DFT, AIM and NBO analysis of 3-methyl-2-thioxo imidazoldin-4-one tautomers and their complexes with iodine

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ABSTRACT

DFT and ab initio theoretical methods were used to calculate the relative stability of complexes of 3-methyl-2-thioxoimidazoldin-4-one (3Me-TIO) with iodine. This molecule (T) has four tautomers (T_1, T_2, T_3, and T_4) and can be used for treatment of hyper thyroidism due to its ability to make complexes with iodine. All tautomers and complexes are optimized using the B3LYP method in conjunction with two different basis sets. The relative energies show that in all tautomers and complexes thione forms are more stable than thiol forms. The NBO calculation is carried out on the tautomers and complexes to obtain atomic charges and find donor-acceptor interactions. These results confirm the ability of 3Me-TIO tautomers to form complexes with iodine and show that the planar complex has more effective interactions than the perpendicular one. The atoms in molecules (AIM) analysis show that the electron charge density and its laplacian at the S-I bond critical point of the planar complex is higher than the perpendicular one.   © 2015 Trade Science Inc. - INDIA

INTRODUCTION

Methimazole, carbimazole and propyltiouracilare anti-thyroid drugs depress the formation of thyroid hormones by inhibiting the first step of the hormonal biosynthesis which is the incorporation of oxidized iodine into tyrosine residues in the large thyroid hormone precursor thyroglobulin molecule[1-4].

Thioimidazoline derivates are also known as iodine absorbent in a human body[5-10]. Each compound with a powerful complex with iodine can be considered as a new drug[3]. Generally, treatment of hyperthyroidism is achieved by two different mechanisms. One mechanism is coordination to iodine and prevention of electrophilic substitution of iodine on tyrosine[11-18] and another one is coordination to a metal ionic center on tyrosine peroxide and deactivation of it[19].

The first mechanism was considered in this study. Therefore, we decided to design new molecules with high ability to form complexes with iodine, which can be used as new drugs for treatment of hyper thyroidism.

In the present work, we used computational quantum chemistry methods to investigate tautomerism

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and stability of the 3-methyl-2-thioxoimidazoldin-4-one (3Me-TIO) complexes in the gas phase. Another important aspect of this molecule is its diversity in tautomerism[20,21]. This molecule has different tautomers, and each tautomer can show unique behavior in the interaction with iodine (See Figure 1 and Figure 2). A study of tautomerism, especially in biologically active molecules, has been one of the most interesting in computational researches because tautomerism plays a vital role in the determination of compound application[22-34], and different tautomers of each molecule behave differently in both chemical and biological systems. Thus, since the biological, chemical, and complexation properties of the 3Me-TIO molecule are different in its tautomers, we attempted a systematic analysis of this molecule
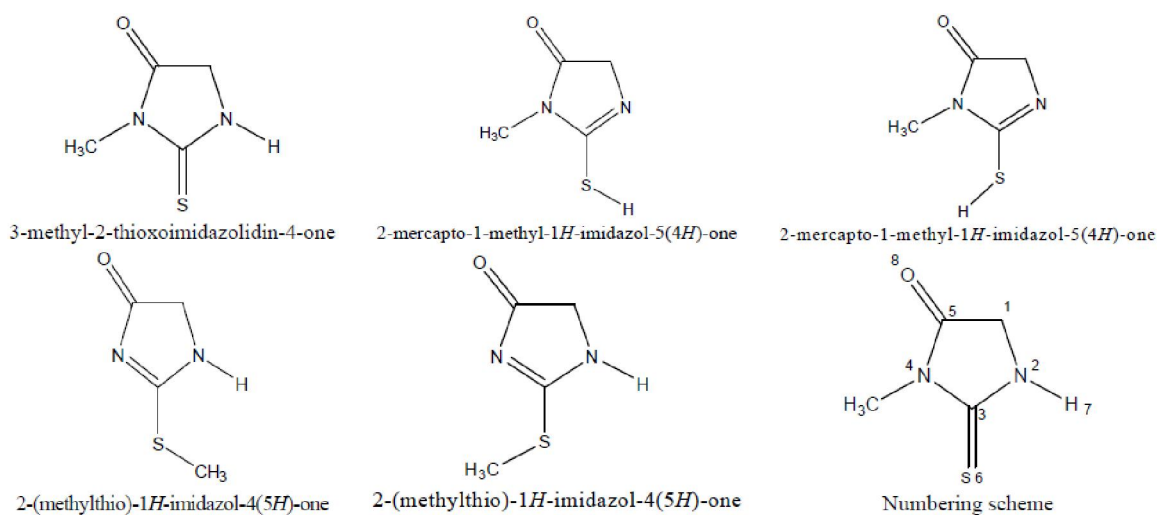

3-methyl-2-thioxoimidazolidin-4-one

2-mercapto-1-methyl-1*H*-imidazol-5(4*H*)-one

2-mercapto-1-methyl-1*H*-imidazol-5(4*H*)-one

2-(methylthio)-1*H*-imidazol-4(5*H*)-one

2-(methylthio)-1*H*-imidazol-4(5*H*)-one

Numbering scheme

Figure 1 : Possible tautomers and numbering scheme for T
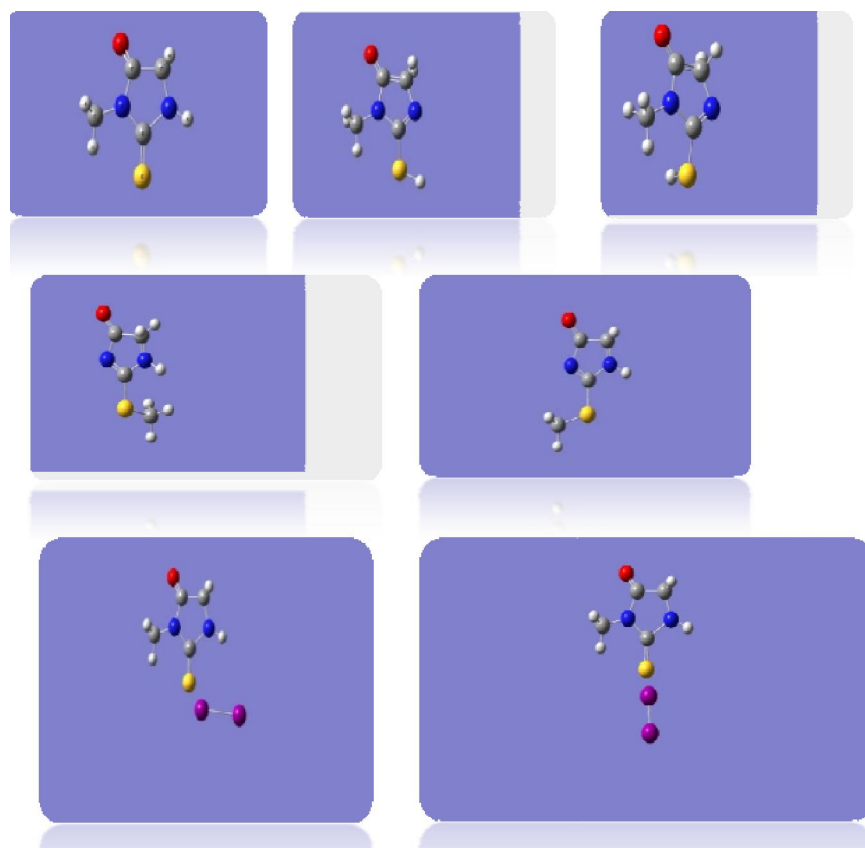

Figure 2 : Optimized structures of the tautomers and complexes

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TABLE 1 : Molecular parameters for the complexes and the most stable isomer of each tautomer in Å and degree

Molecules	T_1	T_2	T_3	T_4
C_3-S_6	1.77	1.77	1.75	1.75
C_3-N_2	1.28	1.281	1.36	1.36
C_3-N_4	1.40	1.41	1.31	1.31
C_5-O_8	1.22	1.22	1.21	1.21
N_2-C_3-N_4	116.30	115.90	116.30	116.20
S_6-C_3-N_4	118.20	122.80	119.40	124.60
C_1-N_2-C_3	105.60	106.00	107.80	108.10
C_5-N_4-C_3	107.60	107.50	106.50	106.40
N_2-C_1-C_5-N_4	0.000	0.20	0.00	0.00

Complexes	T-I_2(perp)	I-I_2(planar)		
C_3-S_6	1.68	1.68		
S_6-I_{15}	3.156	3.03		
I_{15}-I_{16}	2.77	2.80		
C_3-N_2	1.35	1.35		
C_3-N_4	1.38	1.39		
C_5-O_8	1.21	1.27		
N_2-H_7	1.01	1.02		
N_2-C_3-N_4	107.70	107.90		
S_6-C_3-N_4	126.10	124.70		
I_{15}-S_6-C_3	86.80	97.70		
C_1-N_2-C_3	112.70	112.70		
C_5-N_4-C_3	111.60	111.40		
I_{15}-S_6-C_3-N_4	77.40	180.00		
N_2-C_1-C_5-N_4	2.40	0.00		
I_{16}-I_{15}-S_6-C_3	30.90	0.00		

in both the tautomery scheme and complexation properties in our study.

Molecular parameters and relative energies of the 3Me-TIO molecule were calculated using B3LYP/6-311++G** and B3LYP/6-31+G**levels of theory to study its tautomery scheme and properties of all tautomers (TABLES 1 and 2). Frequency calculations were made on the optimized structures at the B3LYP/6-31+G** and B3LYP/6-31+G**levels of theory (TABLE 3).

Moreover, NBO calculations were made to obtain natural atomic charges (TABLE 4). Occupation numbers (TABLE 5), and donor-acceptor interactions (TABLES 6 and 7) of all tautomers and complexes using the B3LYP/6-311++g**level of theory then, AIM analysis (TABLE 8) of the complexes were performed to determine the complexation properties of different tautomers in the interaction with

iodine. Computation details and the results obtained in this work are presented below.

THEORETICAL METHODS

Density functional theory (DFT) has been widely applied by chemists to study the electronic structure of molecule in the past year[35,36]. In this work, all calculation were carried out using Becke'sthree parameter density functional[37] and Lee, Yang, and Parr functional (TABLES 1-3) to describe gradient-corrected correlation effects, which leads to the well-known B3LYP method. The B3LYP method has been validated to give result similar to those of the more computationally expensive MP2 theory for molecular geometry and frequency calculation[39-41].

The geometry optimizations were performed for all tautomers by the B3LYP method in conjunction

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TABLE 2 : Relative Enthalpies and Gibbs Free Energies of All Tautomers (a) and complexes (b) in comparison with the most stable structure in kcal mol^{-1}

(a)						
Tautomers	B3LYP/6-31+G**			B3LYP/6-31++G**		
	ΔZPE	ΔH	ΔG	ΔZPE	ΔH	ΔG
T	0.00	0.00	0.00	0.00	0.00	0.00
T_1	-9.50	51.44	52.90	-9.52	51.48	52.90
T_2	-10.14	62.16	62.21	-9.84	63.37	59.87
T_3	-7.09	69.77	72.43	-7.08	69.64	72.33
T_4	-7.10	54.51	55.87	-7.09	54.43	55.80

(b)						
Complexes	B3LYP/6-31+G**			B3LYP/6-31++G**		
	ΔZPE	ΔH	ΔG	ΔZ$_{PE}$	ΔH	ΔG
T-I$_2$ (planar)	2.85	-41.75	-3.38	3.02	-43.83	-4.91
T-I$_2$(perp)	2.42	-28.01	7.32	2.34	-29.68	5.55

TABLE 3 : The calculated NH stretching wave numbers of T and complexes in cm^{-1}

Method	T	T-I$_2$(Planar)	T-I$_2$(perp)
B3LYP/6-31+G**	3681.2	3544.76	3668.3
B3LYP/6-31++G**	3681.52	3542.47	3668.77

TABLE 4 : Natural atomic charges extracted from NBO calculations in au for tautomers and complexes

Tautomers	C$_3$	N$_2$	N$_4$	O$_8$	H$_{11}$	S$_6$	CH$_3$	C$_5$
T	0.2468	-	-0.4937	-0.5838	0.4536	-1.1592	0.2794	0.6947
T_1	0.2754	-0.5216	-0.5155	-0.5984	0.1718	0.0529	0.2729	0.6896
T_2	0.2657	-0.5026	-0.5185	-0.4612	0.1281	0.0956	-0.2667	0.6893
T_3	0.2756	-0.6620	-0.5823	-0.5716	0.4384	0.3611	-0.0743	0.6516
complexes	C$_3$	N$_2$	N$_4$	O$_6$	H$_{11}$	S$_6$	I$_{15}$	I$_{16}$
T-I$_2$(planar)	0.2676	-0.6017	-0.4832	-0.4877	0.4471	-0.0901	-0.1685	-0.0206
T-I$_2$(perp)	0.2700	-0.6001	-0.4780	-0.4698	0.4491	-0.1516	-0.1264	-0.-229

with 6-31++G**and 6-31++G** basis sets and the NBO analysis[42] was carried out at the B3LYP/6-31++G** level of theory. All optimizations and NBO analysis was carried out using the Gaussion03 program package[43]. AIM analysis were performed using the AIM 2000 program[44] on the wave functions obtained at the B3LYP/6-31++G** level of theory. This method has presented useful information about intermolecular interactions and the characterization of bonds through the analysis of the electron charge densities[45].

RESULTS AND DISCUSSION

All geometries were optimized with the B3LYP method as a part of the Gaussion03 program package[43].

As can be seen from the calculated Gibbs free energy values listed in TABLE 1, all calculations suggest that thione tautomer of 3Me-TIO is more stable than the thiol ones in the gas phase. Data in the TABLE 1 reveal important aspect of the molecular structures. The values of C$_3$-S bond lengths are listed in the first row of the TABLE 1. As can be seen, C$_3$-S bond length in 3Me-TIO is 1.658 Å and in its complexes is in the range of 1.677-1.678Å.

Interaction between non-bonding lone pair of sulfur atom and anti-bonding orbital of Iodine affects on C=S bond lengths in the tautomers and complexes. In the presence of this interaction, charge

transfer from Nitrogen atoms of ring into sulfur atom increases. Thus, C=S bond lengths in the complexes are shorter than tautomers.

In the next rows, S-I and I-I bond lengths of the complexes are listed. The S-I bond is slightly shorter in the planar complexes than that in the perpendicular ones, but there is no any important difference in the values of I-I bond lengths in all complexes.

The next 4 rows of TABLE 1consist of bond angle values. We can follow hybridization changes in the central action of each bond angle by observing bond angle variations. For example, when the central atom of bond angle has SP^2 hybridization, its bond angle is near 120° (as C_3 in all tautomers and N_4 in T_2 and T_4).

But for C_3, the exocyclic bond angle (N_2-C_3-N_4) is smaller than the exocyclic one (S-C_3-N_4) because of a higher mobility of the external sulfur atom.

Dihedral angles are listed in the last columns of the TABLE 1. The values of the N_2-C_1-C_5-N_4 dihedral angles can show the degree of planarity of the molecules. The values of this dihedral angle are near zero in all tautomers and complexes, so that the planarity of all structures is confirmed.

Moreover, the I-I-S-C_3 and I-S-C_3-N_4 dihedral angles determine the situation of the iodine molecule versus tautomers.

ENERGY DATA

The relative zero point energies, enthalpies, and Gibbs free energies for the most stable tautomers and isomers show that T has the lowest enthalpy and Gibbs free energy at both levels of theory. T has both C=S and C=O strong double bonds, so these strong bonds can be responsible for the most stability of this tautomer. The some observation about the relative stability of cyclic tautomers has been observed in various pyrimidine and purine bases[47-49].

The relative stability of other tautomers and geometric isomers obtained at the B3LYP/6-31++g** level of theory is found to be as follows: $T > T_1 > T_4 > T_2 > T_3$.

Moreover, the relative stability of the complexes is found to be as follows: T-I_2 (planar) > T-I_2 (perpendicular).

Data in the TABLE 3 show that ΔG of formation for the planar complex (T-I_2) is by 10.70 kJ mol⁻¹ lower than the perpendicular one. Formation of the complexes is accompanied by decrement of the both enthalpy and entropy. Also, decrement of enthalpy in the planar complex is larger than the perpendicular one.

Stretching vibrational frequencies of the N-H bond for 3Me-TIO and complexes were calculated at the B3LYP/6-31+G** and B3LYP/6-311++G** levels of theory and reported in the TABLE 3. As can be observed, 3Me-TIO has larger wavelength for N-H bond than both complexes. Stretching vibration of N-H bond in the planar complex is more reduced than perpendicular one duo to formation of intermolecular hydrogen bond in this complex.

TABLE 5 : Most important occupancies from NBO calculations for tautomers and complexes in au

	T	T_1	T_2	T_3	T_4	T-I_2(planar)	T-I_2(perp)
δC_3-S_6	1.9840	1.9829	1.9828	1.9803	1.9809	1.9897	1.9867
πC_3-S_6	1.9825	-	-	-	-	1.9872	1.8653
lp₁N_1	1.6979	1.9183	1.9162	1.7118	1.7134	1.3693	1.6495
lp₁N_4	1.6000	1.6275	1.6318	1.9023	1.9081	1.5875	1.5749
lp₁S_6	1.9848	1.9862	1.9844	1.9795	1.9814	1.9865	1.9852
lp₂S_6	1.8661	1.8714	1.8788	1.8080	1.8102	1.9848	1.8761
lp₁O_8	1.9771	1.9771	1.9769	1.9766	1.9764	1.9761	1.9761
lp₂O_8	1.8461	1.8463	1.8463	1.5830	1.8541	1.8188	1.8180
δC_5-O_8	1.0098	0.0110	0.0113	0.0140	0.0139	1.9983	1.9986
πC_5-O_8	1.2644	0.2626	0.2614	0.2413	0.2350	1.9939	1.9948
δC_3-S_6	1.0114	0.0437	0.0420	0.041	0.0464	1.9653	1.9881
πC_3-S_6	1.4495	-	-	-	-	0.2176	0.1543

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NBO ANALYSIS

NBO population analysis was made to obtain natural atomic charges and important donor-acceptor interactions. TABLE 4 presents the natural atomic charges of atoms in all tautomers and complexes. The numbering scheme of this table is the same as the scheme presented in Figure 1.

In tautomers T, T_1, T_2, T_3, and T_4 all nitrogen and oxygen atoms have negative charges and carbon and hydrogen atoms have positive charges. These charges are normal, but interesting charges were observed in the sulfur atom. In T and complexes sulfur has a negative charge, while in the other tautomers it has a positive charge because in T, the sulfur atom is bound only to C_3 with a double bond while in the others sulfur is bond to two atoms by single bonds. Other atomic charges of the atoms in tautomers have usual values with a little variation between the tautomers. In the complexes, the sum of net atomic charges of all atoms in the tautomer is higher than those in simple tautomers, because negative charges are placed on the iodine atoms. These charges provide another proof for the existence of a real complex between the tautomers and iodine. Also, in the planar complex the absolute values of charges placed on the iodine atoms are larger than perpendicular one. This shows that a more effective interaction (between the tautomer and iodine) seems to exist in the planar complex.

One of the important results which obtained from NBO calculations is orbital occupancies and another is donor-acceptor interactions. In TABLE 5, selected occupation numbers for all tautomers and complexes are listed. The values of occupancies show that nearly

all bounding orbitals and lone pairs consist of more than 1.9 electrons, but some lone pairs have occupation numbers between 1.6 and 1.98. These occupancies display that important donor properties can exist on these lone pairs. Also, a significant change in the occupancies of the δ or π bond between the tautomers and complexes has not been observed.

This observation confirms that the δ or π bond do not contribute in electron donation to iodine. On behalf, a significant decrease was observed in the occupation number of the lone pair 2 of sulfur atom in the complexes in comparison with tautomer T which shows that this lone pair is donated to the iodine atom.

The occupation numbers of δ^*C-O and δ^*C-S orbitals in T are larger than its tautomers. This result indicates that charge transfer to these orbitals in T is greater than its tatomers and leads to more stability of T in comparison with corresponding tautomers.

The occupation number of π^*C_5-O_8 in the tautomers show that resonance is between the N_4 lone pair and the C_5=O_8 double bond. Otherwise, the N_4 lone pair has resonance with π^*C_5-O_8. The same result is observed in the π^*C_3-S_6 occupation number in T and other tautomers. Because of a higher capacity of the sulfur atom in electron acceptance, these occupancies are higher in the previous example.

The list of important donor-acceptor interactions is given in TABLE 6. As can be observed, the lone pairs of N_2, N_4, and S_6 are important donors, and C-N, C-S, and C-O bonds are the main acceptors. The most powerful interactions are lp_1N_2 to π^*C_3-S_6 and lp_1N_4 to π^*C_4-O_8. Also, A potent resonance exists between the nitrogen lone pair and the C=S or C=O double bond. Another important interaction is elec-

TABLE 6 : Donor-acceptor interaction energies (in kcal mol⁻¹) in the tautomers and complexes

Donor	Acceptor	T	T_1	T_2	T_3	T_4	T- I_2(planar)	T- I_2(perp)
lp_1N_2	δ_*C_3-S_6	-	0.70	0.84	-	-	102.50	90.93
lp_1N_2	π_*C_3-S_6	73.88	-	-	-	-	-	-
lp_1N_4	δ_*C_3-S_6	-	-	-	0.99	1.02	83.01	85.34
lp_1N_4	π_*C_4-O_8	56.71	54.17	5359	-	-	-	-
lp_1S_6	δ_*C_3-N_4	3.76	-	4.48	-	5.96	-	-
lp_2S_6	δ_*N_2-C_3	11.65	-	0.84	-	-	8.56	12.29
lp_1S_6	δ_*N_2-C_3	4.31	5.07	-	5.59	-	4.09	1.97
lp_2S_6	π_*N_2-C_3	-	24.21	20.56	-	-	-	-
lp_2S_6	δ_*C_3-N_4	14.43	-	0.71	-	29.78	-	-

TABLE 7 : Special donor-acceptor interaction energies (in kcal mol⁻¹) in the complex T-I₂ (planar and perpendicular)

Donor	Acceptor	T-I$_2$(Planar)	T-I$_2$(Perp)
lp$_1$S$_6$	δ^* (I$_{15}$- I$_{16}$)	2.34	1.83
lp$_2$S$_6$	δ^*(I-I)	31.39	0.94
lp$_1$(I$_{15}$)	δ^*(N$_2$-H$_7$)	0.42	-
lp$_3$(I$_{15}$)	δ^*(N$_2$-H$_7$)	7.85	-

TABLE 8 : Calculated critical point properties of the complexes for S-I (a) and C-S (b) bond In Å and au

(a)					
complex	r	ρ(r)		CP,A	CP,B
T-I$_2$(planar)	3.034	0.0272	0.0591	1.5614	1.468
T-I$_2$ (perp)	3.1560	o.o208	0.0492	1.7713	1.5463
(b)					
complex	r	ρ(r)		CP-A	CP-B
T-I2(planar)	1.678	0.2010	0.4589	1.0648	1.6137
T-I2(perp)	1.6778	0.1997	0.4939	1.0643	0.6113

tron donation by lp$_2$S$_6$ to the δ^*C$_3$-N$_4$. This interaction has not been observed in most complexes because of the donation of this lone pair to iodine.

It is obvious that in T$_1$ and T$_2$ the C$_3$=N$_4$ double bond exists. So lp$_2$S$_6$ to the δ^*C$_3$-N$_4$ interaction is replaced by lp$_2$S$_6$ donation to π^*C$_3$-N$_4$ in this tautomers.

In addition, special donor-acceptor interactions were listed only for the complexes in TABLE 7.

The data listed shows that although both sulfur lone pairs contribute in electron donation to iodine, but one of them (lp$_2$) is more effective. Moreover, in the planar complex the donor-acceptor interaction energies are significantly higher than that the perpendicular one for both interactions (lp$_1$ to δ^*I-I and lp$_2$ to δ^*I-I).

AIM ANALYSIS

In the final part of our study, AIM analysis performed for the complexes to obtain important complexation properties, and the results are listed in TABLE 8.

The first column of this table consists of S-I interaction data. In this part, ρ (electron charge destiny) and its laplacian ($\nabla^2\rho$) are very useful parameters to estimate the strengths of the S-I interactions in the complexes.

The low values for the electron charge destiny reflects the weak character of this bond in our complexes. It is noticeable that the planar complex has the larger value of the electron charge density at bond critical point of S-I than the perpendicular one, confirming the higher efficiency of the planar complex for treatment of hyper thyroidism. The negative values of $^2\rho$ at bond critical points of C-S bond reveal the covalent nature of this bond.

CONCLUSIONS

In this report, 3-methyl-4-thioxoimidazolidin-4-one (3Me-TIO) and its tautomers have been studied to find new structures with the effective ability to make a complex with iodine (for treatment of hyperthyroidism).

All structures and complexes with iodine have been optimized using the B3LYP method in conjunction with 6-31+G** and 6-31++G** basis sets to obtain their molecular parameters and relative energies.

Monomer T has four tautomers and the optimized structures show that T makes planar and perpendicular complexes with iodine.

The relative stability of the complexes shows that the planar complex T-I$_2$ is more stable than the perpendicular one.

NBO calculations were performed for the tautomers and complexes to obtain atomic charges, oc-

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cupation numbers, and donor-acceptor interactions. These results confirm the ability of T tautomers to form complexes and show that the planar complex has more effective interaction than the perpendicular one.

The AIM analysis reveals that the planar complex has the larger value of the electron charge density at S-I bond critical point than the perpendicular one. Consequently, planar complex $T-I_2$ has higher efficiency than perpendicular one for treatment of hyper thyroidism.

ACKNOWLEDGEMENT

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