

Theoretical analysis of the interactions of 2,3-dihydro-3-methyl-2-thioxopyrimidin-4(1H)-one tautomers with iodine

T.Hadadi, P.Karimi*

Department of Chemistry, Faculty of Science, University of Zabol, P.O. Box 98613-35856, Zabol, (IRAN)

E-mail: pkarimi@uoz.ac.ir

ABSTRACT

DFT and ab initio theoretical methods were used to calculate the relative stability of 2,3-dihydro-3-methyl-2-thioxopyrimidin-4(1H)-one molecule (DH-3Me-TPO) and its tautomers, also complexes of it 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 because of its ability to build complexes with iodine.

All tautomers and complexes are optimized using the B3LYP method in conjunction with 6-31+G** and 6-311++G** basis sets. Results indicate that in all tautomers and complexes thione form is more stable than thiol ones. The NBO calculation is carried out on optimized tautomers and complexes to obtain atomic charges and donor-acceptor interaction energies. 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 atoms in molecules (AIM) analysis show that the electron charge density (ρ) and its laplacian ($\nabla^2\rho$) at the S-I bond critical point of the planar complex is greater than the perpendicular one.

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KEYWORDS

DH-3Me-TPO;
Hyper thyroidism;
DFT;
NBO;
AIM.

INTRODUCTION

Methimazole, carbimazole and propylthiouracil are anti-thyroid drugs which 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 molecule thyroglobulin^[1-4].

Pyrimidin derivatives are also known as iodine absorbent in a human body^[5-10]. Each compound

which makes a powerful complex with iodine can be considered as a new drug^[3]. In general, treatment of perthyroidism is achieved by two special mechanisms.

One mechanism is the coordination to iodine and makes interference for electrophilic substitution of iodine to tyrosine^[11-18] and another is the coordination to a metal ionic center of tyrosine peroxide and deactivation of it^[19]. The first mechanism was considered in this assay. In fact, we decided to design new molecules with high ability to form complexes

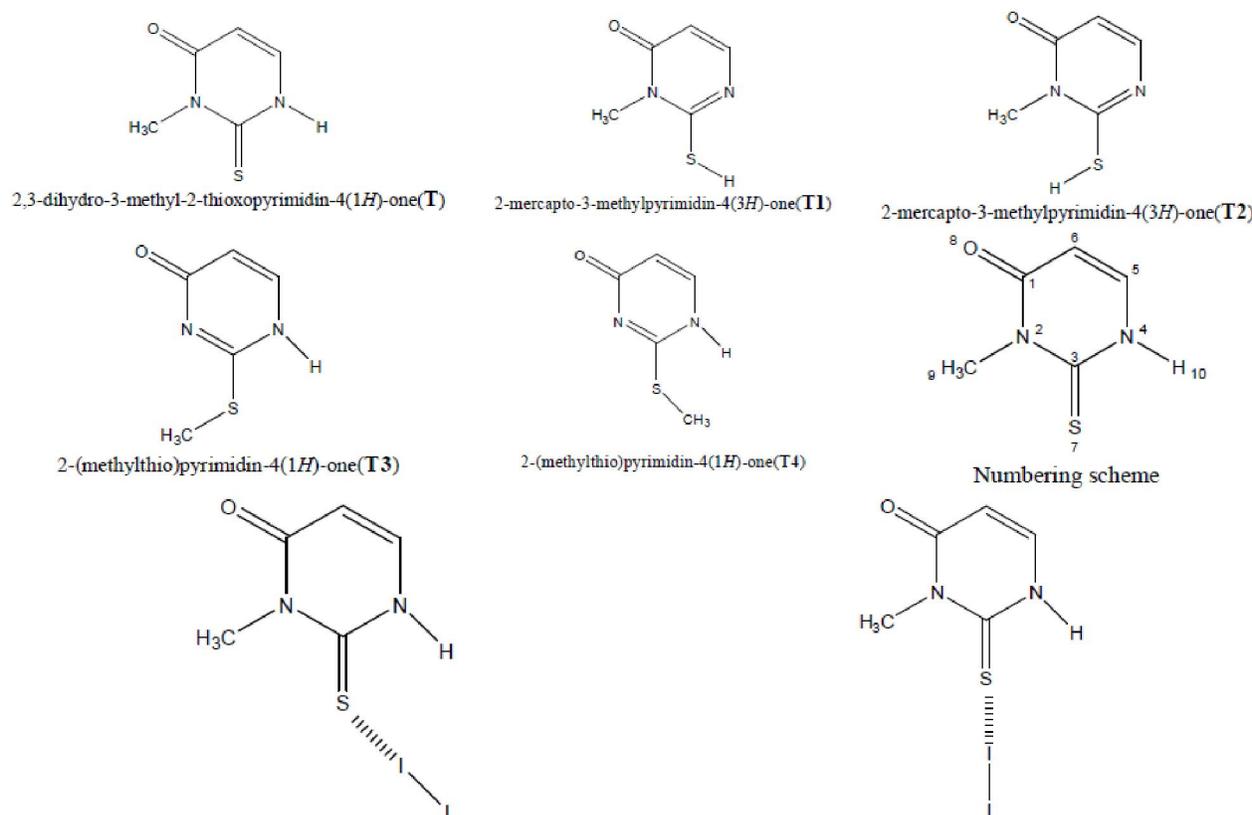


Figure 1 : Possible tautomers and numbering scheme for T and structures of complexes

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 examine tautomerism and stability of 2,3-dihydro-3-methyl-2-thioxopyrimidin-4(1H)-one (DH-3Me-TPO) complexes in the gas phase. Another important feature of DH-3Me-TPO is its variety in tautomerism^[20,21]. This molecule has different tautomers and forms two complexes with iodine (Figure 1).

A study of tautomerism, chiefly in biologically active molecules, has been one of the most interesting examinations in computational researches. In fact, tautomerism plays a key role in the determination of compound application^[22-34], and different tautomers of each molecule behave differently in both chemical and biological systems. Thus, because T has different biological, chemical, and complexation properties in comparison with its tautomers, we performed a systematic analysis on this molecule in both the tautomerism scheme and complexation properties.

In this research, molecular parameters (TABLE 1) and relative energies (TABLE 2) of T tautomers

were calculated using B3LYP/6-311++G** and B3LYP/6-31+G** levels of theory to study tautomerism scheme and properties of all tautomers.

In addition, NBO (natural bond orbital) calculations were made to obtain natural atomic charges (TABLE 4). Occupation numbers (TABLE 5), and donor- acceptor interaction energies (TABLES 6, 7) of all tautomers and complexes were calculated using the B3LYP/6-311++g** level of theory. Also, AIM (atoms in molecules) analyses were performed on wave functions obtained at the above levels of theory (TABLE 8) for the complexes to determine the complexation properties of tautomers in the interaction with the iodine molecule. Computation details and the results obtained in this study are presented below.

Theoretical methods

Density functional theory (DFT) has been widely applied by chemists to study electronic structures of molecules in the past year^[35,36]. In this work, all calculation were carried out using Becke's three parameter density functional^[37] and Lee, Yang, and Parr

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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 ₇	1.782	1.782	1.780	1.781
C ₃ -N ₂	1.308	1.307	1.378	1.376
C ₃ -N ₄	1.366	1.370	1.289	1.290
C ₁ -O ₈	1.227	1.227	1.225	1.224
N ₂ -C ₃ -N ₄	124.9	124.6	124.1	124.2
S ₇ -C ₃ -N ₄	116.5	122.6	122.0	115.9
C ₁ -N ₂ -C ₃	116.4	117.1	119.4	118.9
C ₅ -N ₄ -C ₃	120.9	120.5	120.3	120.4
N ₂ -C ₁ -C ₅ -N ₄	0.0	1.7	0.0	0.0

Complexes	T-I ₂ (perp)	T-I ₂ (planar)
C ₃ - S ₇	1.693	1.696
S ₇ -I ₁₅	3.148	3.021
I ₁₅ - I ₁₆	2.774	2.806
C ₃ -N ₂	1.370	1.365
C ₃ -N ₄	1.364	1.367
C ₁ -O ₈	1.220	1.220
N ₄ -H ₁₀	1.011	1.022
N ₂ -C ₃ -N ₄	116.1	116.4
S ₇ -C ₃ -N ₄	124.7	123.0
I ₁₅ - S ₇ -C ₃	86.4	100.4
C ₁ -N ₂ -C ₃	124.1	123.8
C ₅ -N ₄ -C ₃	124.0	123.9
I ₁₅ - S ₇ -C ₃ -N ₄	85.4	-179
N ₂ -C ₁ -C ₅ -N ₄	0.6	0.0
I ₁₆ -I ₁₅ -S ₇ -C ₃	21.8	0.0

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)						
Tautomer	B3LYP/6-31+G ^{**}			B3LYP/6-31++G ^{**}		
	ΔZPE	ΔH	ΔG	ΔZPE	ΔH	ΔG
T	0	0	0	0	0	0
T ₁	-10.25	25.49	24.29	-10.25	25.53	24.32
T ₂	-10.83	40.74	37.38	-10.59	40.92	38.63
T ₃	-7.42	45.69	39.68	-7.44	45.69	39.69
T ₄	-7.79	68.83	62.82	-7.80	66.62	61.59

(b)						
Complex	B3LYP/6-31+G ^{**}			B3LYP/6-31++G ^{**}		
	ΔZPE	ΔH	ΔG	ΔZPE	ΔH	ΔG
T-I ₂ (planar)	1.81	-45.93	-9.06	1.90	-47.97	-10.85
T-I ₂ (perp)	1.42	-28.88	3.53	1.43	-30.50	2.35

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**	3633.22	3404.16	3625.47
B3LYP/6-31++G**	3633.56	3625.83	340.68

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

molecules	C ₃	N ₂	N ₄	O ₈	H ₁₁	S ₆	CH ₃	C ₅
T	0.24410	-0.5954	-0.4742	-0.5962	0.4621	-0.1757	0.2947	0.6526
T ₁	0.3242	-0.5515	-0.4681	-0.6226	0.1744	0.0569	0.2819	0.6373
T ₂	0.3154	-0.5389	-0.4712	-0.6235	0.1255	0.1103	0.2737	0.6365
T ₃	0.2880	-0.6076	-0.5615	-0.5865	0.4461	0.2564	-0.0092	0.6101
T ₄	0.2810	-0.6121	-0.5376	-0.5863	0.4421	0.3295	-0.0886	0.6070
Complexes	C ₃	N ₂	N ₄	O ₆	H ₁₁	S	I ₁₅	I ₁₆
T-I ₂ (planar)	0.2738	-0.5752	-0.4470	-0.5157	0.4444	-0.0962	-0.0085	-0.1677
T-I ₂ (perp)	0.2712	-0.5722	-0.4411	-0.5078	0.4596	-0.1633	-0.0201	-0.1215

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	1.9817	1.9796	1.9791	1.9764	1.9754	1.9878	1.9846
πC ₃ -S ₆	1.9801	-	-	-	-	1.9857	1.8655
lp ₁ N ₂	1.6066	1.8996	1.8955	1.6322	1.6344	1.5606	1.5721
lp ₁ N ₄	1.5712	1.5628	1.5680	1.8825	1.8788	1.5431	1.5286
lp ₁ S ₆	1.9856	1.9876	1.9849	1.9825	1.9810	1.9872	1.9845
lp ₂ S ₆	1.8757	1.8558	1.8553	1.8340	1.8336	1.6784	1.8909
lp ₁ O ₈	1.9767	1.9761	1.9757	1.9779	1.9781	1.9745	1.9746
lp ₂ O ₈	1.8535	1.8471	1.8449	1.8694	1.8701	1.8285	1.8298
δ*C ₅ -O ₈ ^a	0.0089	0.0092	0.0093	0.0155	0.0157	1.9978	1.9986
π*C ₅ -O ₈ ^b	0.3145	0.3606	0.3630	0.2886	0.2905	1.9934	1.9952
δ*C ₃ -S ₆ ^c	0.4759	1.0434	0.0402	0.0624	0.0523	1.9462	1.9876
πC ₃ -S ₆ ^d	0.0104	-	-	-	-	0.2266	0.1475

^aIn complexes: lp1I₁₅, ^bIn complexes: lp2I₁₅, ^cIn complexes: lp3I₁₅, ^dIn complexes: δ* I₁₅ - I₁₆

functional to describe gradient-corrected correlation effects which leads to the well-known B3LYP method. The B3LYP method has been validated to give results 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 with the 6-31++G** and 6-31++G** basis sets. The NBO analysis^[42] was carried out at the B3LYP/6-31++G** level of theory. All optimizations and NBO analysis was performed using the Gaussian 03 program package^[43]. AIM analyses were performed using the AIM 2000 program^[44]. This method has been presented useful information about intermolecular

interactions and the characterization of bonds through the analysis of the electron charge density^[45].

RESULTS AND DISCUSSION

All geometries of T were optimized with the B3LYP methods as a part of the Gaussian 03^[3]. Data in the TABLE 1 show that value of C₃-S bond length in T is 1.672 Å and in its complexes are in the range of 1.693-1.696 Å.

The difference between the C=S bond length in complexes and monomer may be resulted from interaction between anti-bonding lone pairs of the sulfur and iodine atoms. In the presence of this interaction, the charge-transfer from nitrogen atom of ring

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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 ₁ N ₂	δ* C ₃ -S ₆	-	-	2.37	-	-	88.28	79.24
lp ₁ N ₂	π* C ₃ -S ₆	64.49	-	-	-	-	-	-
lp ₁ N ₄	δ* C ₃ -S ₆	-	2.44	-	3.33	3.04	100.21	100.43
lp ₁ N ₄	π* C ₄ -O ₈	46.10	44.44	-	2.66	-	45.88	45.18
lp ₁ S ₆	δ* C ₃ -N ₄	3.62	-	4.78	5.28	-	10.60	12.45
lp ₂ S ₆	δ* N ₂ -C ₃	10.75	-	-	-	-	8.06	10.91
lp ₁ S ₆	δ* N ₂ -C ₃	3.08	3.78	-	-	4.46	2.92	1.32
lp ₂ S ₆	π* N ₂ -C ₃	-	22.75	21.16	-	-	-	-
lp ₂ S ₆	δ* C ₃ -N ₄	13.40	-	-	25.75	-	-	-

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-I	2.35	1.91
lp ₂ S ₆	δ* (I-I)	34.06	0.06
lp ₁ (I)	δ* (N-H)	0.77	-
lp ₃ (I)	δ* (N-H)	13.12	-

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

Complex	r (Å)	ρ (au)	∇ ² ρ (au)	BCP,A	BCP,B
T-I ₂ (planar)	3.021	0.0284	0.0603	1.5536	1.4597
T-I ₂ (perp)	3.148	0.0210	0.0498	1.6019	1.5435
Complex	r (Å)	ρ (au)	∇ ² ρ (au)	BCP,A	BCP,B
T-I ₂ (planar)	1.6961	0.1979	0.3618	1.0766	0.6189
T-I ₂ (perp)	1.6930	0.1967	0.4141	1.0751	0.6175

to sulfur increases and the C=S bond length decreases relative to monomer.

In the next rows, S-I and I-I bond length of the complexes are listed. The S-I bond is slightly shorter in the planar complex than that in the perpendicular one, but there is no any important difference between I-I bond lengths in these complexes.

The next four rows of TABLE 1 contain bond angles. By analyzing bond angle variations, we can follow hybridization changes in the central action of each angle. For example, when the central atom is SP², its angle is near 120° (as C₃ in all tautomers and N₄ in T₂ and T₄). However, for C₃, the exocyclic angle (N₂-C₃-N₄) is smaller than the exocyclic one (S₇-C₃-N₄) because of a higher mobility of the external sulfur atom.

Dihedral angles are listed in the last columns of TABLE 1. The value of the N₂-C₁-C₅-N₄ dihedral angle can show the degree of planarity in the mol-

ecules. This value is near zero in all tautomers and complexes, so that these values confirm the planarity of all structures.

Moreover, the I₁₆-I₁₅-S₇-C₃ and I₁₅-S₇-C₃-N₄ dihedral angles determine the situation of the iodine molecule versus tautomers.

Energy data

We studied the relative zero point energies, enthalpies, and Gibbs free energies for the most sTABLE tautomers and isomers. As can be seen from the calculated Gibbs free energy values listed in the TABLE 2, thione tautomer of T is more stable than the thiol one in the gas phase. T has the lowest enthalpy and Gibbs free energy at both levels of theory. In fact, this tautomer has both C=S and C=O strong double bonds which these strong bonds may be accountable for the stability of it. The observations about the relative stability of cyclic tautomers were

reported 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: $T > T_1 > T_2 > T_3 > T_4$.

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

The data in the TABLE 2 show that ΔG for formation of planar complex $T-I_2$ is lower than that for perpendicular one by 10.7 kJ mol^{-1} . Also, the equilibrium constant of the planar complex $T-I_2$ is more than perpendicular one.

Formation of the complexes is accompanied by decrement of enthalpy and entropy. The decrease in the enthalpy of the planar complex is more than that for perpendicular one.

In order to support this hypothesis, we calculated the N-H stretching wave numbers of T and the $T-I_2$ complexes. The N-H stretching wave numbers of the T and the $T-I_2$ complexes as computed at B3LYP/6-31++G** and B3LYP/6-31++G* (3-21G** for iodine atom) level of theory, are reported in TABLE 3. The comparison of the calculated vibrational wave number of N-H bond for T (3633.22 cm^{-1}) with the planar form of the complex $T-I_2$ (3404.16 cm^{-1}) reveals that the N-H stretching vibration ν_s undergoes a substantial shift towards a lower wave number in agreement with the IR spectrum. This interaction makes an additional stability to the planar form of the $T-I_2$ complex.

NBO analysis

NBO analyses were made to obtain natural atomic charges and other important complexation properties for tautomers and complexes. 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 , T_4), all nitrogen and oxygen atoms have negative charges and carbon and hydrogen atoms have positive charges. These charges are normal. However, interesting charge was observed in the sulfur atom. In T and complexes sulfur

has a negative charge, while in the other tautomers it has a positive charge. In fact, in T the sulfur atom is bound only to C_3 with a double bond while in the other tautomers sulfur is bound to two atoms by single bonds. Other atomic charges of the atoms in tautomers are usual values with a little variation between the tautomers. Sum of net charges for all atoms of tautomers in the complexes are larger 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 result shows that a more effective interaction (between the tautomer and iodine) seems to exist in the planar complex.

One of the important results obtained from NBO calculations is orbital occupancies and another is acceptor-donor interaction energies. In TABLE 5, selected occupation numbers for all tautomers and complexes are listed. The occupancies show that most bounding orbitals and lone pairs consist of more than 1.90 electrons, but some lone pairs have occupation numbers between 1.60 and 1.98. These occupancies display that important donor properties can exist on these lone pairs. Also, a significant difference has not been observed between the occupancies of the δ or π bonds for the tautomers and complexes. This observation confirms that the δ or π bonds do not contribute in electron donation to iodine. On the other hand, a significant decrease was observed in the occupation number of lone pair 2 of sulfur in the complexes versus tautomer T which shows that this lone pair is donated to the iodine atom.

The occupation numbers of $\pi^*C_5-O_8$ in the tautomers show that there is a resonance between the N_4 lone pair and the $C_5=O_8$ double bond. Otherwise, the N_4 lone pair has resonance with $\pi^*C_5-O_8$. The same result was observed in the occupation numbers of $\pi^*C_3-S_6$ in T and other tautomers. Because of high capacity of the sulfur atom in electron acceptance, these occupancies are higher than those for $\pi^*C_5-O_8$.

The list of important donor-acceptor interactions

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is given in TABLE 6. As shown in this table, the lone pairs of N₂, N₄, and S₆ are important donors, and C₃-N₄, C₃-S₆, and C₄-O₈ bonds are the main acceptors. The most powerful interactions are lp₁N₂ to π*_{C₃-S₆} and lp₁N₄ to π*_{C₄-O₈}, and powerful resonance exists between the nitrogen lone pair and the C=S or C=O double bond. Another important interaction is electron donation by lp₂S₆ to δ*_{C₃-N₄}. This interaction has not been observed in most complexes because of the donation of this lone pair to iodine.

It is obvious that in T₁ and T₂, the C₃=N₄ double bond exists. Thus, lp₂S₆ to δ*_{C₃-N₄} interaction in this tautomers is replaced by lp₂S₆ donation to π*_{C₃-N₄}.

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 (lp₂) is more effective than another one. Moreover, in the planar complex the donor-acceptor interaction energy is significantly higher than in the perpendicular one for both interactions (lp₁ to δ*I-I and lp₂ to δ*I-I).

AIM analyses

In the final part of our study, AIM analyses 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 data for S-I interaction. In this part, ρ (electron charge density) and its laplacian (∇²ρ) may be very helpful parameters to evaluate the strengths of the S-I interaction. The low values for the electron charge density reflect the weak character of this bond in our complexes.

It is noticeable that the planar complex has the larger value of ρ for S-I interaction than perpendicular one which confirm the higher efficiency of the planar complex for treatment of hyper thyroidism. The negative values for the laplacian of the C-S bond show the covalent feature of this bond.

CONCLUSIONS

2,3-dihydro-3-methyl-2-thioxopyrimidin-4(1H)-one and their tautomers were studied to find new structures with effective ability to make a complex

with iodine (for treatment of hyperthyroidism).

All structures and their complexes with iodine have been optimized using the B3LYP method in conjunction with 6-31+G** and 6-31++G** basis sets (for iodine 3-21G**) to obtain their molecular parameters and relative energies. The relative stability of the complexes is found to be: T > T₁ > T₂ > T₃ > T₄

The optimized structures show that T forms planar and perpendicular complexes with iodine. The relative stability of the complexes shows that the planar complex is more stable than perpendicular one.

Results of NBO calculations confirm the ability of T tautomers to form complexes with iodine and show that the planar complex has more valuable interaction than the perpendicular one. Results of AIM analyses indicate that the planar complex T-I₂ has larger value of ρ for S-I interaction than the perpendicular one and has high efficiency for treatment of hyper thyroidism.

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