*Original Research Article*

# Some Molecular Properties and Reaction Mechanism of Synthesized Isatin Thiosemicarbazone and Its Zinc(II) and Nickel(II) Complexes

**Abstract:** The aim of this study is to 1H-Indole-2,3-dione 3-[N-(4-fluorophenyl)-thiosemicarbazone and its zinc(II) and nickel(II) complexes. The structures of the synthesized compounds were confirmed by spectral data and elemental analysis. They were optimized by B3LYP theory with different basis sets. The optimized structures were compared with the experimental values. TD-DFT calculations on electronic absorption spectra in gas phase and DMSO were performed to determine the electronic transitions of the compounds. The Frontier Molecular Orbital analysis were also done in order to identify the charge transfer interaction that takes place between the molecular orbitals. Reaction mechanism of 1H-indole-2,3-dione-3-(N-4-fluorophenyl thiosemicarbazone) molecules were also studied.

**Keywords:** Isatin; metal complexes; thiosemicarbazone; chemical computational calculations

## 1. INTRODUCTION

Isatin thiosemicarbazones are the most important class of biologically active ligands providing potential binding sites through nitrogen and sulphur donor atoms belong to thiosemicarbazone group and oxygen donor atoms belong to indole ring [1-5]. Metal complexes of isatin thiosemicarbazone derivatives, especially Zn(II), Ni(II), Pd(II) and Pt(II), have been extensively synthesized by several researchers because of their biological active properties, such as antibacterial, antiviral, anti-tuberculosis, antifungal activities [6-11].

We have recently experimentally synthesized and characterized some isatin thiosemicarbazones complexes, such as 5-methoxy and 5-fluoro isatin thiosemicarbazone, and theoretically studied the quantum chemical properties [12-18].

In this study, the theoretical vibrational spectrum, UV spectrum, $^{13}C$ and $^{1}H$ NMR values, molecular polarizability, molecular geometry, and atomic charges have been performed for 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone and its zinc(II) and nickel(II) complexes by using B3LYP hybrid functional with basis sets, 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p) and

6-311++G(2d,2p). Fukui functions have been calculated by using AOMix [16-17] from single-point calculations with B3LYP/6-311G(d,p).

## 2. MATERIAL AND METHOD

### 2.1. Experimental

Synthesis of 1H-indole-2,3-dione 3-[N-(4-fluorophenyl)-thiosemicarbazone-I4FPTH$_2$ was carried out by stirring 0.294 g (2 mmol) of isatin in 75 mL ethanol on a hot plate magnetic stirrer until dissolved and adding 0.306 g (2 mmol) of 4-florophenyl-3-thiosemicarbazide dissolved in ethanol and about 2-3 drops of fuming sulphuric acid on isatin solution under stirring, respectively. The mixture was refluxed for about 2-3 hours. The precipitated product was filtered, purified and dried. Orange solid product was obtained.

$C_{15}H_{11}ON_4S$ (Melting point, MP: 240.9 ºC and Molecule weight, MW= 314.34 g/mol), IR($cm^{-1}$): 3293, 3174(NH), 1684(C=O), 1621(C=N), 867(C=S), $^1$H NMR(DMSO-$d_6$,ppm): 7.74(dd, 1H, indol-$C_4$-H), 7.58(dd, 2H, phenyl), 7.35(dt, 1H, indol-$C_5$-H), 7.27(dd, 2H, phenyl), 7.13(dt, 1H, indol-$C_6$-H), 6.92(dd, 1H, indol-$C_7$-H), 10.83(t, 1H, $N_4$-H), 11.26(s, 1H, indol-NH), 12.80(s, 1H, $N_2$-H), (Calc.: C, 57.31; H, 3.53; N, 17.82; S, 10.20%; Found: C, 55.78; H, 2.96; N, 17.43; S, 10.93%).

#### 2.1.1. *Synthesis of bis{1H-indole-2,3-dione 3-[N-(4-fluorophenyl)thiosemicarbazonato}Zn(II) - Zn[(I4FPTH)$_2$]*

0.3142 g (1 mmol) of I4FPTH$_2$ was dissolved in 20 mL methanol at about 50-55 ºC and then 0.1097 g (0.5 mmol) of zinc acetate tetra dehydrate dissolved in 15 mL methanol was slowly added on it to synthesize the Zn[(I4FPTH)$_2$] complex. The mixture was refluxed for about 6-9 hours. A dark orange product was obtained. The Zn[(I4FPTH)$_2$] complex was washed with ethanol and diethyl ether, and then dried (MP: 256 ºC). (Calc.: C, 52.07; H, 2.91; N, 16.19; S, 8.98%; Found: C, 51.66; H, 2.92; N, 15.91; S, 8.98%).

#### 2.1.2. *Synthesis of bis{1H-indole-2,3-dione 3-[N-(4-fluorophenyl)thiosemicarbazonato}Ni(II) Ni[(I4FPTH)$_2$]*

Ni[(I4FPTH)$_2$] complex was synthesized by dissolving 0.3142 g (1 mmol) of I4FPTH$_2$ in 20 mL of methanol at about 50-55 ºC and then slowly adding 15 mL methanol solution containing 0.1244 g (0.5 mmol) of nickel acetate tetradehydrate. The mixture was refluxed for about 2 hours. Brown

Ni[$(I4FPTH)_2$] complex was precipitated, washed with ethanol and diethyl ether, and then dried (MP: 258 ºC). (Calc.: C, 52.57; H, 2.94; N, 15.91; S, 9.35%; Found: C, 50.94; H, 2.90; N, 15.60; S, 8.67%).

### 2.2. Calculation Method

$I4FPTH_2$ ligand was optimized at the level of B3LYP theory with 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets, and Zn[$(I4FPTH)_2$], Ni[$(I4FPTH)_2$] complexes were optimized at the level of B3LYP theory with 6-31G(d,p), 6-311G(d,p) basis sets in gas phase and DMSO solvent. $^{1}H$ and $^{13}C$ NMR chemical shifts were calculated by using the GIAO method at the level of B3LYP theory with 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets for $I4FPTH_2$ ligand. Reaction mechanism of $I4FPTH_2$ ligand was performed with semi-empirical method by using AM1 Package program. Gaussian 09 was used to perform calculations [19].

## 3. Result and Discussion

Figure 1 shows the optimized structure of 1H-indole-2,3-dione 3-[N-(4-fluorophenyl)-thiosemicarbazone molecules with the atom numbering calculated by using B3LYP/6-311G(d,p). Calculated bond lengths of $I4FPTH_2$ molecule with B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p), B3LYP/6-311G(2d,2p) method in gas phase and DMSO solvent are given in Figure 2 and Mulliken charges are presented in Figure 3.

It was observed that there was negative charges density on C17, C11, C5, C4, N6, O9, N21, N20, S7, N19 atoms in both gas and liquid (DMSO) phase. Calculations were completed by using B3LYP method and 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets for $I4FPTH_2$. Charge densities vary in accordance with the basis sets and depending on whether the gas or liquid phases. Mulliken charge of C17 atom calculated with the 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets are -0.125, -0.027, -0.330, -0.302 ē, respectively in gas phase, while in DMSO are -0.148, -0.051, -0.351, -0.315 ē and for N21 atom in gas phase are -0.380, -0.240, -0.068, -0.373 ē while in DMSO -0.386, -0.241, -0.082, -0.396 ē.

The optimized structures for the Zn[$(I4FPTH)_2$] and Ni[$(I4FPTH)_2$] calculated with B3LYP/6-311G(d,p) level are given in Figure 4. Bond lengths calculated with the B3LYP level and 6-311G(d,p) 6-31G(d,p), 6-311G(d,p) basis sets are given in Figure 5 and Mulliken charges are given in Figure 6. As can be seen from the Figure 5, there is no significant difference in bond lengths according to the basis sets. Therefore, either 6-311G(d,p), or 6-311G(d,p) basis sets might be preferred to calculate bond lengths.

Bond lengths of $I4FPTH_2$ ligand, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$ complexes calculated according to B3LYP/6-311G(d,p) theory are given in Figure 7. Bond length for C15-C17 atoms belong to indole ring for $I4FPTH_2$ ligand, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$ complexes is 1.390, 1.393, 1.395 Å; for C10-N6 bond length is 1.403, 1.396, 1.392 Å; for C18-N21 bond length is 1.296, 1.305, 1.310 Å and for N21-N20 bond length is 1.332, 1.357, 1.347 Å, respectively. There is a little increasing in bond lengths at thiosemicarbazone side of complexes.

Negative charge density on C11, C5, C4, N6, O9 atoms and positive charge density on C10, C12, C18 atoms belong to indole ring of $Zn[(I4FPTH)_2]$ complex was found. The negative charge density on C11, C5, C4, N6, O9 atoms are -0.106 ē, -0.092, -0.108 ē, -0.674 ē, -0.476 ē, for 6-31G(d,p) basis set and 0.034, -0.135, -0.083, -0.048, -0.490, -0.316 ē, for 6-311G(d,p) basis set, respectively. The positive charge density on C10, C12, C18 atoms are 0.304, 0.622, 0.261 ē; for 6-31G(d,p) basis set and 0.252, 0.429, 0.204 ē for 6-311G(d,p) basis set, respectively. N21, N20, S7, N19 atoms belong to thiosemicarbazone group have negative charge density, these are 0.499, -0.308¸ -0.227, -0.598 ē for 6-31G(d,p) basis set, and -0.533, -0.220, -0.436, -0.399 ē for 6-311G(d,p) basis set, respectively. Mulliken charge calculated with 6-311G(d,p) is lower than of 6-31G(d,p).

According to B3LYP/6-311G(d,p) theory; the Mulliken charges on C17, C11, C5, C4, C10, C15, N6, C12, O9, C18 atoms are -0.027, -0.100, -0.090, -0.041, 0.239, -0.135, -0.489, 0.422 ē, for $I4FPTH_2$ ligand; 0.034, -0.135, -0.083, -0.048, 0.252, -0.157, -0.490, 0.429, -0.316, 0.204 ē, for $Zn[(I4FPTH)_2$ complex and 0.012, -0.113, -0.082, -0.051, 0.239, -0.132, -0.488, 0.312, -0.322, 0.224 ē, for $Ni[(I4FPTH)_2]$ complex, respectively. Mulliken charges on N21, N20, C16, S7, N19, C13 belong to thiosemicarbazone group are -0.240, -0.270, 0.230, -0.214, -0.462, 0.199 ē, for $I4FPTH_2$ ligand; -0.533, -0.220, 0.164, -0.436, -0.399, 0.143 ē, for $Zn[(I4FPTH)_2$ complex and -0.485, -0.263, 0.195, -0.312, -0.428, 0.169 ē, for $Ni[(I4FPTH)_2]$ complex, respectively. Mulliken charge of Zn atom in $Zn[(I4FPTH)_2$ complex and Ni atom in $Ni[(I4FPTH)_2]$ complex were calculated as 1.379 and 1.045 ē (Figure 8).

### 3.1 Reaction mechanism study of 1H-indole-2,3-dione-3-(N-4-fluorophenyl thiosemicarbazone) molecules

The calculation was caried out on protonated form of 1H-indole-2,3-dione and 4-(4-Fluorophenyl)-3-thiosemicarbazide and continued to protonated form of product in the reaction mechanism study. The reaction mechanism was studied with semi-empirical method Austin Model (AM1). Reactants, transition states (TS), intermediates (IN1) and products of spatial arrangements of atoms are given in Figure 9. Bond lengths and Mulliken charges of 1a-2, TS1, IN1**,** TS2**,** 3b molecules are given in Figure 10.

Gaussian assumes electronic distribution as a function of the molecular geometry (Born-Oppenheimer approximation). The vibrational frequency calculations are required for understanding whether it has been obtained from a stable minimum structure. Negative imaginary frequencies were found in calculations for TS1 and TS2 (the negative frequencies for TS1 and TS2 are 315 and 1743 $cm^{-1}$).

As well as the presence of a negative frequency defining the minima connected through the transition state is required. We chose the intrinsic reaction coordinate (IRC), and defined as the minimum energy reaction pathway (MERP) in mass-weighted Cartesian coordinates that between the transition state of a reaction and its reactants and products (Figure 11).

4-(4-Fluorophenyl)-3-thiosemicarbazide molecule and protonated 1H-indole-2,3-dione molecule are far from each other (C13-N17= 3.00 Å). The distance between N17 atom belong to 34-(4-Fluorophenyl)-3-thiosemicarbazide molecule and C13 atom attached to protonated 1H-indole-2,3-dione molecule in the transition state, intermediate state and product state is 1.950, 1,496, 1,560, 1.314 Å, respectively. C=O bond length belong to indole ring in reactant state, TS1, IN, TS2 and product state is found as 1.226, 1.229, 1.230, 1.232 and 1.226 Å, respectively. The Mulliken charge of N17 atom in reactant state, TS1, IN, TS2 and product state is 0.290, -0.235, -0.001, -0.052, -0.025 ē, respectively and the Mulliken charge of C11 atom in reactant state is 0.276, 0.299, 0.144, 0.107, 0.144 ē, respectively. This explains that, N17 atom belong to 4-(4-Fluorophenyl)-3-thiosemicarbazide molecule attacks to C13 atom attached to protonated 1H-indole-2,3-dione ring as nucleophile.

The reactivity of a molecule is closely related to the highest occupied molecular orbital-HOMO and the lowest empty molecular orbital –LUMO and the parameters such as hardness, softness can be calculated using HOMO and LUMO energies. The higher value of $E_{HOMO}$ means its ability to donate electrons to appropriate acceptor molecules with low energy empty MO. $E_{HOMO}$ value indicates the ability to donate electrons and $E_{LUMO}$ indicates the ability to accept electrons. HOMO, LUMO energies and five molecular orbital energies close to HOMO and LUMO of $I4FPTH_2$ molecule obtained from the calculations with the 6-31G(d,p), 6-311G(d, p), 6-311++G(d,p), 6-311G(2d,2p) basis sets of B3LYP method in gas phase and solvent (DMSO) (Figure 12) and those for $Zn[(I4FPTH)_2]$, $Ni[(I4FPTH)_2]$ calculated with the 6-31G(d,p), 6-311G(d,p) basis sets of B3LYP method are given in Figure 13.

It was observed that $E_{HOMO}$ and $E_{LUMO}$ values calculated with B3LYP method for carried out basis sets in DMSO solvent were lower than those in gas phase. For example, while $E_{HOMO}$ values in the gas phase calculations by using 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets are -0.21723, -0.22651, -0.23083, -0.22967 au, in the DMSO solvent calculations are -

0.22080, -0.22847, -0.23206, -0.23073 au. $E_{LUMO}$ values are -0.09713, -0.10535, -0.11099, -0.10979 au in gas phase, and -0.09283, -0.10157, -0.10648, -0.10528 au in DMSO solvent.

HOMO and LUMO energies for Zn[(I4FPTH)$_2$], Ni[(I4FPTH)$_2$] calculated with 6-31G(d,p) basis set is higher than those calculated with 6-311G(d,p) basis set. HOMO with the 5 molecular orbital energies close to Frontier orbitals and LUMO with the 5 molecular orbital energies close to Frontier orbitals are -0.20833, -0.20901, -0.21880, -0.22292, -0.23609, -0.23976, -0.10223, -0.10212, -0.01653, -0.01576, -0.00909, -0.00879 au for the calculations with 6-31G(d,p) basis set and are 0.21823, -0.21868, -0.22907, -0.23242, -0.24647, -0.24876, -0.11209, -0.11104, -0.02777, -0.02744, -0.02112, -0.02102 au for the calculations with 6-311G(d,p) basis set (Figure 13).

Frontier orbital energies of ligand and its zinc(II) and nickel(II) complexes are given in Figure 14. HOMO energy for I4FPTH$_2$ ligand and Zn[(I4FPTH)$_2$], Ni[(I4FPTH)$_2$ complexes at the level of theory B3LYP/6-311G(d,p) were calculated as -0.22651, 0.19795, -0,21823 au, respectively and LUMO energies of those were calculated as -0,10535, -0,10037, -0,11209 au. HOMO energies of complexes are higher than its ligand.

The electronic energy data for I4FPTH$_2$ calculated with 6-311G(d,p), 6-311++G(d,p), 6-311++G(2d,2p) basis sets in gas phase and DMSO solvent and for Zn[(I4FPTH)$_2$], Ni[(I4FPTH)$_2$] complexes calculated with 6-31G(d,p), 6-311G(d,p) basis sets are given in Table 1 in au units.

The electronic energy for I4FPTH$_2$ calculated with the level of B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p), B3LYP/6-311++G(2d,2p) are -1370.50690942, -1370.75982233, -1370.77771190, -1370.81055509 au, respectively. The lowest electronic energy structure was predicted by B3LYP/6-311++G(2d,2p) in DMSO solvent. Calculated electronic energies in DMSO (-1370.83735522 au) is lower than in gas phase (-1370.81055509 au) for the same basis sets.

Polarizability, α, is the distortion outer electrons under the influence of the electric field as a result of migration from one region to another in the presence of an electric field. As α increase, electron cloud can be polarized easily. Electric dipole polarization may be calculated by the following equation.

$$\alpha = \frac{1}{3}\left(\alpha_{xx} + \alpha_{xx} + \alpha_{zz}\right)$$

Polarizability increases when basis set level increases. Polarizability values calculated with 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311++G(2d,2p) basic sets of B3LYP theory for I4FPTH$_2$ ligand are 246.4, 257.0, 277.5, 283.0 Bohr$^3$, respectively. The polarizability of metal complexes is more than their ligands (Table 2).

### 3.2. NMR Study

$^{1}H$ and $^{13}C$ NMR values for $I4FPTH_2$ ligand calculated with 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets of B3LYP theory in gas phase and DMSO solvent are given in Tables 3 and 4 with the experimental values. $^{1}H$ and $^{13}C$ NMR values of $Zn[(I4FPTH)_2]$ complex calculated with 6-31G(d,p) and 6-311G(d,p) basis sets with the experimental ones are presented in Table 5.

The correlation coefficient excluding Hydrogen atom belonging to indole ring in $^{1}H$ NMR calculations performed with B3LYP and 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets in gas phase is found as 0.856, 0.861, 0.864, 0.888 ppm, respectively and in DMSO solvent 0.773, 0.841, 0.870, 0.870 ppm, respectively (Table 3).

The correlation coefficient of $^{13}C$ NMR calculations performed with B3LYP and 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets in gas phase is found as 0.987, 0.984, 0.984, 0.985 ppm, respectively and in DMSO solvent 0.950, 0.941, 0.983, 0.985 ppm, respectively. Correlation coefficients between calculated and observed chemical shifts for $^{13}C$ NMR carried out with B3LYP and 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p) basis sets are 0.987, 0.984, 0.984, 0.985 ppm, respectively in DMSO solvent and are in 0.950, 0.941, 0.983, 0.985 ppm in gas phase (Table 4). Accordingly, $^{1}H$ NMR calculation performed with B3LYP/6-311G(2d,2p) calculation in DMSO gives excellent correlation between computed and observed $^{13}C$ NMR spectra.

The lack of N-H31 chemical shift belong to thiosemicarbazone group for $Zn[(I4FPTH)_2]$ complex which is observed for $I4FPTH_2$ ligand indicates that deprotonation take place during complexation reaction.

### 3.3. UV Study

UV calculations for molecular structure of $I4FPTH_2$ ligand, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$ were simulated by using TDDFT. Oscillator strengths (f) and excitation energies (eV) for UV spectra values of all studied compounds were summarized in Table 6 with the experimental values.

176th molecular orbital calculated with B3LYP/6-31G(d,p) theory is HOMO and 177th molecular orbital is LUMO in the $Zn[(I4FPTH)_2]$ complex. The transition observed at 479 nm in the TDB3LYP/6-31G(d,p) level consists of mainly HOMO-1↔LUMO and HOMO↔LUMO+1 and transition assigned at 266 nm is belong to HOMO-17↔LUMO+1, HOMO-16↔LUMO, HOMO-

2↔LUMO+2, HOMO-1↔LUMO+2, HOMO↔LUMO+3 transitions. The absorption bands for Zn[(I4FPTH)$_2$] complex observed at 654, 436 and 259 nm were assigned at 744, 431, 310 nm in the calculation with B3LYP/6-31G(d,p) theory, respectively (Table 6).

In the FTIR spectra of I4FPTH$_2$ in Table 7, the experimental bands at 3292, 3174 and 3073 cm$^{-1}$ correspond to the stretching of ν(N6–H26), ν(N19–H30), and ν(N20–H31) bonds, respectively, whereas ν(N6–H) belong to isatin ring and ν(N19-H30) belong to thiosemicarbazone group were assigned at 3381 and 3328 cm$^{-1}$ for Zn[(I4FPTH)$_2$] and at 3405 and 3277 cm$^{-1}$ for Ni[(I4FPTH)$_2$] complexes, respectively. The ν(N6–H26), ν(N19–H30) and ν(N20–H31) bands stretching of I4FPTH$_2$ compound have been calculated at 3643, 3502 and 3428 cm$^{-1}$ with B3LYP/6–31G(d,p). Whereas in the Zn[(I4FPTH)$_2$] complex, the ν(N6-H) belong to isatin ring and ν(N19-H30) belong to thiosemicarbazone group were assigned at 3648 and 3604 cm$^{-1}$, and assigned at 3653 and 3613 cm$^{-1}$ for Ni[(I4FPTH)$_2$]. The ν(N20–H31) for I4FPTH$_2$ observed at 3073 cm$^{-1}$ was disappeared in Zn[(I4FPTH)$_2$] and Ni[(I4FPTH)$_2$] complexes, it is assumed that this could be due to the dissociation of the proton. The presence of the band at 1681 cm$^{-1}$ in the Zn(II) complex agrees with the uncoordinated nature of the CO group, whereas CO group of I4FPTH$_2$ assigned at 1684 cm$^{-1}$ undergoes a negative shift for Ni[(I4FPTH)$_2$] complex. This indicates coordination also occurs via C=O functional groups in addition to C=N and C=S functional groups.

## 4. CONCLUSIONS

Results of quantum chemical calculations of 1H-indole 2,3-dione-3-(N-4-fluorophenyl thiosemicarbazone and its Zinc (II) and Nickel (II) complexes showed that HOMO energies and polarizibility of complexes are found higher than those ligand. In addition to quantum chemical calculations, experimental values indicates that Zn(II) complex of ligand coordinates via C=N and C=S of its ligand while Ni(II) complex coordinates via C=O C=N and C=S. The results of $^{13}$C NMR calculation with B3LYP/6-311G(2d,2p) method were obtained most sensitive in the all methods.

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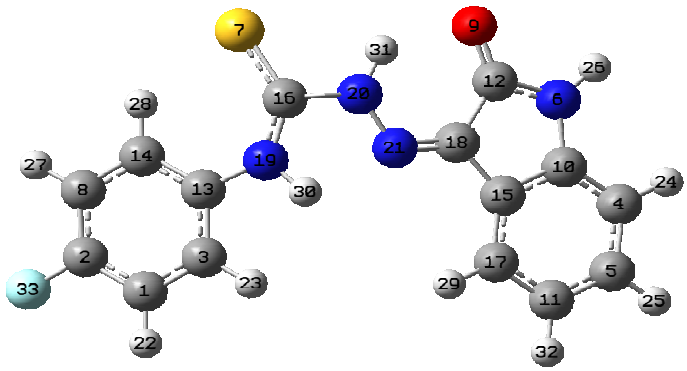



**Figure 1** The optimized structure of 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecules with the atom numbering calculated by using B3LYP/6-311G(d,p)

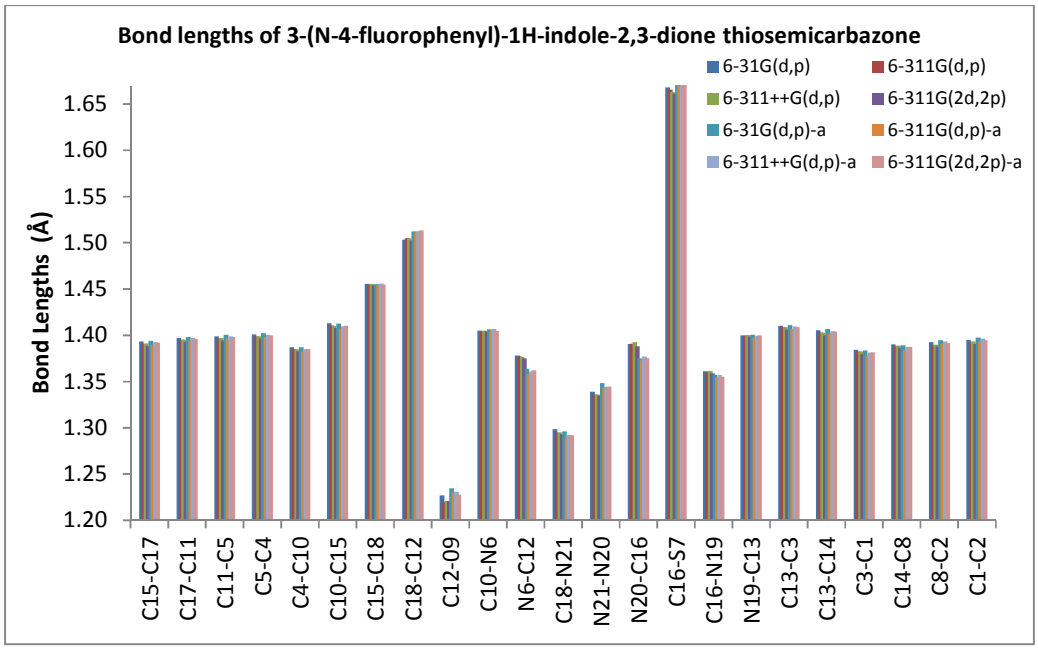



**Figure 2** Bond lengths of 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecules

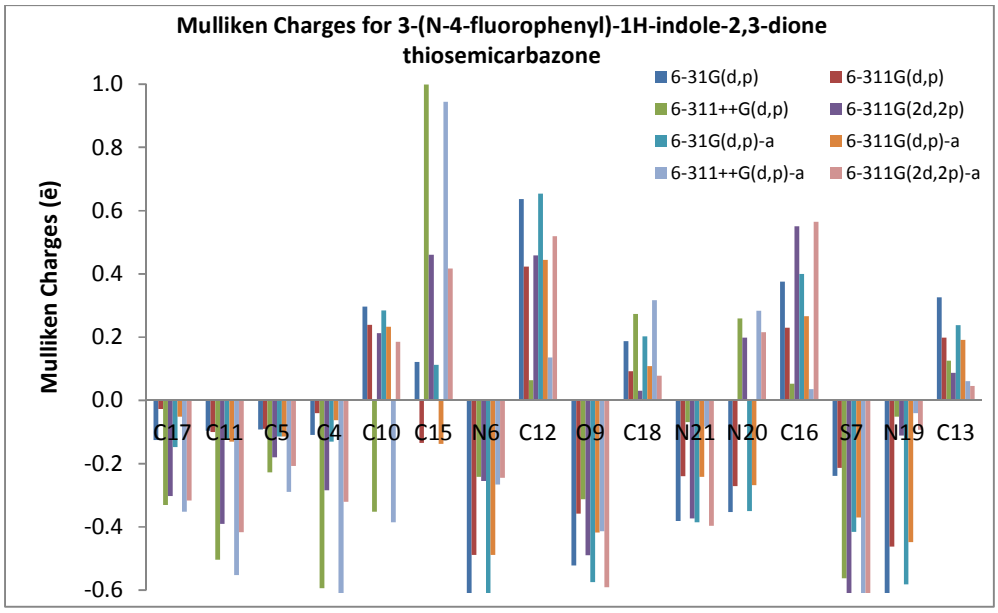
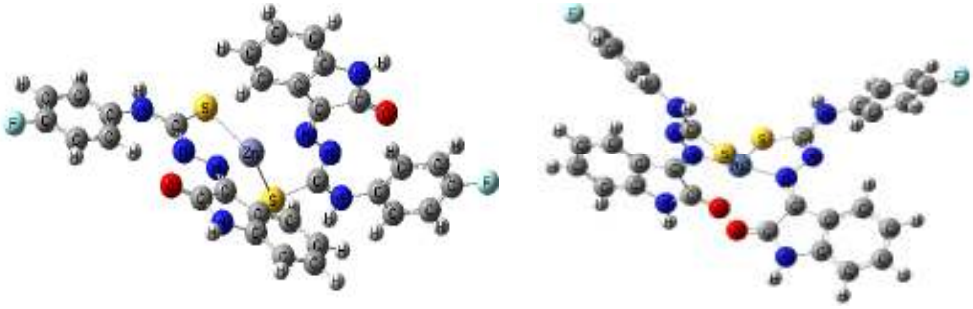
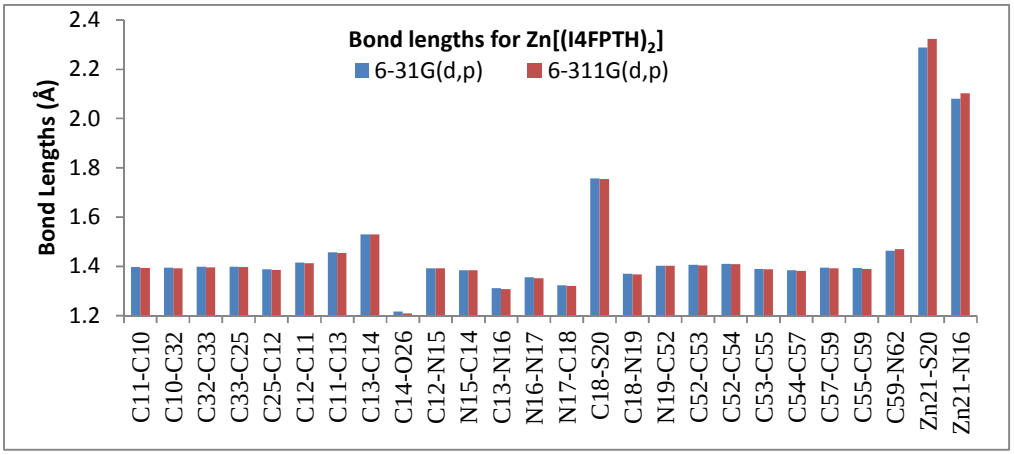



**Figure 3** Mulliken charges of 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecules



$Zn[(I4FPTH)_2]$ $Ni[(I4FPTH)_2]$

**Figure 4** Optimized structure of $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$



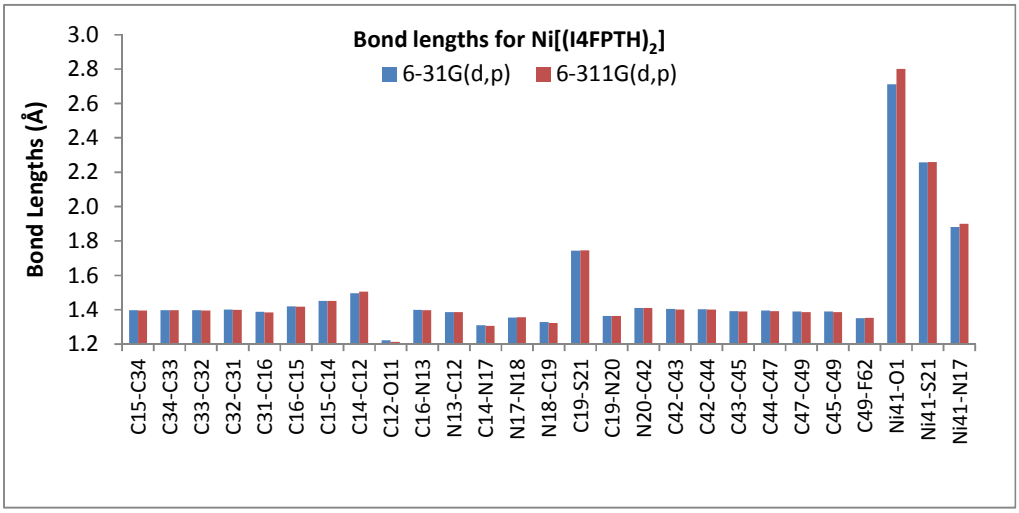




**Figure 5** Bond lengths for (a) Zn[(I4FPTH)$_2$] and (b) Ni[(I4FPTH)$_2$] complexes

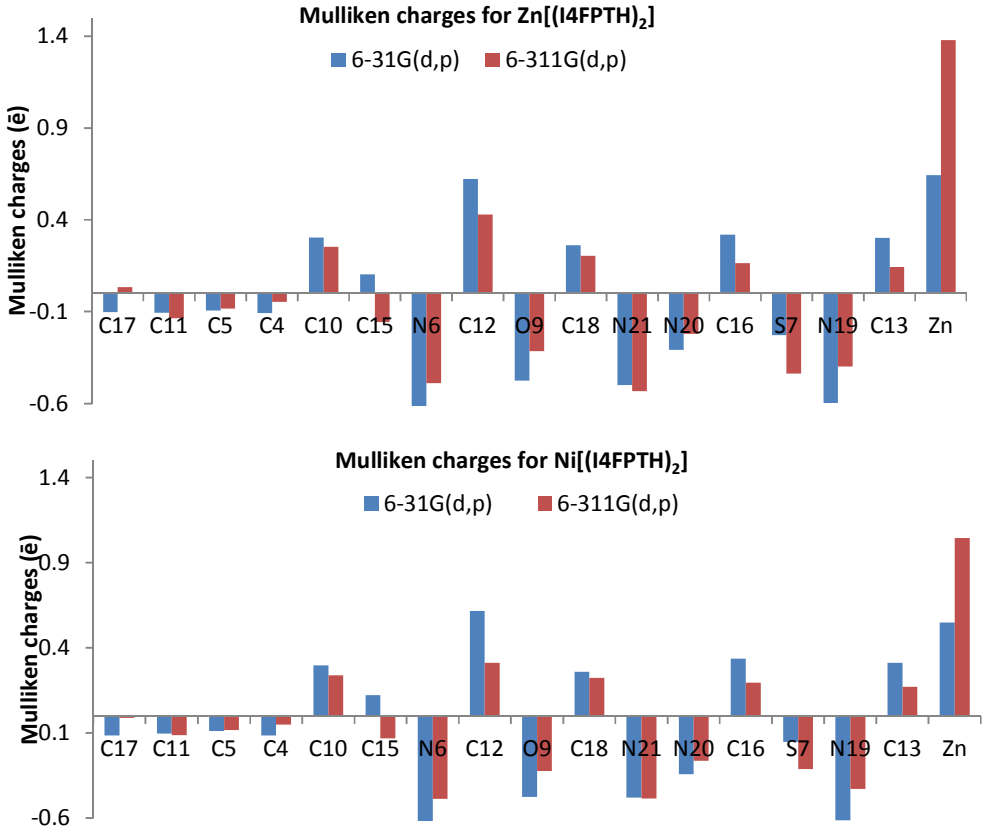



**Figure 6** Mulliken charges for Zn[(I4FPTH)$_2$] and Ni[(I4FPTH)$_2$] complexes

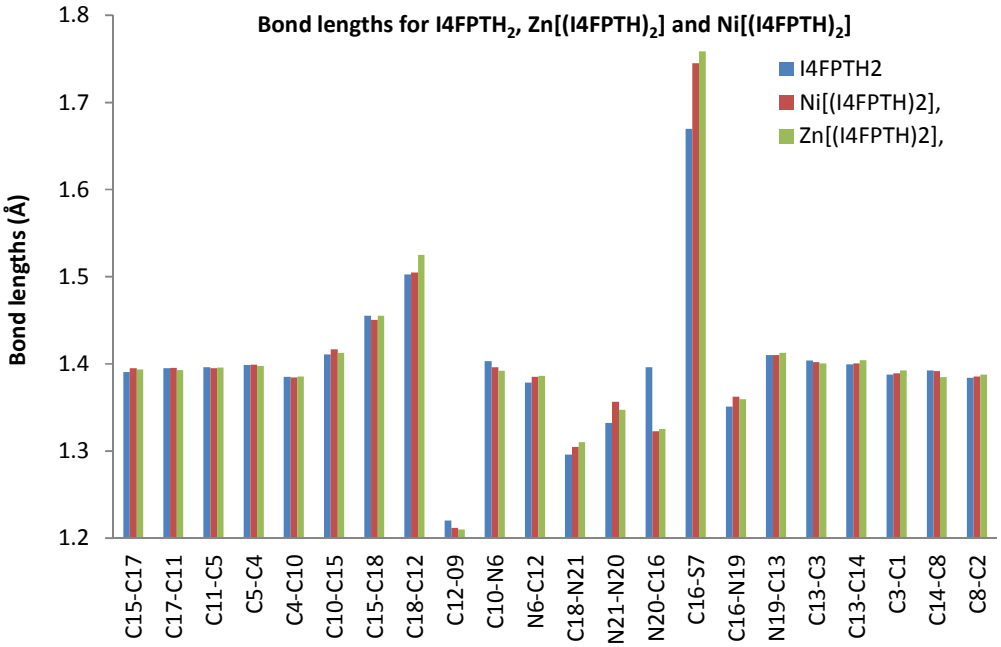



**Figure 7** Bond lengths for $I4FPTH_2$, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$ calculated with B3LYP/6-311G(d,p) method

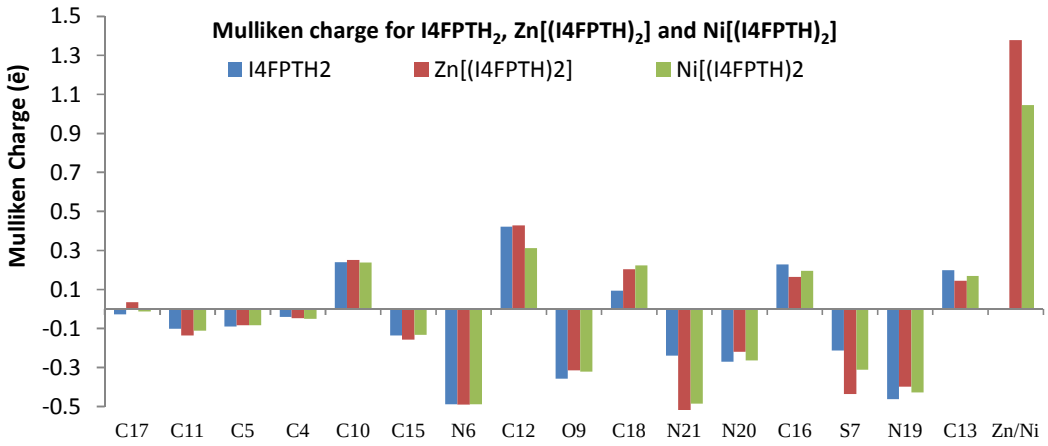



**Figure 8** Mulliken charge for $I4FPTH_2$, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$ calculated with B3LYP/6-311G(d,p) method

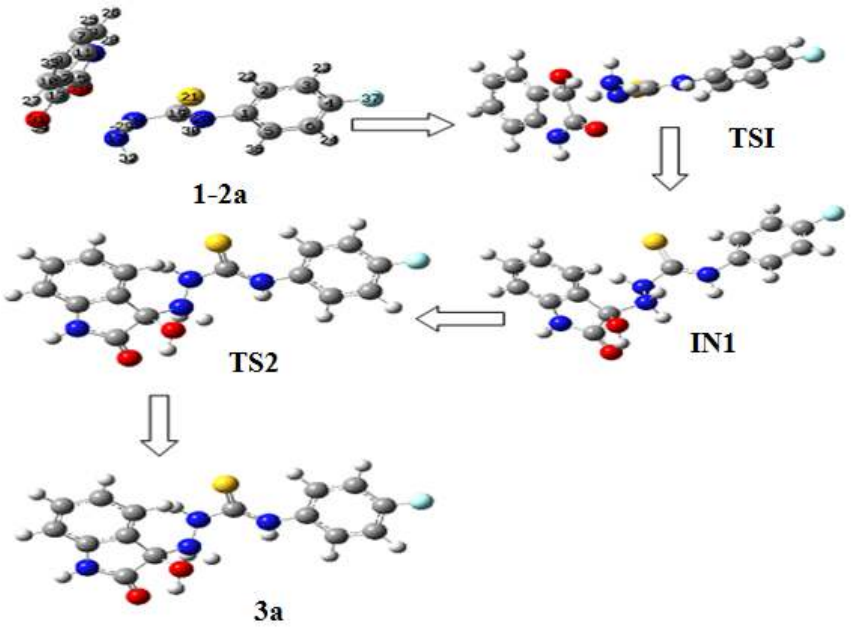



**Figure 9** Optimized structures of Reactants, transition states (TS), intermediates (IN1) and products

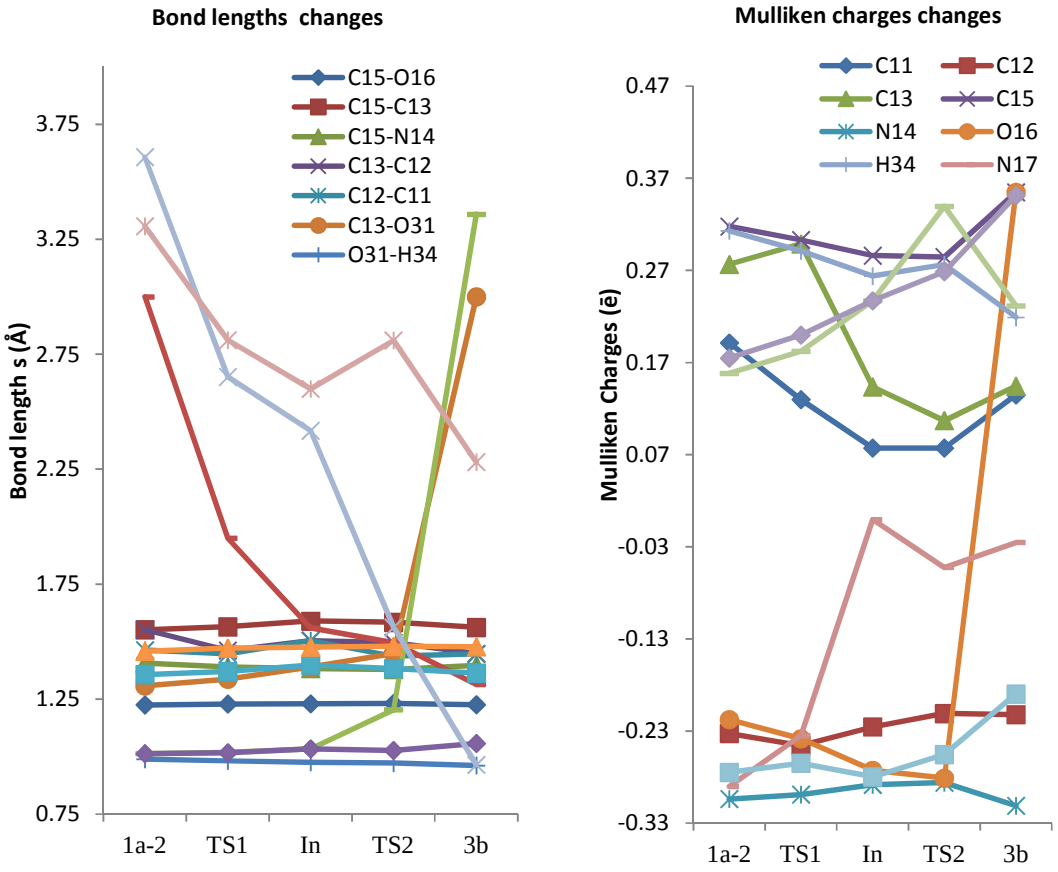



**Figure 10** Bond lengths changes and Mulliken charges changes in the reaction mechanism for 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecule

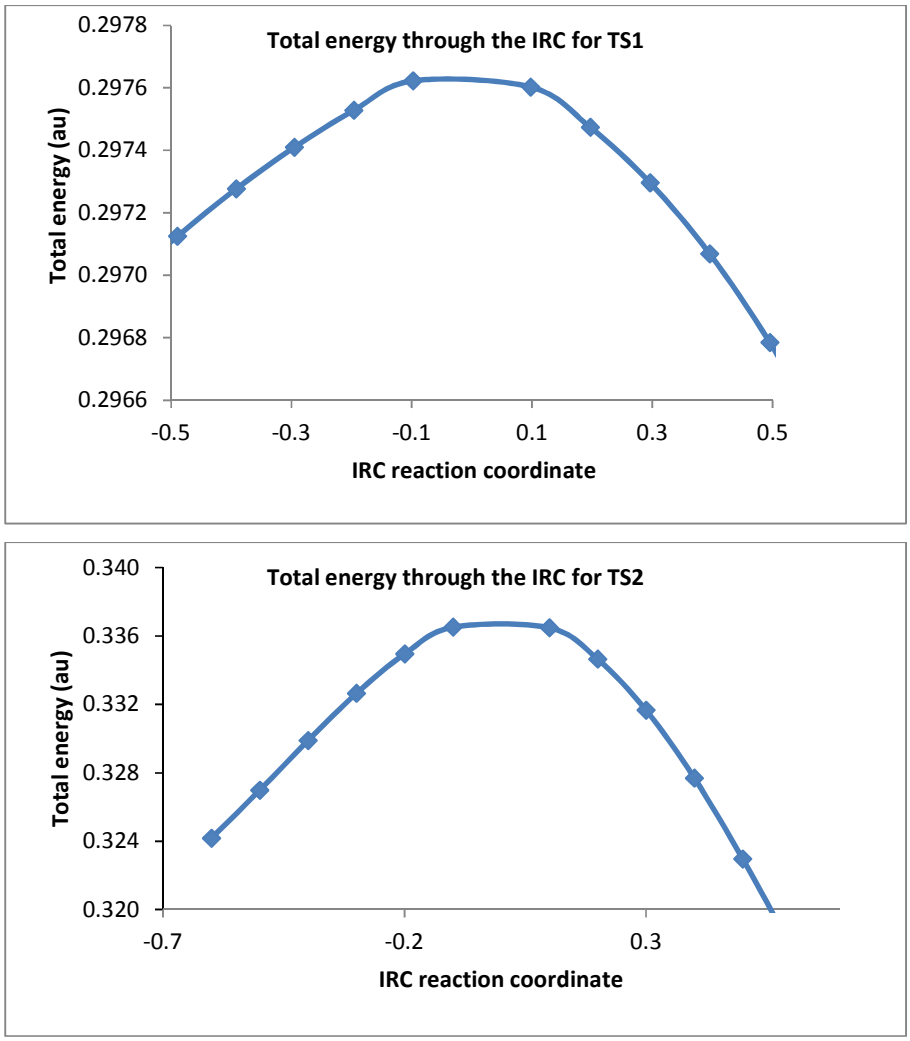



**Figure 11** Total energy through the IRC for 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecule

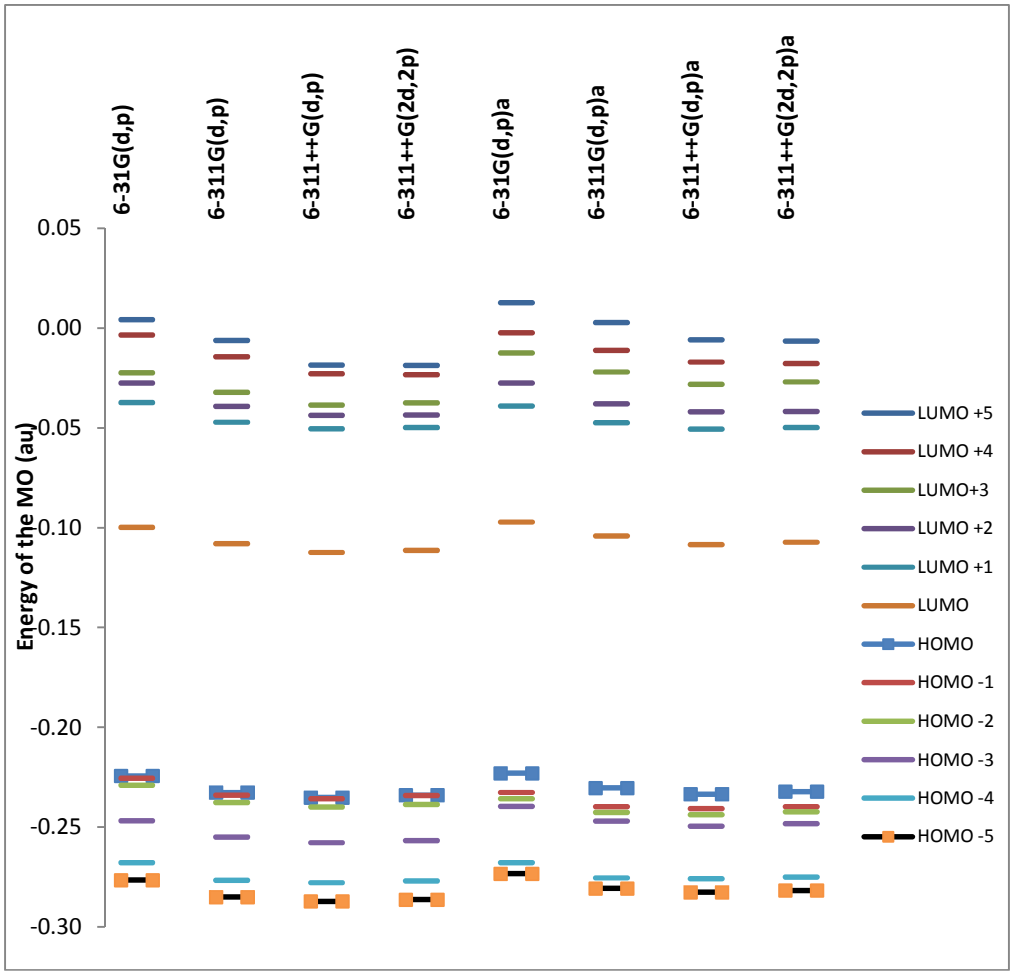



**Figure 12** Molecular orbital energies of 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecules

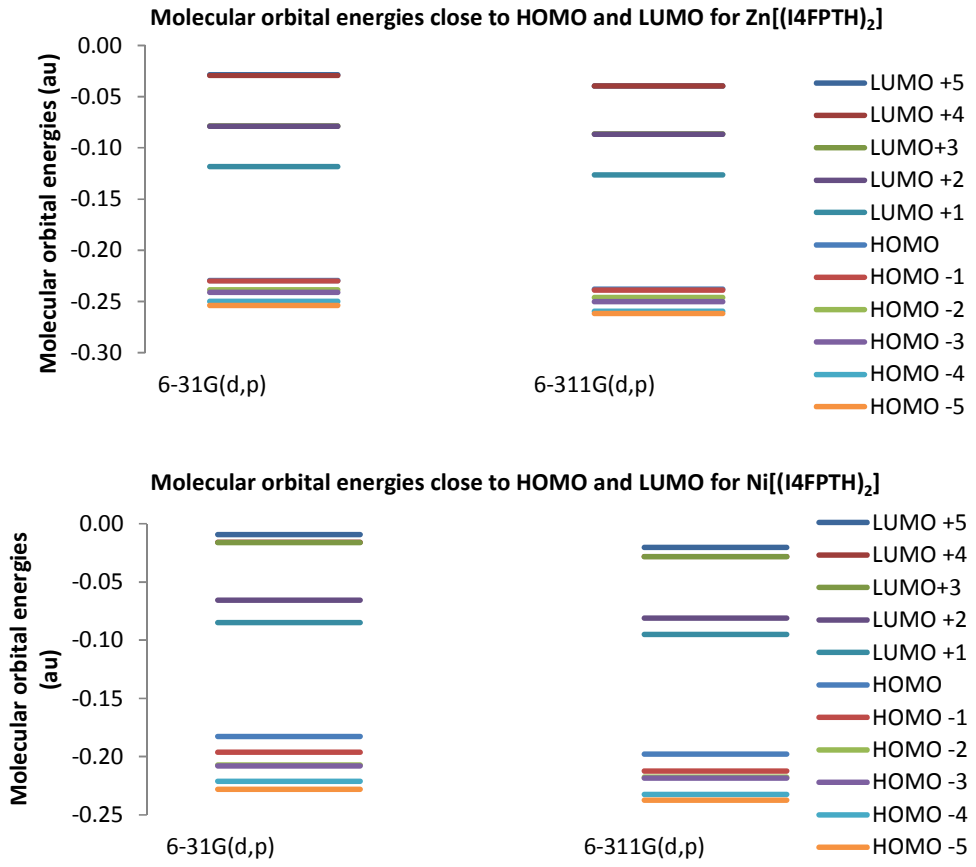



**Figure 13** Molecular orbital energies close to HOMO and LUMO for Zn[$(I4FPTH)_2$] and Ni[$(I4FPTH)_2$]

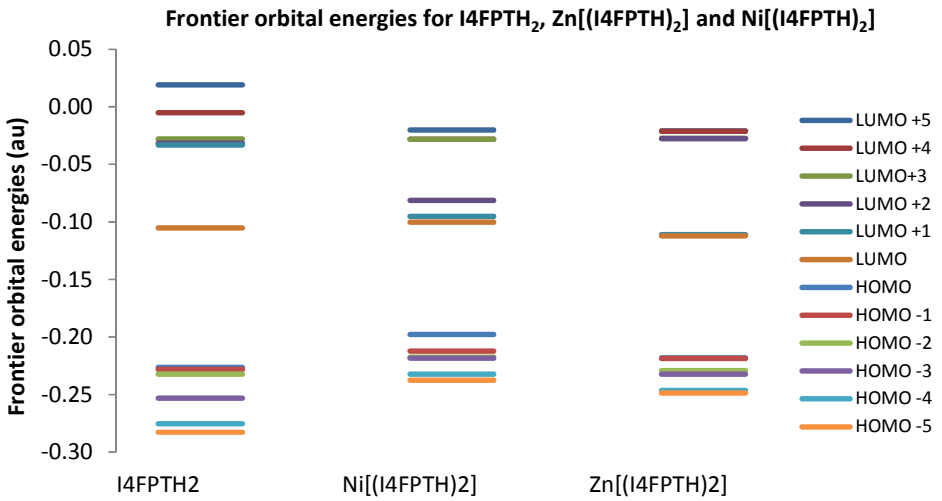



**Figure 14** Frontier orbital energies for $I4FPTH_2$, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$ calculated with B3LYP/6-311G(d,p) method

**Table 1. Electronic energies for $I4FPTH_2$, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$ complexes**

| Compounds | | Electronic Energies (B3LYP) (au) 6-31G(d,p) | 6-311G(d,p) | 6-311++G(d,p) | 6-311++ G(2d,2p) |
|---|---|---|---|---|---|
| $I4FPTH_2$ | gas | -1370.50690942 | -1370.75982233 | -1370.77771190 | -1370.81055509 |
| | DMSO | -1370.53408912 | 1370.78639203 | -1370.80560437 | -1370.83735522 |
| $Ni[(I4FPTH)_2]$ | gas | -4248.03385394 | 4248.66059430 | | |
| $Zn[(I4FPTH)_2]$ | gas | -4519.01672668 | -4519.68637322 | | |

**Table 2. Polarizibilty of $I4FPTH_2$, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$**

| Compounds | 6-31G(d,p) | 6-311G(d,p) | 6-311++G(d,p) | 6-311++G(2d,2p) |
|---|---|---|---|---|
| $I4FPTH_2$ | 246.4 | 257.0 | 277.5 | 283.0 |
| $Zn[(I4FPTH)_2]$ | 542.0 | 554.8 | | |
| $Ni[(I4FPTH)_2]$ | 552.5 | 562.4 | | |

**Table 3. Experimental and theoretical $^{1}$H NMR values of 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecule**

| Atoms | Exp. | 6-31G(d,p) | 6-311G(d,p) | 6-311++G(d,p) | 6-311G(2d,2p) | 6-31G(d,p)-a | 6-311G(d,p)-a | 6-311++G(d,p)-a | 6-311G(2d,2p)-a |
|---|---|---|---|---|---|---|---|---|---|
| H29 | 7.74 | 7.66 | 7.79 | 7.75 | 7.93 | 7.92 | 8.05 | 7.91 | 8.20 |
| H24 | 6.92 | 6.72 | 6.85 | 6.82 | 7.00 | 7.25 | 7.41 | 7.19 | 7.55 |
| H32 | 7.13 | 7.14 | 7.22 | 7.18 | 7.38 | 7.43 | 7.58 | 7.41 | 7.73 |
| H25 | 7.35 | 7.34 | 7.43 | 7.40 | 7.62 | 7.74 | 7.87 | 7.71 | 8.06 |
| H28 | 7.58 | 9.89 | 10.00 | 9.97 | 10.32 | 7.94 | 9.85 | 9.66 | 10.17 |
| H23 | 7.58 | 6.72 | 6.89 | 6.85 | 7.11 | 7.60 | 7.45 | 7.33 | 7.66 |
| H27 | 7.27 | 7.07 | 7.23 | 7.19 | 7.39 | 7.49 | 7.64 | 7.53 | 7.81 |
| H22 | 7.27 | 6.97 | 7.10 | 7.06 | 7.29 | 7.51 | 7.64 | 7.53 | 7.82 |
| H30 | 10.83 | 9.41 | 9.45 | 9.41 | 10.04 | 9.13 | 9.60 | 9.70 | 10.20 |
| H31 | 11.26 | 12.59 | 12.36 | 12.33 | 13.11 | 13.03 | 12.63 | 12.56 | 13.29 |
| H26 | 11.26 | 6.22 | 6.25 | 6.21 | 6.77 | 8.17 | 8.24 | 8.36 | 8.76 |
| $R^2$ | | 0.856 | 0.861 | 0.864 | 0.888 | 0.773 | 0.841 | 0.870 | 0.870 |

**Table 4. Experimental and theoretical $^{13}C$ NMR values of 3-(N-4-fluorophenyl)-1H-indole-2,3-dione thiosemicarbazone molecule**

| Atoms | Exp. | 6-31G(d,p) | 6-311G(d,p) | 6-311++G(d,p) | 6-311G(2d,2p) | 6-31G(d,p)-a | 6-311G(d,p)-a | 6-311++G(d,p)-a | 6-311G(2d,2p)-a |
|---|---|---|---|---|---|---|---|---|---|
| C17 | 122 | 116 | 125 | 125 | 125 | 118 | 111 | 128 | 127 |
| C11 | 128 | 118 | 127 | 127 | 128 | 119 | 112 | 131 | 129 |
| C5 | 133 | 125 | 136 | 136 | 136 | 128 | 121 | 140 | 140 |
| C4 | 111 | 105 | 113 | 113 | 114 | 108 | 101 | 118 | 117 |
| C10 | 142 | 136 | 147 | 147 | 148 | 139 | 132 | 151 | 151 |
| C15 | 128 | 117 | 127 | 127 | 128 | 116 | 109 | 127 | 127 |
| C18 | 132 | 123 | 131 | 131 | 131 | 131 | 124 | 139 | 138 |
| C12 | 161 | 154 | 164 | 164 | 167 | 157 | 150 | 171 | 171 |
| C16 | 177 | 169 | 179 | 179 | 181 | 175 | 168 | 184 | 182 |
| C13 | 135 | 129 | 141 | 141 | 142 | 130 | 122 | 144 | 143 |
| C3 | 121 | 115 | 124 | 124 | 124 | 124 | 117 | 129 | 128 |
| C14 | 120 | 115 | 124 | 124 | 125 | 127 | 120 | 125 | 125 |
| C1 | 115 | 111 | 120 | 120 | 120 | 112 | 105 | 124 | 123 |
| C8 | 115 | 112 | 121 | 121 | 121 | 112 | 105 | 122 | 121 |
| C2 | 163 | 155 | 169 | 169 | 169 | 158 | 151 | 171 | 170 |
| $R^2$ | | 0.987 | 0.984 | 0.984 | 0.985 | 0.950 | 0.941 | 0.983 | 0.985 |

**Table 5. Experimental and theoretical $^{1}$H NMR and $^{13}$C NMR values of Zn[(I4FPTH)$_2$] complex**

| | $^{1}$H NMR | | | | $^{13}$C NMR | | |
|---|---|---|---|---|---|---|---|
| **Atoms** | **Exp.** | **6-31G(d,p)** | **6-311G(d,p)** | **Atoms** | **Exp.** | **6-31G(d,p)** | **6-311G(d,p)** |
| H28 | 6.96 | 6.52 | 6.60 | C17 | 127.8 | 120 | 130 |
| H24 | 7.70 | 7.66 | 7.74 | C31 | 131.3 | 116 | 126 |
| H27 | 7.32 | 6.72 | 6.76 | C5 | 131.5 | 127 | 137 |
| H25 | 7.60 | 7.13 | 7.22 | C4 | 111.7 | 104 | 112 |
| H29 | 6.98 | 6.61 | 6.86 | C10 | 131.7 | 136 | 147 |
| H23 | 7.77 | 10.25 | 10.33 | C15 | 131.3 | 116 | 124 |
| H28 | 7.62 | 7.30 | 7.40 | C18 | 132.1 | 139 | 148 |
| H22 | 7.51 | 6.92 | 7.05 | C12 | 136.3 | 151 | 161 |
| H30 | 10.96 | 6.95 | 7.30 | C16 | 166.6 | 172 | 181 |
| H26 | 10.42 | 6.19 | 6.16 | C13 | 131.6 | 130 | 141 |
| | | | | C3 | 129.6 | 121 | 130 |
| | | | | C1 | 122.8 | 113 | 122 |
| | | | | C8 | 117.2 | 110 | 119 |
| | | | | C2 | 142.7 | 155 | 169 |

**Table 6. Oscillator strengths (f) and excitation energies (eV) for UV spectra values calculated with TDB3LYP and TDB3LYP**

**$I4FPTH_2$**

| | B3LYP | | | | | | | | bp86 | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Exp(nm)** | **6-31G(d,p)** | | **6-311G(d,p)** | | **6-311++G(d,p)** | | **6-311++G(2d,2p)** | | **cep-31g*** | |
| 371 | 356 | 3.47(0.46) | 357 | 3.47(0.46) | 362 | 3.43(0.45) | 362 | 3.42(0.45)E4 | 338 | 3.68(0.40) |
| 257 | 256 | 4.85(0.23) | 259 | 4.78(0.23) | 262 | 4.72(0.19) | 263 | 4.71(0.18) | 243 | 4.71(0.26) |

**B3LYP**

| **$Zn[(I4FPTH)_2]$** | | | | | **$Ni[(I4FPTH)_2]$** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Exp(nm)** | **6-31G(d,p)** | | **6-311G(d,p)** | | **Exp(nm)** | **6-31G(d,p)** | | **6-311G(d,p)** | |
| 368 | 479 | 2.59(0.26)E3 | 484 | 2.56(0.30)E3 | 654 | 744 | 1.66(0.08) | 664 | 1.87(0.06)E3 |
| 256 | 266 | 4.66(0.22)E32 | 267 | 4.64(0.22) | 436 | 431 | 2.87(0.22) | 432 | 2.87(0.19)E12 |
| | | | | | 259 | 310 | 3.99(0.10) | 305 | 4.05(0.08)E35 |

**Table 7. Experimental and theoretical the FTIR spectra of $I4FPTH_2$, $Zn[(I4FPTH)_2]$ and $Ni[(I4FPTH)_2]$**

| **Experimental** | **υ(N6-H26)** | **υ(N19-H30)** | **ν(N20-H31)** | **ν(C=O)** | **ν(C=N)** | **ν(C-S)** |
|---|---|---|---|---|---|---|
| I4FPTH2 | 3292 | 3174 | 3073 | 1684 | 1586 | 835 |
| Zn[(I4FPTH)2] | 3381 | 3328 | - | 1681 | 1575 | 810 |
| Ni[(I4FPTH)2] | 3405 | 3277 | - | 1660 | 1576 | 812 |
| **Theoretical 6-311G(d,p)** | | | | | | |
| $I4FPTH_2$ | 3643 | 3502 | 3428 | 1776 | 1621 | 958 |
| $Zn[(I4FPTH)_2]$ | 3648 | 3604 | - | 1793 | 1591 | 820 |
| $Ni[(I4FPTH)_2]$ | 3653 | 3613 | - | 1791 | 1630 | 833 |