

## **Original Research Article**

# **Theoretical evaluation of some compounds with antifungal effect as corrosion inhibitors for copper in nitric acid solution: DFT calculations**

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### **ABSTRACT**

Quantum chemical calculations based on Density Functional Theory (DFT) at the B3LYP/6-31G (d,p) basis set were used to study the inhibition performance of four antifungal organic molecules in copper corrosion in 1M nitric acid solution. The quantum chemical descriptors analysis shows that the investigated compounds have good inhibitory abilities in combating copper corrosion. It results that the inhibition efficiency of these molecules is a function of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the energy gap. The inhibition performance of these molecules increases when the energy gap decreases. Finally, the areas containing N, S and C atoms are the most likely sites to bind to the copper surface either by donating or receiving electrons.

*Keywords: Quantum chemical calculations, density functional theory, inhibition performance, antifungal, copper corrosion*

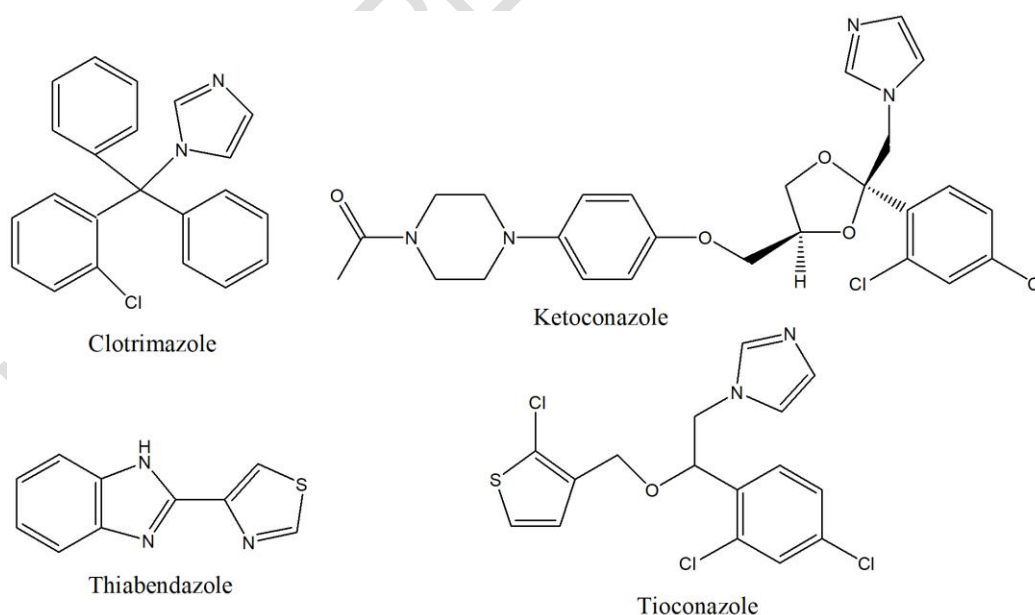
### **1. INTRODUCTION**

The degradation of materials and their physical-chemical properties due to corrosion is a detrimental process that causes huge economic losses and has led to many studies and researches. These various researchers have found suitable organic corrosion inhibitors in various corrosive media [1-3]. Sometimes these research studies are often based on experimentation. Although experimental studies are simple, they are often tedious, time consuming and expensive. Continued advances in hardware and software have opened the door to powerful use of theoretical chemistry in the search for corrosion inhibitors. Several quantum chemical methods and molecular modeling techniques have been used to correlate the inhibitors inhibition efficiency with their molecular properties [4-8]. The theoretical parameters use permits the characterization of the molecular inhibitors structure and proposes their mechanism of interaction with metal surfaces [9,10]. Advances in methodology and implementations have reached a point where predicted properties with reasonable accuracy can be obtained from density functional theory (DFT) calculations. Density functional theory is based on the postulate proposed by Thomas [11] and Fermi [12] that electronic properties can be described in terms of electron density functional. In this theory the multi-electron wave function is replaced by the electron density as the basic quantity for the calculations. The methods for solving the Hartree-Fock and DFT calculations are very similar, and therefore require comparable resources. However the correlation is

included in the DFT, so the results are better for similar computation times. Some research in this area has proven that the protective activity of an inhibitor generally depends on several physicochemical and electronic properties of the protective molecules, in particular, its organic functional groups, steric properties, electron density of the contributing atoms, and the orbital characteristic of the electron sharing [13-15]. Indeed, a number of these inhibitors are also highly hazardous to health and the environment, and are the subject of increasing ecological scrutiny and strict environmental regulations. Current research efforts are now focusing on development of non-toxic, low-cost and environmentally friendly corrosion inhibitors as alternatives [16,17]. The electronic structural features required for corrosion inhibitors, such as the presence of heteroatoms, extensive conjugation, and substituted heterocycles, are readily found in biochemical compounds used as drugs [18-22]. Interestingly, some drugs have been shown to be effective in inhibiting certain metals. In order to comply with the recommendations on the preservation of the environment and to promote the health of all, this work has focused on studying the inhibitory power of four therapeutic molecules with an antifungal effect (Figure 1), which are ketoconazole, clotrimazole, thiabendazole and tioconazole for copper corrosion in acidic medium. These drugs were chosen because they would not be toxic and they all contain the heteroatoms oxygen (O), nitrogen (N) and sulfur (S) which are at the heart of the electronic exchanges between the metal and these molecules. The reactive capacity of the inhibitor is closely related to its frontier molecular orbital (FMO), including the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, as well as other parameters such as the energy gap and the fraction of transferred electrons.

The aim of this study is to theoretically investigate the anticorrosive properties of the four antifungals mentioned above and to propose a mechanism of inhibition of the compounds for copper corrosion in nitric acid medium. This research will help to understand the essential elements of a molecule that are involved in the inhibition process.

Quantum chemistry calculations based essentially on Density Functional Theory (DFT) were used in this study to explain how these molecules will be able to protect copper in an acidic environment.



**Figure 1.** The molecular structures of the investigated inhibitors

## 2. METHODS

### Theoretical calculations details

In this work, theoretical calculations are based on Density Functional Theory (DFT). All calculations in the gas and aqueous phases were performed using the Gaussian 09 software suite [23]. The geometry optimizations were carried out using the hybrid functional B3LYP (Beckes three-parameter with Lee–Yang–Parr) with 6-31G (d) basis set [24, 25].

Moreover the quantum chemical parameters such as as highest occupied molecular orbital energy ( $E_{HOMO}$ ), lowest unoccupied molecular orbital energy ( $E_{LUMO}$ ), energy gap ( $\Delta E$ ), ionization potential (I), electron affinity (A) dipole moment ( $\mu$ ), electronegativity  $\chi$ , hardness  $\eta$ , softness  $S$ , electrophilicity index  $\omega$ , Fukui function  $f_k^+$  or  $f_k^-$  and dual descriptor ( $\Delta f_k^+$  or  $\Delta f_k^-$ ).

The energy gap is determined by the following expression:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (1)$$

The ionization potential (I) and electron affinity (A) of the inhibitors are calculated according to Koopman's theorem [26]

$$I = -E_{HOMO} \quad (2)$$

$$A = -E_{LUMO} \quad (3)$$

The electronegativity ( $\chi$ ) [27] and the hardness ( $\eta$ ) [28] of the inhibitors were estimated using the value of I and A that given by:

$$\chi = -\mu_p = \left( \frac{\partial E}{\partial N} \right)_{v(r)} \quad (4)$$

$$\chi = \frac{I+A}{2} \quad (5)$$

$$\eta = \frac{I-A}{2} \quad (6)$$

The global softness (S) is obtained from the equation [28]:

$$S = \frac{1}{\eta} = \frac{2}{I-A} \quad (7)$$

The global electrophilicity index ( $\omega$ ) [29] is defined as follows:

$$\omega = \frac{(I+A)^2}{4(I-A)} \quad (8)$$

The fraction of electrons transferred ( $\Delta N$ ) from the inhibitor molecule to the metal was performed according to Pearson's electronegativity relationship [30]:

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} \quad (9)$$

where  $\chi_{Cu}$  and  $\eta_{Cu}$ ,  $\chi_{inh}$  and  $\eta_{inh}$  denote the electronegativity and hardness of copper and the inhibitor molecule respectively. In our case we use the theoretical value of  $\chi_{Cu} = 4.98$  eV/mol and  $\eta_{Cu} = 0$  [31] assuming that for a metallic charge  $I = A$  [32], for the calculation of the number of transferred electrons.

In order to locate the sites of reactivity within each molecule, the Fukui functions were determined from Mulliken charges. Fukui functions, which can be determined using the finite difference approximation:

$$\text{Nucleophilic attack} \quad f_k^+ = q_k(N+1) - q_k(N) \quad (13)$$

$$\text{Electrophilic attack} \quad f_k^- = q_k(N) - q_k(N-1) \quad (14)$$

Where  $q_k(N+1)$ ,  $q_k(N)$  and  $q_k(N-1)$  are the electronic population of atom k in  $(N+1)$ ,  $N$  and  $(N-1)$  electrons systems.

The dual descriptor was introduced to unambiguously explain the sites of local reactivity [33,34]. This descriptor can be determined by the following relations:

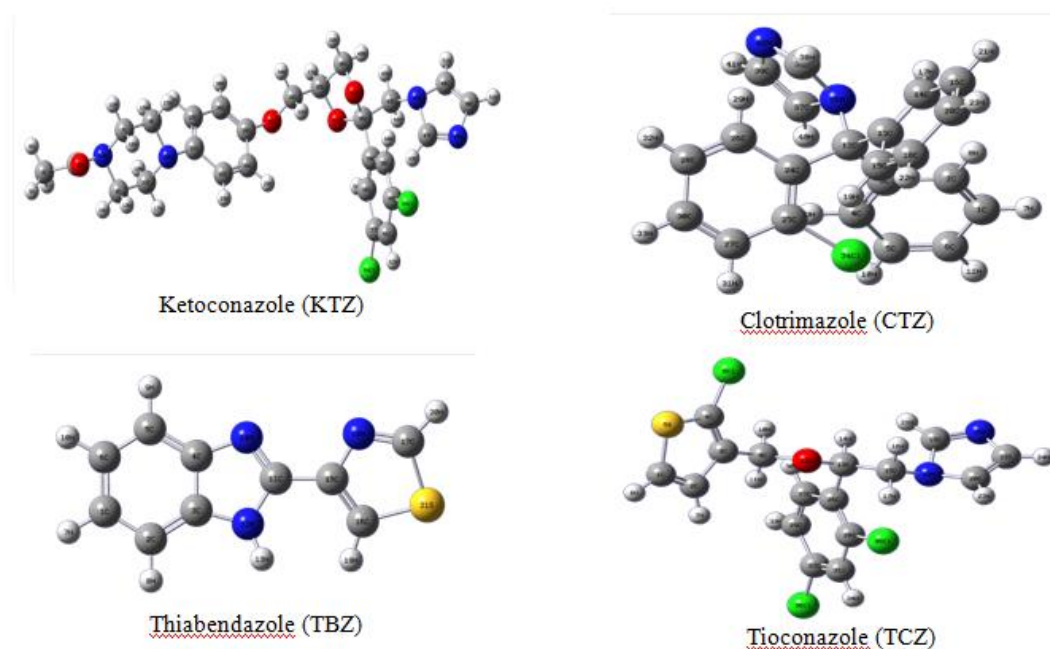
$$\Delta f_k(r) = \left( \frac{\partial f_k(r)}{\partial N} \right)_{v(r)} \quad (15)$$

$$\Delta f_k(r) = f_k^+ - f_k^- \quad (16)$$

### 3. RESULTS AND DISCUSSION

#### 3.1 Molecules optimized forms

The optimized structures of the studied molecules performed by DFT with labels by B3LYP/6-31G (d) are represented by the figure 2.



**Figure 2.** Optimized structure of KTZ, CTZ, TBZ and TCZ calculated with B3LYP/6-31G (d)

### 3.2 Global reactivity parameters analysis

The values of the calculated quantum chemical global parameters with the B3LYP/6-31G (d) are listed in table 1.

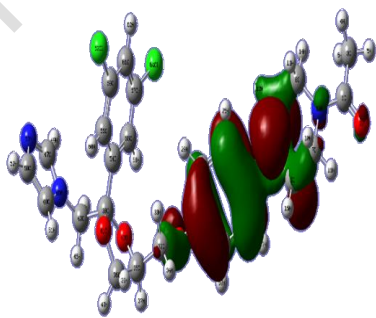
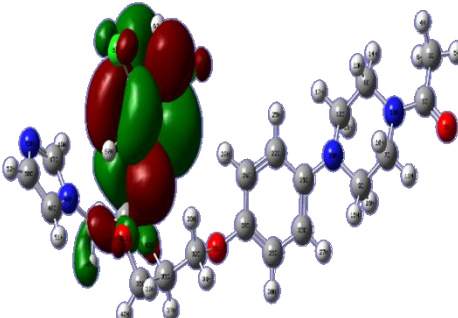
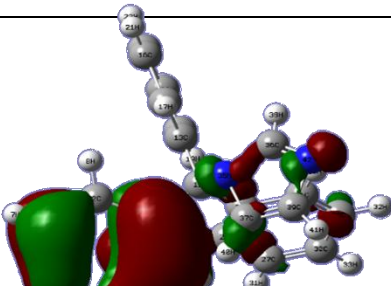
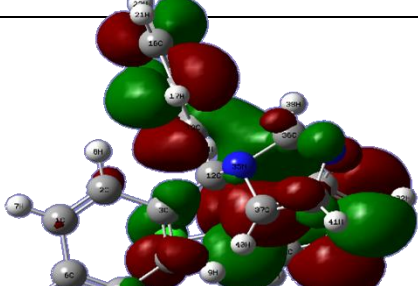
**Table 1.** Quantum chemical parameters of the studied compounds calculated using B3LYP/6-31G (d).

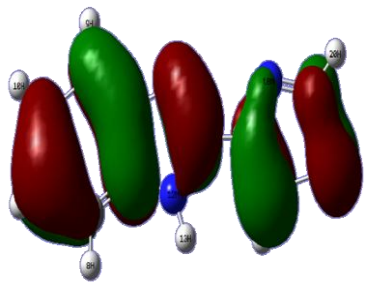
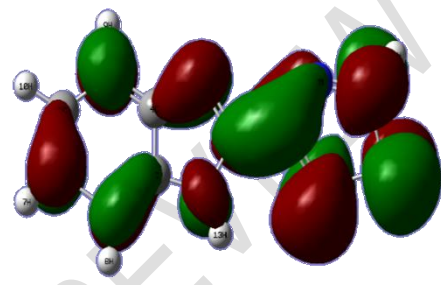
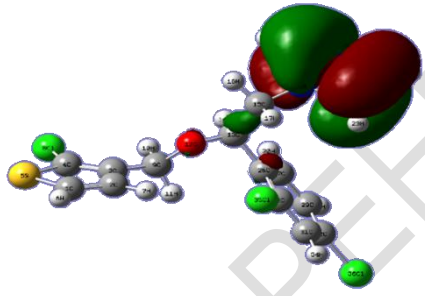
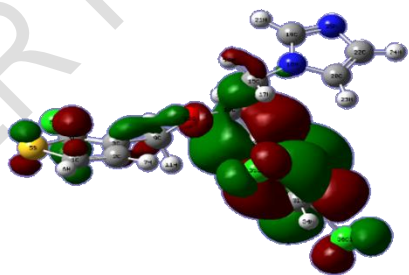
| Parameters                    | Ketoconazole | Clotrimazole | Thiabendazole | Tioconazole |
|-------------------------------|--------------|--------------|---------------|-------------|
| $E_{\text{HOMO}}$ (eV)        | -5,5553      | -5,9233      | -5,8341       | -6,1246     |
| $E_{\text{LUMO}}$ (eV)        | -0,9365      | -0,7115      | -1,3410       | -1,1788     |
| Energy gap $\Delta E$ (eV)    | 4,6188       | 5,2118       | 4,4931        | 4,9458      |
| Dipole moment $\mu$ (D)       | 6,0900       | 2,3297       | 3,4576        | 3,3014      |
| Ionization energy $I$ (eV)    | 5,5553       | 5,9233       | 5,8341        | 6,1246      |
| Electron affinity $A$ (eV)    | 0,9365       | 0,7115       | 1,3410        | 1,1788      |
| Electronegativity $\chi$ (eV) | 3,2459       | 3,3174       | 3,5875        | 3,6517      |

|   |            |            |           |            |
|---|------------|------------|-----------|------------|
| Hardness $\eta$ (eV)                        | 2,3094     | 2,6059     | 2,2466    | 2,4728     |
| Softness $S$ (eV) <sup>-1</sup>             | 0,4330     | 0,3837     | 0,4451    | 0,4043     |
| Fraction of electron transferred $\Delta N$ | 0,3754     | 0,3190     | 0,3099    | 0,2685     |
| Electrophilicity index $\omega$             | 2,2810     | 2.1113     | 2.8644    | 2.6962     |
| Total energy $E_T$ (Ha)                     | -2447.7078 | -1417.9664 | -947.6897 | -2580.8709 |

According to the molecular orbital theory, chemical reactivity is a function of the interaction between the HOMO and LUMO levels of the reacting species [35].  $E_{HOMO}$  is a quantum chemical parameter which indicates that a molecule can give electrons to a suitable acceptor system of low energy molecular orbital empty [36]. The analysis of the values obtained shows that Ketoconazole has the highest value of  $E_{HOMO}$ , however it could have the best ability to donate electrons to the metal.

These molecules do not only supply electrons to the «d» orbitals of metal ions such as  $Cu^{2+}([Ar] 3d^9)$ , but they can also receive electrons from these «d» orbitals, leading to a mutual exchange of electrons [37]. In our case, the low  $E_{LUMO}$  values show that these molecules tend to receive electrons. The lower the values of  $E_{LUMO}$ , the more probable it is that the molecule accepts electrons. The binding capacity of the inhibitor to the metal surface increases with increasing HOMO and decreasing LUMO energy values because the geometry of the inhibitor's base state and the nature of its frontier molecular orbitals, HOMO and LUMO, are involved in the inhibition process [37,38]. It should be noted that the electron density of HOMO location in each molecule is mainly distributed near the nitrogen (N) and oxygen (O) atoms showing that these are the preferred sites for adsorption, whereas the LUMO density was distributed almost of the entire molecules. The HOMO-LUMO diagrams of the molecules are shown in Figure 3.

| Molecule | HOMO  | LUMO   |
|----------|---|--|
| KTZ      |  |  |
|          |  |  |

|     |  |   |
|-----|--|---|
| CTZ |  |   |
| TBZ |   |   |
| TCZ |  |  |

**Figure 3 HOMO and LUMO orbitals of KTZ, CTZ, TBZ and TCZ using DFT at B3LYP/6-31G (d).**

By analyzing the HOMO–LUMO energy gap values for these molecular compounds in table 1, it can be noted that TBZ has the lowest energy gap value. Therefore this compound can be predicted to be best corrosion inhibitor compared to other molecules studied. Indeed when the value of  $\Delta E$  is low, the electronic transfer between HOMO and LUMO orbitals is easier [39,40]. This good inhibition performance that TBZ could possess is due to the presence of heteroatoms (N, S) and  $\pi$  bonds able to ensure a good interaction between the metal and the molecules.

Referring to the table, all the molecules studied have a low electronegativity value compared to that of copper ( $\chi_{\text{Cu}}=4.98$  eV). In this case the movement of electrons will be from each molecule to the metal. It appears therefore that the ability of these molecules to protect copper against corrosion will be by receiving their electrons. In fact, the electron flow will happen from the system with the low electronegativity towards that of a higher value until the chemical potentials are the same [30].

We can observe from Table 1 that the hardness ( $\eta$ ) values of the studied compounds are in the following order:  $\eta(\text{TBZ}) < \eta(\text{KTZ}) < \eta(\text{TCZ}) < \eta(\text{CTZ})$ . This order is the reverse of that obtained for global softness. Thus, the inhibitor with the least value of global hardness (hence the highest value of global softness) could have the best inhibition performance in controlling copper corrosion in acidic media. In this case TBZ could protect the copper better against corrosion than the other compounds studied

The fraction of electrons transferred ( $\Delta N$ ) values of the studied compounds are lower than 3.6. It follows in this case that these compounds give electrons to copper in order to strengthen its surface [41]. In fact during the copper corrosion, it loses electrons. In order to protect it, each compound will give electrons to compensate for the lost electrons.

The studied molecules can be good inhibitors for copper corrosion because on the one hand the unoccupied d orbitals of  $\text{Cu}^{2+}([\text{Ar}]3d^9)$  can accept electrons from the inhibitors to form a coordination bond. On the other hand, the inhibitor molecules can also accept electrons from the  $\text{Cu}^{2+}$  ions with a coordination bond. These donation and back donation processes strengthen the adsorption of the inhibitors molecules onto copper surface.

The total energy values are all negative, this implies that the transfer of electrons metal-molecule is possible [42,43].

### 3.3 Local reactivity parameters Analysis

In order to locate the sites capable of donating or accepting electrons Mulliken charges and Fukui indices of each molecule were calculated [44-47]. In addition, the dual descriptors were also determined to unambiguously locate the active sites of the inhibitor molecules. The results are grouped in tables 2,3,4 and 5. The analysis of these results will allow to understand the interactions of each inhibitor with the metal.

**Table 2. Mulliken atomic charges, Fukui indices and dual descriptor of KTZ DFT using DFT at B3LYP/6-31G (d)**

| Atoms | $q_k(N+1)$ | $q_k(N)$  | $q_k(N-1)$ | $f_k^+$   | $f_k^-$          | $\Delta f_k(r)$  |
|-------|------------|-----------|------------|-----------|------------------|------------------|
| 1 C   | -0.008043  | 0.575909  | 0.012710   | -0.583952 | 0.563199         | <b>-1.147151</b> |
| 2 O   | 0.017543   | -0.506838 | 0.004915   | 0.524381  | -0.511753        | 1.036134         |
| 3 C   | 0.000552   | -0.549299 | -0.001201  | 0.549851  | <b>-0.548098</b> | 1.097949         |
| 4 H   | -0.000195  | 0.168155  | 0.000925   | -0.168350 | 0.167230         | -0.335580        |
| 5 H   | -0.000071  | 0.189323  | 0.000032   | -0.189394 | 0.189291         | -0.378685        |
| 6 H   | -0.000277  | 0.167769  | 0.001297   | -0.168046 | 0.166472         | -0.334518        |
| 7 C   | 0.006127   | -0.144312 | -0.000291  | 0.150439  | -0.144021        | 0.294460         |
| 8 C   | -0.000231  | -0.141538 | -0.000040  | 0.141307  | -0.141498        | 0.282805         |



|           |          |           |           |           |                 |           |                 |
|-----------|----------|-----------|-----------|-----------|-----------------|-----------|-----------------|
| 9         | C        | -0.015238 | -0.136170 | 0.000744  | 0.120932        | -0.136914 | 0.257846        |
| 10        | H        | 0.004257  | 0.148743  | 0.001154  | -0.144486       | 0.147589  | -0.292075       |
| 11        | H        | -0.000050 | 0.194712  | -0.000051 | -0.194762       | 0.194763  | -0.389525       |
| 12        | C        | -0.009774 | -0.132965 | 0.001238  | 0.123191        | -0.134203 | 0.257394        |
| 13        | H        | 0.005975  | 0.152318  | 0.000546  | -0.146343       | 0.151772  | -0.298115       |
| 14        | H        | -0.000474 | 0.159486  | 0.000001  | -0.159960       | 0.159485  | -0.319445       |
| 15        | H        | 0.001118  | 0.156714  | 0.002786  | -0.155596       | 0.153928  | -0.309524       |
| 16        | H        | 0.027730  | 0.134635  | -0.000200 | -0.106905       | 0.134835  | -0.241740       |
| 17        | H        | 0.000584  | 0.156685  | 0.002371  | -0.156101       | 0.154314  | -0.310415       |
| 18        | H        | 0.031058  | 0.134527  | -0.000409 | -0.103469       | 0.134936  | -0.238405       |
| 19        | N        | 0.030384  | -0.423317 | -0.000891 | 0.453701        | -0.422426 | 0.876127        |
| <b>20</b> | <b>N</b> | 0.310112  | -0.503597 | -0.000757 | <b>0.813709</b> | -0.502840 | <b>1.316549</b> |
| 21        | C        | 0.043237  | 0.328785  | -0.024233 | -0.285548       | 0.353018  | -0.638566       |
| 22        | C        | 0.079125  | -0.178086 | 0.094625  | 0.257211        | -0.272711 | 0.529922        |
| 23        | C        | 0.072460  | -0.195317 | 0.059622  | 0.267777        | -0.254939 | 0.522716        |
| 24        | C        | -0.037948 | -0.173642 | 0.071123  | 0.135694        | -0.244765 | 0.380459        |
| 25        | H        | -0.003578 | 0.134319  | -0.005516 | -0.137897       | 0.139835  | -0.277732       |
| 26        | C        | -0.017413 | -0.177690 | 0.092555  | 0.160277        | -0.270245 | 0.430522        |
| 27        | H        | -0.003641 | 0.135763  | -0.003699 | -0.139404       | 0.139462  | -0.278866       |
| 28        | C        | 0.144381  | 0.352328  | -0.026517 | -0.207947       | 0.378845  | -0.586792       |
| 29        | H        | 0.001074  | 0.145943  | -0.001707 | -0.144869       | 0.147650  | -0.292519       |
| 30        | H        | 0.000622  | 0.133315  | -0.005546 | -0.132693       | 0.138861  | -0.271554       |
| 31        | O        | 0.028580  | -0.543523 | 0.000202  | 0.572103        | -0.543725 | 1.115828        |
| 32        | C        | 0.003871  | -0.025738 | 0.000775  | 0.029609        | -0.026513 | 0.056122        |
| 33        | H        | -0.000161 | 0.151449  | 0.001444  | -0.151610       | 0.150005  | -0.301615       |
| 34        | H        | 0.002836  | 0.131351  | -0.000184 | -0.128515       | 0.131535  | -0.260050       |

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|    |   |           |           |           |           |           |           |
|----|---|-----------|-----------|-----------|-----------|-----------|-----------|
| 35 | C | 0.000430  | 0.087967  | -0.000718 | -0.087537 | 0.088685  | -0.176222 |
| 36 | C | 0.000090  | -0.062528 | 0.000519  | 0.062618  | -0.063047 | 0.125665  |
| 37 | H | -0.000042 | 0.163990  | 0.000763  | -0.164032 | 0.163227  | -0.327259 |
| 38 | C | 0.000266  | 0.468778  | -0.000061 | -0.468512 | 0.468839  | -0.937351 |
| 39 | H | 0.000112  | 0.167708  | 0.000242  | -0.167596 | 0.167466  | -0.335062 |
| 40 | H | 0.000550  | 0.150445  | 0.000446  | -0.149895 | 0.149999  | -0.299894 |
| 41 | O | 0.002972  | -0.510863 | 0.003940  | 0.513835  | -0.514803 | 1.028638  |
| 42 | O | 0.000037  | -0.513438 | 0.003260  | 0.513475  | -0.516698 | 1.030173  |
| 43 | C | -0.000042 | -0.158424 | 0.014025  | 0.158382  | -0.172449 | 0.330831  |
| 44 | H | -0.000086 | 0.178099  | -0.000676 | -0.178185 | 0.178775  | -0.356960 |
| 45 | H | 0.000174  | 0.168733  | 0.010427  | -0.168559 | 0.158306  | -0.326865 |
| 46 | N | -0.013430 | -0.373661 | -0.001262 | 0.360231  | -0.372399 | 0.732630  |
| 47 | C | 0.114900  | 0.198498  | 0.000291  | -0.083598 | 0.198207  | -0.281805 |
| 48 | C | 0.125796  | 0.004832  | 0.000153  | 0.120964  | 0.004679  | 0.116285  |
| 49 | H | -0.005636 | 0.154261  | -0.000093 | -0.159897 | 0.154354  | -0.314251 |
| 50 | C | 0.091436  | -0.037201 | 0.000068  | 0.128637  | -0.037269 | 0.165906  |
| 51 | H | -0.005351 | 0.156774  | 0.000035  | -0.162125 | 0.156739  | -0.318864 |
| 52 | H | -0.004638 | 0.135526  | 0.000014  | -0.140164 | 0.135512  | -0.275676 |
| 53 | N | -0.024581 | -0.435374 | 0.000582  | 0.410793  | -0.435956 | 0.846749  |
| 54 | C | 0.000418  | 0.089263  | 0.283483  | -0.088845 | -0.194220 | 0.105375  |
| 55 | C | -0.000186 | -0.170870 | 0.072552  | 0.170684  | -0.243422 | 0.414106  |
| 56 | C | 0.001486  | -0.142347 | 0.011112  | 0.143833  | -0.153459 | 0.297292  |
| 57 | C | 0.000508  | -0.077627 | -0.020696 | 0.078135  | -0.056931 | 0.135066  |
| 58 | H | 0.000027  | 0.185566  | -0.004823 | -0.185539 | 0.190389  | -0.375928 |
| 59 | C | 0.000008  | -0.074801 | 0.043612  | 0.074809  | -0.118413 | 0.193222  |
| 60 | H | -0.000187 | 0.182826  | -0.001753 | -0.183013 | 0.184579  | -0.367592 |

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|    |    |           |           |           |           |           |           |
|----|----|-----------|-----------|-----------|-----------|-----------|-----------|
| 61 | C  | 0.000070  | -0.122688 | 0.326728  | 0.122758  | -0.449416 | 0.572174  |
| 62 | H  | -0.000002 | 0.178012  | -0.018920 | -0.178014 | 0.196932  | -0.374946 |
| 63 | Cl | 0.000155  | -0.001910 | -0.000460 | 0.002065  | -0.001450 | 0.003515  |
| 64 | Cl | 0.000213  | -0.009747 | -0.000614 | 0.009960  | -0.009133 | 0.019093  |

**Table 3. Mulliken atomic charges, Fukui indices and dual descriptor of CTZ DFT using DFT at B3LYP/6-31G (d)**

| Atoms | $q_k(N+1)$ | $q_k(N)$  | $q_k(N-1)$ | $f_k^+$   | $f_k^-$   | $\Delta f_k(r)$ |
|-------|------------|-----------|------------|-----------|-----------|-----------------|
| 1 C   | 0.046440   | -0.158170 | 0.068410   | 0.204610  | -0.226580 | 0.431190        |
| 2 C   | -0.005050  | -0.126960 | -0.022550  | 0.121910  | -0.104410 | 0.226320        |
| 3 C   | 0.013480   | 0.097180  | 0.075040   | -0.083700 | 0.022140  | -0.105840       |
| 4 C   | 0.037600   | -0.298270 | 0.104440   | 0.335870  | -0.402710 | 0.738580        |
| 5 C   | -0.000652  | -0.113810 | -0.036950  | 0.113158  | -0.076860 | 0.190018        |
| 6 C   | 0.006880   | -0.128870 | 0.092370   | 0.135750  | -0.221240 | 0.356990        |
| 7 H   | -0.001930  | 0.132150  | -0.004210  | -0.134080 | 0.136360  | -0.270440       |
| 8 H   | -0.000268  | 0.147160  | 0.001030   | -0.147428 | 0.146130  | -0.293558       |
| 9 H   | -0.001570  | 0.181010  | -0.005580  | -0.182580 | 0.186590  | -0.369170       |
| 10 H  | -0.000161  | 0.132660  | 0.001600   | -0.132821 | 0.131060  | -0.263881       |
| 11 H  | -0.000433  | 0.132510  | -0.005650  | -0.132943 | 0.138160  | -0.271103       |
| 12 C  | -0.013480  | 0.000974  | 0.021260   | -0.014454 | -0.020286 | 0.005832        |
| 13 C  | 0.087180   | 0.105740  | 0.073460   | -0.018560 | 0.032280  | -0.050840       |
| 14 C  | 0.063790   | -0.206790 | 0.119920   | 0.270580  | -0.326710 | 0.597290        |
| 15 C  | -0.028510  | -0.134390 | -0.027780  | 0.105880  | -0.106610 | 0.212490        |
| 16 C  | -0.026250  | -0.135870 | -0.039430  | 0.109620  | -0.096440 | 0.206060        |
| 17 H  | -0.002830  | 0.163300  | -0.006960  | -0.166130 | 0.170260  | -0.336390       |
| 18 C  | 0.057860   | -0.151460 | 0.081050   | 0.209320  | -0.232510 | 0.441830        |
| 19 H  | 0.000652   | 0.155780  | 0.000405   | -0.155128 | 0.155375  | -0.310503       |

|    |    |           |           |           |                 |                 |                  |
|----|----|-----------|-----------|-----------|-----------------|-----------------|------------------|
| 20 | C  | 0.060760  | -0.128470 | 0.097290  | 0.189230        | -0.225760       | 0.414990         |
| 21 | H  | 0.000713  | 0.138450  | 0.001300  | -0.137737       | 0.137150        | -0.274887        |
| 22 | H  | -0.002480 | 0.138570  | -0.005080 | -0.141050       | 0.143650        | -0.284700        |
| 23 | H  | -0.002680 | 0.135370  | -0.005970 | -0.138050       | 0.141340        | -0.279390        |
| 24 | C  | 0.064510  | 0.115430  | 0.089320  | -0.050920       | 0.026110        | -0.077030        |
| 25 | C  | 0.011720  | -0.207190 | 0.164270  | 0.218910        | -0.371460       | 0.590370         |
| 26 | C  | -0.000983 | -0.097570 | -0.045950 | 0.096587        | -0.051620       | 0.148207         |
| 27 | C  | -0.008010 | -0.126560 | -0.033160 | 0.118550        | -0.093400       | 0.211950         |
| 28 | C  | 0.001500  | -0.183930 | 0.144170  | 0.185430        | -0.328100       | 0.513530         |
| 29 | H  | -0.001550 | 0.199950  | 0.001340  | -0.201500       | 0.198610        | -0.400110        |
| 30 | C  | 0.041020  | -0.122150 | 0.082090  | 0.163170        | -0.204240       | 0.367410         |
| 31 | H  | 0.000200  | 0.154280  | 0.000956  | -0.154080       | 0.153324        | -0.307404        |
| 32 | H  | -0.000142 | 0.146160  | -0.008480 | -0.146302       | 0.154640        | -0.300942        |
| 33 | H  | -0.001700 | 0.143920  | -0.005480 | -0.145620       | 0.149400        | -0.295020        |
| 34 | Cl | 0.011890  | 0.089640  | 0.004560  | -0.077750       | 0.085080        | -0.162830        |
| 35 | N  | 0.008430  | -0.420140 | 0.006860  | <b>0.428570</b> | -0.427000       | <b>0.855570</b>  |
| 36 | C  | 0.229250  | 0.127910  | 0.006150  | 0.101340        | 0.121760        | -0.020420        |
| 37 | C  | 0.208730  | 0.020520  | 0.002090  | 0.188210        | 0.018430        | 0.169780         |
| 38 | H  | 0.230390  | -0.025840 | 0.000542  | 0.256230        | -0.026382       | 0.282612         |
| 39 | C  | -0.010740 | 0.199150  | -0.000502 | -0.209890       | <b>0.199652</b> | <b>-0.409542</b> |
| 40 | H  | -0.008880 | 0.175420  | 0.001480  | -0.184300       | 0.173940        | -0.358240        |
| 41 | H  | -0.011170 | 0.150640  | 0.000544  | -0.161810       | 0.150096        | -0.311906        |
| 42 | N  | -0.053520 | -0.417440 | 0.011800  | 0.363920        | -0.429240       | 0.793160         |

**Table 4.**Mulliken atomic charges,Fukui indices and dual descriptor of TBZ DFT using DFT at B3LYP/6-31G (d)

| Atoms | $q_k(N + 1)$ | $q_k(N)$  | $q_k(N - 1)$ | $f_k^+$         | $f_k^-$         | $\Delta f_k(r)$  |
|-------|--------------|-----------|--------------|-----------------|-----------------|------------------|
| 1 C   | 0.296933     | -0.148547 | 0.084021     | 0.445480        | -0.232568       | 0.678048         |
| 2 C   | -0.092226    | -0.173826 | 0.063758     | 0.081600        | -0.237584       | 0.319184         |
| 3 C   | 0.167686     | 0.357305  | -0.018143    | -0.189619       | <b>0.375448</b> | -0.565067        |
| 4 C   | 0.135371     | 0.237262  | -0.015418    | -0.101891       | 0.252680        | -0.354571        |
| 5 C   | 0.071703     | -0.182972 | 0.129682     | 0.254675        | -0.312654       | 0.567329         |
| 6 C   | -0.020661    | -0.142239 | -0.037296    | 0.121578        | -0.104943       | 0.226521         |
| 7 H   | -0.013039    | 0.127719  | -0.005038    | -0.140758       | 0.132757        | -0.273515        |
| 8 H   | 0.002954     | 0.126107  | -0.003950    | -0.123153       | 0.130057        | -0.253210        |
| 9 H   | -0.003990    | 0.143244  | -0.006694    | -0.147234       | 0.149938        | -0.297172        |
| 10 H  | -0.000103    | 0.127025  | 0.001170     | -0.127128       | 0.125855        | -0.252983        |
| 11 C  | 0.140353     | 0.487276  | 0.137379     | -0.346923       | 0.349897        | <b>-0.696820</b> |
| 12 N  | -0.039596    | -0.765538 | 0.024209     | <b>0.725942</b> | -0.789747       | <b>1.515689</b>  |
| 13 H  | 0.000752     | 0.327890  | 0.000615     | -0.327138       | 0.327275        | -0.654413        |
| 14 N  | 0.086376     | -0.532410 | 0.056077     | 0.618786        | -0.588487       | 1.207273         |
| 15 C  | 0.030498     | 0.265186  | 0.019340     | -0.234688       | 0.245846        | -0.480534        |
| 16 C  | 0.163800     | -0.400414 | 0.433023     | 0.564214        | -0.833437       | 1.397651         |
| 17 C  | 0.040562     | -0.117466 | 0.101133     | 0.158028        | -0.218599       | 0.376627         |
| 18 N  | -0.012013    | -0.361397 | -0.036472    | 0.349384        | -0.324925       | 0.674309         |
| 19 H  | -0.007933    | 0.175801  | -0.024772    | -0.183734       | 0.200573        | -0.384307        |
| 20 H  | -0.002257    | 0.191367  | -0.006685    | -0.193624       | 0.198052        | -0.391676        |
| 21 S  | 0.054829     | 0.258626  | 0.104061     | -0.203797       | 0.154565        | -0.358362        |

**Table 5.**Mulliken atomic charges,Fukui indices and dual descriptor of TCZ DFT using DFT at B3LYP/6-31G (d)

| Atoms | $q_k(N + 1)$ | $q_k(N)$ | $q_k(N - 1)$ | $f_k^+$         | $f_k^-$         | $\Delta f_k(r)$  |
|-------|--------------|----------|--------------|-----------------|-----------------|------------------|
| 1 C   | 0.183028     | -0.36171 | 0.104877     | <b>0.544738</b> | -0.466587       | 1.011325         |
| 2 C   | -0.007783    | -0.09464 | -0.010105    | 0.086857        | -0.084535       | 0.171392         |
| 3 C   | 0.052624     | 0.1613   | 0.026748     | -0.108676       | 0.134552        | -0.243228        |
| 4 C   | 0.170657     | -0.35665 | 0.163793     | 0.527307        | -0.520443       | <b>1.04775</b>   |
| 5 S   | -0.030862    | 0.30463  | 0.045116     | -0.335492       | <b>0.259514</b> | <b>-0.595006</b> |
| 6 H   | -0.008462    | 0.18412  | -0.006456    | -0.192582       | 0.190576        | -0.383158        |
| 7 H   | -0.000251    | 0.16843  | 0.000522     | -0.168681       | 0.167908        | -0.336589        |
| 8 Cl  | 0.068457     | 0.02562  | 0.001388     | 0.042837        | 0.024232        | 0.018605         |
| 9 C   | -0.003396    | -0.08773 | 0.007305     | 0.084334        | -0.095035       | 0.179369         |
| 10 H  | 0.001878     | 0.14918  | -0.0004      | -0.147302       | 0.14958         | -0.296882        |
| 11 H  | 0.005323     | 0.15619  | 0.002794     | -0.150867       | 0.153396        | -0.304263        |
| 12 O  | 0.006846     | -0.48606 | 0.008154     | 0.492906        | -0.494214       | 0.98712          |
| 13 C  | -0.000427    | 0.08186  | 0.018161     | -0.082287       | 0.063699        | -0.145986        |
| 14 H  | -0.000135    | 0.13564  | -0.000595    | -0.135775       | 0.136235        | -0.27201         |
| 15 C  | 0.00522      | -0.19138 | 0.00977      | 0.1966          | -0.20115        | 0.39775          |
| 16 H  | 0.000942     | 0.18267  | 0.004681     | -0.181728       | 0.177989        | -0.359717        |
| 17 H  | -0.000027    | 0.19096  | 0.000072     | -0.190987       | 0.190888        | -0.381875        |
| 18 N  | -0.01496     | -0.37081 | -0.000212    | 0.35585         | -0.370598       | 0.726448         |
| 19 C  | 0.192777     | 0.18863  | 0.000446     | 0.004147        | 0.188184        | -0.184037        |
| 20 C  | 0.17348      | 0.00902  | 0.000568     | 0.16446         | 0.008452        | 0.156008         |
| 21 H  | -0.009397    | 0.1511   | 0.000105     | -0.160497       | 0.150995        | -0.311492        |
| 22 C  | 0.176096     | -0.04164 | 0.000428     | 0.217736        | -0.042068       | 0.259804         |
| 23 H  | -0.007427    | 0.15652  | -0.000181    | -0.163947       | 0.156701        | -0.320648        |
| 24 H  | -0.008563    | 0.13547  | -0.000031    | -0.144033       | 0.135501        | -0.279534        |
| 25 N  | -0.051831    | -0.43455 | 0.000043     | 0.382719        | -0.434593       | 0.817312         |

|    |    |           |           |           |           |           |           |
|----|----|-----------|-----------|-----------|-----------|-----------|-----------|
| 26 | C  | 0.043082  | 0.15571   | 0.220647  | -0.112628 | -0.064937 | -0.047691 |
| 27 | C  | -0.003144 | -0.1777   | -0.01918  | 0.174556  | -0.15852  | 0.333076  |
| 28 | C  | 0.008378  | -0.13388  | 0.150551  | 0.142258  | -0.284431 | 0.426689  |
| 29 | C  | 0.010219  | -0.12074  | 0.089913  | 0.130959  | -0.210653 | 0.341612  |
| 30 | H  | -0.000139 | 0.15942   | -0.000357 | -0.159559 | 0.159777  | -0.319336 |
| 31 | C  | -0.003627 | -0.12687  | -0.076773 | 0.123243  | -0.050097 | 0.17334   |
| 32 | C  | 0.025963  | -0.06292  | 0.258173  | 0.088883  | -0.321093 | 0.409976  |
| 33 | H  | -0.000496 | 0.16861   | -0.006203 | -0.169106 | 0.174813  | -0.343919 |
| 34 | H  | 0.000035  | 0.18155   | 0.002656  | -0.181515 | 0.178894  | -0.360409 |
| 35 | Cl | 0.006352  | -3.10E-05 | 0.001145  | 0.006383  | -0.001176 | 0.007559  |
| 36 | Cl | 0.01957   | 6.69E-04  | 0.002438  | 0.018901  | -0.001769 | 0.02067   |

The probable sites for nucleophilic attacks are the sites for which the values of the Fukui index  $f_k^+$  and the dual descriptor are the highest. As for the electrophilic attack sites, they are identified by the highest value of the Fukui index  $f_k^-$  and by the lowest value of the dual descriptor  $\Delta f_k(r)$ . In case of ambiguity the atom with the largest value and the lowest value of  $\Delta f_k(r)$  for the same compound are respectively the probable sites for nucleophilic and electrophilic attacks. Thus in view of the above and after analysis tables 2, 3, 4 and 5, the different sites of reactivity of the studied molecules are recorded in table 6.

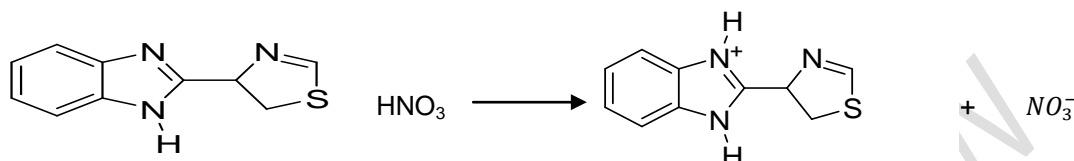
**Table.6 Recap of the different reactivity atoms**

| Molecules | probable sites for nucleophilic attacks | probable sites for electrophilic attacks |
|-----------|---|--|
| KTZ       | N(20)                                   | C(1)                                     |
| CTZ       | N(35)                                   | C(39)                                    |
| TBZ       | N(12)                                   | C(11)                                    |
| TCZ       | C(4)                                    | S(5)                                     |

It appears that the studied inhibitors reactivity strongly depends on N,S heteroatoms and C carbon atom. However the probable sites for nucleophilic attacks are dominated by nitrogen atoms (N). In addition these sites associated with the LUMO orbital could receive electrons that would come from the metal. Regarding the probable sites for electrophilic attacks, they are dominated by carbon atoms (C) with the presence of a sulfur atom (S). These sites are

likely to donate electrons to the metal. Therefore, these electrophilic attack sites are associated with the HOMO. The donor-acceptor properties that these molecules possess give them a good ability to protect copper against corrosion in nitric acid solution.

The inhibitor molecules are protonated in nitric acid medium. Thiabendazole is protonated according to the chemical in following equation:



The inhibitor molecule protonated formed in the solution will permit the compound to adsorb on the copper surface negatively charged by  $\text{NO}_3^-$  ions. Thanks to the charge carried by the proton, the latter, interacting with the negative charge of the nitrate ions, gives rise to electrostatic interactions that promote physisorption. The free electron pairs of the heteroatoms belong to each compound studied, as well as the  $\pi$  electrons of the aromatic rings which help the molecule to adsorb on copper surface. This adsorption is facilitated by the presence of the unfilled d-orbitals gives importance to the donor-acceptor interactions between the molecule and the metal surface favoring the chemisorption. Indeed this chemisorption is due to the heteroatoms and electrons present in the structures of the studied compounds will certainly provide enough electrons to the vacant 3d orbitals of the metal for the formation of a stable coordination bond.

Figure 4 explains the mechanism of adsorption.

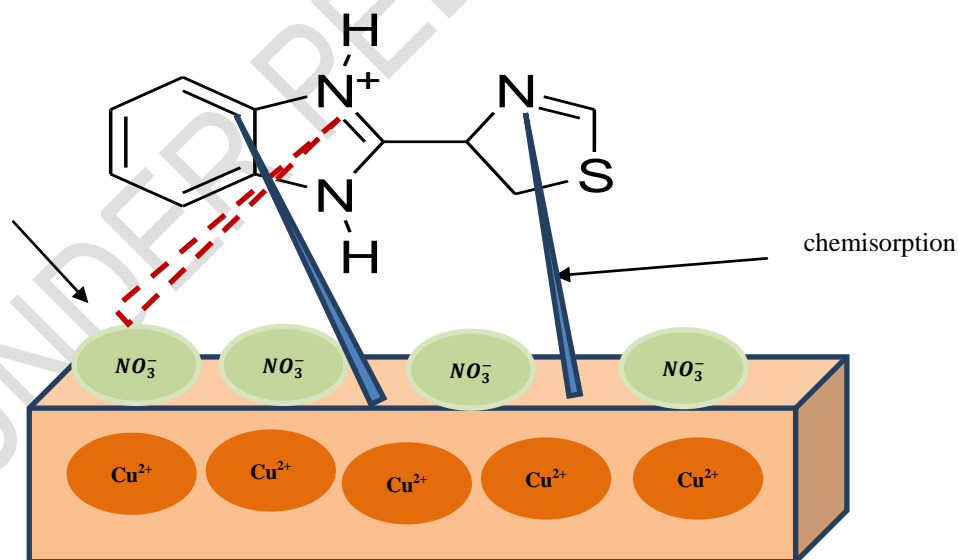


Figure 4. Pictorial representation of Thiabendazole adsorption on copper surface in 1.0 M  $\text{HNO}_3$

## Conclusion



Quantum chemical studies justified by DFT calculations revealed that the inhibitory power of KTZ, CTZ, TBZ and TCZ is promoted by their electron donor-acceptor ability. These inhibition properties could strengthen the copper surface by reducing its degradation. The inhibition capacity of the four studied inhibitors related to highest occupied molecular orbital energy ( $E_{\text{HOMO}}$ ), lowest unoccupied molecular orbital energy ( $E_{\text{LUMO}}$ ), the energy gap ( $\Delta E$ ) and the fraction of transferred electrons ( $\Delta N$ ). The relative ability of the studied molecules to inhibit copper corrosion is found to be dependent on the relative ability of the compounds to donate electrons to the metal. It was found that TBZ could have the best inhibitory performance in copper corrosion in the studied solution. The total energy values of the studied compounds predict that the electronic exchanges between them and copper are favorable. Furthermore, the values of Fukui indices and dual descriptor led to accurate predictions of the positions for electrophilic and nucleophilic attack. These positions also estimated the importance of nitrogen, carbon and sulfur atoms in the local reactivity. In addition, these results could facilitate the design of new corrosion inhibitors with the same chemical functions as the studied compounds that can be used in the protection of metals.

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