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DFT Study on 4(5)-Imidazole-carbaldehyde-N(5)-phenylthiosemicarbazone (ImTPh): NMR Shielding Tensors, Thermodynamic Parameters, NBO Analysis, Molecular Electrostatic Potential (MEP), HOMO and LUMO Studies

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ABSTRACT

The density functional theory (DFT) calculations at the level of B3LYP/6-31G was carried out on the structure 4(5)-Imidazole-carbaldehyde-N(5)-phenylthiosemicarbazone (ImTPh) in gas phase using Gaussian 03. Dipole moment (Debye), energy of structure formation (HF; kcal/mol) and point group, NMR parameters such as isotropic shielding (σ_{iso}) and anisotropic shielding (σ_{aniso}), σ_{11}, σ_{22} and σ_{33} obtained. Also thermodynamic properties and natural bond orbitals (NBO) were calculated. Besides, the frontier molecular orbital (FMO) analysis and the molecular electrostatic potential (MEP) of the compound were investigated by theoretical calculations.

Key words: DFT; ImTPh; NMR parameter; Thermodynamic parameter; NBO; FMO; MEP.

INTRODUCTION

Imidazole is an organic compound with the formula $C_3H_4N_2$. This aromatic heterocyclic is classified as an alkaloid. Imidazole refers to the parent compound whereas imidazoles are a class of heterocycles with similar ring structure but varying substituents. The imidazole nucleus is well known to play an important role in living organisms since it is incorporated into the histidine molecule and many other important biological systems. Imidazole derivatives show various pharmacological activities such as antifungal and anti-bacterial activity[1], anti inflammatory activity and analgesic activity[2], antitubercular activity[3], anti depressant activity, anti cancer activity[4], antiviral activity[5] and antileishmanial activity. Due to their antifungal properties imidazole-derived compounds have been used in agriculture as effective ingredients for controlling plants pests. Imidazole derivatives are employed in the control of spoilage microorganisms or organisms potentially harmful to man, in the protection of wood against fungi and also in food storage[6]. Thiosemicarbazones[7,8] and hydrazones[9] are reported as compounds which

present significant antifungal activity. The imidazole-derived thiosemicarbazones were prepared by reacting of 4(5)-imidazole-carboxaldehyde, 4-(1*H*-imidazole-1-yl)-benzaldehyde or 4-(1*H*-imidazole-1-yl)- acetophenone with the suitable thiosemicarbazide using methanol as solvent[10]. In the present work we carried out theoretical calculations on one of the imidazole-derived thiosemicarbazones, that is named 4(5)-Imidazole-carbaldehyde-N(5)-phenylthiosemicarbazone (ImTPh).

Theoretical calculations

We have carried out quantum theoretical calculations of ImTPh using DFT (B3LYP) method with 6-31G basis set by the Gaussian 03 program[11]. We calculated ^{1}H and ^{13}C NMR chemical shifts of ImTPh using B3LYP/6-31G level within GIAO approach. Moreover was studied thermodynamic parameters of ImTPh using methods listed, and obtained the energy (ΔE), enthalpies (ΔH), Gibbs free energy (ΔG), entropies (S) and constant volume molar heat capacity (C_v) of derivatives[12]. Some electronic properties such as energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (Eg; Δ) between LUMO and HOMO, atomic charges, dipole moment (μ) and Point group were determined. The optimized molecular structures, HOMO and LUMO surfaces were visualized using GaussView 03 program[13].

We also studied electronic structures of ImTPh using Natural Bond Orbital (NBO) analysis using level of B3LYP/6-31G. The main listing of NBOs, displaying the form and occupancy of the complete set of NBOs that span the input AO space and for each orbital gives the type of orbital and the occupancy[14].

DISCUSSION

The optimized molecular structure of ImTPh was calculated using Gaussian 03 software. The optimized geometrical parameters, such as Dipole moment (Debye), energy of structure formation (HF; kcal/mol) and point group, obtained using B3LYP method and 6-31G as the basis set that are listed in Table 1. As shown in Table 1, ImTPh has C_1 point

Table 1: Dipole moment, HF and Point group of ImTPh obtained using B3LYP/6-31G level

HF (kcal/mol)	Dipole moment (Debye)	Point group
-688676.535	5.4185	C_1

Table 2. NMR shielding tensors values of ImTPh obtained using B3LYP/6-31G level

	σ_{iso}	σ_{aniso}	σ_{11}	σ_{22}	σ_{33}
C_1	68.109	105.736	7.598	58.129	138.600
C_2	63.816	114.798	-4.365	55.464	140.347
C_4	61.335	97.839	-8.789	66.234	126.561
C_6	68.474	100.343	-12.944	82.998	135.369
C_9	15.892	121.787	-128.044	78.637	97.084
N_3	-40.283	409.594	-268.882	-84.746	232.779
N_5	102.382	121.185	8.110	115.864	183.172
N_7	-71.636	380.997	-353.853	-43.418	182.361
N_8	79.316	93.185	6.673	89.836	141.440
N_{11}	123.777	105.585	40.554	136.610	194.167
H_{19}	25.353	3.797	22.976	25.199	27.884
H_{20}	23.747	9.631	17.025	24.049	30.168
H_{21}	25.080	5.337	22.776	23.826	28.638
H_{22}	25.696	3.834	22.484	26.352	28.252
H_{23}	26.829	8.131	19.613	28.624	32.250

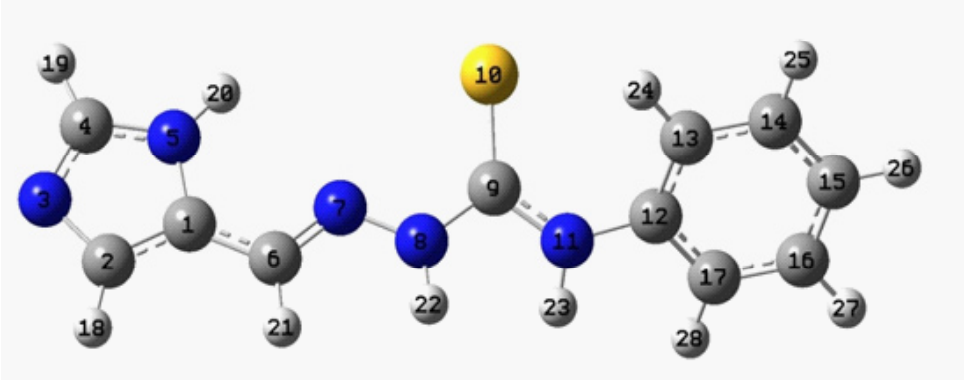

Fig. 1: Structure of ImTPh

group symmetry and Dipole moment (μ) value is 5.4185. Also the energy of structure formation (HF) of ImTPh is negative.

NMR Parameters

In this section we report and analyze NMR shielding tensors of ^{1}H, ^{13}C, ^{15}N-NMR such as isotropic shielding (σ_{iso}) and anisotropic shielding (σ_{aniso}), σ_{11}, σ_{22}, σ_{33} of ImTPh, which obtain using level of B3LYP/6-31G in gas phase. The chemical shielding anisotropy (CSA) tensors provide important information about electronic environment of the nuclei, which depends on the molecular geometry. The results of our studies are listed Table 2. According to Table 2, isotropic shielding value (σ_{iso}) and anisotropic shielding value (σ_{aniso}) for C_1, C_2, C_4, C_6, C_9 atoms are a positive values. Of carbon atoms mentioned, C_9 has the lowest isotropic shielding and the highest anisotropic shielding value. The isotropic shielding value of N_3 and N_7 (-C=N) is negative and anisotropic shielding for these atoms is the highest value. The isotropic and anisotropic shielding values of hydrogen atoms are positive. The H_{20} has the lowest isotropic shielding and the highest anisotropic shielding value. Therefore H_{20} is the most acidic hydrogen.

Table 3. The calculated thermodynamic parameters of ImTPh using B3LYP/6-31G level

ΔE(Kcal/mol)	ΔG(Kcal/mol)	ΔH(Kcal/mol)	S(cal/molK)	C_V(cal/molK)
-688530.795	-688568.278	-688530.202	127.707	55.106

Frequency calculations

Thermodynamic parameters such as the relative energy (ΔE), standard enthalpies (ΔH), entropies (ΔS), Gibbs free energy (ΔG) and constant volume molar heat capacity (C_v) values of ImTPh were obtained using B3LYP/6-31G level. The values are listed in Table 3 showed that relative energy, Gibbs free energy and standard enthalpies of ImTPh are negative that we found this structure is stable.

NBO analysis

In accordance with the simple bond orbital picture, each bonding NBO is introduced as an orbital formed from two directed valence hybrids (NHOs) hA, hB on atoms A and B, with corresponding polarization coefficients cA, cb. Table 3 show share of orbitals contribute in the bonds (BD for 2-center bond). As shown in Table 4, in the N_5-H_{20} bond, BD= $0.8603sp^{2.19}$ + 0.5097s reported. Thus polarization coefficients of the N_5-H_{20} bond N_5= 0.8603 and H_{20}= 0.5097 reported, that sizes of these coefficients show hybrid of N_5 is more important in the formation of the N_5-H_{20} bond. Also in N_8-H_{22} and N_{11}-H_{23} bonds, polarization coefficient values of N_8 and N_{11} is larger than H_{22} and H_{23}. The of polarization coefficient values of H_{20}, H_{22} and H_{23} is 0.5097, 0.5366 and 0.5344, respectively. This show

Table 4: Calculated natural bond orbitals (NBO) and the polarization coefficient for each hybrid in N-H bonds of ImTPh

BD*			BD		
B	**A**	**A-B**	**B**	**A**	**A-B**
s (-0.8603)	$sp^{2.19}$ (0.5097)	N_5-H_{20}	s(0.5097)	$sp^{2.19}$ (0.8603)	N_5-H_{20}
s (-0.8438)	$sp^{2.59}$ (0.5366)	N_8-H_{22}	s(0.5366)	$sp^{2.37}$ (0.8438)	N_8-H_{22}
s (-0.8452)	$sp^{2.59}$ (0.5344)	N_{11}-H_{23}	s(0.5344)	$sp^{2.90}$ (0.8452)	N_{11}-H_{23}

* Antibonding

that share of contribute H_{20} in bond N_5-H_{20} is lower than share of H_{22} and H_{23} in N_8-H_{22} and N_{11}-H_{23} bonds, respectively.

Frontier Molecular Orbital (FMO) Analysis

The E_{HOMO}, E_{LUMO} and HOMO-LUMO energy gap (Eg; Δ) of ImTPh was calculated using the B3LYP method and 6-31G basis set. The properties of molecular orbitals such as energy and frontier electron density are important and are used to determine the reactive position.

According to Fig. 2, the HOMO energy and the LUMO energy (E_{LUMO}) of ImTPh is -5.61 eV and -1.74 eV, respectively. Also Fig.2 and spectrum DOS (Fig. 3) show that energy gap of ImTPh is 3.87 eV. As shown in Fig. 2, the HOMO is focused mainly around and sulfur atom and imidazole ring.

Molecular Electrostatic Potential

Molecular electrostatic potential (MEP) is relevant to the electronic density and it to specify the locations sites of electrophilic and nucleophilic[15].

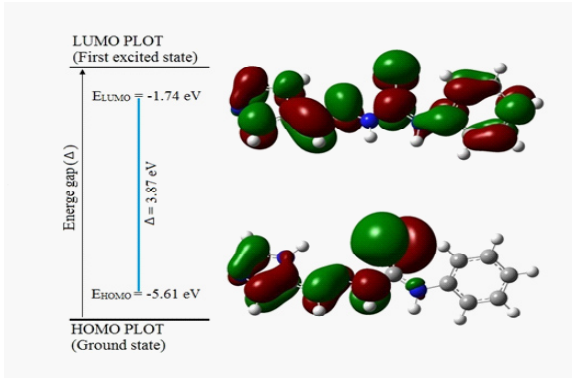

Fig. 2: Frontier molecular orbitals of ImTPh. (Δ: Energy gap between LUMO and HOMO)

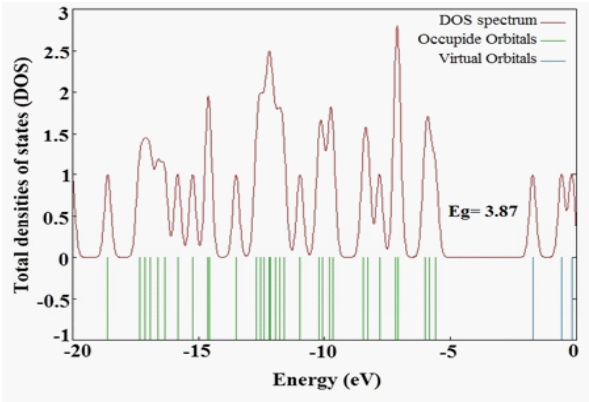

Fig. 3: Total densities of states (DOSs) for ImTPh

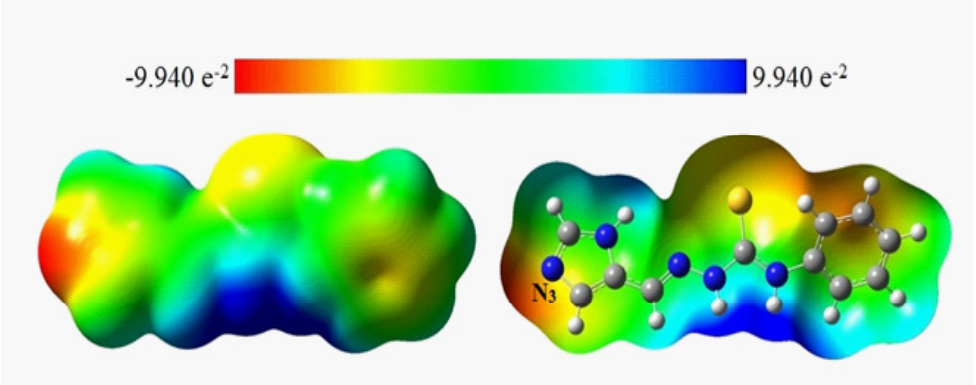

Fig. 4: Molecular electrostatic potential map of ImTPh

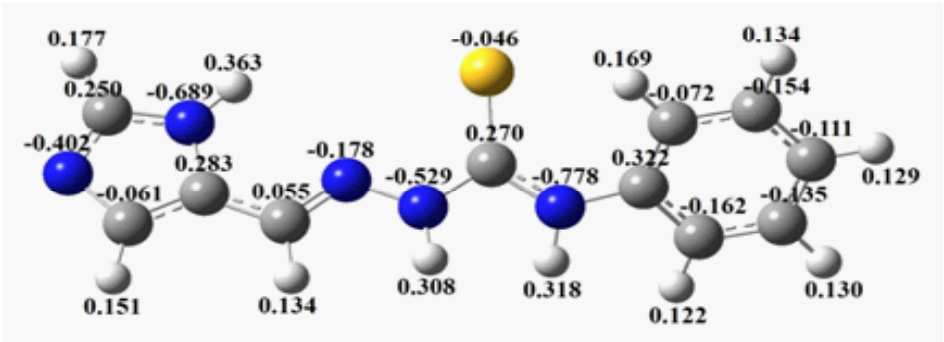

Fig. 5: Atomic charge of atoms of ImTPh

MEP methodology studies the electronic distribution in the molecule[16]. The optimized geometry of ImTPh to indicate sites of electrophilic and nucleophilic, MEP was calculated using B3LYP method and 6-31G basis set.

As shown in Fig. 4, nitrogen atom of imidazole ring (N_3) has maximum electronic density (red color). Therefore N_3 is main negative center. Also lowest electron density is observed for hydrogen atoms bound to nitrogen (blue color).

The atomic charge of atoms of ImTPh is shown in Fig. 5. As can be seen in Fig. 5, H_{20} (Hydrogen attached to the nitrogen in the imidazole ring) has the most positive charge.

CONCLUSION

In the present work, we have performed theoretical analyses of 4(5)-Imidazole-carbaldehyde-N(5)-phenylthiosemicarbazone (ImTPh). The following conclusions are obtained from the current study:

1. The point group symmetry, Dipole moment (μ) and energy of structure formation (HF) of ImTPh is C1, 5.4185 and -688676.535, respectively.
2. As regards hydrogen bonded to nitrogen of imidazole ring (H_{20}) has the lowest valu of σ_{iso} and σ_{aniso}, therefore H_{20} the most acidic hydrogen of ImTPh.
3. According to the thermodynamic parameters, we find that amount of Gibbs free energy (ΔG), standard enthalpies (ΔH) and internal thermal energy (ΔE) of ImTPh is negative value, therefore ImTPh is stable structure.
4. Among hydrogens bonded to nitrogen, H_{20} in bond N_5-H_{20} has the lowest polarization coefficient. This suggests that H_{20} in imidazole ring is the most acidic hydrogen of ImTPh.
5. According to FMO analysis, the HOMO is focused mainly around and sulfur atom and imidazole ring.

6. As shown MEPs, the maximum electron density is located on the nitrogen atom (N_3) imidazole ring.
7. Finally, Our results confirm the biological properties of compounds containing the imidazole ring among 4(5)-Imidazole-carbaldehyde-N(5)-phenylthiosemi carbazone (ImTPh).

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