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Theoretical Prediction of Some Antimalarial Molecules Behavior as Aluminium Inhibition Corrosion in Acidic Media

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Abstract Use of organic molecules to reduce metal degradation in acid solutions has become a widespread means of protection. With this in mind, the present study investigates the inhibition performance of five (05) organic antimalarial molecules, namely chloroquine, hydroxychloroquine, amodiaquine, primaquine and quinine, in protecting aluminum against corrosion. These performances were proven by Density Functional Theory (DFT) calculations. These DFT calculations were performed with B3LYP functional and in 6-31G (d, p) basis set. It was found that the inhibition activities of these compounds are based on electronic exchanges with aluminum. The sites at which the various electronic transactions are within the inhibitor have been identified from the reactivity on the basis of the reactivity parameters.

Keywords Organic antimalarial molecules, Inhibition performance, Density Functional Theory, Aluminium, Reactivity parameters

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1. Introduction

Computational insight into the inhibition potential of organic molecules in metal corrosion is now a reality. This technique has been popularized thanks to powerful computers and high-quality software (Gaussian, Gamess, Molpro, NWchem, etc.) which have enabled the development of numerical simulation and molecular modeling methods [1-2]. These methods, which permit to describe the anti-corrosive properties of molecules, are not only less costly, but also help guide researchers in the design of new, more appropriate molecules to combat the corrosion phenomenon. Metal corrosion is inevitable, but it can be reduced by the use of organic compounds. Corrosion is the deterioration of metals and alloys under atmospheric action or chemical agents. When metals and alloys are used in various sectors, they often come into contact with chemical products such as acid solutions. This contact causes the metal to lose electrons, transforming it into oxides. This transformation also leads to the loss of the metal physico-chemical properties, rendering it unusable.

The use of environmentally-friendly, less toxic organic compounds will help to reduce this corrosion phenomenon, while at the same time extending service life of metals in various sectors [3-4]. These organic compounds contain a non-polar, hydrophobic and relatively voluminous part made up mainly of carbon and hydrogen atoms, and a polar, hydrophilic part made up of one or more heteroatoms such as nitrogen, oxygen, phosphorus or sulfur. During inhibition, the polar part of the molecule binds to the metal surface, while the larger, non-polar part blocks the active surface. The active centers likely to exchange electrons with the metal are the heteroatoms. It has been shown that the inhibition efficiency varies inversely with the electronegativity of these atoms [5-8]. It increases in the following order: O<N<S<P.

It is in this context that the present study proposes to predict the behavior of five antimalarial compounds in inhibiting aluminum corrosion using density functional theory. This work will explain how these inhibitors react with this metal, preventing its degradation and creating a defensive layer on its surface to combat corrosive attack. As for the choice of metal, it was motivated by its massive use in several sectors.

2. Material and Methods

2.1. Molecules Structure

The chemical structures of the compounds studied are given in Figure 1.

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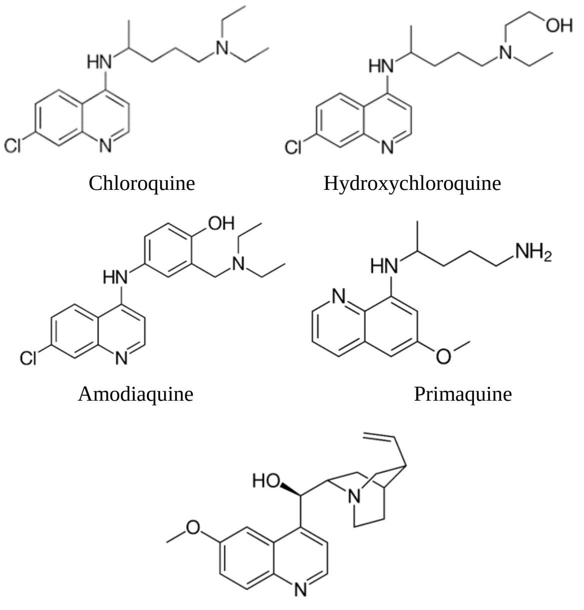


Chloroquine Hydroxychloroquine

Amodiaquine Primaquine

Quinine

Figure 1. The molecular structures of the investigated inhibitors

2.2. Quantum Chemical Computations

Full geometry optimization of the inhibitors were performed using DFT (density functional theory) with Beck's three - parameter exchange functional along with Lee-Yang-Parr non local correlation functional (B3LYP) with 6-31G (d,p) basic set [9-10], using the Gaussian 09 program package [11]. Energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), ΔE (HOMO − LUMO energy gap), dipole moment (μ), total energy (TE), electronegativity (χ), hardness (ή), the number of transferred electrons (ΔN), electron affinity ($A = -E_{LUMO}$) [12], ionization energy ($I = -E_{HOMO}$) [12] etc. are identified. Some parameters such electronegativity (χ), hardness (ɳ), softness (σ), affinity and electrophylicity index (ω) are related to ionization energy (I) and electron affinity (A). They are expressed from the following relationships [13-15]:

$$\chi = \frac{I+A}{2} \tag{1}$$

$$\eta = \frac{I-A}{2} \tag{2}$$

$$\sigma = \frac{1}{\eta} \tag{3}$$

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

Moreover, for a reaction of two systems with different electronegativities the electronic flow will occur from the molecule with the lower electronegativity (usually the organic inhibitor) towards that of higher value (usually the metallic surface), until the chemical potentials are equal [16]. Therefore, the fraction of electrons transferred (ΔN) was calculated according to Pearson electronegativity scale as follows [17].

$$\Delta N = \frac{\chi^{Al}-\chi^{inh}}{2(\eta_{Al}+\eta_{inh})} \tag{5}$$

Where χ^{Al} and χ^{inh} represent the absolute electronegativity of Al and the inhibitor molecule, respectively, η_{Al} and η_{inh} represent the absolute hardness of Al and the inhibitor molecule, respectively. By assuming that for a metallic bulk $I = A$; because they are softer than the neutral metallic atoms [18]; theoretical values for the electronegativity $\chi^{Al} = 4.28\, eV$ and $\eta_{Al} = 0$ the global hardness were hence used.

Net atomic charges have been obtained using the Natural Population Analysis (NPA) of Weinhold [19]. The population analysis has been performed on the neutral, cationic and anionic species at the same obtained optimized geometry of each inhibitor in order to determine their Fukui functions.

Molecules local selectivity parameters such as Fukui functions and dual descriptor responsible for nucleophilic and electrophilic attacks was also determined [20-24]. The following equations were used to determine these parameters [25]:

$$f_k^+ = [q_k(N+1) - q_k(N)] \tag{6}$$

$$f_k^- = [q_k(N) - q_k(N-1)] \tag{7}$$

$$f_k^0 = \frac{[q_k(N+1) - q_k(N-1)]}{2} \tag{8}$$

Where f_k^+, f_k^- and f_k^0 are respectively nucleophilic, electrophilic and radical Fukui functions, (N+1), (N) and (N−1) are the electronic population of atom k in (N+1), N and (N−1) electrons systems. The condensed form of dual descriptor is given in equation (13)

$$\Delta f_k(r) = f_k^+ - f_k^- \tag{9}$$

3. Results and Discussions

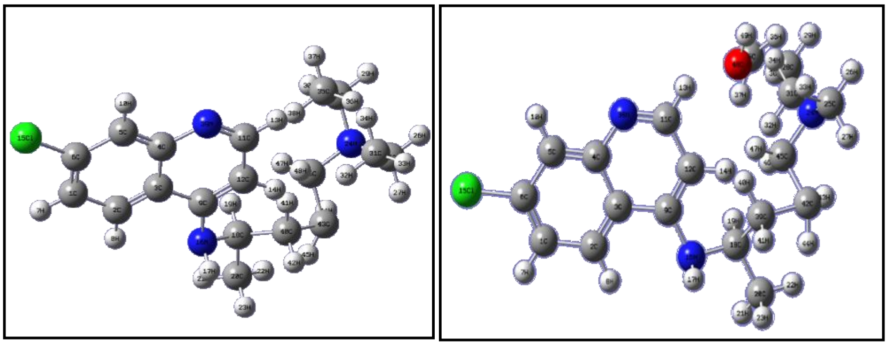
3.1. Molecular Geometric

The geometries of the five studied molecules are fully optimized at B3LYP/6-31G (d, p) level of theory in gaseous phase. The final geometries are given in Figures 2.

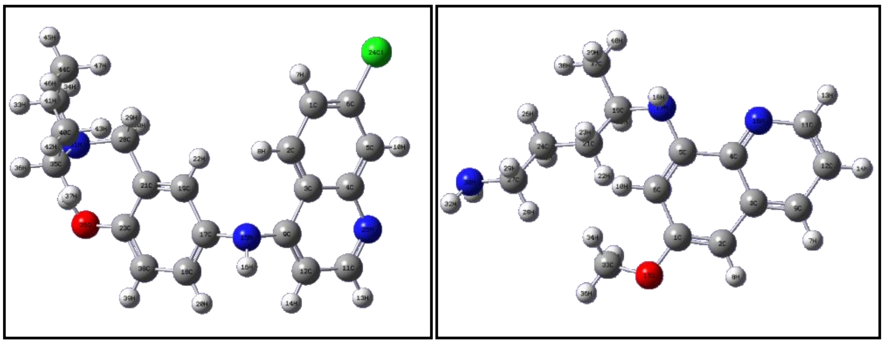
3.2. Global Reactivity and HOMO-LUMO Orbitals

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 [26].

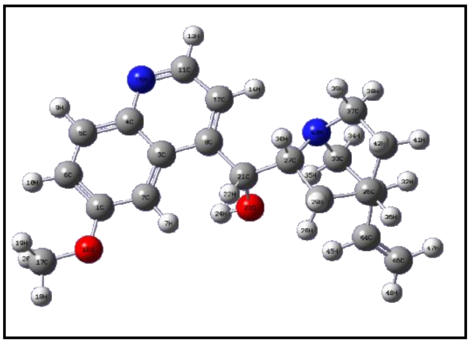
The corrosion inhibitor reactivity of anti-malaria derivatives is studied by quantum chemical calculation. The studied molecules are investigated quantum chemical parameter such as E_{HOMO}, E_{LUMO}, ΔE energy gap (HOMO-LUMO), electronegativity, chemical potential, chemical hardness, electrophilicity, nucleophilicity, global softness and proton affinity. These parameters are very important parameters which are compared the reactivity of studied molecules.



Chloroquine (CLQ) Hydroxychloroquine (HCQ)



Amodiaquine (ADQ) Primaquine (PRQ)



Quinine (QNN)

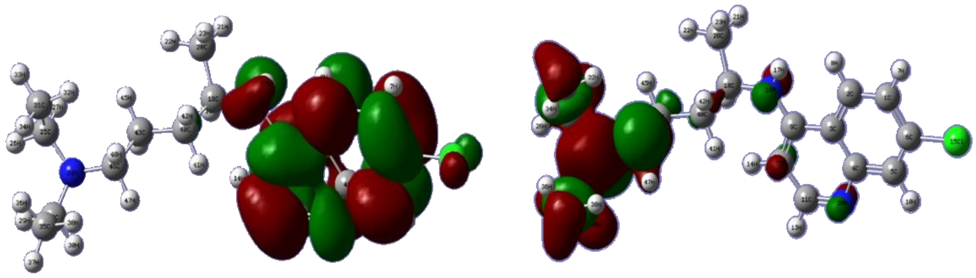
Figure 2. Optimized structure of CLQ, HCQ, ADQ, PRQ, and QNN with B3LYP/6-31G (d, p) method

Table 1. Molecules global reactivity parameters calculated using B3LYP/6-31G(d, p)

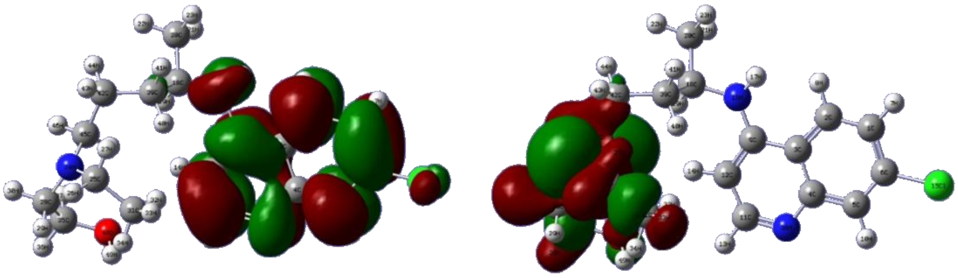
Parameters	**Chloroquine**	**Hchloroquine**	**Amodiaquine**	**Primaquine**	**Quinine**
E_{LUMO} (*eV*)	-1.167152	-1.09235	-1.488928	-0.962064	-1.392096
E_{HOMO} (*eV*)	-5.434016	-5.344256	-5.392400	-4.792096	-5.532752
Energy gap ΔE (*eV*)	4.266864	4.251904	3.903472	3.830032	4.140656
Dipole moment μ (D)	3.070200	5.056700	5.555600	2.268900	2.387800
Electron affinity A (eV)	1.167152	1.092352	1.488928	0.962064	1.392096
Ionization energy I (eV)	5.434016	5.344256	5.392400	4.792096	5.532752
Electronegativity χ (eV)	3.300584	3.218304	3.440664	2.877080	3.462424
Hardness η (eV)	2.133432	2.125952	1.951736	1.915016	2.070328
Softness σ $(eV)^{-1}$	0.468728	0.470378	0.512364	0.522189	0.483015
Fraction of electron transferred ΔN	0.229540	0.249699	0.215023	0.366295	0.197451
Electrophylicity index ω	2.209147	6.013827	7.906984	1.344090	1.376977
Total energy E_T (Ha)	-1325.439342	-1400.111560	-1474.791215	-823.465141	-1035.971348

As it is well known that the properties of chemical reactivity of studied molecules were compared by molecular orbitals of an inhibitor molecule that have got two molecular orbitals whose the name is Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

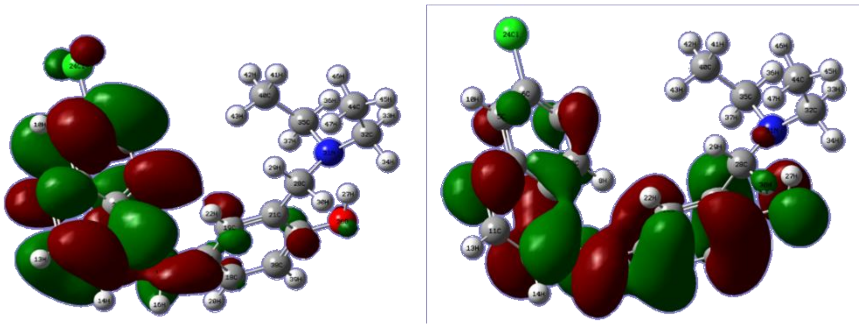
The energy level of HOMO has defined the electron donating ability of studied molecules. The molecule has got the high values of energy of HOMO that is showing the tendency to donate electrons of the molecule to appropriate that the acceptor molecules have low energy and empty molecular orbital [27-31]. From the light of the result given in the information, the energy level of LUMO of molecules is indicated electron accepting abilities of studied molecules. When the energy value of LUMO of inhibitor molecule is lower, this molecule has more electron accepting ability in lower energy of molecular orbitals. The calculated of HOMO and LUMO energy value is given in Table 1.



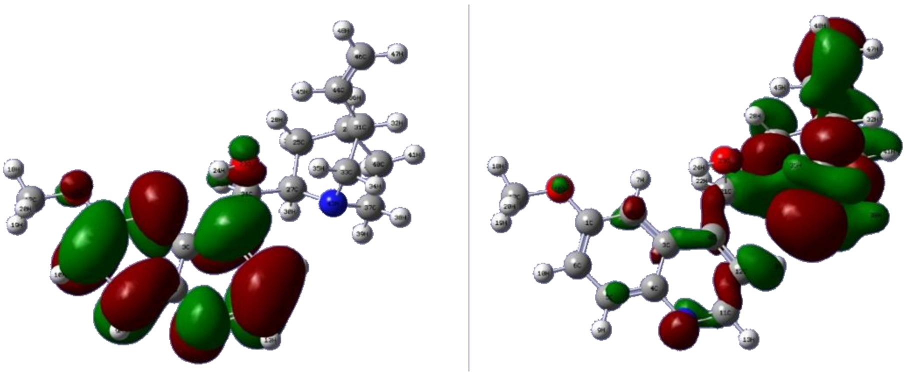
LUMO_CLQ HOMO_CLQ



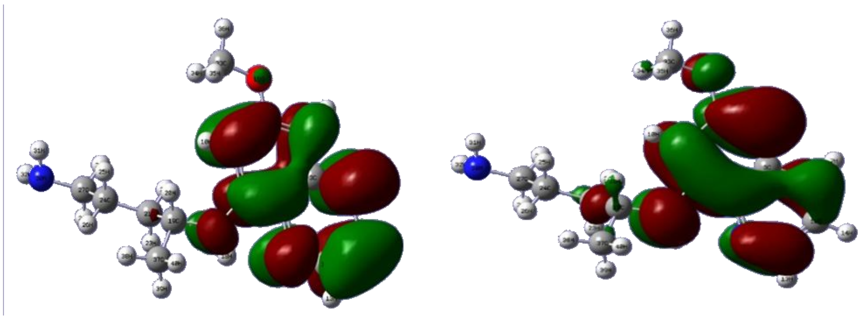
LUMO_ HCQ HOMO_HCQ



LUMO_ADQ HOMO_ADQ



LUMO_QN HOMO_QN



LUMO_PRQ HOMO_PRQ

Figure 3

The energy gap value (ΔE) in chemical reactivity of inhibitor molecule is a very important parameter in corrosion. As it is well known, that inhibitor molecule has a small energy gap value, this molecule is a good corrosion inhibitor. Since the energy gap value of inhibitor molecule is indicated that the binding ability of inhibitor molecules on metal surfaces [32]. On the basis of the calculated the energy gap value given in Table 1, the corrosion inhibition activity of malaria derivatives molecules can be written as: $PRQ < ADQ < QN < HCQ < CLQ$ in B3LYP method. Therefore, their higher reactivity can allowed them to be easily adsorbed onto the metal (Al) surface leading to increase their inhibitive efficiencies compared respectively.

The results also show that ADQ and QNN have the lowest E_{LUMO} compared to others molecules respectively which indicate a better capability of ADQ and QNN to accept electrons and since a good corrosion inhibitor should not only be a good electrons donor but also a good electron acceptor through the back donation mechanism. This result can lead to increase their adsorption on the metal surface and accordingly increases their inhibition efficiency.

Absolute hardness and softness are very important parameters to describe the molecular reactivity and stability.

The absolute hardness η exemplifies the resistance of a molecule to electron charge transfer. Given that the corrosion inhibition process always involves the transfer of electrons between the inhibitor and the metallic surface. Thereby, soft molecules of low hardness are more responsive to charge transfer. Soft molecules are more reactive than hard ones because they can easily offer electrons. Hence, inhibitors with the highest values of global softness (the least values of the global hardness) are expected to be good corrosion inhibitors for bulk metals in acidic media.

The calculations from table 1 indicate that PRQ (0.522189) and ADQ (0.512364) have the highest softness (σ) values compared to QNN (0.483015), HCQ (0.470378) and CLQ (0.468728), respectively. This result was consistent with the general belief that hard molecules should have large ΔE and a soft molecule should have small ΔE [32].

As for the dipole moment, there is an inconsistent in the literature on the correlation between the dipole moment and inhibition efficiency [33,34]. However, it is generally agreed that the adsorption of compounds possessing high dipole moments on the metal surface should lead to better inhibition efficiency [35]. Indeed, the results indicate that ADQ and HCQ have the highest values of μ compared to CLQ, QNN and PRQ, respectively.

The fraction of electrons transferred describes the trend of electrons donation within a set of inhibitors. Indeed, the fraction of electron transferred ΔN presents the particularity of considering both the metal and the inhibitor (in terms of χ and η) to determine the direction and intensity of the electrons' flow. The positive values of ΔN for both inhibitors indicate that the flow of electrons takes place probably from the inhibitors towards the metal. Also, it is generally assumed that if ΔN<3.6 the inhibition efficiency is found to amplify as the values of ΔN increase [36].

According to Lukovits's study [37], if ΔN < 3.6 then the inhibition efficiency increased with increasing electron-donating ability at the metal surface. The obtained values of ΔN reported in Table 1 are all below 3.6 and PRQ and HCQ have higher values of ΔN than ADQ, CLQ and QNN respectively. This result implies good disposition of PRQ and HCQ molecules to donate their electrons leading to increase their adsorption on the metal surface and to increase their inhibition efficiencies.

3.3. Local Molecular Reactivity

Besides the global reactivity indicators, the analysis of atoms selectivity within inhibitors is very useful in indicating the reactive sites towards electrophilic and nucleophilic attacks. In the case of an electron-transfer for reaction control, the selectivity descriptors of choice are the condensed Fukui functions on atoms the dual descriptor [38]. These functions help to distinguish each part of the molecule according to its behaviour due to the different functional groups. Thus, the site for nucleophilic attack will be the site where f_k^+ value is maximum and $\Delta f_k(r)$ is positive whereas the site for electrophilic attack will be the site where f_k^- is maximum and $\Delta f_k(r)$ is negative.

It has been reported in the literature that the dual descriptor is more accurate local reactivity descriptor than Fukui function [38]. Although, the Fukui function has the capability of revealing nucleophilic and electrophilic regions in a molecule, the dual descriptor is able to unambiguously expose truly nucleophilic and electrophilic regions. Moreover, dual descriptor is less affected by the lack of relaxation terms than the Fukui function [39]. Local parameters calculated through

Fukui functions and dual descriptor for different molecules are listed in the tables 1, 2, 3, 4, and 5 below. These sites constitute electronic exchange center where the molecule can lose or gain electrons. From the light of the result given in table 2, 3, 4, 5 and 6, we can summarize the various probable attack sites for each compound studied in Table 7.

Table 2. Mulliken atomic charges, Fukui functions and dual descriptor of Chloroquine (**CLQ**)

Atoms	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	$\Delta f_k(r)$
13H	0.135080	0.123312	0.007366	0.011768	0.115946	-0.104178
14H	0.116236	-0.007280	0.007555	0.123516	-0.014835	0.138351
15Cl	0.050335	-0.005693	-0.146598	0.056028	**0.140905**	**-0.084877**
16N	-0.562102	-0.568310	-0.615072	0.006208	0.046762	-0.040554
17H	0.279426	0.257001	0.223388	0.022425	0.033613	-0.011188
18C	0.036949	0.022871	0.088938	0.014078	-0.066067	0.080145
19H	0.132546	0.125859	0.088968	0.006687	0.036891	-0.030204
20C	-0.341233	-0.336954	-0.326311	-0.004279	-0.010643	0.006364
21H	0.146003	0.128869	0.110263	0.017134	0.018606	-0.001472
39N	-0.473653	-0.502178	-0.585555	0.028525	0.083377	-0.054852
40C	-0.178554	-0.190362	-0.162696	0.011808	-0.027666	0.039474
41H	0.114115	0.188749	0.117139	-0.074634	0.071610	-0.146244
42H	0.111563	0.106218	0.069103	0.005345	0.037115	-0.031770
43C	-0.206032	-0.427480	-0.186039	**0.221448**	-0.241441	**0.462889**
44H	0.125826	0.213228	0.095697	-0.087402	0.117531	-0.204933
45H	0.122537	0.165360	0.081992	-0.042823	0.083368	-0.126191
46C	-0.049489	-0.001969	-0.024346	-0.047520	0.022377	-0.069897
47H	0.126273	0.111821	0.096776	0.014452	0.015045	-0.000593
48H	0.13197	-0.014715	0.069109	0.146685	-0.083824	0.230509

Table 3. Mulliken atomic charges, Fukui functions and dual descriptor of Hydroxychloroquine **(HCQ)**

Atoms	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	$\Delta f_k(r)$
1C	-0.078019	0.000000	-0.097063	-0.078019	0.097063	-0.175082
2C	-0.162058	0.000000	-0.185771	-0.162058	0.185771	-0.347829
3C	0.097876	0.000000	0.095689	0.097876	-0.095689	0.193565
4C	0.248027	-0.000001	0.252532	**0.248028**	-0.252533	**0.500561**
5C	-0.097096	0.000000	-0.127037	-0.097096	0.127037	-0.224133
6C	-0.092618	0.000000	-0.100906	-0.092618	0.100906	-0.193524
7H	0.135952	0.000000	0.074310	0.135952	-0.074310	0.210262
13H	0.144444	0.000991	0.149569	0.143453	-0.148578	0.292031
14H	-0.048901	-0.000664	0.008787	-0.048237	-0.009451	-0.038786
15Cl	0.037860	0.000000	-0.072168	0.037860	0.072168	-0.034308
16N	-0.546861	0.000000	-0.576584	-0.546861	**0.576584**	**-1.123445**
17H	0.275195	0.000000	0.234061	0.275195	-0.234061	0.509256
18C	0.009472	0.000000	0.038914	0.009472	-0.038914	0.048386
19H	0.141420	0.000000	0.117337	0.141420	-0.117337	0.258757

Table 4. Mulliken atomic charges, Fukui functions and dual descriptor of Amodiaquine **(ADQ)**

Atoms	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	$\Delta f_k(r)$
9C	0.201930	0.218008	0.134904	-0.016078	0.083104	-0.099182
10H	0.135104	0.127562	0.062031	0.007542	0.065531	-0.057989
11C	0.122418	0.112861	0.019298	0.009557	**0.093563**	**-0.084006**
12C	-0.149329	-0.161388	-0.195256	0.012059	0.033868	-0.021809
13H	0.149478	0.137269	0.065482	0.012209	0.071787	-0.059578
14H	0.127794	0.112477	0.050320	0.015317	0.062157	-0.046840

Atoms	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	$\Delta f_k(r)$
22H	0.146224	0.101188	0.095189	0.045036	0.005999	0.039037
23C	0.352250	0.305198	0.297898	0.047052	0.007300	0.039752
24Cl	-0.008254	-0.017896	-0.089837	0.009642	0.071941	-0.062299
25N	-0.513874	-0.527141	-0.605529	0.013267	0.078388	-0.065121
26O	-0.508808	-0.620704	-0.626259	**0.111896**	0.005555	**0.106341**
27H	0.380364	0.346980	0.344507	0.033384	0.002473	0.030911
28C	-0.067565	-0.062711	-0.062738	-0.004854	0.000027	-0.004881
29H	0.144629	0.111564	0.109082	0.033065	0.002482	0.030583
30H	0.179423	0.138419	0.134364	0.041004	0.004055	0.036949
31N	-0.482785	-0.488711	-0.487724	0.005926	-0.000987	0.006913
32C	-0.054390	-0.043313	-0.042698	-0.011077	-0.000615	-0.010462

Table 5. Mulliken atomic charges, Fukui functions and dual descriptor of Primaquine **(PRQ)**

Atoms	$q_k(N+1)$	$q_k(N)$	f_k^+	f_k^-	$q_k(N-1)$	$\Delta f_k(r)$
1C	0.377366	0.349947	0.322342	0.027419	0.027605	-0.000186
2C	-0.110033	-0.183902	-0.233749	0.073869	0.049847	0.024022
11C	0.097789	0.067021	0.043841	0.030768	0.023180	0.007588
12C	-0.081776	-0.093099	-0.106521	0.011323	0.013422	-0.002099
13H	0.163081	0.107882	0.030851	0.055199	0.077031	-0.021832
14H	0.147706	0.091185	0.009312	0.056521	0.081873	-0.025352
15O	-0.480949	-0.536283	-0.562431	0.055334	0.026148	0.029186
16N	-0.509518	-0.535143	-0.612500	0.025625	**0.077357**	**-0.051732**
17N	-0.481616	-0.540865	-0.549134	**0.059249**	0.008269	**0.050980**
18H	0.292304	0.249582	0.217625	0.042722	0.031957	0.010765
19C	-0.000372	0.036459	0.061980	-0.036831	-0.025521	-0.011310
20H	0.137125	0.105478	0.085955	0.031647	0.019523	0.012124
21C	-0.191191	-0.175863	-0.159341	-0.015328	-0.016522	0.001194

Table 6. Mulliken atomic charges. Fukui functions and dual descriptor of Quinine **(QNN)**

Atoms	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	$\Delta f_k(r)$
11C	0.123788	0.109342	0.070473	0.014446	0.038869	-0.024423
12C	-0.169827	-0.165594	-0.189902	-0.004233	0.024308	-0.028541
13H	0.146713	0.114188	0.048140	0.032525	0.066048	-0.033523
14H	0.111331	0.107629	0.056025	0.003702	0.051604	-0.047902
15N	-0.457107	-0.493184	-0.557452	0.036077	**0.064268**	**-0.028191**
16O	-0.524177	-0.531848	-0.548644	0.007671	0.016796	-0.009125
17C	-0.097126	-0.083181	-0.061528	-0.013945	-0.021653	0.007708
18H	0.144889	0.122920	0.085063	0.021969	0.037857	-0.015888
19H	0.131911	0.121433	0.104452	0.010478	0.016981	-0.006503
20H	0.127743	0.116054	0.101326	0.011689	0.014728	-0.003039
21C	-0.006325	0.023703	0.022648	-0.030028	0.001055	-0.031083
22H	0.204077	0.142173	0.105529	0.061904	0.036644	0.025260
23O	-0.448653	-0.463757	-0.475273	0.015104	0.011516	0.003588
24H	0.363034	0.335420	0.325655	0.027614	0.009765	0.017849
25C	-0.247394	-0.218428	-0.216499	-0.028966	-0.001929	-0.027037
26C	-0.080322	-0.047617	-0.039818	-0.032705	-0.007799	-0.024906
27C	0.029064	-0.094243	-0.079337	**0.123307**	-0.014906	**0.138213**
28H	0.190557	0.128535	0.082512	0.062022	0.046023	0.015999
29H	0.253193	0.171400	0.149244	0.081793	0.022156	0.059637
30H	0.194623	0.126151	0.078870	0.068472	0.047281	0.021191
31C	-0.117921	-0.106888	-0.095952	-0.011033	-0.010936	-0.000097

Table 7. Mulliken atomic charges. Fukui functions and dual descriptor reactivity sites for the compounds studied

Compounds	Atoms	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	$\Delta f_k(r)$
ADQ	**11C**	0.122418	0.112861	0.019298	0.009557	**0.093563**	**-0.084006**
	26O	-0.508808	-0.620704	-0.626259	**0.111896**	0.005555	**0.106341**
CLQ	**15Cl**	0.050335	-0.005693	-0.146598	0.056028	**0.140905**	**-0.084877**
	43C	-0.206032	-0.427480	-0.186039	**0.221448**	-0.241441	**0.462889**
HCQ	**4C**	0.248027	-0.000001	0.252532	**0.248028**	-0.252533	**0.500561**
	16N	-0.546861	0.000000	-0.576584	-0.546861	**0.576584**	**-1.123445**
PRQ	**16N**	-0.509518	-0.535143	-0.612500	0.025625	**0.077357**	**-0.051732**
	17N	-0.481616	-0.540865	-0.549134	**0.059249**	0.008269	**0.050980**
QN	**15N**	-0.457107	-0.493184	-0.557452	0.036077	**0.064268**	**-0.028191**
	27C	0.029064	-0.094243	-0.079337	**0.123307**	-0.014906	**0.138213**

Table 8. Different reactivity sites for the compounds studied

Compounds	Nucleophilic attack site	Electrophilic attack site
Chloroquine (CLQ)	**26C**	**15Cl**
Hydrochloroquine (HCQ)	**4C**	**16N**
Amodiaquine (ADQ)	**26O**	**11C**
Primaquine (PRQ)	**17N**	**16N**
Quinine (QNN)	**27C**	**15N**

Analysis of the table shows that the reactivity sites are generally located on carbon atoms (C) and heteroatoms (N,O). These data reveal that the various electronic transactions are based on these atoms. It turns out that carbon atoms (C) are more prone to nucleophilic attack. This justifies the fact that the electron gain of inhibitors occurs on carbon atoms. While the molecule loses electrons through the likely sites of electrophilic attack, which are usually nitrogen (N) atoms.

4. Conclusions

The quantum chemistry study, using Density Functional Theory (DFT) method, on five antimalarial molecules also chloroquine (CLQ), hydroxychloroquine (HCQ), amodiaquine (ADQ), primaquine (PRQ) and quinine (QNN) has shown that they could have excellent inhibition properties of corrosion in acid media.

They have the ability to give or receive electrons from the unfilled orbitals of aluminium showing their capacity to form covalent bonds.

Furthermore, Primaquine would have the best inhibition performance due to the heteroatoms disposition and its large molecular surface area. This is confirmed on the one hand by the low value of energy gap and hardness, and on the other hand by the higher value of softness and the fraction of electron transferred. The presence of free electron pairs on the heteroatoms or π electrons can strongly contribute to the adsorption process on metal surface. From the local reactivity indices, it was found that the nucleophilic attack sites for CLQ, HCQ, ADQ, PRQ and QNN are C(26), C(14), O(26), N(17) and C(27) respectively, while the electrophilic attack sites are denoted by Cl(15), N(16), C(11), N(16) and N(15). Finally, these compounds may be good inhibitors of metal corrosion.

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