-N-(3-methoxy phenyl) methylene Thiosemicarbazone Schiff base by *Ab-initio* methods

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## ABSTRACT

*The molecular geometry, net atomic charge and atom electron densities, HOMO-LUMO energy, ionization energy and thermodynamic parameters of the β-N-(3-methoxy phenyl) methylene thiosemicarbazone, are examined theoretically at the ab-initio HF/STO-3G, HF/3-21G & HF/6-31G levels. The correlation coefficients for bond lengths obtained HF/STO-3G, HF/3-21G and HF/6-31G levels are 0.9391, 0.9927 and 0.8931 respectively. It is evident that HF/3-21G level gives the maximum correlation (CC=0.9927) for bond lengths. In the case of bond angles, correlation coefficients are 0.8460, 0.8472, and 0.7997 for HF/STO-3G, HF3-21G and HF/6-31G methods respectively. It is evident that HF/3-21G method gives most satisfactory correlation (CC=0.8472) for bond angles. Net atomic charge & atom electron density data reveal the coordination sites in β-N-(3-methoxy phenyl) methylene thiosemicarbazone when it undergoes complexation with transition metal ions. Consequently, performance of ab-initio method at different levels of calculations has been tested to find the best auxiliary tool for the designing of a novel biological active compound.*

**Keywords:** β-N-(3-methoxy phenyl) methylene thiosemicarbazone, HF/STO-3G, HF/3-21G and HF/6-31G *ab-initio* levels, Correlation Coefficient (CC) and HOMO-LUMO energy.

## INTRODUCTION

Thiosemicarbazones exhibit various biological activities and have therefore attracted considerable pharmaceutical interest. They have been evaluated as antiviral, antibacterial and anticancer therapeutics. X-ray crystallography studies of this compound was first reported by Jian Zhang et al[1].The literature contains no computational study of this tridentate ligand; therefore, we report here the theoretical parameters of title compound by using *ab-initio* quantum chemical methods[2]**.** The success of quantum chemical methods in predicting a large number of important molecular properties has been an important part of their emergence as a legitimate tool for many chemical problems[3]. The most frequently used for quantum chemical studies of molecular properties are semi-empirical, *ab-initio,* Density functional and molecular mechanics methods. *Ab-initio* methods have been employed by different workers to study molecular structure, vibrational spectra, NMR, HOMO-LUMO energy and other different parameters[4-7].

D. Kumar et al reported the theoretical studies of the benzaldehyde thiosemicarbazone and also studied the geometry and HOMO-LUMO energy of the pyridine-2-carbaldehyde thiosemicarbazone[8-14]. In the present study, we have been employed HF/STO-3G[15], HF/3-21G[16] and HF/6-31G[17] levels of *ab-initio* methods with standard HF/STO-3G basis set. Thus, we report here the geometrical parameters like as bond length, bond angle, HOMO and LUMO energy, atom electron densities and net atomic charges and thermodynamic parameters by above mentioned quantum chemical methods.

## MATERIALS AND METHODS

Quantum chemical calculations were carried out by *ab-initio* HF/STO-3G, HF/3-21G and HF/6-31G methods by Gaussian programs of Hyperchem 8.0 Molecular Modeling program[18] to calculate geometry, net atomic charge, electron density, HOMO-LUMO energy and thermodynamic parameters. Intel based core i5-2450M CPU @ 2.50 GHz processor machine having 4 GB RAM and 500 GB hard disc was used to run all the calculations.

## RESULTS AND DISCUSSION

**Optimized Geometry:** Optimized geometry of β-N-(3-methoxy phenyl) methylene thiosemicarbazone is shown in fig.1The correlation coefficients (CC) for bond lengths obtained by *ab-initio* HF/STO-3G, HF/3-21G and HF/6-31G levels are 0.9391, 0.9927 and 0.8931 respectively. It is evident that HF/3-21G method gives the maximum correlation (CC=0.9927) for bond lengths. In the case of bond angles, correlation coefficients are 0.8460, 0.8472, and 0.7997 for HF/STO-3G, HF3-21G and HF/6-31G methods respectively. It is evident that HF/3-21G method gives most satisfactory correlation (CC=0.8472). The calculated and experimental bond lengths and bond angles are given in table 1 respectively and graph between experimental versus calculated bond lengths and bond angles are given in figure 2 , 3 respectively.

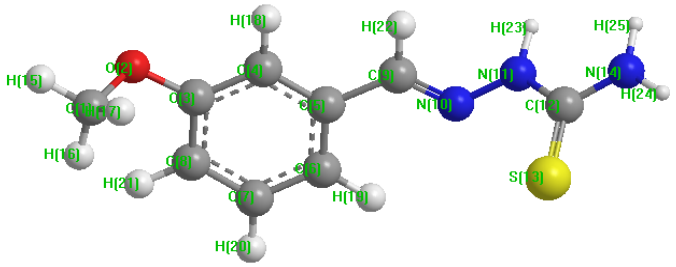


**Figure 1.** Optimized geometry of β-N-(3-methoxy phenyl) methylene thiosemicarbazone

**Table 1**. Calculated and experimental bond lengths and bond angles of β-N-(3-methoxy phenyl) methylene thiosemicarbazone by *ab-initio* HF/STO-3G, HF/3-21G and HF/6-31G levels

| **Bond Lengths** | **Experimental** | **Calculated** | | |
|---|---|---|---|---|
| | | **HF/STO-3G** | **HF/3-21G** | **HF/6-31G** |
| C1-O2 | 1.422 | 1.432 | 1.437 | 1.429 |
| O2-C3 | 1.371 | 1.399 | 1.368 | 1.396 |
| C3-C4 | 1.382 | 1.398 | 1.385 | 1.413 |
| C3-C8 | 1.377 | 1.392 | 1.384 | 1.406 |
| C5-C9 | 1.454 | 1.493 | 1.470 | 1.502 |
| C9-N10 | 1.270 | 1.287 | 1.261 | 1.300 |
| N10-N11 | 1.370 | 1.404 | 1.396 | 1.401 |

| | | | | |
|---|---|---|---|---|
| N11-C12 | 1.346 | 1.420 | 1.343 | 1.441 |
| C12-S13 | 1.683 | 1.610 | 1.745 | 1.574 |
| C12-C14 | 1.309 | 1.386 | 1.319 | 1.407 |
| **Correlation Coefficients (CC)** | --- | **0.9391** | **0.9927** | **0.8931** |
| **Bond Angles ($^0$)** | | | | |
| C1-O2-C3 | 116.9 | 114.9 | 121.0 | 114.5 |
| O2-C3-C4 | 114.8 | 114.5 | 115.1 | 114.8 |
| C4-C5-C9 | 122.0 | 121.2 | 121.3 | 120.3 |
| C5-C6-C7 | 119.8 | 119.8 | 119.4 | 120.0 |
| C5-C9-N10 | 120.3 | 121.0 | 122.7 | 121.0 |
| C6-C5-C9 | 118.0 | 119.4 | 118.6 | 119.6 |
| C7-C8-C3 | 119.1 | 119.4 | 119.8 | 119.7 |
| C9-N10-N11 | 116.4 | 115.1 | 117.8 | 115.4 |
| N10-N11-C12 | 119.1 | 121.9 | 120.0 | 122.3 |
| N11-C12-S13 | 118.7 | 122.2 | 119.3 | 122.6 |
| S13-C12-N14 | 124.1 | 126.3 | 123.6 | 126.9 |
| N11-C12-N14 | 117.1 | 111.4 | 117.0 | 110.3 |
| **Correlation Coefficients (CC)** | | **0.8460** | **0.8472** | **0.7997** |

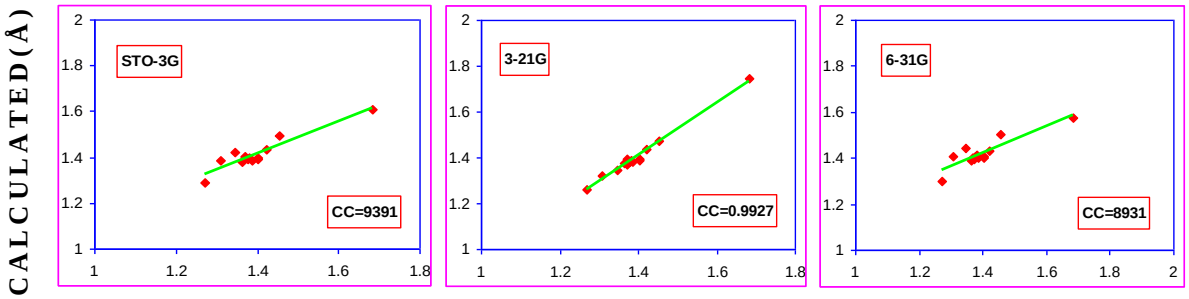


**Figure 2.** Graphic correlation between the experimental and calculated bond lengths obtained by *ab-initio* HF/STO-3G, HF/3-21Gand HF/6-31G methods

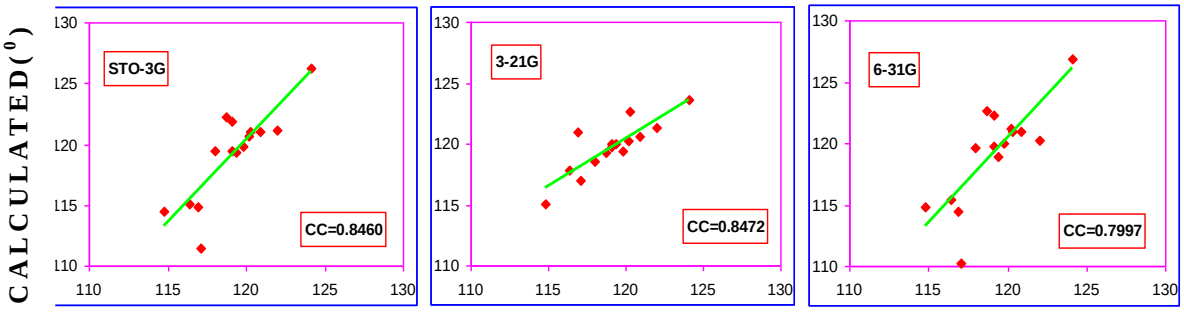


**Figure 3.** Graphic correlation between the experimental and calculated bond angles obtained by *ab-initio* HF/STO-3G, HF/3-21G and HF/6-31G methods

**Net atomic charges and Atom electron densities:** Calculated net atomic charges and electron densities are presented in Table 2. From this table, it is clear that different methods predicted different net atomic charges and electron densities on different atoms. The graphical presentation of electron densities on different atoms is also shown in figure 4. The table 2 shows that O(2), N(10), N(11), S(13) and N(14) have -0.233, -0.134, -0.270, -0.088 & -0.418 (HF/STO-3G) ; -0.737, -0.373, -0.690, -0.130 & -0.907(HF/3-21G) and -0.232, -0.139, -0.316, 0.111 & -0.673 (HF/6-31G) net atomic charges and 8.233, 7.134, 7.270, 16.088 & 7.418 (HF/STO-3G) ; 8.737, 7.373, 7.690, 16.130 & 7.907 (HF/3-21G) and 8.232, 7.139, 7.316, 16.889 & 7.673 (HF/6-31G) electron densities respectively. N(10), N(11), S(13) & N(14) are the probable coordination centre in this Schiff base. However, N(11) & N(14) if coordinated to central metal ion will form a 4-membered chelating ring, which is unstable. N(10) & S(13) , if coordinated to central metal ion will form a 5-membered chelating ring which is very stable. It is confirmed by experimental results. Although no complex of this Schiff base reported. But *m*-cyano benzaldehyde thiosemicarbazone is reported[19] to form a square planner complex with palladium(II) coordinating to through the azomethine nitrogen (N10) & thiolato sulfur (S13) atoms in the trans arrangement. Obviously (β-N-(3-methoxy phenyl) methylene thiosemicarbazone) should also form a square planner complex with central metal ion forming a 5-membered stable ring.

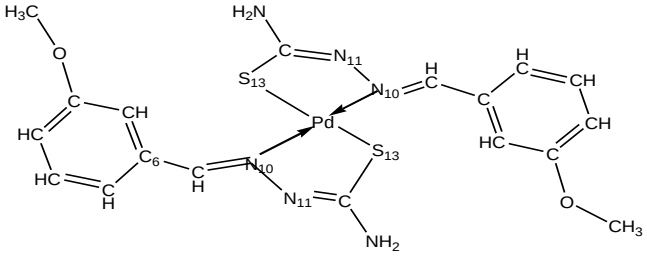


**Table 2.** Net atomic charges (NAC) and electron densities (ED) calculated *by ab-initio* HF/STO-3G, HF/3-21G & HF/6-31G levels

| Atom | HF/STO-3G | | HF/3-21G | | HF/6-31G | |
|---|---|---|---|---|---|---|
| | **NAT** | **ED** | **NAT** | **ED** | **NAT** | **ED** |
| O2 | -0.233 | 8.233 | -0.737 | 8.737 | -0.232 | 8.232 |
| N10 | -0.134 | 7.134 | -0.373 | 7.373 | -0.139 | 7.139 |
| N11 | -0.270 | 7.270 | -0.690 | 7.690 | -0.316 | 7.316 |
| S13 | -0.088 | 16.088 | -0.130 | 16.130 | 0.111 | 15.889 |
| N14 | -0.418 | 7.418 | -0.907 | 7.907 | -0.673 | 7.673 |

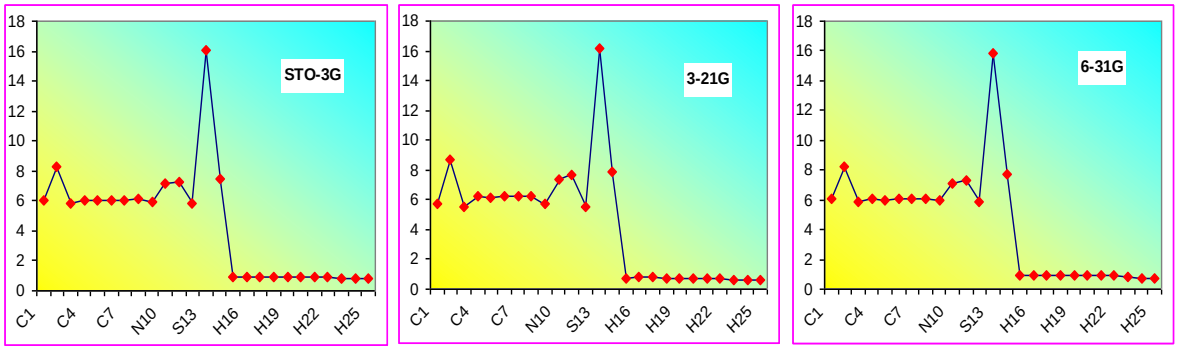


**Figure 4.** Graphical presentation of calculated electron densities on all atoms obtained by *ab-initio* HF/STO-3G, HF/3-21G & HF/6-31G levels

**HOMO-LUMO Energy:** The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity[20,21]. Higher value of HOMO of a molecule has a tendency to donate electrons to appropriate acceptor molecule with low energy, empty molecular orbitals. The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, hardness ($\eta$) and ionization energies (I) have been calculated and are given in table 3. Based on *ab-initio* HF/STO-3G, HF/3-21G and HF/6-31G levels, reveals that the energy gap reflects the chemical activity of the molecule are presented table 3. An electron system with a large HOMO-LUMO gap should be less reactive than having smaller gap. The ionization energy (IE) can be expressed through HOMO orbital energies as IE = $-E_{HOMO}$ and electron affinity (EA) can be expressed through LUMO orbital energies as EA = $-E_{LUMO}$. The hardness ($\eta$) corresponds to the gap between the HOMO and LUMO orbital energies. In the present study, the HOMO-LUMO gap of the molecule is 10.858608, 10.123712 and 11.368456 eV for HF/STO-G, HF/3-21G and HF/6-31G respectively as shown in table 3, which clearly indicates that the molecule is very stable.

**Table 3.** HOMO-LUMO energy calculated by *ab-initio* HF/STO-G, HF/3-21G and HF/6-31G levels for β-N-(3-methoxy phenyl) methylene thiosemicarbazone

| **PARAMETERS** | **HF/STO-3G** | **HF/3-21G** | **HF/6-31G** |
|---|---|---|---|
| $\varepsilon_{HOMO}$ | -5.362673 | -8.109756 | -6.125190 |
| $\varepsilon_{LUMO}$ | 5.495935 | 2.013956 | 5.243266 |
| $\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ | 10.858608 | 10.123712 | 11.368456 |
| $I = -\varepsilon_{HOMO}$ | 5.362673 | 8.109756 | 6.125190 |

**Thermodynamic parameters:** The computed total energy, electronic Kinetic energy, Nuclear repulsion energy and RMS Gradient for Schiff base by HF/STO-3G HF/3-21G and HF/6-31G ab-initio methods are given in table 4 and its graphical representations are presented in figure 5. HF/6-31G gives highest electronic kinetic energy value of 615663.2859 and HF/STO-3G gives lowest electronic kinetic energy value of 603519.3831. HF/3-21G gives higher value of Nuclear repulsion energy value of 556828.9747 (ev) and HF/STO-3G gives lowest nuclear repulsion energy value of 556828.9747 (ev). The HF/STO-3G gives higher value of RMS gradient value of 40.7537150 and HF/3-21G gives lowest RMS gradient value of 24.1557068.

**Table 4.** Computed Total energy, Electronic Kinetic energy, Nuclear repulsion energy and RMS Gradient obtained by *ab-initio* HF/STO-3G, HF/3-21G and HF/6-31G levels

| **PARAMETERS** | **HF/STO-3G** | **HF/3-21G** | **HF/6-31G** |
|---|---|---|---|
| Total energy (kcal/mol) | -609399.9162 | -613496.3663 | -616753.7692 |
| Electronic Kinetic energy (eV) | 603519.3831 | 612132.0682 | 615663.2859 |
| Nuclear Repulsion Energy | 556828.9747 | 556828.9747 | 556828.9747 |
| RMS Gradient | 40.7537150 | 24.1557068 | 27.7710192 |

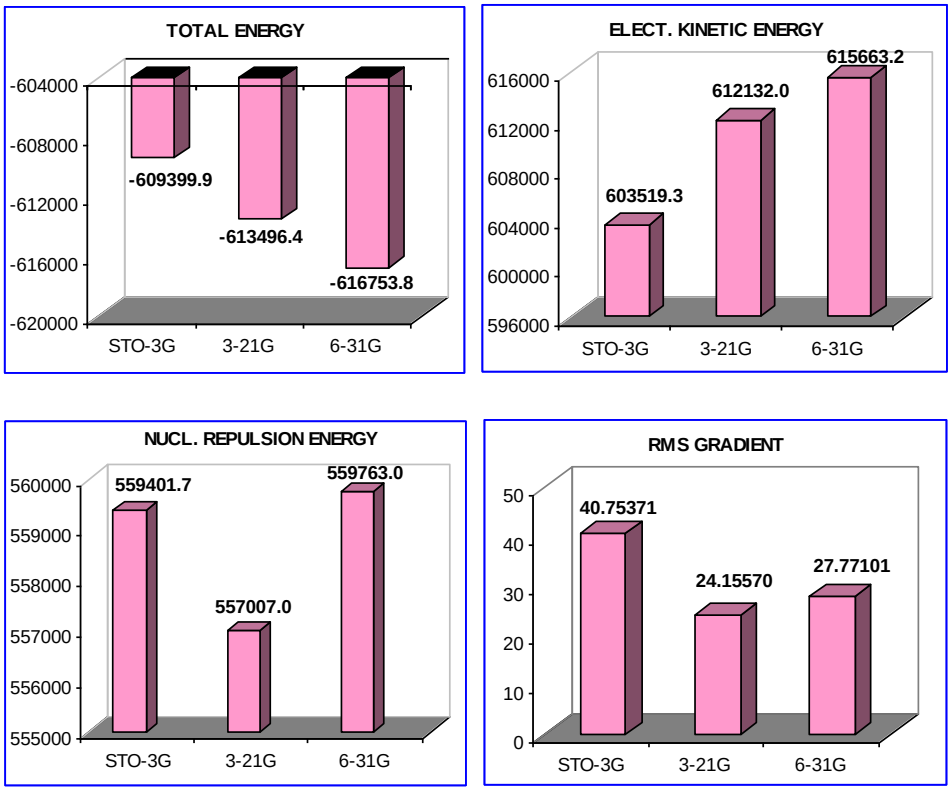


**Figure 5.** Graphic presentation of Total energy, Electronic kinetic energy and RMS gradient obtained by *ab-initio* HF/STO-3G, HF/3-21G and HF/6-31G levels

## APPLICATIONS

The *ab-initio* method at different levels of calculations has been applicable to find the best auxiliary tool for the designing of a novel biological active compound.

## CONCLUSIONS

*Ab-initio* HF/3-21G, HF/6-31G & HF/STO-3G levels proved to be important auxiliary tools for geometry optimization. The correlation coefficients for bond lengths obtained by HF/STO-3G, HF/3-21G and HF/6-31G methods are 0.9391, 0.9927 and 0.8931 respectively. It is obvious that **HF/3-21G** method gives the maximum correlation (CC=0.9927) for bond length. In the case of bond angles, correlation coefficients are 0.8460, 0.8472, and 0.7997 for HF/STO-3G, HF3-21G and HF/6-31G methods respectively. Unmistakably, **HF/3-21G** method present most satisfactory correlation (CC=0.8472). Atom electron densities and net atomic charges indicate the coordination sites in the molecule during complex formation with transition metal ions. Almost all *ab-initio* methods for electron densities are supported by experimental data electron densities. It is clear that 6-31G method give highest HOMO-LUMO gap and 3-21G lowest HOMO-LUMO gap energy. All three ab-initio methods predict different values for hardness. While 6-31G and STO-3G levels predict a highest value for hardness, the 3-21G level predicts a smallest value for hardness. Softness values are reciprocal of hardness value. Consequently, performance of *ab-initio* method at different levels of calculations has been tested to find the best auxiliary tool for the designing of a novel compound.

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