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Quantum chemical studies on inhibiting copper corrosion in nitric acid using some coumarin derivatives

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Abstract

Efforts have been made to limit copper corrosion. Among the many strategies available to protect copper against corrosion, the use of inhibitors is one of the most practical and effective methods. In recent years, quantum chemical calculations have been used to search for new inhibitors. The aim of this work is to study the inhibiting properties of nine coumarins derivatives in the fight against copper corrosion in 1M nitric acid. The studies were carried out using density functional theory with B3LYP hybrid functional associated with the 6-31G(d, p) orbital basis. Quantum descriptor analysis shows that all coumarin derivatives can accept and donate electrons to the metal. These electron exchanges will promote the formation of covalent bonds. These bonds create a protective layer on the metal's surface to reduce dissolution. The sites of reactivity likely to react with the vacant (metal) copper orbitals are the zones containing C and O atoms. Finally, these compounds have good inhibition performances to slow down metal corrosion in acid solutions. Future studies will focus on gravimetric measurements.

Keywords: coumarin, corrosion, functional

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1. Introduction

Copper and copper alloys are among the first metals known to man. Their widespread use depends on a combination of excellent thermal and electrical conductivity, good mechanical properties at both high and low temperatures, and good resistance to corrosion in a variety of environments.

Corrosion is a constant threat, as it is the cause of major material and economic losses (Cramer *et al.*, 2003; Shreir *et al.*,1994). The use of organic inhibitors is one of the most cost-effective ways of protecting metal surfaces against corrosion in order to preserve industrial installations (Schmitt, 2024; Mihit *et al*., 2006; Zarrouk *et al*., 2012b; Vastri, 2001). For this reason, a number of studies have been reported on the use of corrosion inhibitors to mitigate the corrosion of metals in aggressive media (Tigori *et al*., 2020; Benbouya *et al.*, 2018; Olasunkanmi *et al.*, 2015; Obot *et al.*, 2015; Xu *et al.*, 2014; Kosari et al., 2014; Niamien *et al.*, 2012).

On the other hand, organic compounds, because of their ability to donate electrons to the unoccupied d-orbitals of metal surfaces and to accept eletrons from the metal surface using the antibonding orbitals, adsorb onto the metal surface forming a protective film. Effective inhibitors are mainly organic molecules containing nitrogen, oxygen, sulphur heteroatoms, electronegative functional groups of an aromatic ring and/or π electrons systems in triple or double bonds (Singh *et al.*, 2018; Elshakre *et al.*, 2017; Dafali *et al.*, 2002). Among these organic compounds, Coumarins are a large family of compounds from of natural or synthetic origin (Kennedy and Thornes, 1997; Hoult and Paya, 1996). They are the focus of much attention because of their interesting biological and pharmacological activities. Methylcoumarins have choleretic, analgesic, anti-spermatogenic, antitubercular and diuretic properties (Verma *et al.*, 2021; Fitoz *et al.*, 2018; Al-Amiery *et al.*, 2016; Leal *et al.*, 2000; Lino *et al.*, 1998). Some research in this area has shown that the protective activity of an inhibitor generally relies on several physicochemical and electronic properties of the protective molecules, in particular its organic functional groups, steric hindrance, planarity of the molecule, electron density of contributing atoms and electron sharing orbital characteristic (Musa *et al.*, 2012; Cisse *et al.*, 2011).

In recent years, the theoretical study of corrosion inhibitors has become essential, as it allows the structural electronic properties of compounds to be explored in order to determine the intrinsic properties responsible for their ability to protect metals in aggressive environments (Cissé *et al.*, 2024; Obot *et al.*, 2015; El Adnani *et al.*, 2014; Ongun *et al.*, 2014; Nataraja *et al.*, 2012).

The aim of this project is to study the reactivity of a number of coumarin derivatives in the inhitbition of copper corrosion in HNO_3, using computational chemistry (DFT) to predict the action of each derivative on the metal surface. This prediction will lead to a better understanding of the inhibition mechanism of each compound.

2. Materials and methods

In this work, the theoretical calculations are based on density functional theory (DFT). All calculations were performed in the gas phase using Gaussian 09 software (Frisch *et al.*, 2009). This theory represents a judicious compromise between accuracy of results and computational cost. It is based on the use of electron density, rather than the full wave function, making it a more efficient approach. It also enables reliable prediction of the chemical reactivity of molecules. The geometry optimisations were obtained using the hybrid B3LYP (three-parameter Becke Lee-Yang-Parr) functional with the 6-31G (d) basis set (Lopez and Illas, 1998; Yang and Parr, 1985).

In addition, quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), ionization potential (I), electron affinity (A), dipole moment (μ), electronegativity (χ), hardness (η), fraction of electrons transferred (ΔN), bulk molarity (S), electrophilicity index (ω), Fukui functions and dual descriptor can be calculated (Parr *et al.*, 1999; Pearson, 1988; Parr and Yang, 1986; Koopmans, 1934):

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

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

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

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

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

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

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

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

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

χ_{Cu}= 4.98 eV/mol et η_{Cu}= 0, I = A (Dewar et *al.*, 1985),

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

For a nucleophilic attack : $f_k^+ = q_k(N+1) - q_k(N)$ (10)

For an electrophilic attack : $f_k^- = q_k(N) - q_k(N-1)$ (11)

Where $q_k(N+1)$, $q_k(N)$ and $q_k(N-1)$ are the electron population of atom k in N+1 , N and N-1 electron systems. The dual descriptor has been introduced to unambiguously explain local reactivity sites

(Martinez-Araya, 2015). This descriptor can be determined by the following relationship:

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

3. Results and discussion

3.1. Optimized structures

The gas phase optimized geometries of the studied molecules are shown in (**Figure 2**) The optimized geometries were confirmed to correspond to energy minima by the absence of imaginary frequencies in the vibrational frequency calculations.

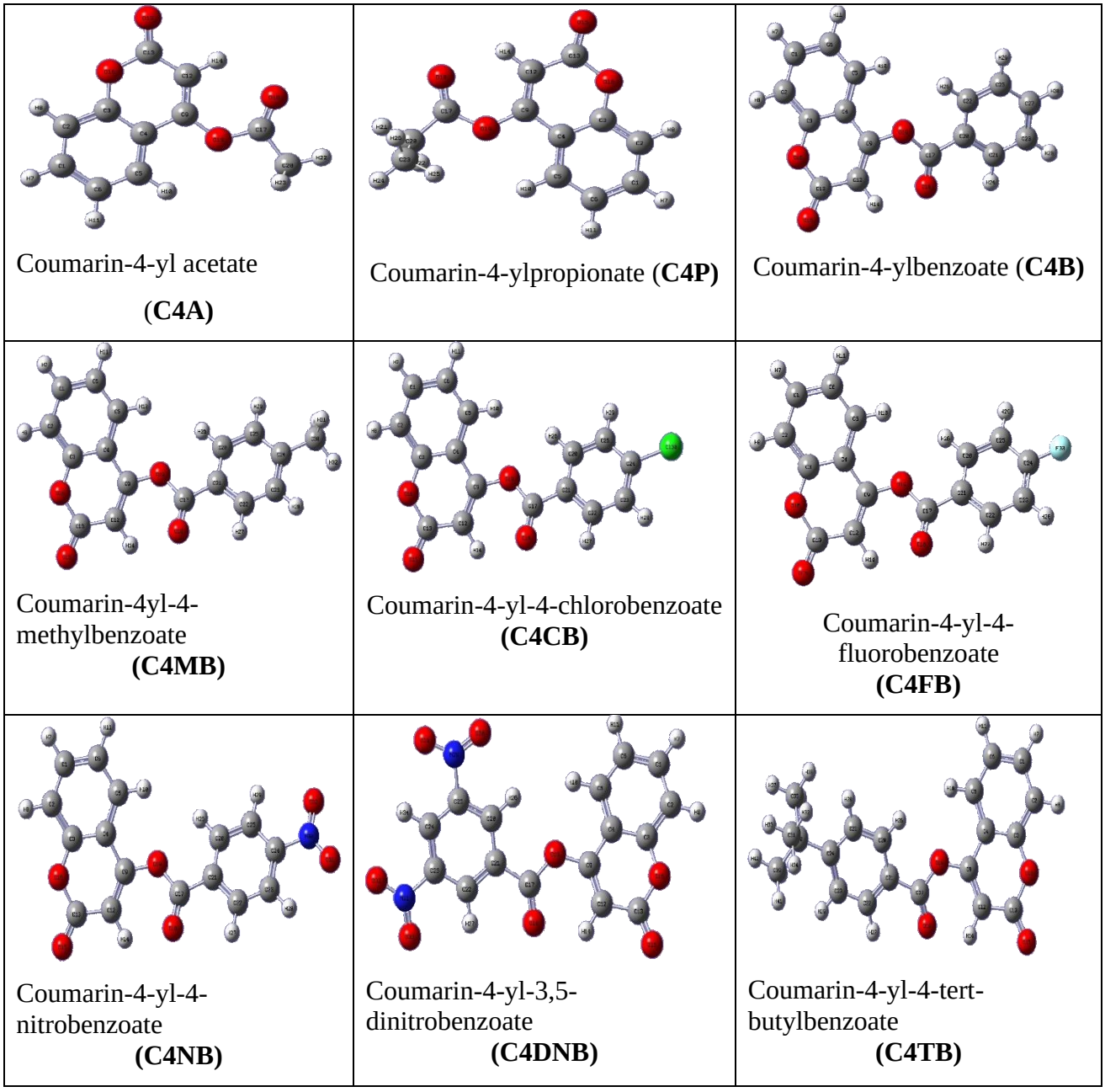


Figure 2. Optimized structures of the studied compounds.

N = blue; O = red; H = white, C = grey colour ; Cl = green and F = colour cyan

3.2. Global reactivity parameters

The corrosion inhibitive process of organic molecules is defined as reaction involving the transfer of electrons between the inhibitor and the material surface. Various chemical reactivity parameters were calculated for the studied compounds and are listed in (**Table 1**). They include the energy of the HOMO (E_{HOMO}), the energy of the LUMO (E_{LUMO}), absolute hardness (η), absolute softness (σ), fraction of electron transferred (ΔN) and dipole moment (μ).

Table 1: Quantum descriptors of the studied molecules

	Base 6-31G(d, p)								
Parameters	**C4A**	**C4P**	**C4B**	**C4MB**	**C4CB**	**C4FB**	**C4NB**	**C4DNB**	**C4TB**
E_{LUMO}(eV)	-1.8645	-1.8572	-2.0799	-2.0022	-2.2614	-2.1219	-3.2303	-3.5123	-1.9875
E_{HOMO}(eV)	-6.4891	-6.4763	-6.4497	-6.4053	-6.5375	-6.4994	-6.6985	-6.8171	-6.3955
Energy gap ΔE (eV)	4.6245	4.6191	4.3697	4.4031	4.2761	4.3776	3.4683	3.3048	4.4080
Dipole moment μ (D)	6.7181	6.8296	7.5215	8.0771	6.1080	6.4453	4.9132	4.6316	8.2465
Electron affinity A(eV)	1.8646	1.8572	2.0799	2.0022	2.2614	2.1219	3.2303	3.5123	1.9875
Ionization energy I(eV)	6.4891	6.4763	6.4497	6.4053	6.53752	6.4994	6.6985	6.8171	6.3955
Electronegativity χ (eV)	4.1768	4.1668	4.2648	4.2038	4.3995	4.3106	4.9644	5.1647	4.1915
Hardness η (eV)	2.3123	2.3095	2.1848	2.2016	2.1380	2.1888	1.7341	1.6524	2.2040
Softness σ $(eV)^{-1}$	0.4325	0.4330	0.4577	0.4542	0.4677	0.4569	0.5766	0.6052	0.4537
Fraction of electron transferred ΔN	0.0223	0.0245	0.0035	0.0173	-0.0279	-0.0070	-0.1973	-0.2677	0.0201
Electrophylicity index ω	9.7594	10.09794	12.9467	14.8166	8.7247	9.4897	6.9601	6.4911	15.4275
Total energy E_T (Ha)	-724.8085	-764.1238	-916.5445	-955.8994	-1376.1157	-1015.8094	-1120.9997	-1325.5398	-1073.7833

The frontier orbitals (Highest Occupied Molecular Orbital, HOMO) and (Lowest Unoccupied Molecular Orbital, LUMO) of reacting species are very important in defining their reactivity. Fukui was the first one to recognize this particularity (Fukui, 1952). The literature showed that the adsorption of most of organic inhibitors onto copper surface can occur on the basis of donor–acceptor interaction between the lone pairs and π electrons of the inhibitors and the vacant d orbitals of the (metal) copper surface atoms (Yuce and Kardas, 2012).

The trend of E_{HOMO} for the studied coumarin is:

C4TB > C4MB > C4B > C4P > C4A > C4FB > C4CB > C4NB > C4DNB.

This suggests that compound C4TB has the highest tendency to donate electrons to the appropriate low-lying empty or partially filled orbitals of metal atom, while compound C4DNB has the least tendency to donate electrons to metal.

Substitution in a carbonyl position by or with Et, tBu, Ph, MePh (methyl, ethyl, tertbutyl, phenyl) groups leads to an increase of the E_{HOMO} in coumarin-4-yl when compared to coumarin-4-yl acetate, in the gas phase. This would probably provide these inhibitors with a better ability to yield their electrons to adsorb to metal surface. Such property may result from the inductive donor effect of tBuPh-, Ph, Et-, MePh- groups. Indeed, due to the inductive donor effect (+I), these groups would bring an additional electron density to the carbonyl moiety, which results in a higher value of HOMO energy, and therefore a better reactivity. In contrast to these data, the substitution in a carbon position of the phenyl ring by Cl, F, N_2O chlorine, fluorine, nitro and dinitro group provides a decrease of E_{HOMO}, which results in a reduction of the donor effect of this inhibitor.

Likewise, E_{LUMO} is associated with the electron accepting ability of the molecule, consequently, the low value of E_{LUMO} the high tendency to accept electrons from suitable electron donors. The values of E_{LUMO} presented in (**Table 1**) show the trend C4DNB > C4NB > C4CB > C4FB > C4MB > C4TB > C4A > C4P suggesting that C4DNB has the highest tendency to accept electrons from the occupied orbitals of metal atom in retro-donation step. This can also be explained by the electron deficiency on the phenyl ring resulting of the withdrawing effect of N_2O^-, Cl- and F- atoms.

The energy gap, ΔE between HOMO and LUMO orbitals reflects the static chemical reactivity of the studied molecules. The obtained values of ΔE indicate that the substitution of the hydrogen atom in H- by N_2O and $2N_2O$ decreases the value of the energy gap. However, the values of N_2O (~3.468272 eV) and $2N_2O$ (~3.304800 eV) are much lower than the one of Me-PP (5,170eV) indicating that the (-I) effect of the dinitro and nitro in the meta and para of the phenyl ring have probably greater influence on the reactivity of the studied inhibitors than the (+I) electronic effect of the tBuPh-, Ph-, Et-, MePh- group in the same position. Therefore, the adsorption of Cl-, F-, N_2O^- and $2N_2O^-$ dinitro and nitro onto the mild steel surface through the back donating mechanism will probably be stronger than the adsorption of tBuPh-, Ph-, Et-, MePh- and Me- , respectively. The decreasing energy gap is as follows:

C4A > C4P > C4TB > C4MB > C4FB> C4B > C4CB > C4NB > C4DNB

The dipole moment μ is a measure of the polarity of a covalent bond, which is related to the distribution of electrons in a molecule. However, its relation to the efficiency of corrosion inhibitors is not yet well established and there is no agreement in the literature on the way of interpreting the trend of the dipole moment values in a set of corrosion inhibitors (Nahlé *et al.*, 2021; Arrousse *et al.*, 2021; Elmsellem *et al.*, 2014; Kovacevic and Kokalj (2011). In fact, the computed values of the dipole moment do not allow any kind of interpretation with regards to the literature.

The global hardness η is a very important parameter that describes the molecular reactivity. It is well established that hard molecules (atoms or ions) are more resistant to eventual deformation or polarization

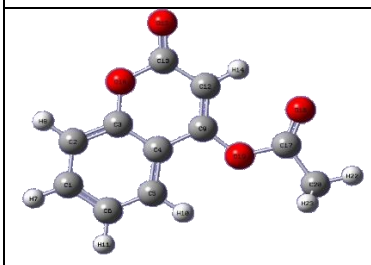
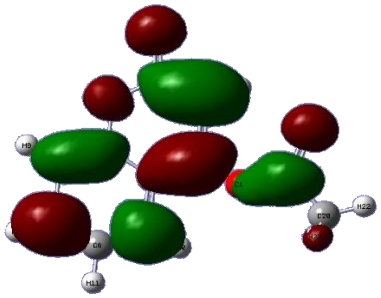
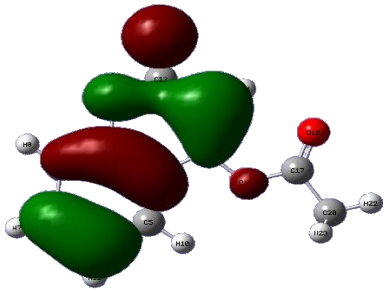
of the electronic cloud caused by a relatively small perturbation of molecular reactions (Al Hamzi *et al.*, 2013; El Adnani *et al.*, 2013; Zarrouk *et al.*, 2012; Yuce and Kardas 2012; Kovacevic and Kokalj, 2011). Hence, inhibitors with the lowest values of global hardness are expected to be good corrosion inhibitors. The global hardness results presented in (**Table 1**) show that C4DNB and C4NB have the lowest value of η (1.734136 1.652400 eV), followed by C4CB and C4FB (2.138056 eV, 2.188784 eV) when C4A and C4P presents the highest value of η (2.312272eV, 2.309552 eV). These results corroborate the previous predictions, derived from gap of energy, of the high reactivity of C4DNB and C4NB in comparison to C4A and C4P, respectively. The increasing global hardness for the studied inhibitors is as follows:

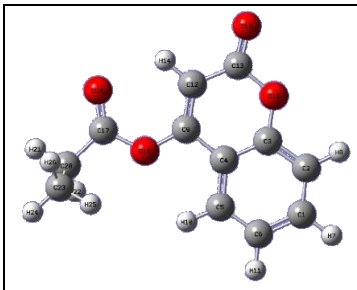
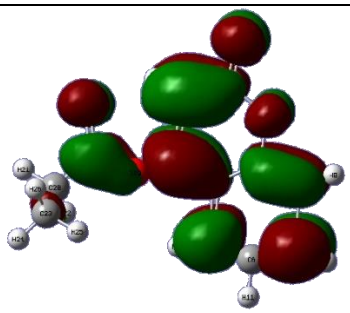
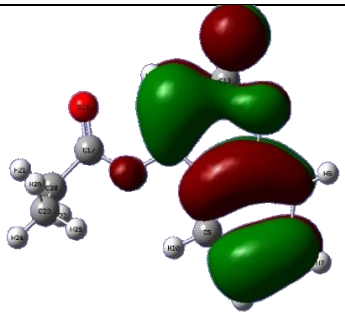
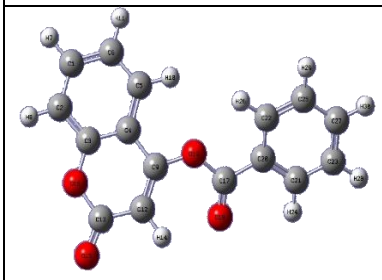
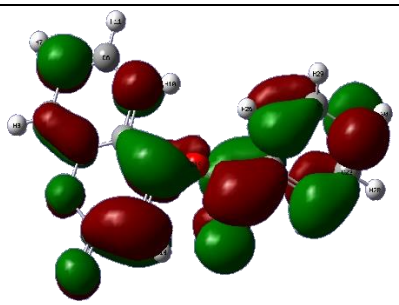
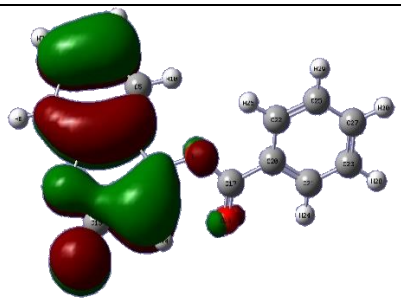
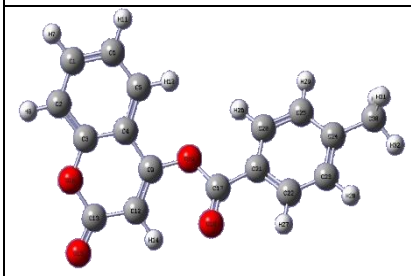
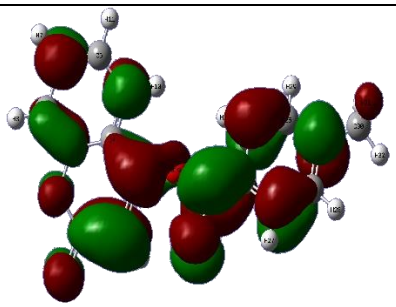
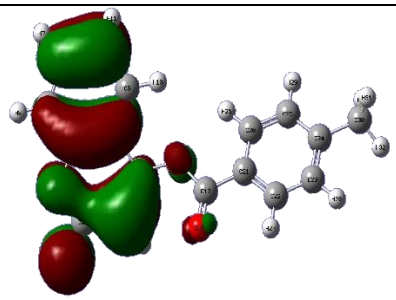
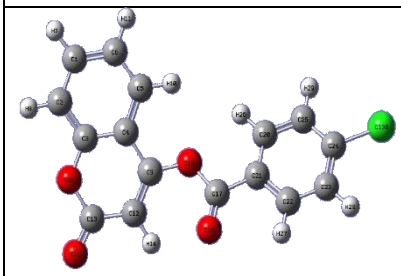
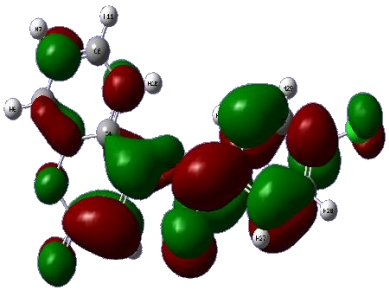
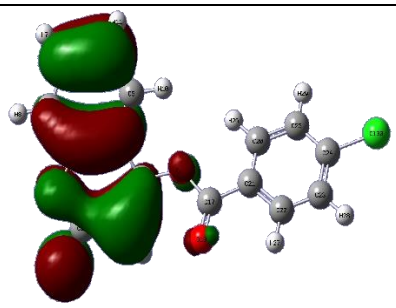
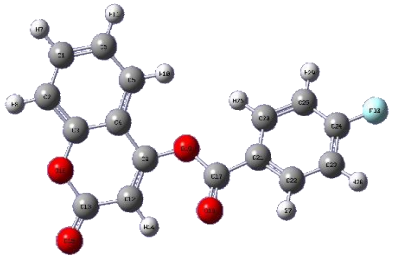
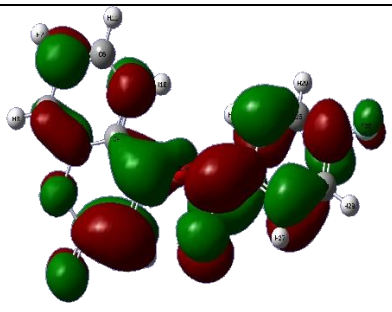
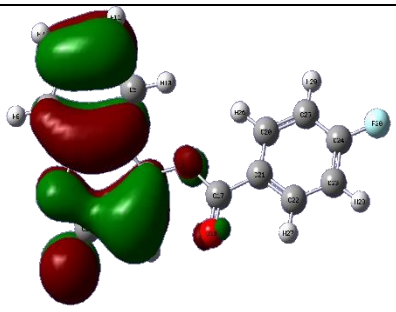
η(C4DNB) < η(C4NB) < η(C4CB) < η(C4B) < η(C4FB) < η (C4MB)< η(C4TB) < η(C4P) < η(C4A)

According to Lukovits's study (Lukovits *et al.*, 2001), the fraction of transferred electrons describes the trend of electrons donation within a set of inhibitors. Generally, in the case of ΔN less than 3.6, the inhibition efficiency increases with the increase in electron-donating ability to metal surface. The obtained values of ΔN reported in (**Table 1**) are all below 3.6 and show that C4A presents the higher value of ΔN, which implies good disposition of this inhibitor to donate electrons to the mild steel surface, especially, when compared to C4DNB, probably as a result of the high withdrawing effect of the chlorine atom on the electron density of the phenyl ring in C4DNB, which agree well with the above results of HOMO and LUMO energies tendency. The transferred electrons increase as follows:

ΔN (C4DNB) < ΔN (C4DNB) < ΔN(C4P) < ΔN (C4A).

As shown in (**Figure 3**), the HOMO of nine coumarins derivatives comprises essentially π-orbitals together with few σ-type orbitals and delocalized mainly on the C atoms of the core of 2H-1-benzopyran-2-one. This implies that coumarins can interact with a metal atom by donating its HOMO π- or σ-orbital electrons to the respective low-lying vacant d- or p-orbitals of the metal.

Inhibitor	LUMO	HOMO
 **C4A**		

 **C4P**		
 **C4B**		
 **C4MB**		
 **C4CB**		
		

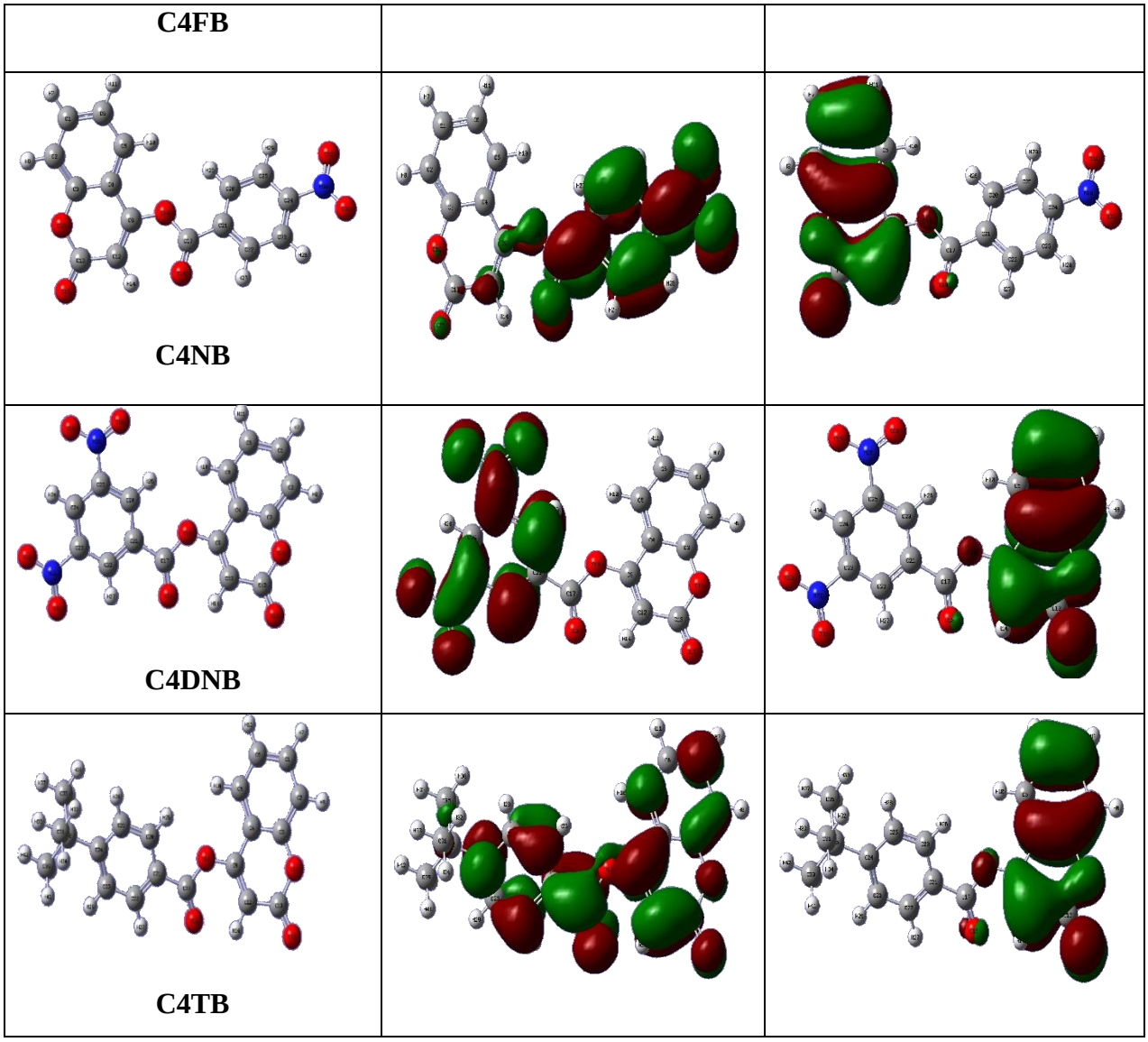


Figure 3. HOMO and LUMO electron density distributions for the studied coumarine 4-yl.
N = blue; O = red; H = white, C = grey colour ; Cl = green and F = cyan

On the other hand, in (**Figure 3**), LUMO of studied compounds comprises a mixture of π and σ type orbitals, delocalised both on C atoms of the coumarin rings and on O atoms of the ester group except in the case of C4NB and C4DNB where the LUMO is mainly delocalised on the coumarin core atoms.This suggests that coumarine derivatives can receive electrons from π- and/or σ-orbitals of Al metal) during retro-donation.

3.3 Local reactivity analysing

The corrosion inhibitive process of organic molecules is defined as reaction involving the transfer of electrons between the inhibitor and the material surface. Hence, it can be explained according to Fukui's frontier molecular orbital theory, by the interaction between HOMO and LUMO of the reacting species

(Rodriguez-Valdez *et al.*, 2006; Fuentealba *et al.*, 2000; Ayers and Parr, 2000). The condensed Fukui functions ($f_k^+$and f_k^-) are used to assess the susceptibility of individual atomic sites in a molecule to nucleophilic or electrophilic attacks. The nucleophilic Fukui function, f_k^+ measures the change in electron density at various sites when a molecule gains electrons and it corresponds to the reactivity of the sites with respect to nucleophilic attack. On the other hand, the electrophilic Fukui function, f_k^- corresponds to reactivity with respect to electrophilic attack when the molecule loses electrons (Yang and Parr, 1985; Udhayakala *et al.*, 2012). The values of f_k^+ and f_k^- or the studied coumarins derivatives are listed in (**Tables 2, 3, 4, 5, 6, 7, 8, 9, 10**) respectively.

Table 2: Values of local reactivity parameters for C4A

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.113698	-0.080166	-0.037066	0.033532	0.0431	0.009568
2 C	-0.176661	-0.152087	-0.12596	0.024574	0.026127	0.001553
3 C	0.318276	0.328976	0.363155	0.0107	0.034179	0.023479
4 C	0.064322	0.066958	0.084929	0.002636	0.017971	0.015335
5 C	-0.202715	-0.160248	-0.127018	0.042467	0.03323	-0.009237
6 C	-0.094457	-0.089159	-0.054161	0.005298	0.034998	0.0297
7 H	0.031087	0.103494	0.182293	0.072407	0.078799	0.006392
8 H	0.053932	0.116507	0.18196	0.062575	0.065453	0.002878
9 C	0.226343	0.290979	0.343677	0.064636	0.052698	-0.011938
10 H	0.052536	0.111456	0.172378	0.05892	0.060922	0.002002
11 H	0.032224	0.097882	0.175492	0.065658	0.07761	0.011952
12 C	-0.198615	-0.157744	-0.098252	0.040871	0.059492	0.018621
13 C	0.499067	0.575905	0.608435	0.076838	0.03253	-0.044308
14 H	0.151814	0.212912	0.273589	0.061098	0.060677	-0.000421
15 O	-0.566799	-0.461357	-0.337753	0.105442	**0.123604**	**0.018162**
16 O	-0.566843	-0.531512	-0.48308	0.035331	0.048432	0.013101
17 C	0.544386	0.592866	0.602958	0.04848	0.010092	-0.038388
18 O	-0.490593	-0.439646	-0.413115	**0.050947**	0.026531	**-0.024416**
19 O	-0.546727	-0.52691	-0.49887	0.019817	0.02804	0.008223
20 C	-0.375847	-0.381749	-0.382945	-0.005902	-0.001196	0.004706
21 H	0.127172	0.167174	0.193433	0.040002	0.026259	-0.013743
22 H	0.121901	0.168321	0.202877	0.04642	0.034556	-0.011864
23 H	0.109895	0.147151	0.173046	0.037256	0.025895	-0.011361

Table 3: Values of local reactivity parameters for C4P

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.113181	-0.080374	-0.037717	0.032807	0.042657	0.00985
2 C	-0.17624	-0.152133	-0.126709	0.024107	0.025424	0.001317
3 C	0.31854	0.3289	0.36208	0.01036	0.03318	0.02282
4 C	0.063793	0.066393	0.083658	0.0026	0.017265	0.014665
5 C	-0.202192	-0.160728	-0.12735	0.041464	0.033378	-0.008086
6 C	-0.094471	-0.089272	-0.055671	0.005199	0.033601	0.028402
7 H	0.03214	0.103273	0.181076	0.071133	0.077803	0.00667
8 H	0.054765	0.116268	0.180769	0.061503	0.064501	0.002998
9 C	0.228103	0.290628	0.343513	0.062525	0.052885	-0.00964
10 H	0.053738	0.111143	0.1713	0.057405	0.060157	0.002752
11 H	0.033189	0.0976	0.173951	0.064411	0.076351	0.01194
12 C	-0.197831	-0.158001	-0.099363	0.03983	0.058638	0.018808
13 C	0.499552	0.575418	0.60804	**0.075866**	0.032622	**-0.043244**
14 H	0.152878	0.212688	0.273126	0.05981	0.060438	0.000628
15 O	-0.565509	-0.461676	-0.3398	0.103833	**0.121876**	**0.018043**
16 O	-0.566508	-0.531768	-0.484483	0.03474	0.047285	0.012545
17 C	0.546879	0.601362	0.615049	0.054483	0.013687	-0.040796
18 O	-0.501345	-0.449703	-0.421385	0.051642	0.028318	-0.023324
19 O	-0.551394	-0.531545	-0.502945	0.019849	0.0286	0.008751
20 C	-0.225559	-0.239282	-0.248555	-0.013723	-0.009273	0.00445
21 H	0.106998	0.15341	0.187626	0.046412	0.034216	-0.012196
22 H	0.095976	0.133693	0.160405	0.037717	0.026712	-0.011005
23 C	-0.321374	-0.335934	-0.342167	-0.01456	-0.006233	0.008327
24 H	0.079289	0.129135	0.166766	0.049846	0.037631	-0.012215
25 H	0.119454	0.129933	0.132304	0.010479	0.002371	-0.008108
26 H	0.130308	0.140573	0.146482	0.010265	0.005909	-0.004356

Table 4: Values of local reactivity parameters for C4B

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.100267	-0.079427	-0.045473	0.02084	0.033954	0.013114
2 C	-0.167335	-0.148632	-0.122704	0.018703	0.025928	0.007225
3 C	0.316489	0.323605	0.358154	0.007116	0.034549	0.027433
4 C	0.087164	0.095055	0.115355	0.007891	0.0203	0.012409
5 C	-0.19807	-0.171193	-0.147428	0.026877	0.023765	-0.003112
6 C	-0.090585	-0.086728	-0.051669	0.003857	0.035059	0.031202
7 H	0.053337	0.105702	0.17491	0.052365	0.069208	0.016843
8 H	0.069721	0.117799	0.177652	0.048078	0.059853	0.011775
9 C	0.31876	0.34321	0.369348	0.02445	0.026138	0.001688
10 H	0.093796	0.108767	0.148575	0.014971	0.039808	0.024837
11 H	0.05821	0.100336	0.166943	0.042126	0.066607	0.024481
12 C	-0.176835	-0.147162	-0.100395	0.029673	0.046767	0.017094
13 C	0.54699	0.592963	0.615532	0.045973	0.022569	-0.023404
14 H	0.085993	0.138395	0.197187	0.052402	0.058792	0.00639
15 O	-0.534995	-0.460008	-0.355903	0.074987	**0.104105**	**0.029118**
16 O	-0.553345	-0.525728	-0.479775	0.027617	0.045953	0.018336
17 C	0.51379	0.572483	0.575458	0.058693	0.002975	-0.055718
18 O	-0.521452	-0.454935	-0.437227	**0.066517**	0.017708	**-0.048809**
19 O	-0.580128	-0.552764	-0.536228	0.027364	0.016536	-0.010828
20 C	0.034053	0.035069	0.032503	0.001016	-0.002566	-0.003582
21 C	-0.154579	-0.114688	-0.101407	0.039891	0.013281	-0.02661
22 C	-0.106021	-0.095715	-0.079847	0.010306	0.015868	0.005562
23 C	-0.093501	-0.089367	-0.069034	0.004134	0.020333	0.016199
24 H	0.087753	0.134156	0.161451	0.046403	0.027295	-0.019108
25 C	-0.10552	-0.095259	-0.080747	0.010261	0.014512	0.004251
26 H	0.081578	0.115055	0.137179	0.033477	0.022124	-0.011353
27 C	-0.110267	-0.076513	-0.063697	0.033754	0.012816	-0.020938
28 H	0.052574	0.107461	0.150942	0.054887	0.043481	-0.011406
29 H	0.050425	0.103462	0.143324	0.053037	0.039862	-0.013175
30 H	0.042267	0.104601	0.147021	0.062334	0.04242	-0.019914

Table 5: Values of local reactivity parameters for C4MB

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.096981	-0.080354	-0.045787	0.016627	0.034567	0.01794
2 C	-0.166641	-0.152499	-0.132295	0.014142	0.020204	0.006062
3 C	0.326632	0.329746	0.354746	0.003114	0.025	0.021886
4 C	0.060907	0.066567	0.079076	0.00566	0.012509	0.006849
5 C	-0.17651	-0.160302	-0.131727	0.016208	0.028575	0.012367
6 C	-0.094197	-0.0891	-0.064974	0.005097	0.024126	0.019029
7 H	0.058398	0.102445	0.167698	0.044047	0.065253	0.021206
8 H	0.076475	0.11567	0.16973	0.039195	0.05406	0.014865
9 C	0.278544	0.293462	0.336656	0.014918	0.043194	0.028276
10 H	0.094944	0.110244	0.155297	0.0153	0.045053	0.029753
11 H	0.059226	0.096561	0.158501	0.037335	0.06194	0.024605
12 C	-0.16556	-0.155805	-0.105621	0.009755	0.050184	0.040429
13 C	0.524759	0.575295	0.604458	0.050536	0.029163	-0.021373
14 H	0.186994	0.212558	0.264395	0.025564	0.051837	0.026273
15 O	-0.525484	-0.462668	-0.36192	0.062816	**0.100748**	**0.037932**
16 O	-0.554439	-0.532035	-0.495207	0.022404	0.036828	0.014424
17 C	0.500091	0.604925	0.617966	**0.104834**	0.013041	**-0.091793**
18 O	-0.557541	-0.4742	-0.456103	0.083341	0.018097	-0.065244
19 O	-0.567578	-0.548115	-0.523628	0.019463	0.024487	0.005024
20 C	-0.106832	-0.090757	-0.080779	0.016075	0.009978	-0.006097
21 C	0.035938	0.029667	0.038924	-0.006271	0.009257	0.015528
22 C	-0.163122	-0.113132	-0.100182	0.04999	0.01295	-0.03704
23 C	-0.138588	-0.13106	-0.111312	0.007528	0.019748	0.01222
24 C	0.085204	0.106616	0.116379	0.021412	0.009763	-0.011649
25 C	-0.126761	-0.109429	-0.095868	0.017332	0.013561	-0.003771
26 H	0.071542	0.110701	0.122429	0.039159	0.011728	-0.027431
27 H	0.079859	0.132274	0.159196	0.052415	0.026922	-0.025493
28 H	0.041999	0.099373	0.140001	0.057374	0.040628	-0.016746
29 H	0.04097	0.097114	0.131428	0.056144	0.034314	-0.02183
30 C	-0.372414	-0.375783	-0.378808	-0.003369	-0.003025	0.000344
31 H	0.103619	0.141044	0.168333	0.037425	0.027289	-0.010136
32 H	0.094911	0.126896	0.150894	0.031985	0.023998	-0.007987
33 H	0.091636	0.124082	0.148104	0.032446	0.024022	-0.008424

Table 6: Values of local reactivity parameters for C4CB

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.093264	-0.079864	-0.044781	0.0134	0.035083	0.021683
2 C	-0.164119	-0.151917	-0.130962	0.012202	0.020955	0.008753
3 C	0.327871	0.329816	0.356269	0.001945	0.026453	0.024508
4 C	0.060919	0.0674	0.080728	0.006481	0.013328	0.006847
5 C	-0.170888	-0.160005	-0.131941	0.010883	0.028064	0.017181
6 C	-0.093852	-0.088742	-0.062656	0.00511	0.026086	0.020976
7 H	0.065252	0.104156	0.170242	0.038904	0.066086	0.027182
8 H	0.08221	0.117199	0.17204	0.034989	0.054841	0.019852
9 C	0.287263	0.292747	0.336238	0.005484	0.043491	0.038007
10 H	0.101738	0.109063	0.155651	0.007325	0.046588	0.039263
11 H	0.065872	0.09808	0.16133	0.032208	0.06325	0.031042
12 C	-0.160074	-0.155852	-0.105257	0.004222	0.050595	0.046373
13 C	0.532517	0.57663	0.605064	0.044113	0.028434	-0.015679
14 H	0.19359	0.212956	0.264741	0.019366	0.051785	0.032419
15 O	-0.514897	-0.460763	-0.358573	0.054134	**0.10219**	**0.048056**
16 O	-0.55118	-0.531123	-0.492906	0.020057	0.038217	0.01816
17 C	0.495827	0.609285	0.620919	**0.113458**	0.011634	**-0.101824**
18 O	-0.561714	-0.469936	-0.455188	0.091778	0.014748	-0.07703
19 O	-0.56768	-0.547522	-0.524501	0.020158	0.023021	0.002863
20 C	-0.098513	-0.07948	-0.070721	0.019033	0.008759	-0.010274
21 C	0.030582	0.027346	0.034234	-0.003236	0.006888	0.010124
22 C	-0.157048	-0.103547	-0.090924	0.053501	0.012623	-0.040878
23 C	-0.094763	-0.08636	-0.070593	0.008403	0.015767	0.007364
24 C	-0.116952	-0.082816	-0.077273	0.034136	0.005543	-0.028593
25 C	-0.09189	-0.076797	-0.066338	0.015093	0.010459	-0.004634
26 H	0.076438	0.1224	0.13088	0.045962	0.00848	-0.037482
27 H	0.085869	0.143001	0.167201	0.057132	0.0242	-0.032932
28 H	0.069834	0.128929	0.164186	0.059095	0.035257	-0.023838
29 H	0.06359	0.122345	0.152313	0.058755	0.029968	-0.028787
30 Cl	-0.102537	0.01337	0.110581	0.115907	0.097211	-0.018696

Table 7: Values of local reactivity parameters for C4FB

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.095911	-0.079972	-0.043541	0.015939	0.036431	0.020492
2 C	-0.165888	-0.15207	-0.130553	0.013818	0.021517	0.007699
3 C	0.327006	0.329841	0.357039	0.002835	0.027198	0.024363
4 C	0.061148	0.06716	0.080755	0.006012	0.013595	0.007583
5 C	-0.174906	-0.160068	-0.130638	0.014838	0.02943	0.014592
6 C	-0.094071	-0.088826	-0.062106	0.005245	0.02672	0.021475
7 H	0.060535	0.103759	0.171824	0.043224	0.068065	0.024841
8 H	0.0783	0.11686	0.173259	0.03856	0.056399	0.017839
9 C	0.280739	0.292902	0.338429	0.012163	0.045527	0.033364
10 H	0.095772	0.108984	0.157546	0.013212	0.048562	0.03535
11 H	0.061138	0.097664	0.16293	0.036526	0.065266	0.02874
12 C	-0.164034	-0.15577	-0.103057	0.008264	0.052713	0.044449
13 C	0.526788	0.576273	0.605759	0.049485	0.029486	-0.019999
14 H	0.188752	0.212839	0.266627	0.024087	0.053788	0.029701
15 O	-0.522539	-0.461223	-0.355499	0.061316	**0.105724**	**0.044408**
16 O	-0.553488	-0.531364	-0.492088	0.022124	0.039276	0.017152
17 C	0.498488	0.608287	0.620126	**0.109799**	0.011839	**-0.09796**
18 O	-0.559543	-0.471685	-0.456085	0.087858	0.0156	-0.072258
19 O	-0.568469	-0.548132	-0.523734	0.020337	0.024398	0.004061
20 C	-0.099018	-0.081264	-0.072237	0.017754	0.009027	-0.008727
21 C	0.032573	0.026398	0.033567	-0.006175	0.007169	0.013344
22 C	-0.163925	-0.108469	-0.095407	0.055456	0.013062	-0.042394
23 C	-0.157533	-0.151058	-0.13346	0.006475	0.017598	0.011123
24 C	0.297535	0.358583	0.387852	0.061048	0.029269	-0.031779
25 C	-0.156927	-0.139073	-0.126292	0.017854	0.012781	-0.005073
26 H	0.08032	0.122378	0.130819	0.042058	0.008441	-0.033617
27 H	0.08683	0.142493	0.167271	0.055663	0.024778	-0.030885
28 H	0.059332	0.121634	0.161085	0.062302	0.039451	-0.022851
29 H	0.057574	0.11824	0.15168	0.060666	0.03344	-0.027226
30 F	-0.316579	-0.275321	-0.241871	0.041258	0.03345	-0.007808

Table 8: Values of local reactivity parameters for C4NB

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.085922	-0.079126	-0.040787	0.006796	0.038339	0.031543
2 C	-0.158582	-0.151139	-0.127322	0.007443	0.023817	0.016374
3 C	0.329567	0.329964	0.361237	0.000397	0.031273	0.030876
4 C	0.060232	0.068238	0.083943	0.008006	0.015705	0.007699
5 C	-0.161283	-0.159748	-0.130361	0.001535	0.029387	0.027852
6 C	-0.092051	-0.088267	-0.056385	0.003784	0.031882	0.028098
7 H	0.080941	0.106586	0.17781	0.025645	0.071224	0.045579
8 H	0.095475	0.119391	0.178672	0.023916	0.059281	0.035365
9 C	0.302014	0.291677	0.33942	-0.010337	0.047743	0.05808
10 H	0.117953	0.108348	0.162248	-0.009605	0.0539	0.063505
11 H	0.081839	0.100263	0.169941	0.018424	0.069678	0.051254
12 C	-0.152692	-0.156063	-0.101128	-0.003371	0.054935	0.058306
13 C	0.556675	0.578622	0.606803	0.021947	0.028181	0.006234
14 H	0.207753	0.213776	0.26842	0.006023	0.054644	0.048621
15 O	-0.487154	-0.45778	-0.346538	0.029374	**0.111242**	**0.081868**
16 O	-0.542662	-0.52982	-0.486188	0.012842	0.043632	0.03079
17 C	0.528676	0.616739	0.626285	0.088063	0.009546	-0.078517
18 O	-0.537987	-0.461312	-0.452678	0.076675	0.008634	-0.068041
19 O	-0.560529	-0.545608	-0.524153	0.014921	0.021455	0.006534
20 C	-0.115899	-0.093522	-0.089628	0.022377	0.003894	-0.018483
21 C	0.033649	0.044397	0.043907	0.010748	-0.00049	-0.011238
22 C	-0.154961	-0.117497	-0.106217	0.037464	0.01128	-0.026184
23 C	-0.142342	-0.107739	-0.100142	0.034603	0.007597	-0.027006
24 C	0.251835	0.277122	0.288829	0.025287	0.011707	-0.01358
25 C	-0.107389	-0.081743	-0.071047	0.025646	0.010696	-0.01495
26 H	0.071342	0.131353	0.130247	0.060011	-0.001106	-0.061117
27 H	0.091979	0.152478	0.169163	0.060499	0.016685	-0.043814
28 H	0.102731	0.161577	0.183905	0.058846	0.022328	-0.036518
29 H	0.085722	0.141944	0.163164	0.056222	0.02122	-0.035002
30 N	0.277274	0.310735	0.316093	0.033461	0.005358	-0.028103
31 O	-0.528879	-0.397763	-0.344797	**0.131116**	0.052966	**-0.07815**
32 O	-0.447325	-0.326086	-0.292715	0.121239	0.033371	-0.087868

Table 9: Values of local reactivity parameters for C4DNB

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.083773	-0.078423	-0.038118	0.00535	0.040305	0.034955
2 C	-0.15672	-0.150436	-0.124347	0.006284	0.026089	0.019805
3 C	0.329805	0.330243	0.365046	0.000438	0.034803	0.034365
4 C	0.06158	0.069046	0.086383	0.007466	0.017337	0.009871
5 C	-0.16152	-0.160491	-0.130695	0.001029	0.029796	0.028767
6 C	-0.090554	-0.087687	-0.051134	0.002867	0.036553	0.033686
7 H	0.087419	0.108954	0.183499	0.021535	0.074545	0.05301
8 H	0.100694	0.121323	0.183703	0.020629	0.06238	0.041751
9 C	0.299856	0.290177	0.339927	-0.009679	0.04975	0.059429
10 H	0.129092	0.109801	0.167801	-0.019291	0.058	0.077291
11 H	0.091721	0.103893	0.177656	0.012172	0.073763	0.061591
12 C	-0.156421	-0.156222	-0.100015	0.000199	0.056207	0.056008
13 C	0.566508	0.580752	0.6086	0.014244	0.027848	0.013604
14 H	0.211117	0.214582	0.270619	0.003465	0.056037	0.052572
15 O	-0.477465	-0.454699	-0.338156	0.022766	**0.116543**	**0.093777**
16 O	-0.53915	-0.528672	-0.481147	0.010478	0.047525	0.037047
17 C	0.593053	0.635974	0.644161	0.042921	0.008187	-0.034734
18 O	-0.494171	-0.456696	-0.451761	0.037475	0.004935	-0.03254
19 O	-0.548531	-0.546562	-0.526697	0.001969	0.019865	0.017896
20 C	-0.158615	-0.092231	-0.08843	0.066384	0.003801	-0.062583
21 C	0.020327	0.00848	0.00801	-0.011847	-0.00047	0.011377
22 C	-0.156987	-0.078943	-0.066779	0.078044	0.012164	-0.06588
23 C	0.24752	0.259732	0.265658	0.012212	0.005926	-0.006286
24 C	-0.096823	-0.075681	-0.061515	0.021142	0.014166	-0.006976
25 C	0.237057	0.262173	0.270169	0.025116	0.007996	-0.01712
26 H	0.10915	0.170242	0.162505	0.061092	-0.007737	-0.068829
27 H	0.11931	0.18106	0.191998	0.06175	0.010938	-0.050812
28 N	0.28551	0.313751	0.313761	0.028241	1E-05	-0.028231
29 O	-0.49406	-0.373625	-0.343255	**0.120435**	0.03037	**-0.090065**
30 O	-0.435323	-0.329753	-0.32288	0.10557	0.006873	-0.098697
31 N	0.288071	0.311477	0.314247	0.023406	0.00277	-0.020636
32 O	-0.481365	-0.381474	-0.345143	0.099891	0.036331	-0.06356
33 O	-0.401465	-0.315616	-0.298481	0.085849	0.017135	-0.068714
34 H	0.155151	0.195551	0.21481	0.0404	0.019259	-0.021141

Table 10: Values of local reactivity parameters for C4TB

Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
1 C	-0.096329	-0.080427	-0.047435	0.015902	0.032992	0.01709
2 C	-0.16617	-0.152527	-0.133192	0.013643	0.019335	0.005692
3 C	0.326766	0.329633	0.353302	0.002867	0.023669	0.020802
4 C	0.061063	0.066668	0.078556	0.005605	0.011888	0.006283
5 C	-0.175579	-0.160398	-0.133034	0.015181	0.027364	0.012183
6 C	-0.094164	-0.089145	-0.066413	0.005019	0.022732	0.017713
7 H	0.059667	0.102307	0.165148	0.04264	0.062841	0.020201
8 H	0.077536	0.11554	0.167649	0.038004	0.052109	0.014105
9 C	0.280015	0.293451	0.334526	0.013436	0.041075	0.027639
10 H	0.096248	0.110402	0.152904	0.014154	0.042502	0.028348
11 H	0.060417	0.096431	0.155764	0.036014	0.059333	0.023319
12 C	-0.164522	-0.155768	-0.107936	0.008754	0.047832	0.039078
13 C	0.526077	0.575173	0.603534	0.049096	0.028361	-0.020735
14 H	0.18816	0.212502	0.262318	0.024342	0.049816	0.025474
15 O	-0.523649	-0.462873	-0.366306	0.060776	**0.096567**	**0.035791**
16 O	-0.553829	-0.532078	-0.496878	0.021751	0.0352	0.013449
17 C	0.499943	0.605605	0.618875	**0.105662**	0.01327	**-0.092392**
18 O	-0.558504	-0.474826	-0.45633	0.083678	0.018496	-0.065182
19 O	-0.567771	-0.54838	-0.524714	0.019391	0.023666	0.004275
20 C	-0.121812	-0.105073	-0.093967	0.016739	0.011106	-0.005633
21 C	0.03889	0.032067	0.042044	-0.006823	0.009977	0.0168
22 C	-0.170147	-0.119203	-0.106431	0.050944	0.012772	-0.038172
23 C	-0.150614	-0.141305	-0.117801	0.009309	0.023504	0.014195
24 C	0.11311	0.141757	0.156168	0.028647	0.014411	-0.014236
25 C	-0.124475	-0.105545	-0.090678	0.01893	0.014867	-0.004063
26 H	0.071367	0.109435	0.122252	0.038068	0.012817	-0.025251
27 H	0.079944	0.131149	0.158171	0.051205	0.027022	-0.024183
28 H	0.045584	0.096278	0.127678	0.050694	0.0314	-0.019294
29 H	0.045902	0.096559	0.134114	0.050657	0.037555	-0.013102
30 C	-0.029453	-0.050786	-0.069974	-0.021333	-0.019188	0.002145
31 C	-0.296436	-0.303295	-0.307186	-0.006859	-0.003891	0.002968
32 H	0.095954	0.102574	0.107802	0.00662	0.005228	-0.001392
33 H	0.070232	0.103087	0.128141	0.032855	0.025054	-0.007801
34 H	0.100903	0.111759	0.121286	0.010856	0.009527	-0.001329
35 C	-0.281143	-0.286374	-0.288927	-0.005231	-0.002553	0.002678
36 H	0.09775	0.107285	0.115873	0.009535	0.008588	-0.000947

37 H	0.071081	0.106777	0.134922	0.035696	0.028145	-0.007551
38 H	0.097065	0.106128	0.113755	0.009063	0.007627	-0.001436
39 C	-0.298282	-0.305566	-0.311438	-0.007284	-0.005872	0.001412
40 H	0.097151	0.104636	0.111462	0.007485	0.006826	-0.000659
41 H	0.102326	0.113305	0.123251	0.010979	0.009946	-0.001033
42 H	0.069729	0.103062	0.129143	0.033333	0.026081	-0.007252

The probable nucleophilic attack sites are those for which the values of the Fukui index and the dual descriptor are the highest. Electrophilic attack sites are identified by the highest value of the Fukui index and the lowest value of the dual descriptor. In the event of ambiguity, the atom with the largest and smallest dual descriptor values for the same compound are the likely nucleophilic and electrophilic attack sites respectively. In view of the above, and after analysing (**Tables 2, 3, 4, 5, 6, 7, 8, 9, 10**) the different sites of reactivity for the molecules studied are shown in (**Table 11**).

Table 11: Summary of local reactivity sites for each compound

Compounds	Atoms	$q_k(N-1)$	$q_k(N)$	$q_k(N+1)$	f_k^-	f_k^+	$\Delta f_k(r)$
(C4A)	**15 O**	-0.566799	-0.461357	-0.337753	0.105442	**0.123604**	**0.018162**
	18 O	-0.490593	-0.439646	-0.413115	**0.050947**	0.026531	**-0.024416**
(C4P)	**15 O**	-0.565509	-0.461676	-0.3398	0.103833	**0.121876**	**0.018043**
	13 C	0.499552	0.575418	0.60804	**0.075866**	0.032622	**-0.043244**
(C4B)	**15 O**	-0.534995	-0.460008	-0.355903	0.074987	**0.104105**	**0.029118**
	18 O	-0.521452	-0.454935	-0.437227	**0.066517**	0.017708	**-0.048809**
(C4MB)	**15 O**	-0.525484	-0.462668	-0.36192	0.062816	**0.100748**	**0.037932**
	17 C	0.500091	0.604925	0.617966	**0.104834**	0.013041	**-0.091793**
(C4CB)	**15 O**	-0.514897	-0.460763	-0.358573	0.054134	**0.10219**	**0.048056**
	17 C	0.495827	0.609285	0.620919	**0.113458**	0.011634	**-0.101824**
(C4FB)	**15 O**	-0.522539	-0.461223	-0.355499	0.061316	**0.105724**	**0.044408**
	17 C	0.498488	0.608287	0.620126	**0.109799**	0.011839	**-0.09796**
(C4NB)	**15 O**	-0.487154	-0.45778	-0.346538	0.029374	**0.111242**	**0.081868**
	31 O	-0.528879	-0.397763	-0.344797	**0.131116**	0.052966	**-0.07815**
(C4DNB)	**15 O**	-0.477465	-0.454699	-0.338156	0.022766	**0.116543**	**0.093777**
	29 O	-0.49406	-0.373625	-0.343255	**0.120435**	0.03037	**-0.090065**
(C4TB	**15 O**	-0.523649	-0.462873	-0.366306	0.060776	**0.096567**	**0.035791**
	17 C	0.499943	0.605605	0.618875	**0.105662**	0.01327	**-0.092392**

As a result, it appears that the reactivity of the inhibitors studied is highly dependent on carbon atoms. The probable nucleophilic attack sites are dominated by carbon atoms (O). These sites associated with

the LUMO orbital could receive electrons from the metal. Probable electrophilic attack sites are dominated by oxygen atoms (C). These sites are likely to donate electrons to the metal. The donor-acceptor properties of these molecules give them a good ability to protect copper against corrosion in nitric acid solution.

Conclusion

The analysis of the global reactivity parameters (E_{LUMO}-E_{HOMO}, η, σ, ΔN, ω,...) points to molecules C4A, C4P, C4B, C4MB, C4CB, C4FB, C4NB, C4DNB and C4TB with good reactivity for copper inhibition in nitric acid solution. These calculations predict that these molecules are capable of donating electrons to the metal, thereby reducing the dissolution of copper in the nitric acid solution.

These descriptor parameters indicate that their inhibition efficiency increases in the following order : coumarin-4-yl-acetate (C4A) < coumarin-4-ylpropionate (C4P) < coumarin-4-ylbenzoate(C4B) < coumarin-4-yl-4-methylbenzoate(C4MB) < coumarin-4-yl-4-chlorobenzoate(C4CB) < coumarin-4-yl-4-fluorobenzoate(C4FB) <coumarin-4-yl-4-tertbutylbenzoate(C4TB< coumarin-4-yl-4-nitrobenzoate (C4NB) < coumarin-4-yl-4-dinitrobenzoate (C4DNB)

The determination of the local parameters (f_k^+,f_k^- and $\Delta f_k(r)$) of the studied molecules permitted to specify the centre of electrophilic and nucleophilic attack.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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