



ORIGINAL ARTICLE

Quantum chemical study of thiazole derivatives as corrosion inhibitors based on density functional theory



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Abstract Quantum chemical and theoretical calculations were carried out in the present study of some thiazole derivatives. Relationship between electronic parameters of thiazole derivatives 5-benzylidene-2,4-dioxo tetrahydro-1,3-thiazole (5-BDT) 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (5IPBDT), 5-(3'-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-TDT) and 5-(3',4'-dimethoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-MBDT) and corrosion inhibition efficiency have been investigated by the Hartree-Fock (HF) and Becke, 3-parameter, Lee-Yang-Parr (B3LYP), M06-2X method with 3-21G, 6-31G, and sdd basis set. All calculations have been performed using the Gaussian 09W suite of programs. The properties most relevant to their potential action as corrosion inhibitors: EHOMO, ELUMO, ΔE (HOMO-LUMO energy gap), electronegativity (χ), chemical potential (μ), chemical hardness (η), electrophilicity (ω), nucleophilicity (ϵ), global softness (σ) and proton affinity (PA) have been studied.

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1. Introduction

Corrosion inhibitory properties of derivatives consisting of five-ring atom groups containing heteroatoms such as nitrogen and sulfur are compared with theoretical methods. Previous studies have shown that the most important features of a good inhibitor are a good electron donor, high purity at low cost

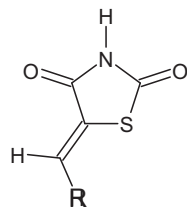
(Kaya et al., 2016; Tüzün, 2014; Tüzün, 2019). It appears that Thiazole and its derivatives 5-benzylidene-2,4-dioxo tetrahydro-1,3-thiazole (5-BDT) 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (5IPBDT), 5-(3'-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-TDT) and 5-(3',4'-dimethoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-MBDT) have these properties. The corrosion inhibition of copper in acidic solution by Thiazole and its derivatives as inhibitor has been studied experimentally by Shaban et al. (2015) and they find that 5-IPBDT showed higher inhibition efficiency. Theoretical studies have shown that the molecular structure of inhibitors is very important to be a good inhibitor. According to the HSAB (hard and soft Acid-Base) theorem (Pearson, 1997; Pearson, 1963; Kovačević and Kokalj, 2011), molecules containing sul-

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fur in the structure are in the class of soft bases. Soft chemical species do not show resistance to electron cloud polarization or deformation. As a result, thiazole and its derivatives give electrons to metal atoms more easily.



Inhibitor	R	Inhibitor	R
5-BDT		5-MBDT	
5-IPBDT		5-TDT	

2. Methods

The theoretical methods used to compare the biological and chemical activities of molecules have become more widespread today. There are many programs used to obtain numerical values of chemical activities of molecules. Many parameters and data are obtained with these programs. In this study, these programs whose names are GaussView 5.0.8, Gaussian09 AS64L-G09RevD.01, ChemDraw Professional 15.1, Chemcraft V1.8 package programs were used in the preparation of molecules (Kovačević and Kokalj, 2011; Dennington et al., 2016; Frisch et al., 2009; PerkinElmer, 2012; Chemissan, 2016). These studied molecules were performed by the Hartree-Fock (HF) (Vautherin and Brink, 1972; Becke, 1993) and Becke, 3-parameter, Lee-Yang-Parr (B3LYP) (Wiberg, 2004; Becke, 1993), M06-2X (Hohenstein et al. 2008) method with 3-21G, 6-31G, and sdd basis set. As a result of the calculations made on these basis sets, many parameters can be obtained. HOMO that is Highest Occupied Molecular Orbital and LUMO that is Lowest Unoccupied Molecular Orbital values are used to obtain information about the activities of molecules by using these methods. There are many parameters obtained from quantum chemical calculations and these are called quantum chemical parameters such as

E_{HOMO} , E_{LUMO} , ΔE (HOMO-LUMO energy gap), electronegativity (χ), chemical potential (μ), chemical hardness (η), electrophilicity (ω), nucleophilicity (ϵ), global softness (σ) and proton affinity (PA) (Bilgiçli et al., 2020; Tüzün, 2020; Günsel et al., 2020a; Günsel et al., 2020b; Günsel et al., 2019a, 2019b).

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_{v(r)} \quad (1)$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right) \quad (2)$$

Ionization energy (I) and electron affinity (A) of studied molecules are calculated with HOMO and LUMO energy that are interested Electronegativity, global softness and chemical hardness obtaining the following equations (Brus,1983).

$$\chi = -\mu = \left(\frac{I + A}{2} \right) \quad (3)$$

$$\eta = \frac{I - A}{2} \quad (4)$$

As it is well known that global softness is defined as the inverse of the chemical hardness.

$$\sigma = 1/\eta \quad (5)$$

$$\chi = -\mu = \left(\frac{-E_{HOMO} - E_{LUMO}}{2} \right) \quad (6)$$

$$\eta = \left(\frac{E_{LUMO} - E_{HOMO}}{2} \right) \quad (7)$$

The global electrophilicity index (Parr and Yang,1989) (ω) that is investigated by Parr et al., is the inverse of nucleophilicity and are given in equality (8). Electrophilicity and nucleophilicity are used for the prediction organic and inorganic reaction mechanisms. Nucleophilicity (ϵ) is defined as the inverse of the electrophilicity in Eq. (9).

$$\omega = \mu^2/2\eta = \chi^2/2\eta \quad (8)$$

$$\epsilon = 1/\omega \quad (9)$$

3. Results and discussion

Many previous experimental and theoretical studies have shown that molecules with hetero atoms in their structure are more likely to be good inhibitors. Therefore, both experimental studies and theoretical studies have influenced each other very much. It is seen that the experimental studies conducted are more in terms of both time and material. Therefore, theoretical studies have become widespread and have guided experimental studies (Tüzün and Kaya, 2018). The studied molecules are optimized using the gaussian software program. With these calculations, many quantum chemical parameters are obtained. By using these parameters, the corrosion inhibition values of the molecules are compared. All parameters obtained from the quantum chemical calculations are given in Table 1. (see Tables 2, 3, 4, 5).

The two most important parameters among these quantum chemical parameters are the HOMO and LUMO of the mole-

Table 1 The calculated quantum chemical parameters with B3LYP method in gas phase (eV).

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	Pi	ω	ε	dipol	Energy
B3LYP/3-21 g LEVEL													
Thiazole	-6,963	-2,061	6,963	2,061	4,901	2,451	0,408	4,512	-4,512	4,153	0,241	1,428	-20507,636
5BDT	-6,356	-2,278	6,356	2,278	4,078	2,039	0,490	4,317	-4,317	4,570	0,219	2,525	-26758,646
5IPBDT	-5,828	-2,053	5,828	2,053	3,775	1,888	0,530	3,941	-3,941	4,113	0,243	4,694	-32955,536
5MBDT	-6,193	-2,184	6,193	2,184	4,008	2,004	0,499	4,188	-4,188	4,377	0,228	3,288	-29948,631
5TDT	-6,325	-2,247	6,325	2,247	4,078	2,039	0,490	4,286	-4,286	4,504	0,222	1,727	-35445,772
B3LYP/6-31 g LEVEL													
Thiazole	-7,206	-2,446	7,206	2,446	4,761	2,380	0,420	4,826	-4,826	4,892	0,204	1,895	-20611,193
5BDT	-6,492	-2,533	6,492	2,533	3,959	1,980	0,505	4,512	-4,512	5,143	0,194	3,609	-26895,371
5IPBDT	-5,848	-2,335	5,848	2,335	3,513	1,757	0,569	4,092	-4,092	4,765	0,210	4,049	-33124,218
5MBDT	-6,323	-2,435	6,323	2,435	3,887	1,944	0,514	4,379	-4,379	4,933	0,203	4,414	-30101,924
5TDT	-6,473	-2,515	6,473	2,515	3,958	1,979	0,505	4,494	-4,494	5,102	0,196	2,733	-35623,987
B3LYP/SDD LEVEL													
Thiazole	-7,412	-2,747	7,412	2,747	4,665	2,333	0,429	5,079	-5,079	5,530	0,181	2,084	-20612,884
5BDT	-6,685	-2,802	6,685	2,802	3,883	1,941	0,515	4,743	-4,743	5,795	0,173	3,968	-26897,476
5IPBDT	-6,214	-2,613	6,214	2,613	3,601	1,800	0,555	4,413	-4,413	5,410	0,185	6,083	-33127,661
5MBDT	-6,490	-2,683	6,490	2,683	3,807	1,903	0,525	4,587	-4,587	5,527	0,181	4,983	-30104,290
5TDT	-6,665	-2,766	6,665	2,766	3,900	1,950	0,513	4,716	-4,716	5,702	0,175	3,197	-35626,061
HF/3-21 g LEVEL													
Thiazole	-10,013	1,983	10,013	-1,983	11,997	5,998	0,167	4,015	-4,015	1,344	0,744	2,246	-20433,552
5BDT	-8,868	1,331	8,868	-1,331	10,199	5,100	0,196	3,768	-3,768	1,392	0,718	3,567	-26643,058
5IPBDT	-8,386	1,368	8,386	-1,368	9,755	4,877	0,205	3,509	-3,509	1,262	0,792	2,482	-32804,842
5MBDT	-8,630	1,422	8,630	-1,422	10,052	5,026	0,199	3,604	-3,604	1,292	0,774	4,256	-29809,846
5TDT	-8,974	1,389	8,974	-1,389	10,362	5,181	0,193	3,792	-3,792	1,388	0,721	2,188	-35326,025
HF/6-31 g LEVEL													
Thiazole	-10,187	1,557	10,187	-1,557	11,744	5,872	0,170	4,315	-4,315	1,585	0,631	2,805	-20535,602
5BDT	-8,915	1,070	8,915	-1,070	9,984	4,992	0,200	3,922	-3,922	1,541	0,649	4,544	-26777,852
5IPBDT	-8,443	1,125	8,443	-1,125	9,567	4,784	0,209	3,659	-3,659	1,399	0,715	5,519	-32970,777
5MBDT	-8,676	1,163	8,676	-1,163	9,839	4,919	0,203	3,756	-3,756	1,434	0,697	5,288	-29960,859
5TDT	-9,037	1,111	9,037	-1,111	10,149	5,074	0,197	3,963	-3,963	1,548	0,646	3,075	-35501,936
HF/SDD LEVEL													
Thiazole	-10,322	1,209	10,322	-1,209	11,531	5,766	0,173	4,556	-4,556	1,800	0,555	2,862	-20536,918
5BDT	-9,069	0,775	9,069	-0,775	9,844	4,922	0,203	4,147	-4,147	1,747	0,572	4,574	-26779,589
5IPBDT	-8,673	0,836	8,673	-0,836	9,509	4,755	0,210	3,918	-3,918	1,615	0,619	5,295	-32973,792
5MBDT	-8,810	0,904	8,810	-0,904	9,714	4,857	0,206	3,953	-3,953	1,609	0,622	5,474	-29962,962
5TDT	-9,189	0,864	9,189	-0,864	10,053	5,026	0,199	4,162	-4,162	1,723	0,580	3,234	-35503,414
M062X/3-21 g LEVEL													
Thiazole	-8,426	-0,960	8,426	0,960	7,467	3,733	0,268	4,693	-4,693	2,950	0,339	1,590	-20502,460
5BDT	-7,710	-1,360	7,710	1,360	6,350	3,175	0,315	4,535	-4,535	3,238	0,309	2,577	-26750,850
5IPBDT	-7,494	-1,314	7,494	1,314	6,179	3,090	0,324	4,404	-4,404	3,138	0,319	3,290	-32945,182
5MBDT	-7,523	-1,275	7,523	1,275	6,249	3,124	0,320	4,399	-4,399	3,097	0,323	3,281	-29939,201
5TDT	-7,664	-1,288	7,664	1,288	6,375	3,188	0,314	4,476	-4,476	3,143	0,318	1,755	-35437,959
M062X/6-31 g LEVEL													
Thiazole	-8,622	-1,331	8,622	1,331	7,291	3,645	0,274	4,976	-4,976	3,397	0,294	1,980	-20606,232
5BDT	-7,801	-1,602	7,801	1,602	6,199	3,100	0,323	4,701	-4,701	3,565	0,280	3,433	-26887,913
5IPBDT	-7,615	-1,582	7,615	1,582	6,033	3,017	0,331	4,598	-4,598	3,504	0,285	4,005	-33114,198
5MBDT	-7,612	-1,521	7,612	1,521	6,091	3,046	0,328	4,566	-4,566	3,423	0,292	4,155	-30092,866
5TDT	-7,768	-1,547	7,768	1,547	6,221	3,110	0,321	4,658	-4,658	3,487	0,287	2,533	-35616,519
M062X/SDD LEVEL													
Thiazole	-8,830	-1,651	8,830	1,651	7,180	3,590	0,279	5,240	-5,240	3,825	0,261	2,204	-20608,124
5BDT	-8,002	-1,889	8,002	1,889	6,113	3,056	0,327	4,946	-4,946	4,001	0,250	3,805	-26890,351
5IPBDT	-7,473	-1,721	7,473	1,721	5,752	2,876	0,348	4,597	-4,597	3,674	0,272	6,795	-33118,076
5MBDT	-7,775	-1,771	7,775	1,771	6,004	3,002	0,333	4,773	-4,773	3,794	0,264	4,757	-30095,593
5TDT	-7,972	-1,814	7,972	1,814	6,157	3,079	0,325	4,893	-4,893	3,888	0,257	3,022	-35618,945

cules. The HOMO energy value of the molecules indicates the ability of the molecule to donate electron to metal atoms. indicates whether the molecules are a good corrosion inhibitor (Günsel et al., 2019a, 2019b). The molecule has the highest

HOMO energy value and is a good corrosion inhibitor. Because the molecule with the highest value is likely to give electrons to metal atoms. As a result, the probability of the molecule becoming a good inhibitor increases as the probab-

Table 2 Parameter values of copper metal.

Metal	E_{HOMO}	E_{LUMO}	I	A	η	χ
Cu	-7,618	1,445	7,618	-1,445	4,532	3,087

Table 3 ΔN values between copper metal and inhibitor.

	Thiazole	5BDT	5IPBDT	5MBDT	5TDT
ΔN	-6,388	-3,976	-2,664	-3,161	-4,207

Table 4 The Gibbs free energy values of the interaction between molecules and metal.

	Molecule	Metal atom	Complexes	ΔG
Thiazole	-20535.60198	-44567.32281	-85661.09865	-22.57189
5BDT	-26777.85175	-44567.32281	-58862.34902	39260.67729
5IPBDT	-32970.77710	-44567.32281	-71247.20940	39261.66760
5MBDT	-29960.85913	-44567.32281	-65228.37103	39260.67005
5TDT	-35501.93574	-44567.32281	-65228.44227	50342.75203

Table 5 The Enthalpy energy values of the interaction between molecules and metal.

	Molecule	Metal atom	Complexes	ΔH
Thiazole	-754.62497	-1637.78717	-85659.15033	-23.23539
5BDT	-984.00859	-1637.78717	-58859.76381	39259.94182
5IPBDT	-1211.58066	-1637.78717	-71243.93821	39260.96786
5MBDT	-1100.97225	-1637.78717	-65225.24781	39259.99442
5TDT	-1304.61227	-1637.78717	-65225.32561	50342.65826

ity of giving electrons to the metal atoms of the molecule increases (Kaya et al. 2016). The inhibition efficiency of organic and inorganic inhibitor increases with increasing electron donating ability at the metal surface. On the other hand, the LUMO energy value of the molecule indicates the ability of the molecule to accept electrons (Günsel et al., 2019a, 2019b; Obi-Egbedi et al., 2011; Bhawsar et al., 2018). The lowest energy value of this parameter of the molecule increases the probability of accepting electrons from the metal atom. accordingly, the molecule becomes a better corrosion inhibitor as the probability of accepting electrons increases. It should be well known that molecules can be explained by the HOMO and LUMO energy values to be a good corrosion inhibitor. As a result of calculations, the best inhibitor is 5IPBDT according to the HOMO energy value of the inhibitors. If the best inhibitor is ranked according to the HOMO energy value: Thiazole < 5TDT < 5BDT < 5MBDT < 5IPBDT. The HOMO, LUMO, and ESP shapes of all inhibitors studied are given in Fig. 1.

With the theoretical calculations, the interactions between metal and molecules are examined in more detail. A good corrosion inhibitor must have a strong Lewis base. Because this contains a pair of lone electrons on the base. The electronegativity value of the strong inhibitor gives information about the electron transfer that takes place between the metal and the inhibitor (Verma et al., 2018). The electronegativity value of the inhibitors is used to explain the reactivity in organic and inorganic chemistry. The electronegativity of inhibitors is another important parameter used to explain the inhibitory properties. This parameter shows the power of inhibitors to attract bond electrons in the gas phase. It is understood by the theoretical calculations that the metal atom or the inhibitor will give electrons. From the equation given below, it is clearly seen that as the inhibitor's electronegativity values decrease, the electron transfer value between the metal and the inhibitor increases, according to Sanderson's electronegativity equalization (10) (Kaya et al., 2016; Bratsch, 1984).

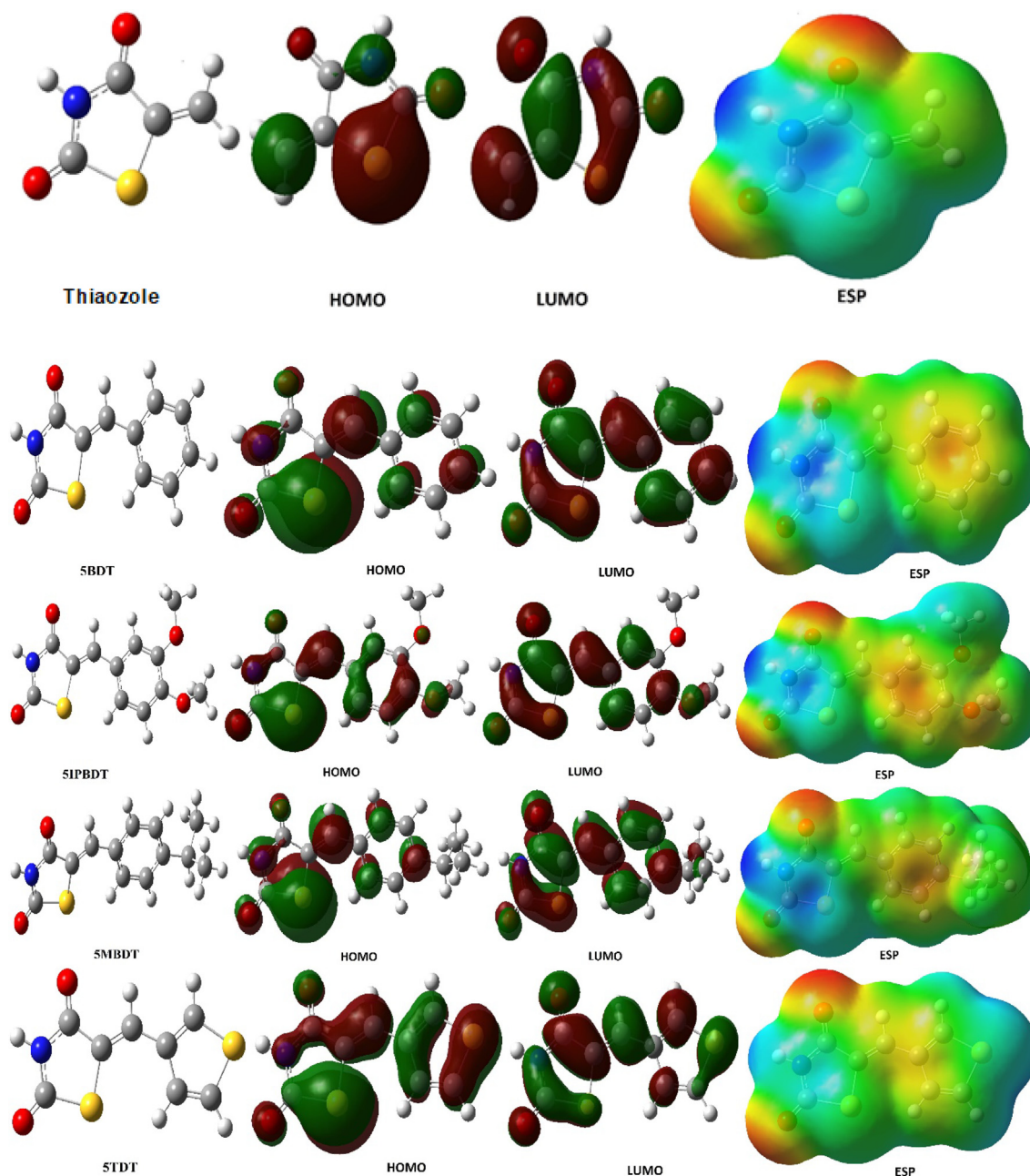


Fig. 1 Optimization structures of inhibitors, HOMO, LUMO, and ESP shapes representation.

$$\Delta N_{max} = \frac{\chi_M - \chi_L}{2(\eta_M + \eta_L)} \quad (10)$$

where χ_M and χ_L are electronegativity of metal and ligand, respectively. η_M and η_L are chemical hardness of ligand and metal, respectively.

Various quantum chemical parameters of the copper metal atom were calculated using the HF/6-31g basis set. The neutral state of copper metal was calculated. However, these parameters were substituted at equalization 10 and the ΔN value was calculated. As a result of the calculations, it is seen that the electron density is high on the oxygen atom bound to the carbonyl carbon in the Thiazole ring (Kaya et al., 2016). This is shown in the ESP forms of inhibitors. The red colored region is electron-rich. The blue colored region is electron-poor (Tüzün,

2014). Therefore, these inhibitors are expected to bond with these oxygens when binding with metal atoms. Using Eq. (10), the value of electron transfer between this oxygen atom and the copper metal atom is calculated.

The ΔN values calculated for these five inhibitors can be both negative and positive. If the value of the calculated ΔN of the inhibitors is negative, the copper metal atom supplies the inhibitor with electrons. If the value of the calculated ΔN of the inhibitors is positive, it should be well known that there is an electron transfer from the inhibitor to the copper metal atom (Kaya et al., 2016; Bratsch, 1984). The calculated ΔN value of the inhibitors shows that the whole ΔN value is negative and the copper metal atom has been shown to give electrons to the inhibitors. As a result of the calculations of the ΔN

value, it was seen that the most electron transfer value was seen in Thiazole. On the other hand, the least electron transfer value was seen in 5IPBDT. It is seen that the order of ΔN values and the order of most inhibitors are similar.

An interaction occurs between the copper metal atom of Thiazole and its derivatives. As a result of this interaction, a chemical event occurs between them. In order to explain these events theoretically, enthalpy and the Gibbs free energy values were calculated. Enthalpy that is symbolized by H , is the sum of all kinds of energies stored in the structure of matter. Gibbs free energy is a thermodynamic variable obtained by subtracting the product of entropy and absolute temperature from enthalpy. In the calculation of these two terms, the following Eq. (11) is used.

$$\Delta E = E_{M-L_{\text{complex}}} - \left[E_{M^{2+}} + \sum E_{Ligand} \right] \quad (11)$$

where $E_{M-L_{\text{complex}}}$ is the energy of the metal complex, E_{Ligand} is the energy of the Thiazole and its derivatives and $E_{M^{2+}}$ is energy of the metal ion.

The Gibbs free energy value can have three different values. In the first, if this value is greater than zero, this interaction does not happen spontaneously. Secondly, this value is equal to zero, the system is in equilibrium. In the latter, this value is less than zero, the interaction is automatic. On the other hand, the enthalpy value being less than zero indicates that heat is given to the environment during interaction. The reaction enthalpy can be positive or negative depending on the process. In endothermic events (the system takes heat from the environment) the ΔH value is positive (ie $\Delta H > 0$), in exothermic events (the system releases heat to the environment) ΔH is negative (ie $\Delta H < 0$).

In the light of the explanations above, it is seen that the Gibbs free energy values are negative only for thiazole. In this case it was observed only for Thiazole. This is not the case for others. On the other hand, when the enthalpy values are examined, it appears that the gene is only negative for Thiazole. This is not the case for others.

4. Conclusion

As a result of the theoretical calculations, many parameters were obtained. As a result of the calculations made, many theoretical parameters for molecules have been calculated. HOMO and LUMO values of the molecules are at the top of these parameters. However, when the ΔN values of the molecules against the copper atom are calculated, the electron values taken into the molecules are calculated. It was seen that the least electron transfer was at 5IPBDT with $-2,664$ values. Apart from these, ΔG and ΔH values were calculated. The Thiazole molecule was calculated to be both ΔG with a value of -22.57189 and ΔH with a value of -23.23539 . These values of the Thiazole molecule are both the most negative and the only molecule that is spontaneous. Given the numerical value of these parameters, all five inhibitors can be good inhibitors against copper metal. but to compare among themselves, the best inhibitor is 5IPBDT. It should be well known that the best inhibitor has been shown to have fewer electron transfer values. The numerical values obtained as a result of the theoretical calculations show that both the E_{HOMO} value and the ΔN value for thiazole are more negative than the values of other molecules. When the experimental results were compared with

these calculations, it was seen that only 5-IPBDT activity was similar. The reason for the difference in sequencing of other molecules is due to too much experimental input in experimental processes. but the theory is done in a completely isolated and pure environment.

Declaration of Competing Interest

None.

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