*Int. J. Electrochem. Sci.*, 7 **(2012)** 5643 - 5676

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

# Quantum Chemical Investigations on Quinoline Derivatives as Effective Corrosion Inhibitors for Mild Steel in Acidic Medium

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*Received:* 1 April 2012 / *Accepted:* 3 May 2012 / *Published:* 1 June 2012

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The Density Functional Theory (DFT) and *ab initio* (HF and MP2) calculations were performed on the quinoline molecule (QL) and its derivatives, namely quinaldine (QLD) and quinaldic acid (QLDA) to investigate their possible role as corrosion inhibitors for mild steel in acidic medium. Calculations were done for non-protonated and protonated forms *in vacuo* and in water. Some quantum chemical parameters were calculated and discussed in order to provide insight into the reactivity and selectivity of the molecules. The performance of the different calculation methods were also compared with available experimental data. The results show that DFT/B3LYP basis set is adequate in describing the geometry and quantum chemical parameters of the studied systems. Both experimental and theoretical results established that QLDA has the highest inhibition efficiency. A comparison in the trends of the quantum chemical parameters in water solution and *in vacuo* shows minimal influence of the solvent effects.

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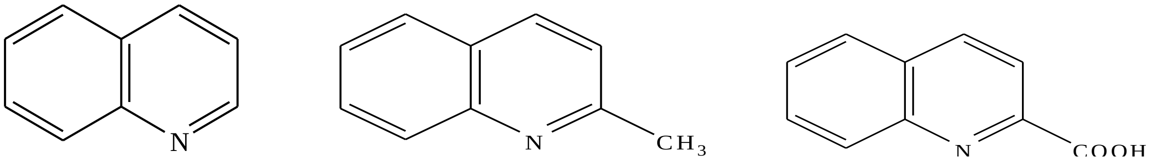
**Keywords:** Reactivity descriptors, DFT, *ab initio*, solute-solvent, quinoline, quinaldine, quinaldic acid.

## 1. INTRODUCTION

Mild steel is widely used in many industrial applications such as storage and transportation of various chemical solutions. However, some substances that are stored or transported in pipes or other materials made out of mild steel have corrosive properties and in most cases lead to the dissolution of the metal, resulting in great economic and financial losses for various industries. The dissolution of mild steel is a result of its direct contact with the corrosive substances (e.g., acidic solutions that are widely used in industries for various applications such as pickling, acid cleaning, oil well acidizing, etc. [1]). Several approaches, including anodic and cathodic protection, lubrication, painting and electroplating, have been proposed to protect the metal from corrosion. Another important method is the use of corrosion inhibitors [2]. Corrosion inhibitors are substances that adsorb (both physically and chemically) at the metal-solution interface and in the process block or reduce the contact surface between the metal and the corrosive materials. In order to achieve its objectives, a corrosion inhibitor molecule should have specific properties that allow it to adsorb at the metal-solution interface [2]. Such properties are encoded in the molecular structure of the inhibitor e.g. electron density and the geometry of the molecule. Molecules that have high electron density have a greater tendency to donate electrons to species that are electron deficient and in the case of metal, the donated electrons could be accepted into the partially filled or vacant d orbitals resulting in the formation of a coordination bond (i.e., chemical adsorption) between the metal and the inhibitor. Therefore, molecules containing atoms with lone pair of electrons (e.g., N, O, S and P heteroatoms), $\pi$-electrons in triple or conjugated bonds, aromatic systems, etc are highly utilised as corrosion inhibitors because they have a high electron density at those specific centres [3]. The geometry of an inhibitor also has an important influence in determining its adsorbability at the metal-solution interface. Molecules that are planar have a greater tendency to adsorb at the metal surface than molecule that have less planar geometry [4–6]. Therefore, understanding the nature of the molecule provides useful information on its applicability as corrosion inhibitor. Although the focus of the current work is on the nature of the inhibitor, we hasten to remind that there are several inter-dependent factors, beside the nature of the inhibitor, which influence the adsorption of the inhibitor on the metal surface (e.g., the nature of the metal, the environment and the electrochemical potential at the metal-solution interface). Hence, to understand the adsorption of inhibitor at the metal-solution interface, it is necessary to have an insight into the effect of all the factors as much as possible.

In the search for effective corrosion inhibitors in a given class of compounds, having a similar central moiety and differing only in the substituent’s, it is important to identify the main characterising features that distinguish a particular compound as a likely effective inhibitor from the rest of the other compounds. Such studies are usually done using both experimental and quantum chemical approaches. Quantum chemical calculations have become an effective tool in the analysis and elucidation of many experimental observations. Moreover, its use in corrosion science as a tool to explain experimental results is growing, as is noted by the increasing number of published articles that are increasingly reporting both experimental and quantum chemical results. In the current work, quantum chemical methods are utilised to study a group of quinoline derivative in order to investigate their possible role as effective corrosion inhibitors.

Quinoline derivatives in general are known to have a variety of pharmacological and biological activities, such as immunodepresant activity [7], antimalarial activity [8] and antitubecular activity [9]. A few reports have been presented in literature on the use of quinoline and some of its derivatives as corrosion inhibitors in different media [10–15].The present work reports the results of quantum chemical calculations on quinoline (QL) and two of its derivatives namely quinalidine (QLD) and quinaldic acid (QLDA) in order to understand their possible role as corrosion inhibitors of mild steel in hydrochloric acid. Their molecular structures are shown in figure 1 below.



QL QLD QLDA

**Figure 1.** The molecular structures of the studied quinoline compounds.

These compounds have a pyridine ring (i.e., an aromatic ring containing an N atom) and a benzene ring fused together. In our previous work on these structures (i.e., QL, QLD and QLDA), we reported experimental results on their corrosion inhibitory role in hydrochloric acid medium and concluded that the inhibition efficiency follows the order QLDA > QLD > QL [16]. In the current work, the quantum chemical results on these compounds are discussed and compared with the experimental results in order to obtain a better understanding of the molecular features that distinguishes one compound from the others as a better corrosion inhibitor and to provide supportive explanations for the observed experimental trends. Moreover, any differences in the results of the quantum chemical calculations and experimental results are highlighted and discussed.

## 2. COMPUTATIONAL DETAILS

Different quantum molecular properties may be described better by different computational methods, depending on the sophistication of the computational approaches. In view of this, three different computational methods, viz., Density Functional Theory (DFT), Hartree Fock (HF) and second order Møller–Plesset perturbation theory method (MP2) were selected for the study of the compounds used as corrosion inhibitors. Although HF does not take into account correlation and dispersion effects, it provided useful results for comparison with other methods, Moreover, for cases where HF provided results that are closer to those of sophisticated methods; further study at HF level was done because it is less computationally expensive. DFT takes into account a part of correlation and it has been reported to provide fairly good results for the description of various molecular properties such as the energy of the Highest Occupied Molecular Orbital (HOMO), the energy of the Lowest Unoccupied Molecular orbital (LUMO), electronegativity ($\chi$), ionization potential, etc., [17]. In the present study, DFT in combination with the B3LYP and the BP8 functionals were utilized in order to compare the effect of the different functionals on the calculated molecular properties for the systems under study. DFT/B3LYP has been widely used in the description of the inhibitor metal surface mechanism and is also recommended for the study of chemical reactivity and selectivity of molecules [18, 19].

MP2 takes into account both correlation effects and dispersion effects and its use in the current study provided good description of molecular properties for which such effects might be predominant. In this way, the selected methods give wide possibilities for obtaining reasonable estimations of trends in the molecular properties of the studied molecules. The basis set selected for a particular molecular calculation provided an idea of the sophistication of the model chemistry (i.e., method plus basis set) utilised for a particular study. The selection of model chemistry on the other hand is strongly dependent on the size of the system to be studied, type of calculations to be carried out and available computational facilities. It is therefore essential to select a model chemistry that does not compromise the meaningful-ness of the results and at the same time it is not too computationally demanding for the available facilities. Since the current study is done both *in vacuo* and in water solution, four basis sets were selected and considered adequate enough to take into account necessary features of the desired molecular properties. Calculations at HF level were done using the 6-31G(d,p) basis set; calculations at MP2 level were done by using both 3-21G and 6-31G (d,p) basis sets; calculations at DFT/B3LYP were done using the 6-31G(d,p) and 6-31++G(d,p) basis sets and calculations at DFT/BP8 were done by using the CEP-31G basis set.

Molecular properties, related to the reactivity and selectivity of the compounds, were estimated following the Koopmans's theorem relating the energy of the HOMO and the LUMO [20]. Electronegativity is estimated using the following the equation:

$$\chi \cong -\tfrac{1}{2}\,(E_{HOMO} + E_{LUMO}) \tag{1}$$

Chemical hardness (η) measures the resistance of an atom to a charge transfer [21], it is estimated by using the equation:

$$\eta \cong -\tfrac{1}{2}\,(E_{HOMO} - E_{LUMO}) \tag{2}$$

Global electrophilicity index (ω) is estimated by using the electronegativity and chemical hardness parameters through the equation:

$$\omega = \frac{\chi^2}{2\eta} \tag{3}$$

A high value of electrophilicity describes a good electrophile while a small value of electrophilicity describes a good nucleophile.

Electron polarizability, also called chemical softness (σ), describes the capacity of an atom or group of atoms to receive electrons [21] and is estimated by using the equation:

$$\sigma = 1/\eta \cong -2/(E_{HOMO} - E_{LUMO}) \tag{4}$$

Electron affinity (A) is related to $E_{LUMO}$ through the equation:

$$A \cong - E_{LUMO} \tag{5}$$

Ionization potential (I) is related to the $E_{HOMO}$ through the equation:

$$I \cong - E_{HOMO} \tag{6}$$

The maximum number of electrons transferred ($\Delta N_{max}$) in a chemical reaction is given by the equation;

$$\Delta N_{max} = \frac{\chi}{2\eta} \tag{7}$$

and on using the I and A terms can be written as

$$\Delta N_{max} = \frac{(I + A)}{2(I - A)} \tag{8}$$

The study in solution considers the bulk solvent effects and are estimated with the polarisable continuum model (PCM) with its default settings as described in [22] and as implemented in the Gaussian03 package [23]. The inhibition efficiencies of the quinoline derivatives were obtained experimentally using the weight loss method [16].

## 3. RESULTS AND DISCUSSIONS

The calculated quantum chemical descriptors provide trends in the reactivity and selectivity features of the studied compounds. Calculations were done *in vacuo* and in water solution and by considering both the protonated and the non-protonated species. The results of the calculations in solution provide information that would be more realistic, considering that electrochemical processes are mostly done in solution.

The results show that QLDA is the most preferred compound as corrosion inhibitor with the order of inhibition efficiency being QLDA > QL > QLD. A comparison of the protonated and the non-protonated species show that there are some significant quantum chemical parameter differences between the protonated and the non-protonated species as a result of difference in electron density distribution between the protonated and the non-protonated species. The results in solution, however, are similar to the results *in vacuo,* both for the protonated and the non-protonated species, probably due to the lack of significant molecular geometry changes. The difference in the trends between the theoretical results and experimental results are related to two competing factors; geometry planarity and electron density of the inhibitors, with the electron density factor appearing to be preferred as evidenced by experimental results.

### *3.1. Results of the calculations in vacuo for the non-protonated species*

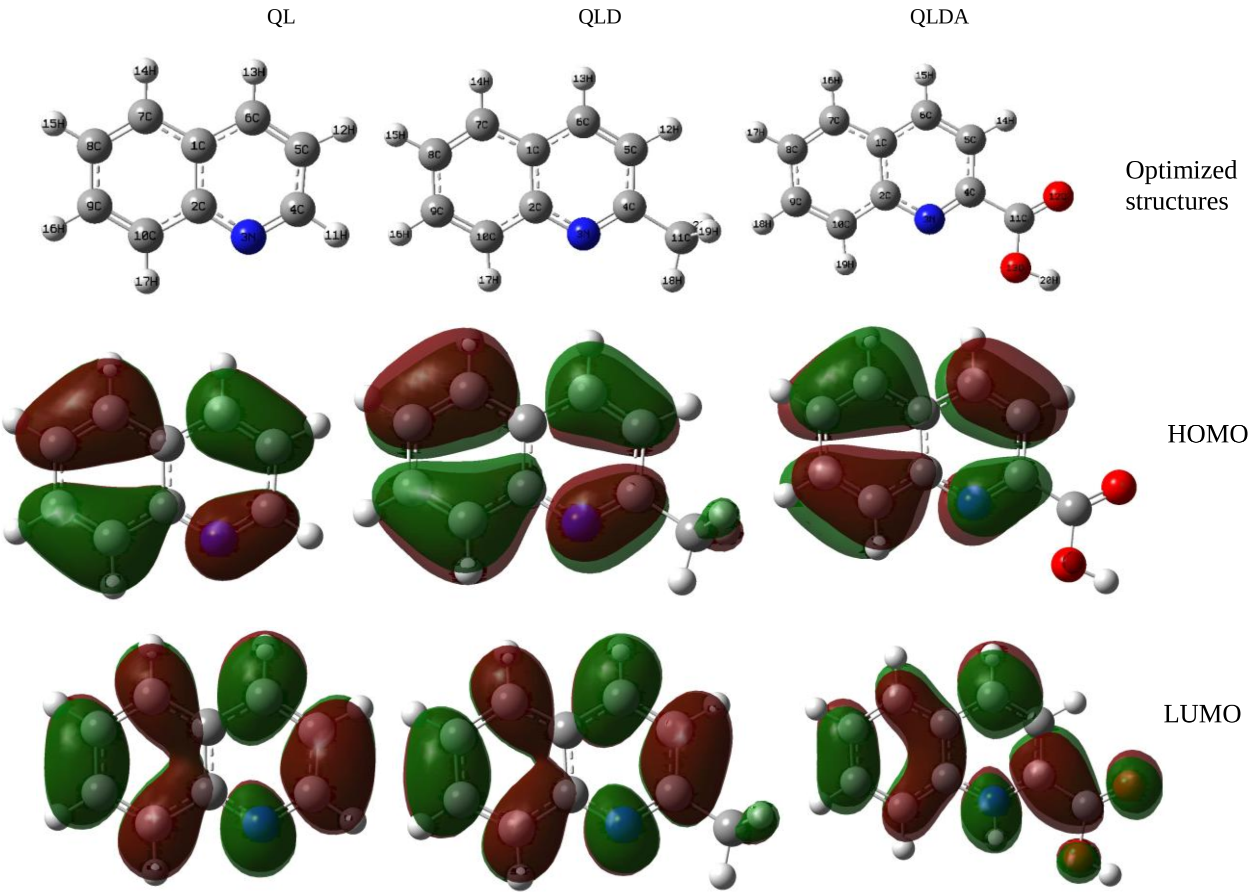


**Figure 2.** The optimized structures, HOMO and LUMO of the non-protonated inhibitor molecules (using B3LYP/6-31++G (d, p) results).

The optimised geometries of the non-protonated species are show in figure 2 above together with the atom numbering utilised throughout this work; the HOMO, the LUMO and the total electron density of each compound. Table 1 shows the bond length of the C–C and C–N for the studied systems. In the absence of experimental results on geometrical parameters of quinoline, the calculated bond lengths reported in Table 1 are compared with the experimental bond lengths of naphthalene reported in [24]. The results show that for the C1–C2, C4–C5, C1–C6, C1–C7, C8–C9 and C2–C10 bond lengths, HF and DFT/B3LYP results are closer to experimental results than MP2, which appears to overestimate the length of the C–C bond. A comparison of the C5–C6, C7–C8 and C9–C10 bond lengths using different calculation methods and those for naphthalene show that HF underestimates the bond length, but both MP2 and DFT/BP86 overestimates the bond lengths, while DFT/B3LYP results are closer to the experimental results. In this way, DFT/B3LYP results provide the best estimate for the geometry of quinoline and its derivatives. Addition of diffuse orbital to DFT/B3LYP does not seem to have a significant influence on the length of the C−C bonds or C−N bond. Moreover, DFT/B3LYP results on geometry are in good agreement with the C−C and C−N bond lengths for quinoline obtained by using the force field refinement method reported in [25]. Based on these results any further discussion on the geometry of quinoline and its derivatives (e.g., the geometry of the protonated species and that of the non-protonated species) will be exclusively based on the DFT/B3LYP results.

The overall geometry of the molecule is better described by taking into account not only the bond lengths, but also the bond angles and torsion angles of the atoms of the molecule. A comparison of the geometries of the molecules shows that QL and QLDA are highly planar while, QLD is less planar because of off-plane orientation of the H atoms of the methyl group.

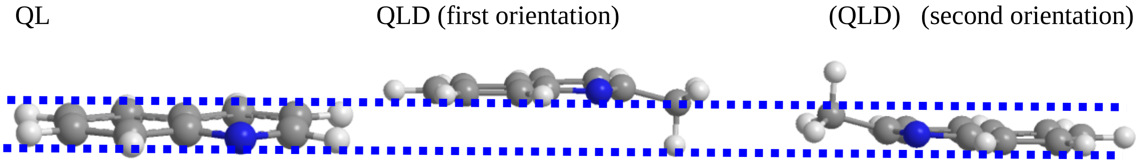


**Figure 3.** Planarity influencing factor in quinoline (QL) and quinaldine (QLD). The region between the dotted lines represents the surface of the metal.

Figure 3 shows the two orientations of the QLD molecule compared with the orientation of QL on the metal surface. Both orientations of QLD do not cover the surface of the metal desirably and therefore would not result in effective corrosion inhibition; the QL molecule, on the other hand, has maximum coverage of the surface of the metal and therefore would theoretically be a better corrosion inhibitor than QLD. Therefore, in terms of adsorbability on the metal surface, the trends, as predicted by the geometry of the molecules, would most probably be such that QLDA > QL > QLD.

Beside the geometries of the compounds, an analysis of other quantum chemical parameters provided valuable information on the reactivity and selectivity of quinoline and its derivatives. These pieces of information were valuable in selecting a suitable compound or compounds (among compounds of similar structural features) to use as corrosion inhibitor as they inform which molecule has greater tendency to donate electrons, receive electrons or bind more strongly to the metal surface. Quantum chemical parameters such as the energy of the Highest Occupied Molecular Orbital ($E_{HOMO}$) and the energy of the Lowest Unoccupied Molecular Orbital ($E_{LUMO}$), the $E_{HOMO} - E_{LUMO}$ energy difference ($\Delta E$) [$E_{HOMO} - E_{LUMO}$], the dipole moment (D), the charges on the atoms, the molecular volume (MV) and sum of the total negative charge (TNC) are often sighted among the most important quantities that provide information on the reactivity of the systems under consideration. Other quantities include the global hardness ($\eta$), global softness ($\sigma$), electronegativity ($\chi$), chemical potential ($\pi$) and fraction of transferred electrons (N). The various parameters are collectively reported in Table 2.

The HOMO and the LUMO for the studied molecules are shown in figure 2 together with the total electron density. In the quinoline molecule, the HOMO and the LUMO are delocalised throughout the system with the HOMO having the maximum amplitude coefficients on C7 and C10 atoms while the LUMO has the maximum amplitude coefficient on C6 and N3. The LUMO on these centres has an anti-bonding character; the total electron density shows that the negative charge (indicated in red colour) is strongly localised on the N atom while the rest of the molecule appears to have a neutral distribution of charges (green colour). The negative charge on the N atom is likely due to the electron cloud of the lone pair of electrons.

In the QLD, the HOMO and LUMO orbitals are also strongly distributed across the molecule, with the exception of the $CH_3$ group. As is the case in quinoline, the maximum amplitude of the HOMO coefficient is on C7 and C10 atoms while the maximum amplitude of the LUMO coefficients is on C6 and N3. The total electron density of QLD reveals that only the N atom has the highest negative charge density, which may also be related to the electron cloud of the lone pair of electron on the N atom. However, in comparison to the QL molecule, the total electron density of the QLD molecule shows significant distribution of negative charge in the rest of the ring (i.e., there is more yellow colour in the benzofused heterocyclic ring of QLD than in the benzofused heterocyclic ring of QL). This phenomenon is the result of the electron donating inductive effect of the $CH_3$ to the ring, resulting in the spread of the negative charge to some parts of the benzofused heterocyclic ring

In the quinaldic acid (QLDA), the HOMO is delocalised only on the two rings, with a strong maximum amplitude coefficient on C6 and C10. The LUMO is distributed not only on the rings but also on the C atom of the carbonyl group, and has its maximum amplitude on the C6 and N3 atoms. The total electron density of QLDA reveals that the negative charge is strongly delocalised in two regions namely in the region between the N atom and the $sp^3$ O of the carboxylic functional group and in the region ahead of the $sp^3$ O of the carbonyl functional group. This high negative charge density is also strongly related to the lone pair of electrons of the three heteroatoms (N, $sp^3$ O and $sp^2$ O atoms). The two regions would readily interact with electrophilic species resulting in the electron rich QLDA molecule providing electrons to the vacant orbitals of an incoming electron deficient species. The total electron density of QLDA also reveals that the H atom of the carboxylic functional group is strongly electron deficient (excess blue colour) and therefore it is most likely to be attacked by electron rich species. A comparison of the total electron densities for the three molecules shows that QLDA has the least electron density distributed in the benzofused heterocyclic ring. This phenomenon is a result of the electron withdrawing effect of the COOH group, which results in the deactivation of the rings.

Collectively, the electron density distribution for the three molecules is such that QLDA > QLD> QL, suggesting that QLDA would have the greatest tendency to adsorb on the metal-solution interface while QL would have the least tendency to adsorb onto the metal-solution interface.

The $E_{HOMO}$ informs of the tendency of a molecule to donate electrons to the electron deficient species. The higher the $E_{HOMO}$ value the greater the tendency to donate electrons. The $E_{HOMO}$ for the three compounds follow the order; QLD > QL > QLDA which implies that the molecule which has the highest tendency to donate electrons is QLD. The trend may be explained as follows: QLD has a high electron density than QL and therefore it is understandable that it would have a greater tendency to donate electrons than QL. QLDA on the other hand has the highest electron density because of the presence of O atoms that have lone pair of electrons. However, because O atoms are highly electronegative, the lone pairs of electrons on the O atoms are tightly held so that the tendency to donate electrons is minimal. The $E_{LUMO}$ informs of the tendency of a molecule to accept electrons from an electron rich species. The lower the $E_{LUMO}$ value the greater the tendency to accept electrons. The $E_{LUMO}$ for the three compounds follows the order; QLDA > QL > QLD which implies that QLDA has the greatest tendency to accept electrons. Three regions in the QLDA molecule are significantly electron deficient namely the benzene ring (due to the electron withdrawing effect of the carboxylic functional group), the C and H atoms of the carboxylic functional group (because of the great electronegativity difference with respect to the O atom attached to both C and H atoms of the carboxylic group). These high number of electron deficient centres make the QLDA molecule possess the highest tendency to accept electron. The ring in the QLD molecule is however electron rich because of the presence of the $CH_3$ group that donates electrons to the benzofused heterocyclic ring, therefore in relation to the parent compound QL, QLD has a less tendency to accept electrons. $\Delta E$ value informs of the reactivity of the molecular systems. Molecules with the lowest value of $\Delta E$ have the highest tendency to react. The trend for the $\Delta E$ values follows the order QLDA > QL > QLD which suggests that QLDA has the highest reactivity in comparison to the other compounds and would therefore likely interact strongly with the metal surface. Collectively, the results show that the trend in the $E_{HOMO}$, $E_{LUMO}$ and $\Delta E$ does not correlate with the trend in the observed inhibition efficiency. However, both the theoretical and experimental results agree that QLDA has the highest tendency to interact with the metal surface.

The dipole moment of the molecule gives information on the polarity of the given system. Molecules that have high dipole moment have a tendency to interact with other molecule through electrostatic interactions (e.g., dipole-dipole interactions). The dipole moment of a molecule is strongly determined by the shape of the molecule, size of the molecule and type of atoms constituting the molecule. The relationship between inhibition efficiencies and dipole moment of similar molecules have often given results that are not univocal, i.e., in some instances the dipole moment appears to increase with increasing inhibition efficiencies [26] while in other systems the dipole moment appears to decrease with increase in the inhibition efficiencies of the inhibitors [27]. The results of the dipole moment for the QL, QLD and QLDA are reported in Table 2. The dipole moment of QL has been earlier reported experimentally in literature [26]. A comparison of the experimentally determined dipole moment and the theoretical results obtained from this work show that *ab initio* HF method gives results that are much closer to experimental results; DFT underestimates the magnitude of the dipole moment while MP2 overestimates the magnitude of the dipole moment. Overall, the trend in the dipole moment follows the order; QLDA > QL > QLD, which is not in agreement with trends in the experimental inhibition efficiencies of the inhibitors earlier reported in literature[16].

A comparison of the sum of the total negative charge (TNC) across structures shows that it follows the order; QLDA > QLD > QL. This result is consistent with the analysis of the electron density that showed that the electron density is highest for QLDA and lowest for QL. The trend in the total negative charge is also in line with the trend in the experimentally obtained inhibition efficiencies of the inhibitors.

The partial charges on the individual atoms in a molecule also indicate the reactive centres for a particular inhibitor. Atoms with the highest negative charge are considered to have an electron donor role when interacting with metal surfaces. The Mulliken atomic charges for the heteroatoms of the quinoline derivatives are reported in table 1 and show that N3 has the highest negative charge with

MP2/3-21G, MP2/6-31G(d,p), HF/6-31G(d,p) and DFT/6-31G(d,p) methods. Moreover, the negative charge on the N atom increases across the structures following the order; QLDA < QL < QLD. This result is consistent with the fact that the electron withdrawing effect of the COOH group in QLDA decreases the negative charge on the N atom in the ring while the electron donating role of the $CH_3$ increases the negative charge on the N atom in QLD. The negative charge on the O atoms of QLDA shows that it is highest on the $sp^2$ O atom than on the $sp^3$ O atom, which suggests greater electron donor role of the $sp^2$ O than the $sp^3$ O atom. In view of the above results, QLDA has greater tendency to adsorb on the metal surface because it has three highly negative charged centres while QL is preferentially the molecule with the least negative charge.

The fraction of electron transferred follows the order; QLDA < QL < QLD. This is understandable considering that QLDA has the least number of electrons that are loosely bound (because the high electronegativity of O atoms causes the electron density to be tightly bound to the molecule) while QLD has the highest electron density (due to the electron donating effect of the $CH_3$ group).

The local selectivity descriptor of an inhibitor also indicates the centers in the molecule on which certain types of relativities are most likely to occur. These descriptors are often described in terms of the condensed Fukui functions. Fukui functions provide information related to the atoms in a molecule that have a higher tendency to either loose (i.e., a site that is susceptible to an electrophilic attack) or accept (i.e., a site that is susceptible to a nucleophilic attack) an electron or pair of electrons. In most cases, the Fukui functions for the electron rich centers (i.e., atoms susceptible to electrophilic attack) and electron deficient centers (i.e., atoms that are susceptible to nucleophilic attack) are calculated using the finite difference approximation approach as follows [28];

$$f^+ = q_{(N+1)} - q_N \tag{9}$$

$$f^- = q_N - q_{(N-1)} \tag{10}$$

where $q_{(N+1)}$, q and $q_{(N-1)}$ are the charges of the atoms on the systems with N+1, N and N−1 electrons respectively. The preferred site for nucleophilic attack is the atom (or region) in the molecule where $f^+$ has the highest value while the site for electrophilic attack is the atom (or region) in the molecule where the value of $f^-$ is the highest. The calculated values of the Fukui functions for the non-hydrogen atoms in the three studied molecules are reported in Table 3 and Table 4 for $f^-$ and $f^+$ respectively, for the non-protonated species. The preferred site for nucleophilic attack is the C6 atom for both QL and QLD while the preferred site for nucleophilic attack in QLDA is N3. The electrophilic attack (shown by the highest value of $f^-$) would preferably occur at the C7 and C10 atoms.

### *3.2. Results of the calculations in vacuo for the protonated species*

The inhibitor protects the metal surface by blocking or reducing its interaction in acidic medium. However, because of the presence of heteroatom with a number of lone pair of electrons, the interaction between the acidic medium and the inhibitor may result in the protonation of the inhibitor at the heteroatom centers. In such cases, it is interesting to investigate the characteristics of the corrosion inhibitor in the protonated form so as to compare it with the non-protonated form. Such a comparison provides information on the preferred form of the inhibitor to interact with the metal surface.

In the quinoline derivatives considered in this work, the N atom is the only heteroatom that is common to all the systems, therefore, for the purpose of comparison of trends across structures, it is meaningful to investigate only the protonation on the N atom. The charges on the heteroatoms and the bond distances for the protonated species are reported in Table 5. The results show that, in comparison to the results of the non-protonated species, the charge (*e*) on the N atom obtained using the MP2/3-21G, MP2/6-31G(d,p), HF/6-31G(d,p) and DFT/6-31G(d,p) methods is higher in the protonated form than in the non-protonated form; the charge (*e*) on the O atoms of QLDA decreases by 0.066 for DFT, 0.093 for HF and 0.100 for MP2 for sp$^2$ O atom and increases by 0.014 for DFT, 0.043 for HF and 0.05 for MP2 for the sp$^3$ O atom with respect to the non-protonated form.

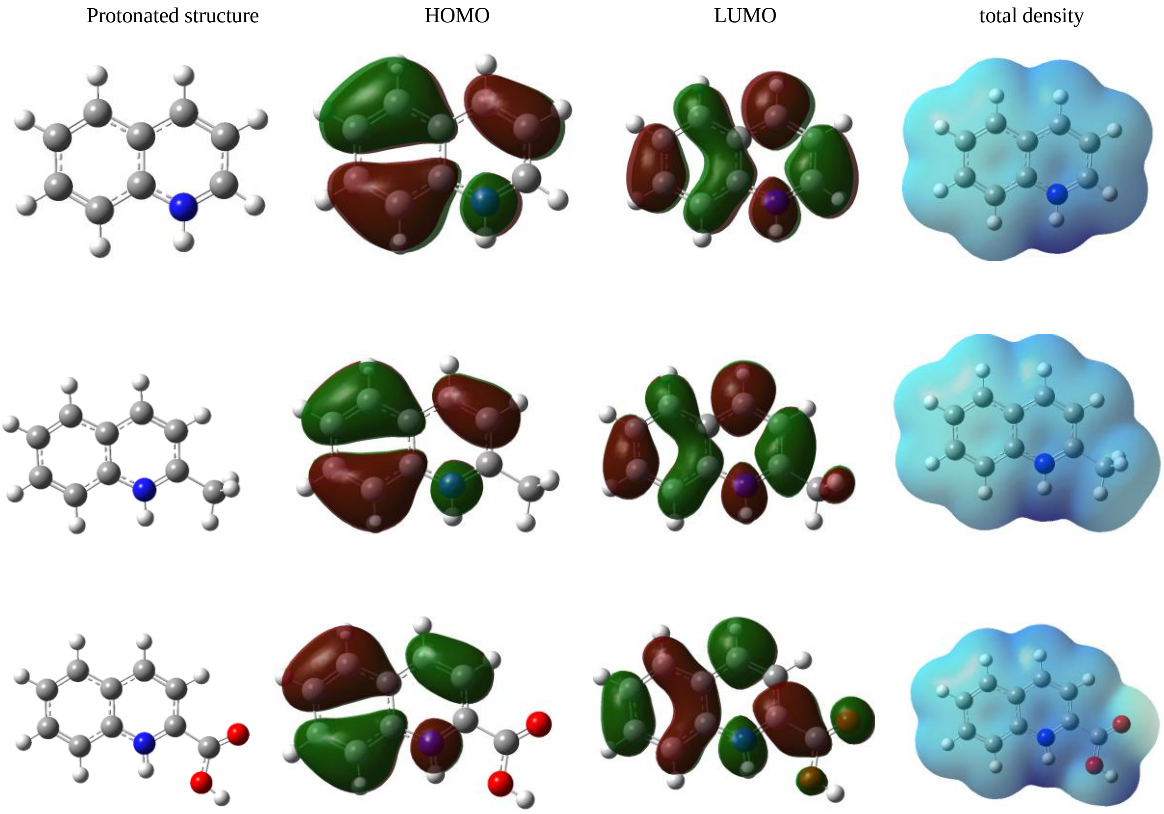


**Figure 4**. The optimised structures, HOMO, LUMO and the total electron density for the protonated inhibitor molecules (using B3LYP/6-31++G (d,p) results *in vacuo*).

A comparison of the bond lengths using the DFT/B3LYP method shows that the C−C bond lengths (Å) are often longer in the non-protonated form than in the protonated form (by ~ 0.004−0.024 Å) while the C2−N3 and N3−C4 bond lengths (Å) are consistently shorter in the non-protonated form than in the protonated form (by 0.011 and 0.021 for QL, 0.014 and 0.042 for QLD and 0.011 and 0.023 for QLDA respectively).The HOMO and LUMO of the protonated species are shown in figure 4 while the quantum chemical parameters related to the reactivity of the protonated species are reported in Table 4. Like in the non-protonated species, the HOMO is strongly localized (i.e., it has a high amplitude) on C7 and C10 atoms for all the species. The LUMO on the other hand has the highest amplitude on C4 and C6. The electron density mapped onto the potential surface for the three molecules show that electron deficient regions (blue color) dominate much of the molecule and is strongly localized in the region ahead of the N atoms. This phenomenon is a result of the high electronegative charge of the N atom that leaves the H atom attached to it highly electron deficient. The electron deficient regions are more spread in QLD than in QL and are highest in QLDA, probably because of the presence of two proton species, one on the N atom and the other on the $sp^3$ O atom. Overall, the results reveal that the protonated species are electron deficient and therefore have a less tendency to donate electrons to the electron deficient species as compared to the non-protonated species.

The Mulliken charges obtained using DFT/B3LYP/6-31++G (d,p) are significantly different from the results of other methods. This result is consistent with the fact that Mulliken atomic charges are strongly basis-set sensitive and in most instances tend to become unphysical when large basis sets with diffuse functions are employed [27]. The Mulliken atomic charges on the N atom obtained by using the DFT/BP86/CEP-31G method are also not realistic (Table 5).

A comparison of the quantum chemical parameters of the protonated species (Table 6) and those of the non-protonated species (Table 2) show similarity for the two forms. For instance, in protonated and non-protonated form, the order of the $E_{HOMO}$ is such that QLDA > QLD > QL; the order of the $E_{LUMO}$ is such that QLDA > QL > QLD. A comparison of the individual values of the $E_{HOMO}$, $E_{LUMO}$ and $\Delta E$ show that $E_{HOMO}$ for the protonated form is lower than for the non-protonated form, which suggests that the non-protonated form has greater tendency to donate electron pair than the protonated form; $E_{LUMO}$ has lower values in the protonated form than in the non-protonated form, implying that the protonated form has a greater tendency to accept electrons than the non-protonated species; $\Delta E$ is smaller for the protonated form than for the non-protonated form, meaning that the protonated form has greater reactivity than the non-protonated form (i.e., the protonated form has a greater tendency to adsorb on the metal surface than the non-protonated form). These results are in agreement with the analysis of the electron density mapped on the potential surface for the non-protonated and the protonated species.

The dipole moment is higher for the protonated species than for the non-protonated species (for the HF and DFT results) suggesting that dipole-dipole interactions are more predominant in the interaction between the metal surface and the protonated form than in the interaction between the metal surface and the non-protonated form. The sum of the negative charges appears to be higher for the protonated form than for the non-protonated form obtained using HF and MP2 methods. DFT results do not give a specific trend on the sum of the negative charges.

Tables 7 and 8 show the $f^+$ and the $f^-$ values respectively for the condensed Fukui functions of the protonated species. $f^+$ has the highest values for the C4 and C6 atoms, indicating that these are the preferred centers for a nucleophilic attack on the protonated species. This result is slightly different from the results obtained for the non-protonated species where it was shown that the preference for nucleophilic attack was on N3 and C6. The highest $f^-$ values correspond to the C7 and C10 atoms; these atoms would therefore be the preferred centers for an electrophilic attack.

### *3.3. Results of the calculations on the quinoline derivatives in water solution.*

Tables 9 and 10 show the C–C and C–N bond lengths for the non-protonated and protonated species respectively. The C–C and C–N bond lengths do not change substantially (the changes are less than 0.003Å) with respect to the results *in vacuo* which suggest that the solvent has minimal effects on the geometry of the inhibitors. The minimal geometric change is the result of the absence of significant rotatable single bonds in the molecules of QL, QLD and QLDA.

Tables 11 and 12 show the quantum chemical parameters for the non-protonated and the protonated species respectively. These parameters give information on the chemical reactivity of the studied molecules in solution. Trends in the quantum chemical parameters are similar for the results *in vacuo* and in water solution. $E_{HOMO}$, $E_{LUMO}$ and $\Delta E$ show only a slight increase (absolute values) with respect to the results i*n vacuo*. The dipole moment is higher in water solution than *in vacuo*, which is also a result of the polarization of the solute (inhibitors) by the solvent, resulting in an increased charge separation in the solute. The Mulliken charge on the individual atoms (table 9 for the non-protonated and table 10 for the protonated species) is higher in solution than *in vacuo*. This observation is also a consequence of the increased charge polarization induced by the solvent. The total negative charge of the molecule is higher in water solution than *in vacuo*.

The condensed Fukui functions for the inhibitor are reported in tables 13 and 14 for the non-protonated and tables 15 and 16 for the protonated species. The results show similar trends which suggests that the centers for the electrophilic and nucleophilic attack are the same *in vacuo* and in water solution.

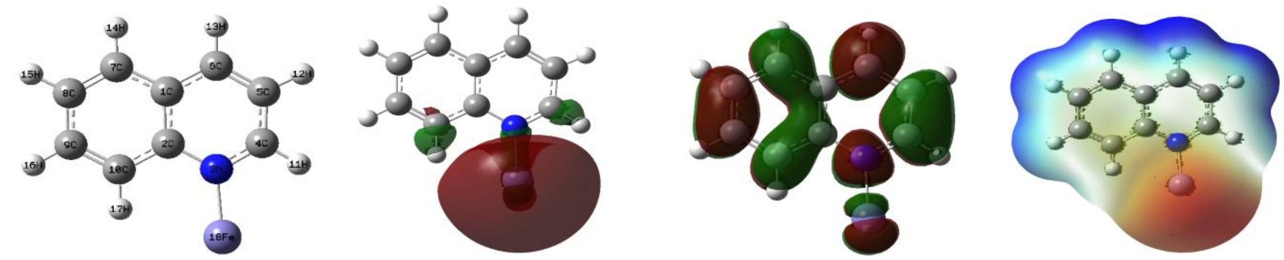
The similarity in the trends in the geometry and other quantum chemical parameters *in vacuo* and in water solution is attributed to the fact that the geometry of the molecules do not change significantly between the results *in vacuo* and the results in water solution, because of the absence of rotatable single bonds. Significant differences in some quantum chemical parameters (e.g., the dipole moment) between the results *in vacuo* and in water solution arise mainly due to the effect of the solvent on those properties.

### *3.4. The adsorption of the quinoline derivatives on the metal surface*

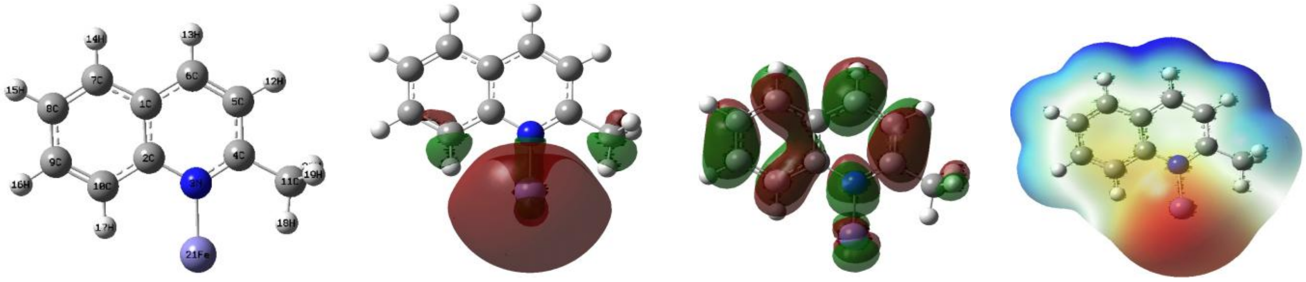
The binding capability of the metal on the inhibitor depends strongly on the electronic charge of the active site [29]. The Mulliken atomic charges of the non-protonated species show that the N atom, in all the calculated compounds, has the highest negative charge. Based on these results, each inhibitor molecule was allowed to interact with the Fe metal at the N atom. The interaction energy between the inhibitor and the metal was then estimated as the difference between the energy of the complex ($E_{Fe\text{-}X}$) and the sum of the energy of the isolated inhibitor and isolated Fe atom ($E_X + E_{Fe}$) resulting in the equation;

$$E_{interation} = E_{Fe.\text{-}X} - (E_X + E_{Fe}) \qquad (9)$$

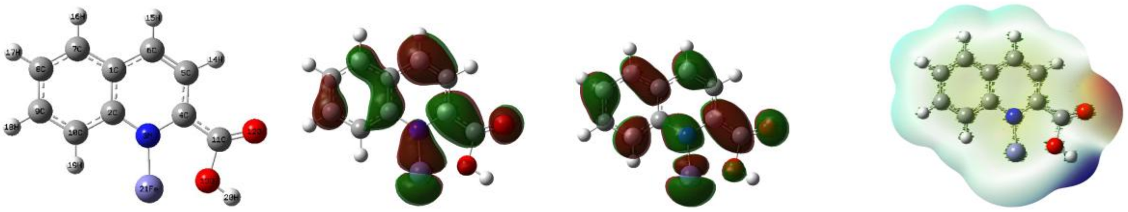
The interaction energy between the metal and the inhibitor is reported in table 17 and show that the trend follows the order; QLDA-Fe > QL-Fe > QLD-Fe, which confirm that QLDA has the strongest interaction with the metal surface (i.e., it is the most efficient inhibitor). These results are also supported by the comparison of the N3-Fe18 bond distances (reported in Table 1) that show that QLDA-Fe has the shortest N3-Fe18 bond distance (therefore stronger interactions between QLDA and the Fe atom) while QLD-Fe has the longest N3-F18 bond distance. Shorter bond distance implies stronger interactions while longer bond distance implies weaker interactions between concerned species. Both results (the interaction energy and the bond distances), therefore imply that QLDA bind strongly to the metal surface, resulting in a stronger adsorption on the metal surface.



QL (Fe-N3) HOMO LUMO total charge densıty



QLD (Fe-N3) HOMO LUMO total charge densıty



QLDA (Fe-N3) HOMO LUMO total charge densıty

**Figure 5.** The optimized structures, HOMO, LUMO of Fe–inhibitor complexes and total charge density (using DFT/B3LYP/6-31++G (d, p) results *in vacuo*).

Figure 5 shows the HOMO, the LUMO and the total electron density for the metal-inhibitor complexes. Both QL and QLD have the HOMO orbital strongly localized on the Fe ion. The electron density potential surface shows that there is a high negative charge (indicated by the red color) on the Fe ion (or on the Fe-inhibitor bond) than in the rest of the molecule. In fact, the electron density in this region (i.e., near the N3 atom) is higher than in the individual QL and QLD molecules, which indicates that the interaction between the inhibitor and the metal surface results in increased reactivity (i.e., the interaction does not necessary lead to stability). The HOMO and LUMO of the QLDA-Fe complex are delocalized throughout the molecule. The total electron density reveals that there is complete negative charge depletion on the N atom and the $sp^3$ O atom as well as on the Fe ion. Moreover, the charge density on the two rings appears more neutral than in the QL and QLD molecules, suggesting that QLDA-Fe complex is the least reactive (i.e. the interaction between QLDA and the Fe ion results in the most stable system). This observation is strengthened by the analysis of the $\Delta E$ values that show that QLDA-Fe has the highest $\Delta E$ value and is therefore the least reactive complex. All these results point to the fact that the interaction between QLDA and the metal surface give rise to the strongest adsorption on the metal surface which is also in agreement with experimental results that show that QLDA has the highest inhibition efficiency.

Both experimental and theoretical results point to the fact that QLDA has the highest inhibition efficiency. However, theoretical results differ from experimental results on the preference of inhibition efficiency of QLD and QL, with theoretical results showing that QL would be a better inhibitor than QLD and experimental results showing the opposite. There are two competing factors in the two structures that should be considered; planarity and electron density. QL is more planar than QLD because the methyl hydrogen atoms do not lie on the plane of the benzofused heterocyclic ring of QLD, resulting in a less planar geometry for the overall molecule. As a consequence, when the QLD molecule is placed on the metal surface, a part of it that is closer to the methyl group would not lie flat on the surface (i.e., there would be an angle between the metal surface and the inhibitor), which in principle should result in reduced inhibition efficiency and this would agree with predicted results. However, despite the fact that QLD is less planar than QL, it has a higher electron density than QL. Since a higher electron density molecule leads to greater inhibition efficiency, QLD has a greater tendency to donate electrons than QL and therefore its absorbability on the metal surface (and therefore its inhibitor efficiency) is greater than that of QL, which agrees with experimentally determined inhibition efficiency trends. In this case, therefore, experimental results have provided decisive information as to which of these two factors (planarity and electron density) pre-dominates the other.

## 4. CONCLUSION

The results of DFT and *ab initio* HF and MP2 calculations on quinoline (QL), quinaldine (QLD) and quinalic acid (QLDA) have been presented *in vacuo* and in water solution, taking into account both the non-protonated and protonated species. The results of the calculated molecular properties show interesting patterns across structures, across media and on the protonated and non-protonated species. The HOMO, LUMO, condensed Fukui functions and charges on the atoms predict similar centre that are preferably attacked by nucleophilic or electrophilic species. A comparison of the results *in vacuo* and in water solution shows that trends in the molecular properties across structures are similar, which may be related to the planar geometry of the studied systems (i.e., the geometry of the molecules are not significantly different *in vacuo* and in water solution). However, some parameters (e.g., charges on the atoms and dipole moment) are strongly influenced by the solute-solvent interactions

A comparison of the protonated species and the non-protonated species show that the protonated species are more electron deficient than the non-protonated species. However the ΔE values suggest that protonated species have greater tendency to interact with the metal surface. Quantum chemical calculations on the Fe-inhibitor complex also reveal that QLDA has a tendency to form the most stable complex and therefore as an inhibitor has the highest tendency to adsorb strongly onto the metal surface.

A comparison of the different utilized quantum chemical methods show that DFT/B3LYP gave results that are more realistic and in the case of the geometry of the conformers, DFT/B3LYP results are closer to experimental data. MP2 results appear to overestimate the magnitude of the bond length while HF appears to underestimate the magnitude of the bond lengths.

ACKNOWLEDGEMENTS

M. M. Kabanda, A. K. Singh and S. K. Shukla are grateful to the North-West University for granting them Postdoctoral Fellowships enabling them to participate in this work. E.E. Ebenso thanks the National Research Foundation (NRF) of South Africa for funding.

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**Table 1.** The calculated Mulliken charges (e) for selected atoms and bond distances (Å) for non-protonated compounds.

| Method and Molecule | Net atomic charge | | | | Bond Distance | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | N3 | O12 | O13 | Fe18 | C1-C2 | C2-N3 | N3-C4 | C4-C5 | C5-C6 | C1-C6 | C1-C7 | C7-C8 | C8-C9 | C9-C10 | C2-C10 | C4-C11 | C11-O12 | C11-13 | **N3-Fe18** |
| **MP2/3-21G** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.688 | - | - | - | 1.436 | 1.396 | 1.345 | 1.428 | 1.385 | 1.431 | 1.431 | 1.386 | 1.430 | 1.386 | 1.427 | - | - | - | - |
| **QLD** | -0.786 | - | - | - | 1.434 | 1.396 | 1.346 | 1.433 | 1.382 | 1.432 | 1.430 | 1.387 | 1.429 | 1.386 | 1.427 | 1.522 | - | - | - |
| **QLDA** | -0.730 | -0.625 | -0.703 | - | 1.438 | 1.393 | 1.342 | 1.425 | 1.383 | 1.431 | 1.430 | 1.387 | 1.430 | 1.385 | 1.428 | 1.499 | 1.243 | 1.382 | - |
| **MP2/6-31G(d,p)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.570 | - | - | - | 1.442 | 1.399 | 1.350 | 1.432 | 1.392 | 1.435 | 1.436 | 1.394 | 1.434 | 1.394 | 1.431 | - | - | - | - |
| **QLD** | -0.616 | - | - | - | 1.440 | 1.399 | 1.352 | 1.439 | 1.390 | 1.435 | 1.434 | 1.394 | 1.433 | 1.394 | 1.430 | 1.517 | - | - | - |
| **QLDA** | -0.537 | -0.573 | -0.707 | - | 1.443 | 1.394 | 1.351 | 1.433 | 1.391 | 1.433 | 1.434 | 1.394 | 1.434 | 1.393 | 1.431 | 1.498 | 1.257 | 1.388 | - |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.587 | - | - | - | 1.407 | 1.356 | 1.292 | 1.417 | 1.356 | 1.417 | 1.419 | 1.358 | 1.418 | 1.358 | 1.419 | - | - | - | - |
| **QLD** | -0.631 | - | - | - | 1.404 | 1.359 | 1.292 | 1.428 | 1.352 | 1.420 | 1.417 | 1.359 | 1.415 | 1.360 | 1.417 | 1.506 | - | - | - |
| **QLDA** | -0.582 | -0.584 | -0.601 | - | 1.407 | 1.352 | 1.292 | 1.417 | 1.356 | 1.416 | 1.419 | 1.357 | 1.419 | 1.357 | 1.420 | 1.502 | 1.191 | 1.318 | - |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.506 | - | - | - | 1.432 | 1.367 | 1.318 | 1.418 | 1.374 | 1.418 | 1.420 | 1.376 | 1.417 | 1.377 | 1.420 | - | - | - | - |
| **QLD** | -0.554 | - | - | - | 1.430 | 1.367 | 1.320 | 1.427 | 1.371 | 1.419 | 1.418 | 1.377 | 1.416 | 1.377 | 1.419 | 1.508 | - | - | - |
| **QLDA** | -0.554 | -0.480 | -0.487 | - | 1.434 | 1.361 | 1.320 | 1.420 | 1.373 | 1.418 | 1.419 | 1.377 | 1.418 | 1.376 | 1.421 | 1.501 | 1.216 | 1.346 | - |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.130 | - | - | - | 1.433 | 1.367 | 1.319 | 1.420 | 1.376 | 1.419 | 1.421 | 1.378 | 1.419 | 1.378 | 1.421 | - | - | - | - |
| **QLD** | -0.145 | - | - | - | 1.431 | 1.368 | 1.321 | 1.429 | 1.373 | 1.420 | 1.420 | 1.379 | 1.418 | 1.379 | 1.420 | 1.509 | - | - | - |
| **QLDA** | -0.159 | -0.493 | -0.411 | - | 1.434 | 1.361 | 1.320 | 1.422 | 1.374 | 1.419 | 1.420 | 1.378 | 1.420 | 1.377 | 1.422 | 1.502 | 1.218 | 1.347 | - |
| **BP86/CEP-31G** | | | | | | | | | | | | | | | | | | | |
| **QL** | 0.607 | - | - | - | 1.461 | 1.382 | 1.338 | 1.445 | 1.404 | 1.441 | 1.444 | 1.407 | 1.442 | 1.408 | 1.444 | - | - | - | - |
| **QLD** | 0.685 | - | - | - | 1.459 | 1.382 | 1.341 | 1.452 | 1.401 | 1.442 | 1.443 | 1.408 | 1.441 | 1.409 | 1.443 | 1.527 | - | - | - |
| **QLDA** | 0.735 | -0.058 | -0.141 | - | 1.462 | 1.376 | 1.340 | 1.445 | 1.402 | 1.441 | 1.443 | 1.407 | 1.443 | 1.407 | 1.445 | 1.522 | 1.240 | 1.370 | - |
| **B3LYP/6-31G ++(d.p) (Fe-Complex)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.153 | - | - | -0.002 | 1.431 | 1.391 | 1.341 | 1.406 | 1.377 | 1.418 | 1.422 | 1.377 | 1.416 | 1.380 | 1.416 | - | - | - | **1.871** |
| **QLD** | -0.144 | - | - | -0.217 | 1.428 | 1.397 | 1.346 | 1.417 | 1.372 | 1.418 | 1.420 | 1.378 | 1.414 | 1.381 | 1.416 | 1.507 | - | - | **1.883** |
| **QLDA** | **-0.186** | **-0.496** | **-0.482** | **0.168** | **1.425** | **1.401** | **1.390** | **1.414** | **1.369** | **1.435** | **1.414** | **1.386** | **1.408** | **1.387** | **1.408** | **1.432** | **1.216** | **1.433** | **1.779** |

**Table 2.** The calculated quantum chemical parameters[a] for non- protonated compounds *in vacuo*.

| **Method and molecule** | **$E_{HOMO}$ (eV)** | **$E_{LUMO}$ (eV)** | **ΔE (eV)** | **dipole moment μ (D)** | **molecular volume MV ($cm^3$/mol)** | **sum of the total negative charge TNC (e)** | **global hardness η (eV)** | **Softness σ ($eV^{-1}$)** | **chemical potential Pi (eV)** | **electronegativity χ (eV)** | **fraction of electrons transferred ΔN (e)** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | |
| ***MP2/3-21G*** | | | | | | | | | | | |
| **QL** | -8.41 | 2.11 | 10.52 | 2.309 | 88.480 | -2.148 | 5.260 | 0.190 | -3.150 | 3.150 | **0.366** |
| **QLD** | -8.33 | 2.25 | 10.58 | 2.006 | 101.864 | -2.765 | 5.290 | 0.189 | -3.040 | 3.040 | **0.374** |
| **QLDA** | -8.72 | 1.35 | 10.07 | 3.215 | 125.567 | -3.318 | 5.035 | 0.199 | -3.685 | 3.685 | **0.329** |
| | | | | | | | | | | | |
| ***MP2/6-31G(d,p)*** | | | | | | | | | | | |
| **QL** | -8.30 | 2.02 | 10.32 | 2.547 | 132.422 | -1.737 | 5.160 | 0.194 | -3.140 | 3.140 | **0.374** |
| **QLD** | -8.21 | 2.16 | 10.37 | 2.255 | 121.916 | -2.272 | 5.185 | 0.193 | -3.025 | 3.025 | **0.383** |
| **QLDA** | -8.66 | 1.11 | 9.77 | 3.455 | 114.953 | -2.901 | 4.885 | 0.205 | -3.775 | 3.775 | **0.330** |
| | | | | | | | | | | | |
| ***RHF/ 6-31G(d.p)*** | | | | | | | | | | | |
| **QL** | -8.41 | 2.43 | 10.84 | 2.231 | 113.487 | -1.478 | 5.420 | 0.185 | -2.990 | 2.990 | **0.370** |
| **QLD** | -8.32 | 2.58 | 10.90 | 1.983 | 96.671 | -1.878 | 5.450 | 0.183 | -2.870 | 2.870 | **0.379** |
| **QLDA** | -8.67 | 1.79 | 10.46 | 2.231 | 123.138 | -2.556 | 5.230 | 0.191 | -3.440 | 3.440 | **0.340** |
| | | | | | | | | | | | |
| ***B3LYP/6-31G(d.p)*** | | | | | | | | | | | |
| **QL** | -6.30 | -1.40 | 4.90 | 2.030 | 103.193 | -1.196 | 2.450 | 0.408 | -3.850 | 3.850 | **0.643** |
| **QLD** | -6.20 | -1.25 | 4.95 | 1.710 | 116.591 | -1.534 | 2.475 | 0.404 | -3.725 | 3.725 | **0.662** |
| **QLDA** | -6.56 | -1.98 | 4.58 | 2.847 | 134.400 | -2.078 | 2.290 | 0.437 | -4.270 | 4.270 | **0.596** |
| | | | | | | | | | | | |
| ***B3LYP/6-31G ++(d.p)*** | | | | | | | | | | | |
| **QL** | -6.59 | -1.77 | 4.82 | 2.180 | 96.484 | -2.746 | 2.410 | 0.415 | -4.180 | 4.180 | **0.585** |
| **QLD** | -6.48 | -1.60 | 4.88 | 1.873 | 121.233 | -3.342 | 2.440 | 0.410 | -4.040 | 4.040 | **0.607** |
| **QLDA** | -6.86 | -2.36 | 4.50 | 2.912 | 132.993 | -4.075 | 2.250 | 0.444 | -4.610 | 4.610 | **0.531** |
| | | | | | | | | | | | |
| ***BP86/CEP-31G*** | | | | | | | | | | | |
| **QL** | -5.76 | -2.42 | 3.34 | 2.078 | 83.767 | -2.468 | 1.670 | 0.599 | -4.090 | 4.090 | **0.871** |
| **QLD** | -5.64 | -2.26 | 3.38 | 1.725 | 116.338 | -2.568 | 1.690 | 0.592 | -3.950 | 3.950 | **0.902** |
| **QLDA** | -6.05 | -2.99 | 3.06 | 2.750 | 116.976 | -2.642 | 1.530 | 0.654 | -4.520 | 4.520 | **0.810** |

[a] μ is the dipole moment, MV is the Molecular Volume, TNC is the sum of the total negative charge, η is the global hardness, σ is the global softness, π is the chemical potential, χ is the electronegativity and ΔN is the fraction of the electrons transferred

**Table 3.** The calculated condensed Fukui functions for the electrophilic attack ($f^{-}$) for the non-protonated compounds.

| **Method and Molecule** | **Atom of interest** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C2 | N3 | C4 | C5 | C6 | C7 | C8 | C9 | **C10** |
| ***MP2/3-21G*** | | | | | | | | | |
| **QL** | – | 12.09 | 4.26 | 7.47 | 11.28 | 22.57 | 10.07 | 8.28 | **23.09** |
| **QLD** | 2.01 | 12.85 | 5.98 | 4.72 | 10.31 | 21.68 | 12.84 | 5.75 | **23.03** |
| **QLDA** | – | 10.53 | 2.76 | 10.13 | 11.64 | 23.07 | 7.87 | 10.26 | **22.57** |
| | | | | | | | | | |
| ***MP2/6-31G*** | | | | | | | | | |
| **QL** | 1.03 | 11.98 | 3.85 | 7.44 | 10.91 | 22.88 | 10.11 | 8.38 | **23.32** |
| **QLD** | 2.44 | 12.76 | 5.59 | 4.54 | 9.87 | 21.95 | 13.08 | 5.69 | **23.29** |
| **QLDA** | 4.38 | 10.30 | 2.47 | 10.16 | 11.32 | 23.41 | 7.80 | 10.44 | **22.71** |
| | | | | | | | | | |
| ***RHF/ 6-31G(d.p)*** | | | | | | | | | |
| **QL** | 1.91 | 10.02 | 3.90 | 6.50 | 9.70 | 23.36 | 12.04 | 8.12 | **23.94** |
| **QLD** | 5.05 | 10.41 | 6.72 | 2.54 | 8.05 | 21.54 | 16.96 | 3.97 | **22.80** |
| **QLDA** | – | 8.90 | 2.23 | 9.57 | 10.19 | 23.69 | 9.05 | 10.76 | **23.47** |
| | | | | | | | | | |
| ***B3LYP/6-31G(d.p)*** | | | | | | | | | |
| **QL** | 1.35 | 10.53 | 3.56 | 7.43 | 10.39 | 23.60 | 9.78 | 8.66 | **23.96** |
| **QLD** | 2.44 | 11.40 | 5.07 | 4.81 | 9.62 | 22.59 | 12.17 | 6.40 | **24.08** |
| **QLDA** | 1.06 | 9.51 | 2.65 | 8.98 | 10.40 | 23.90 | 8.72 | 9.57 | **23.67** |
| | | | | | | | | | |
| ***B3LYP/6-31G ++(d.p)*** | | | | | | | | | |
| **QL** | 1.22 | 10.40 | 3.33 | 7.49 | 10.28 | 23.81 | 9.76 | 8.65 | **24.31** |
| **QLD** | – | 11.24 | 4.69 | 5.04 | 9.43 | 22.80 | 12.23 | 6.36 | **24.28** |
| **QLDA** | – | 9.22 | 2.21 | 9.37 | 10.32 | 24.17 | 8.50 | 9.75 | **23.91** |
| | | | | | | | | | |
| ***BP86/CEP-31G*** | | | | | | | | | |
| **QL** | 1.35 | 9.99 | 3.33 | 7.66 | 9.88 | 24.07 | 9.47 | 8.88 | **24.48** |
| **QLD** | 2.27 | 10.89 | 4.72 | 5.23 | 9.15 | 23.08 | 11.60 | 6.79 | **24.71** |
| **QLDA** | 1.05 | 8.89 | 2.34 | 9.48 | 9.81 | 24.34 | 8.29 | 9.87 | **24.11** |
| | | | | | | | | | |
| ***B3LYP/6-31G ++(d.p)*** | | | | | | | | | |
| **QL** | – | 18.82 | – | 3.01 | – | 2.36 | – | – | **–** |
| **QLD** | **–** | **19.62** | **3.12** | **–** | **3.60** | **1.62** | **–** | **3.09** | **–** |
| **QLDA** | **3.27** | **2.72** | **14.39** | **1.15** | **14.09** | **1.96** | **–** | **–** | **–** |

**Table 4.** The calculated condensed Fukui functions for the nucleophilic attack ($f^{+}$) for the non-protonated compounds.

| **Method and Molecule** | **Atom of interest** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | N3 | C4 | C5 | C6 | C7 | C8 | C9 | **C10** |
| **MP2/3-21G** | | | | | | | | |
| **QL** | 16.07 | 8.83 | 8.98 | 22.49 | 14.81 | 5.91 | 8.11 | **14.50** |
| **QLD** | 14.59 | 7.80 | 10.44 | 22.31 | 15.36 | 5.17 | 8.90 | **14.56** |
| **QLDA** | 20.42 | 14.89 | | 14.58 | 7.78 | 9.92 | 1.81 | **10.93** |
| **MP2/6-31G(d,p)** | | | | | | | | |
| **QL** | 16.15 | 9.81 | 8.80 | 23.20 | 14.16 | 5.71 | 7.88 | **13.69** |
| **QLD** | 14.49 | 8.49 | 10.53 | 23.18 | 14.77 | 4.82 | 8.85 | **13.70** |
| **QLDA** | 20.44 | 15.46 | | 13.23 | 6.38 | 9.66 | 1.35 | **9.69** |
| **RHF/ 6-31G(d.p)** | | | | | | | | |
| **QL** | 13.72 | 9.87 | 9.80 | 22.28 | 14.10 | 6.07 | 8.59 | **13.74** |
| **QLD** | 12.04 | 8.23 | 11.88 | 22.14 | 22.14 | 4.97 | 9.77 | **13.83** |
| **QLDA** | 17.53 | 16.87 | 1.11 | 15.26 | 15.26 | 10.26 | 2.37 | **10.57** |
| **B3LYP/6-31G(d.p)** | | | | | | | | |
| **QL** | 16.22 | 10.67 | 8.51 | 22.38 | 13.48 | 6.28 | 7.44 | **13.22** |
| **QLD** | 14.76 | 9.36 | 10.19 | 22.09 | 14.09 | 5.61 | 8.12 | **13.33** |
| **QLDA** | 19.18 | 15.13 | | 14.55 | 7.16 | 9.18 | 2.39 | **10.42** |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | |
| **QL** | 15.00 | 11.25 | 10.28 | 21.55 | 12.89 | 6.59 | 7.52 | **13.52** |
| **QLD** | 13.76 | 9.81 | 11.51 | 22.02 | 13.72 | 5.75 | 8.53 | **13.38** |
| **QLDA** | 18.44 | 15.91 | | 14.44 | 6.35 | 9.54 | 2.17 | **10.61** |
| **BP86/CEP-31G** | | | | | | | | |
| **QL** | 15.92 | 10.75 | 8.64 | 22.63 | 13.23 | 6.31 | 7.31 | **13.29** |
| **QLD** | 14.30 | 8.99 | 10.75 | 22.36 | 14.03 | 5.45 | 8.21 | **13.34** |
| **QLDA** | 18.85 | 14.84 | | 14.24 | 6.56 | 9.09 | 2.36 | **10.55** |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | |
| **QL** | 14.98 | 13.56 | 7.02 | 21.68 | 10.05 | 4.97 | 7.04 | **9.35** |
| **QLD** | 14.73 | 11.73 | 7.94 | 22.50 | 10.44 | 4.28 | 7.70 | **8.96** |
| **QLDA** | 14.82 | 5.42 | | 3.71 | 2.41 | 6.42 | | **5.51** |

**Table 5.** The calculated Mulliken charges (e) for selected atoms and bond distances (Ǻ) for protonated compounds.

| **Method and Molecule** | **Net atomic charge** | | | **Bond Distance** | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | N3 | O12 | O13 | C1-C2 | C2-N3 | N3-C4 | C4-C5 | C5-C6 | C1-C6 | C1-C7 | C7-C8 | C8-C9 | C9-C10 | C2-C10 | C4-C11 | C11-O12 | **C11-O13** |
| | | | | | | | | | | | | | | | | | |
| **MP2/3-21G** | | | | | | | | | | | | | | | | | |
| **QL-P** | -1.001 | - | - | 1.437 | 1.389 | 1.354 | 1.407 | 1.393 | 1.424 | 1.433 | 1.385 | 1.432 | 1.385 | 1.423 | - | - | - |
| **QLD-P** | -0.999 | - | - | 1.432 | 1.394 | 1.352 | 1.416 | 1.387 | 1.427 | 1.431 | 1.386 | 1.431 | 1.387 | 1.422 | 1.515 | - | - |
| **QLDA-P** | -1.001 | -0.518 | -0.691 | 1.442 | 1.384 | 1.350 | 1.405 | 1.391 | 1.427 | 1.431 | 1.386 | 1.432 | 1.386 | 1.423 | 1.501 | 1.233 | **1.385** |
| **QLDA-2P** | -0.988 | -0.588 | -0.609 | 1.461 | 1.379 | 1.368 | 1.411 | 1.395 | 1.424 | 1.424 | 1.391 | 1.436 | 1.387 | 1.423 | 1.462 | 1.305 | **1.316** |
| | | | | | | | | | | | | | | | | | |
| **MP2/6-31G** | | | | | | | | | | | | | | | | | |
| **QL-P** | -0.992 | - | - | 1.442 | 1.393 | 1.357 | 1.413 | 1.399 | 1.429 | 1.437 | 1.392 | 1.437 | 1.393 | 1.427 | - | - | - |
| **QLD-P** | -1.056 | - | - | 1.437 | 1.397 | 1.360 | 1.421 | 1.395 | 1.430 | 1.435 | 1.393 | 1.435 | 1.394 | 1.426 | 1.511 | - | - |
| **QLDA-P** | -1.038 | -0.473 | -0.757 | 1.446 | 1.387 | 1.360 | 1.416 | 1.398 | 1.430 | 1.435 | 1.393 | 1.437 | 1.392 | 1.428 | 1.499 | 1.245 | **1.390** |
| **QLDA-2P** | -1.046 | -0.575 | -0.610 | 1.465 | 1.382 | 1.376 | 1.423 | 1.400 | 1.430 | 1.427 | 1.399 | 1.441 | 1.394 | 1.427 | 1.458 | 1.315 | **1.326** |
| | | | | | | | | | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | | | | | | | | |
| **QL-P** | -0.738 | - | - | 1.405 | 1.368 | 1.320 | 1.385 | 1.374 | 1.409 | 1.419 | 1.358 | 1.416 | 1.363 | 1.404 | - | - | - |
| **QLD-P** | -0.793 | - | - | 1.400 | 1.375 | 1.321 | 1.401 | 1.365 | 1.416 | 1.415 | 1.361 | 1.412 | 1.366 | 1.402 | 1.499 | - | - |
| **QLDA-P** | -0.790 | -0.491 | -0.644 | 1.409 | 1.360 | 1.324 | 1.381 | 1.378 | 1.404 | 1.422 | 1.355 | 1.420 | 1.361 | 1.408 | 1.509 | 1.176 | **1.317** |
| **QLDA-2P** | -0.793 | -0.504 | -0.541 | 1.438 | 1.342 | 1.352 | 1.366 | 1.404 | 1.380 | 1.433 | 1.348 | 1.434 | 1.358 | 1.410 | 1.467 | 1.258 | **1.264** |
| | | | | | | | | | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | | | | | | | | |
| **QL-P** | -0.550 | - | - | 1.429 | 1.378 | 1.339 | 1.394 | 1.386 | 1.414 | 1.420 | 1.376 | 1.417 | 1.380 | 1.407 | - | - | - |
| **QLD-P** | -0.604 | - | - | 1.424 | 1.381 | 1.342 | 1.407 | 1.380 | 1.416 | 1.418 | 1.378 | 1.415 | 1.382 | 1.405 | 1.496 | - | - |
| **QLDA-P** | -0.627 | -0.414 | -0.501 | 1.432 | 1.372 | 1.343 | 1.395 | 1.386 | 1.413 | 1.420 | 1.376 | 1.419 | 1.379 | 1.408 | 1.504 | 1.203 | **1.345** |
| **QLDA-2P** | -0.638 | -0.306 | -0.417 | 1.454 | 1.361 | 1.362 | 1.397 | 1.395 | 1.404 | 1.419 | 1.376 | 1.429 | 1.377 | 1.411 | 1.456 | 1.285 | **1.293** |
| | | | | | | | | | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | | | | | | | | |
| **QL-P** | -0.129 | - | - | 1.430 | 1.379 | 1.340 | 1.395 | 1.387 | 1.415 | 1.422 | 1.377 | 1.418 | 1.382 | 1.408 | - | - | - |
| **QLD-P** | -0.135 | - | - | 1.425 | 1.383 | 1.343 | 1.408 | 1.381 | 1.418 | 1.420 | 1.379 | 1.416 | 1.383 | 1.407 | 1.497 | - | - |
| **QLDA-P** | -0.163 | -0.402 | -0.475 | 1.433 | 1.372 | 1.344 | 1.396 | 1.387 | 1.413 | 1.421 | 1.377 | 1.420 | 1.380 | 1.410 | 1.504 | 1.204 | **1.347** |
| **QLDA-2P** | -0.130 | -0.364 | -0.373 | 1.455 | 1.361 | 1.362 | 1.398 | 1.395 | 1.405 | 1.420 | 1.377 | 1.430 | 1.378 | 1.412 | 1.456 | 1.286 | **1.294** |
| | | | | | | | | | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | | | | | | | | | |
| **QL-P** | 0.548 | - | - | 1.456 | 1.394 | 1.357 | 1.421 | 1.414 | 1.437 | 1.444 | 1.406 | 1.442 | 1.410 | 1.431 | - | - | - |
| **QLD-P** | 0.634 | - | - | 1.451 | 1.397 | 1.361 | 1.433 | 1.407 | 1.439 | 1.443 | 1.407 | 1.441 | 1.411 | 1.430 | 1.514 | - | - |
| **QLDA-P** | 0.640 | 0.019 | -0.202 | 1.459 | 1.389 | 1.361 | 1.422 | 1.412 | 1.437 | 1.444 | 1.406 | 1.443 | 1.409 | 1.432 | 1.523 | 1.225 | **1.370** |
| **QLDA-2P** | 0.598 | -0.046 | -0.087 | 1.479 | 1.379 | 1.378 | 1.427 | 1.417 | 1.431 | 1.440 | 1.407 | 1.453 | 1.407 | 1.435 | 1.475 | 1.309 | **1.317** |
| | | | | | | | | | | | | | | | | | |

**Table 6.** The calculated quantum chemical parameters[a] for protonated compounds.

| Method and Molecule | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) | Dipole moment μ (D) | Molecular volume MV (cm$^3$/mol) | sum of the total negative charge TNC (e) | Global hardness η (eV) | Softness σ (eV$^{-1}$) | Chemical potential Pi (eV) | Electronegativity χ (eV) | ΔN (e) fraction of electrons transferred |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ***MP2/3-21G*** | | | | | | | | | | | |
| **QL-P** | -13.24 | -3.47 | 9.77 | 3.499 | 97.524 | -2.233 | 4.885 | 0.205 | -8.355 | 8.355 | **-0.139** |
| **QLD-P** | -13.06 | -3.12 | 9.94 | 3.029 | 103.093 | -3.053 | 4.970 | 0.201 | -8.090 | 8.090 | **-0.110** |
| **QLDA-P** | -13.31 | -4.09 | 9.22 | 2.552 | 107.381 | -3.609 | 4.610 | 0.217 | -8.700 | 8.700 | **-0.184** |
| **QLDA-2P** | -16.51 | -9.09 | 7.42 | 8.592 | 129.950 | -3.533 | 3.710 | 0.270 | -12.800 | 12.800 | **-0.782** |
| ***MP2/6-31G*** | | | | | | | | | | | |
| **QL-P** | -13.12 | -3.42 | 9.70 | 3.437 | 100.582 | -2.128 | 4.850 | 0.206 | -8.270 | 8.270 | **-0.131** |
| **QLD-P** | -12.95 | -3.11 | 9.84 | 2.960 | 95.208 | -2.700 | 4.920 | 0.203 | -8.030 | 8.030 | **-0.105** |
| **QLDA-P** | -13.26 | -4.19 | 9.07 | 2.942 | 129.511 | -3.346 | 4.535 | 0.221 | -8.725 | 8.725 | **-0.190** |
| **QLDA-2P** | -16.46 | -9.11 | 7.35 | 8.204 | 132.006 | -3.270 | 3.675 | 0.272 | -12.785 | 12.785 | **-0.787** |
| ***RHF/ 6-31G(d.p)*** | | | | | | | | | | | |
| **QL-P** | -13.22 | -3.16 | 10.06 | 3.290 | 104.776 | -1.600 | 5.030 | 0.199 | -8.190 | 8.190 | **-0.118** |
| **QLD-P** | -13.04 | -2.79 | 10.25 | 2.808 | 124.005 | -2.040 | 5.125 | 0.195 | -7.915 | 7.915 | **-0.089** |
| **QLDA-P** | -13.30 | -3.63 | 9.67 | 2.794 | 116.677 | -2.668 | 4.835 | 0.207 | -8.465 | 8.465 | **-0.151** |
| **QLDA-2P** | -16.56 | -8.30 | 8.26 | 8.576 | 101.379 | -2.457 | 4.130 | 0.242 | -12.430 | 12.430 | **-0.657** |
| ***B3LYP/6-31G(d.p)*** | | | | | | | | | | | |
| **QL-P** | -11.14 | -6.85 | 4.29 | 3.130 | 114.222 | -1.082 | 2.145 | 0.466 | -8.995 | 8.995 | **-0.465** |
| **QLD-P** | -10.93 | -6.51 | 4.42 | 2.621 | 104.896 | -1.553 | 2.210 | 0.452 | -8.720 | 8.720 | **-0.389** |
| **QLDA-P** | -11.18 | -7.20 | 3.98 | 2.984 | 120.565 | -2.051 | 1.990 | 0.503 | -9.190 | 9.190 | **-0.550** |
| **QLDA-2P** | -14.64 | -11.96 | 2.68 | 7.332 | 115.924 | -1.863 | 1.340 | 0.746 | -13.300 | 13.300 | **-2.351** |
| ***B3LYP/6-31G ++(d.p)*** | | | | | | | | | | | |
| **QL-P** | -11.28 | -7.03 | 4.25 | 2.984 | 110.201 | -2.720 | 2.125 | 0.471 | -9.155 | 9.155 | **-0.507** |
| **QLD-P** | -11.07 | -6.69 | 4.38 | 2.637 | 112.560 | -2.928 | 2.190 | 0.457 | -8.880 | 8.880 | **-0.429** |
| **QLDA-P** | -11.36 | -7.43 | 3.93 | 2.953 | 130.329 | -3.576 | 1.965 | 0.509 | -9.395 | 9.395 | **-0.609** |
| **QLDA-2P** | -14.75 | -12.12 | 2.63 | 7.703 | 105.154 | -3.617 | 1.315 | 0.760 | -13.435 | 13.435 | **-2.447** |
| ***BP86/CEP-31G*** | | | | | | | | | | | |
| **QL-P** | -10.47 | -7.65 | 2.82 | 2.870 | 93.413 | -2.077 | 1.410 | 0.709 | -9.060 | 9.060 | **-0.730** |
| **QLD-P** | 10.25 | -7.30 | -17.55 | 2.579 | 99.624 | -2.184 | -8.775 | -0.114 | 1.475 | -1.475 | **-0.483** |
| **QLDA-P** | -10.54 | -8.00 | 2.54 | 2.987 | 112.121 | -1.984 | 1.270 | 0.787 | -9.270 | 9.270 | **-0.894** |
| **QLDA-2P** | -14.00 | -12.62 | 1.38 | 7.499 | 141.924 | -1.739 | 0.690 | 1.449 | -13.310 | 13.310 | **-4.572** |

[a] μ is the dipole moment, MV is the Molecular Volume, TNC is the sum of the total negative charge, η is the global hardness, σ is the global softness, π is the chemical potential, χ is the electronegativity and ΔN is the fraction of the electrons that the inhibitor could transferred to the metal. The letter P in the name denote the protonated species.

**Table 7.** The calculated condensed Fukui functions for electrophilic attack ($f^{-}$) for the protonated species.

| Method and molecule | Atom of interest | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C1 | C2 | N3 | C5 | C6 | C7 | C8 | C9 | **C10** |
| **MP2/3-21G** | | | | | | | | | |
| **QL** | 1.01 | 5.17 | 6.91 | 7.25 | 4.15 | 28.29 | 15.29 | 4.33 | **27.49** |
| **QLD** | | 5.68 | 6.72 | 6.69 | 3.95 | 28.47 | 15.69 | 4.01 | **27.56** |
| **QLDA** | | 4.96 | 6.97 | 7.34 | 4.66 | 28.26 | 15.05 | 4.51 | **27.11** |
| | | | | | | | | | |
| **MP2/6-31G** | | | | | | | | | |
| **QL** | 1.41 | 5.24 | 6.96 | 8.15 | 4.07 | 27.84 | 14.01 | 4.52 | **27.76** |
| **QLD** | 1.41 | 5.68 | 6.85 | 7.64 | 3.85 | 27.96 | 14.32 | 4.25 | **27.95** |
| **QLDA** | 1.13 | 5.29 | 7.07 | 7.94 | 4.63 | 27.91 | 14.37 | 4.38 | **27.18** |
| | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | |
| **QL** | 2.23 | 4.15 | 6.46 | 8.95 | 3.77 | 27.12 | 12.38 | 6.32 | **28.15** |
| **QLD** | 3.28 | 3.70 | 5.91 | 9.62 | 3.49 | 27.00 | 10.70 | 7.18 | **28.63** |
| **QLDA** | 1.82 | 3.95 | 6.71 | 8.86 | 4.22 | 27.07 | 12.88 | 6.33 | **27.65** |
| | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | |
| **QL** | 2.46 | 4.58 | 6.72 | 8.67 | 4.22 | 28.28 | 11.60 | 5.64 | **27.32** |
| **QLD** | 2.56 | 4.61 | 6.65 | 8.53 | 4.12 | 28.36 | 11.44 | 5.66 | **27.46** |
| **QLDA** | 2.36 | 4.39 | 6.74 | 8.81 | 4.54 | 28.09 | 11.54 | 5.79 | **27.08** |
| | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | |
| **QL** | 2.41 | 4.57 | 6.61 | 8.86 | 4.27 | 28.38 | 11.51 | 5.58 | **27.44** |
| **QLD** | 2.52 | 4.60 | 6.54 | 8.74 | 4.15 | 28.44 | 11.37 | 5.59 | **27.60** |
| **QLDA** | 2.33 | 4.35 | 6.63 | 8.95 | 4.58 | 28.25 | 11.43 | 5.73 | **27.22** |
| | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | |
| **QL** | 2.65 | 4.87 | 6.33 | 8.76 | 4.12 | 28.54 | 11.37 | 5.49 | **27.29** |
| **QLD** | 2.61 | 4.91 | 6.35 | 8.51 | 4.05 | 28.62 | 11.45 | 5.39 | **27.40** |
| **QLDA** | 2.67 | 4.61 | 6.31 | 8.99 | 4.39 | 28.28 | 11.13 | 5.73 | **27.12** |

**Table 8.** The calculated condensed Fukui functions for nucleophilic attack ($f^{+}$) for the protonated species.

| **Method and molecule** | **Atom of interest** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C1 | C2 | N3 | C4 | C5 | C6 | C7 | C8 | C9 | **C10** |
| **MP2/3-21G** | | | | | | | | | | |
| **QL** | | 5.23 | 13.75 | 23.02 | 2.07 | 31.55 | 8.09 | 2.30 | 9.13 | **4.16** |
| **QLD** | | 4.73 | 12.77 | 22.34 | 3.35 | 31.10 | 8.51 | 1.97 | 9.26 | **4.38** |
| **QLDA** | 3.18 | 3.03 | 15.43 | 24.11 | | 22.90 | 4.85 | 3.74 | 5.14 | **3.73** |
| | | | | | | | | | | |
| **MP2/6-31G** | | | | | | | | | | |
| **QL** | | 5.50 | 12.33 | 23.91 | 1.90 | 31.61 | 8.49 | 2.29 | 9.22 | **4.09** |
| **QLD** | | 5.27 | 11.25 | 22.22 | 3.14 | 31.50 | 8.90 | 1.83 | 9.52 | **4.10** |
| **QLDA** | 3.26 | 3.52 | 13.76 | 24.11 | | 22.40 | 4.90 | 3.80 | 5.17 | **3.55** |
| | | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | |
| **QL** | 1.11 | 5.72 | 11.80 | 22.49 | 3.02 | 31.21 | 8.08 | 2.47 | 9.43 | **4.19** |
| **QLD** | | 5.00 | 10.89 | 21.93 | 4.55 | 30.88 | 8.53 | 2.07 | 9.49 | **4.42** |
| **QLDA** | 2.85 | 4.34 | 13.00 | 23.75 | | 25.41 | 5.81 | 3.67 | 6.50 | **3.82** |
| | | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | |
| **QL** | 1.74 | 5.44 | 15.11 | 23.01 | 2.38 | 28.91 | 7.33 | 3.10 | 8.43 | **4.06** |
| **QLD** | 1.20 | 4.94 | 14.10 | 22.02 | 3.55 | 28.49 | 7.79 | 2.74 | 8.51 | **4.25** |
| **QLDA** | 3.44 | 4.25 | 15.72 | 22.27 | | 21.83 | 4.73 | 4.21 | 5.74 | **3.80** |
| | | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | |
| **QL** | 1.85 | 5.51 | 13.86 | 23.81 | 2.77 | 29.04 | 7.04 | 3.17 | 8.43 | **4.01** |
| **QLD** | 1.15 | 5.18 | 13.25 | 22.30 | 3.59 | 29.16 | 7.51 | 2.79 | 8.55 | **4.10** |
| **QLDA** | 3.58 | 4.16 | 14.95 | 22.76 | | 21.86 | 4.35 | 4.35 | 5.59 | **3.73** |
| | | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | | |
| **QL** | 2.06 | 5.39 | 14.98 | 23.33 | 2.39 | 28.68 | 6.96 | 3.33 | 8.26 | **4.00** |
| **QLD** | 1.40 | 5.01 | 13.97 | 21.90 | 3.67 | 28.42 | 7.55 | 2.89 | 8.49 | **4.16** |
| **QLDA** | 3.80 | 4.26 | 15.60 | 22.13 | | 20.96 | 4.20 | 4.50 | 5.56 | **3.75** |

**Table 9**. The calculated Mulliken atomic charges (e) and the bond distances (Ǻ) for non-protonated compounds in water solution.

| **Method and** | **Net atomic charge** | | | | **Bond Distance** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Molecule** | N3 | O12 | O13 | Fe18 | C1-C2 | C2-N3 | N3-C4 | C4-C5 | C5-C6 | C1-C6 | C1-C7 | C7-C8 | C8-C9 | C9-C10 | C2-C10 | C4-C11 | C11-O12 | C11-13 | **N3-Fe18** |
| **MP2/3-21G** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0742 | - | - | - | 1.437 | 1.398 | 1.348 | 1.428 | 1.386 | 1.432 | 1.433 | 1.387 | 1.431 | 1.387 | 1.429 | - | - | - | - |
| **QLD** | -0.769 | - | - | - | 1.435 | 1.399 | 1.347 | 1.434 | 1.383 | 1.433 | 1.431 | 1.388 | 1.430 | 1.388 | 1.429 | 1.522 | - | - | - |
| **QLDA** | -0.728 | -0.664 | -0.723 | - | 1.439 | 1.395 | 1.345 | 1.425 | 1.384 | 1.431 | 1.431 | 1.388 | 1.431 | 1.387 | 1.429 | 1.504 | 1.244 | 1.371 | - |
| **MP2/6-31G** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.654 | - | - | - | 1.442 | 1.401 | 1.353 | 1.431 | 1.393 | 1.435 | 1.437 | 1.395 | 1.435 | 1.394 | 1.432 | - | - | - | - |
| **QLD** | -0.689 | - | - | - | 1.440 | 1.401 | 1.354 | 1.438 | 1.390 | 1.436 | 1.436 | 1.395 | 1.434 | 1.395 | 1.432 | 1.517 | - | - | - |
| **QLDA** | -0.617 | -0.647 | -0.764 | - | 1.444 | 1.395 | 1.355 | 1.432 | 1.392 | 1.433 | 1.435 | 1.395 | 1.436 | 1.394 | 1.433 | 1.500 | 1.259 | 1.378 | - |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.639 | - | - | - | 1.407 | 1.360 | 1.296 | 1.417 | 1.357 | 1.419 | 1.420 | 1.360 | 1.418 | 1.360 | 1.419 | - | - | - | - |
| **QLD** | -0.674 | - | - | - | 1.404 | 1.363 | 1.296 | 1.427 | 1.353 | 1.421 | 1.417 | 1.361 | 1.416 | 1.362 | 1.417 | 1.506 | - | - | - |
| **QLDA** | -0.633 | -0.614 | -0.614 | - | 1.408 | 1.353 | 1.295 | 1.415 | 1.358 | 1.415 | 1.421 | 1.359 | 1.420 | 1.358 | 1.421 | 1.505 | 1.197 | 1.309 | - |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.556 | - | - | - | 1.433 | 1.370 | 1.322 | 1.418 | 1.375 | 1.419 | 1.421 | 1.378 | 1.418 | 1.378 | 1.421 | - | - | - | - |
| **QLD** | -0.597 | - | - | - | 1.430 | 1.370 | 1.323 | 1.427 | 1.372 | 1.420 | 1.419 | 1.379 | 1.417 | 1.379 | 1.420 | 1.508 | - | - | - |
| **QLDA** | -0.604 | -0.523 | -0.519 | - | 1.434 | 1.363 | 1.323 | 1.419 | 1.374 | 1.417 | 1.420 | 1.377 | 1.419 | 1.377 | 1.422 | 1.503 | 1.221 | 1.337 | - |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.266 | - | - | - | 1.433 | 1.371 | 1.323 | 1.419 | 1.377 | 1.420 | 1.422 | 1.380 | 1.420 | 1.380 | 1.422 | - | - | - | - |
| **QLD** | -0.273 | - | - | - | 1.431 | 1.372 | 1.324 | 1.428 | 1.373 | 1.421 | 1.421 | 1.381 | 1.419 | 1.381 | 1.421 | 1.508 | - | - | - |
| **QLDA** | -0.265 | -0.565 | -0.494 | - | 1.435 | 1.363 | 1.324 | 1.420 | 1.376 | 1.418 | 1.421 | 1.379 | 1.421 | 1.379 | 1.423 | 1.504 | 1.225 | 1.336 | - |
| **BP86/CEP-31G** | | | | | | | | | | | | | | | | | | | |
| **QL** | 0.559 | - | - | - | 1.462 | 1.386 | 1.343 | 1.444 | 1.406 | 1.442 | 1.446 | 1.409 | 1.444 | 1.410 | 1.445 | - | - | - | - |
| **QLD** | 0.648 | - | - | - | 1.459 | 1.386 | 1.344 | 1.452 | 1.402 | 1.443 | 1.445 | 1.410 | 1.443 | 1.411 | 1.444 | 1.527 | - | - | - |
| **QLDA** | 0.690 | -0.101 | -0.183 | - | 1.462 | 1.378 | 1.343 | 1.444 | 1.404 | 1.441 | 1.444 | 1.409 | 1.445 | 1.408 | 1.446 | 1.524 | 1.245 | 1.360 | - |
| **B3LYP/6-31G ++(d.p) (Fe-Complex)** | | | | | | | | | | | | | | | | | | | |
| **QL** | -0.181 | - | - | - | 1.435 | 1414 | 1.382 | 1.391 | 1.393 | 1.421 | 1.425 | 1.384 | 1.412 | 1.389 | 1.409 | - | - | - | **1.798** |
| **QLD** | -0.693 | - | - | - | 1.428 | 1.408 | 1.362 | 1.409 | 1.376 | 1.418 | 1.420 | 1.379 | 1.412 | 1.381 | 1.414 | 1.506 | - | - | **1.814** |
| **QLDA** | -0.241 | -0.733 | -0.624 | - | 1.427 | 1.415 | 1.429 | 1.421 | 1.365 | 1.449 | 1.410 | 1.395 | 1.401 | 1.396 | 1.405 | 1.403 | 1.248 | 1.419 | **1.804** |

**Table 10.** The calculated Mulliken atomic charges for the heteroatom and selected the bond distances (Å) for protonated compounds in water solution.

| **Method and** | **Net atomic charge** | | | | **Bond Distance** | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Molecule** | N3 | O12 | O13 | Fe18 | C1-C2 | C2-N3 | N3-C4 | C4-C5 | C5-C6 | C1-C6 | C1-C7 | C7-C8 | C8-C9 | C9-C10 | C2-C10 | C4-C11 | C11-O12 | C11-13 |
| **MP2/3-21G** | | | | | | | | | | | | | | | | | | |
| **QL** | -0954 | - | - | - | 1.434 | 1.388 | 1.349 | 1.409 | 1.390 | 1.425 | 1.433 | 1.384 | 1.432 | 1.385 | 1.424 | - | - | - |
| **QLD** | -0.995 | - | - | - | 1.430 | 1.390 | 1.350 | 1.416 | 1.386 | 1.426 | 1.432 | 1.385 | 1.431 | 1.386 | 1.423 | 1.515 | - | - |
| **QLDA** | -0.993 | -0.576 | -0.689 | - | 1.440 | 1.383 | 1.348 | 1.406 | 1.388 | 1.426 | 1.431 | 1.385 | 1.432 | 1.384 | 1.424 | 1.499 | 1.235 | 1.376 |
| **MP2/6-31G** | | | | | | | | | | | | | | | | | | |
| **QL** | -0.983 | - | - | - | 1.439 | 1.391 | 1.352 | 1.414 | 1.396 | 1.429 | 1.437 | 1.392 | 1.436 | 1.392 | 1.428 | - | - | - |
| **QLD** | -1.037 | - | - | - | 1.435 | 1.395 | 1.355 | 1.423 | 1.393 | 1.430 | 1.436 | 1.392 | 1.435 | 1.393 | 1.427 | 1.510 | - | - |
| **QLDA** | -1.046 | -0.549 | -0.768 | - | 1.444 | 1.385 | 1.358 | 1.416 | 1.396 | 1.429 | 1.435 | 1.392 | 1.437 | 1.392 | 1.429 | 1.496 | 1.249 | 1.381 |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | | | | | | | | | |
| **QL** | -0.717 | - | - | - | 1.402 | 1.366 | 1.315 | 1.390 | 1.368 | 1.414 | 1.418 | 1.358 | 1.416 | 1.362 | 1.407 | - | - | - |
| **QLD** | -0.772 | - | - | - | 1.397 | 1.373 | 1.316 | 1.405 | 1.360 | 1.420 | 1.415 | 1.362 | 1.412 | 1.365 | 1.404 | 1.497 | - | - |
| **QLDA** | -0.771 | -0.533 | -0.618 | - | 1.407 | 1.357 | 1.321 | 1.381 | 1.377 | 1.404 | 1.423 | 1.355 | 1.421 | 1.359 | 1.410 | 1.507 | 1.183 | 1.309 |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | | | | | | | | | |
| **QL** | -0.570 | - | - | - | 1.427 | 1.375 | 1.335 | 1.396 | 1.383 | 1.414 | 1.420 | 1.376 | 1.417 | 1.379 | 1.408 | - | - | - |
| **QLD** | -0.627 | - | - | - | 1.422 | 1.379 | 1.339 | 1.408 | 1.377 | 1.418 | 1.418 | 1.378 | 1.415 | 1.381 | 1.407 | 1.495 | - | - |
| **QLDA** | -0.642 | -0.448 | -0.503 | - | 1.431 | 1.369 | 1.340 | 1.395 | 1.385 | 1.412 | 1.420 | 1.375 | 1.419 | 1.378 | 1.410 | 1.501 | 1.209 | 1.338 |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | | | | | | | | | |
| **QL** | -0.093 | - | - | - | 1.427 | 1.376 | 1.336 | 1.397 | 1.384 | 1.415 | 1.421 | 1.378 | 1.418 | 1.381 | 1.409 | - | - | - |
| **QLD** | -0.088 | - | - | - | 1.422 | 1.380 | 1.339 | 1.410 | 1.378 | 1.419 | 1.419 | 1.379 | 1.416 | 1.382 | 1.408 | 1.495 | - | - |
| **QLDA** | -0.104 | -0.477 | -0.475 | - | 1.432 | 1.369 | 1.342 | 1.395 | 1.386 | 1.412 | 1.421 | 1.376 | 1.421 | 1.379 | 1.411 | 1.501 | 1.211 | 1.338 |
| **BP86/CEP-31G** | | | | | | | | | | | | | | | | | | |
| **QL** | 0.454 | - | - | - | 1.454 | 1.390 | 1.352 | 1.425 | 1.411 | 1.439 | 1.444 | 1.408 | 1.443 | 1.411 | 1.432 | - | - | - |
| **QLD** | -0.454 | - | - | - | 1.449 | 1.394 | 1.357 | 1.435 | 1.405 | 1.440 | 1.442 | 1.408 | 1.440 | 1.411 | 1.431 | 1.513 | - | - |
| **QLDA** | 0.535 | -0.055 | -0.223 | - | 1.458 | 1.384 | 1.359 | 1.422 | 1.411 | 1.436 | 1.443 | 1.406 | 1.444 | 1.408 | 1.433 | 1.520 | 1.232 | 1.361 |

**Table 11.** The calculated quantum chemical parameters[a] for non-protonated compounds in water solution.

| Method and molecule | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) | dipole moment μ (D) | molecular volume MV ($cm^3$/mol) | sum of the total negative charge TNC (e) | global hardness η (eV) | Softness σ ($eV^{-1}$) | chemical potential Pi (eV) | Electronegativity χ (eV) | fraction of electrons transferred ΔN (e) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **MP2/3-21G** | | | | | | | | | | | |
| **QL** | -9.47 | 0.67 | 10.14 | 5.170 | 90.362 | -2.471 | 5.070 | 0.197 | -4.400 | 4.400 | 0.256 |
| **QLD** | -9.48 | 0.67 | 10.15 | 3.872 | 103.717 | -3.131 | 5.075 | 0.197 | -4.405 | 4.405 | 0.256 |
| **QLDA** | -9.60 | -0.14 | 9.46 | 2.876 | 95.310 | -3.705 | 4.730 | 0.211 | -4.870 | 4.870 | 0.255 |
| | | | | | | | | | | | |
| **MP2/6-31G(d,p)** | | | | | | | | | | | |
| **QL** | -9.27 | 0.69 | 9.96 | 5.092 | 100.433 | -2.177 | 4.980 | 0.201 | -4.290 | 4.290 | 0.272 |
| **QLD** | -9.28 | 0.75 | 10.03 | 3.855 | 113.590 | -2.737 | 5.015 | 0.199 | -4.265 | 4.265 | 0.273 |
| **QLDA** | -9.42 | -0.29 | 9.13 | 3.438 | 126.618 | -3.432 | 4.565 | 0.219 | -4.855 | 4.855 | 0.235 |
| | | | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | | |
| **QL** | -9.33 | 0.99 | 10.32 | 5.108 | 119.635 | -1.639 | 5.160 | 0.194 | -4.170 | 4.170 | 0.274 |
| **QLD** | -9.33 | 1.11 | 10.44 | 3.935 | 129.998 | -2.068 | 5.220 | 0.192 | -4.110 | 4.110 | 0.277 |
| **QLDA** | -9.46 | 0.31 | 9.77 | 3.104 | 134.173 | -2.746 | 5.885 | 0.205 | -4.575 | 4.575 | 0.248 |
| | | | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | | |
| **QL** | -7.20 | -2.74 | 4.46 | 4.651 | 93.002 | -1.097 | 2.230 | 0.448 | -4.970 | 4.970 | 0.455 |
| **QLD** | -7.36 | -2.82 | 4.51 | 6.487 | 123.068 | -1.562 | 2.270 | 0.441 | -5.090 | 5.490 | 0.421 |
| **QLDA** | -7.33 | -3.30 | 4.03 | 3.401 | 131.698 | -2.098 | 2.015 | 0.496 | -5.315 | 5.315 | 0.418 |
| | | | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | | |
| **QL** | -7.35 | -2.93 | 4.42 | 4.776 | 79.355 | -2.783 | 2.210 | 0.452 | -5.140 | 5.140 | 0.421 |
| **QLD** | -7.33 | -2.82 | 4.51 | 3.748 | 114.015 | -3.097 | 2.255 | 0.443 | -5.075 | 5.075 | 0.427 |
| **QLDA** | -7.50 | -3.53 | 3.97 | 3.672 | 122.182 | -3.717 | 1.985 | 0.504 | -5.515 | 5.515 | 0.374 |
| | | | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | | | |
| **QL** | -6.57 | -3.60 | 2.97 | 4.642 | 104.412 | -2.298 | 1.485 | 0.673 | -5.085 | 5.085 | 0.645 |
| **QLD** | -6.54 | -3.48 | 3.06 | 3.681 | 140.928 | -2.246 | 1.530 | 0.654 | -5.010 | 5.010 | 0.650 |
| **QLDA** | -6.71 | -4.14 | 2.57 | 3.774 | 125.006 | -2.272 | 1.285 | 0.778 | -5.425 | 5.425 | 0.613 |

[a] μ is the dipole moment, MV is the Molecular Volume, TNC is the sum of the total negative charge, η is the global hardness, σ is the global softness, π is the chemical potential, χ is the electronegativity and ΔN is the fraction of the electrons transferred.

**Table 12.** The calculated quantum chemical parameters[a] for protonated compounds in water solution.

| Method and molecule | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) | dipole moment μ (D) | Molecular volume MV ($cm^3$/mol) | sum of the total negative charge (e) | global hardness η (eV) | Softness σ ($eV^{-1}$) | chemical potential Pi (eV) | Electronegativity χ (eV) | fraction of electrons transferred ΔN (e) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **MP2/3-21G** | | | | | | | | | | | |
| **QL** | -9.47 | 0.67 | 10.14 | 5.170 | 90.362 | -2.471 | 5.070 | 0.197 | -4.400 | 4.400 | 0.256 |
| **QLD** | -9.48 | 0.67 | 10.15 | 3.872 | 103.717 | -3.131 | 5.075 | 0.197 | -4.405 | 4.405 | 0.256 |
| **QLDA** | -9.60 | -0.14 | 9.46 | 2.876 | 95.310 | -3.705 | 4.730 | 0.211 | -4.870 | 4.870 | 0.255 |
| | | | | | | | | | | | |
| **MP2/6-31G(d,p)** | | | | | | | | | | | |
| **QL** | -9.27 | 0.69 | 9.96 | 5.092 | 100.433 | -2.177 | 4.980 | 0.201 | -4.290 | 4.290 | 0.272 |
| **QLD** | -9.28 | 0.75 | 10.03 | 3.855 | 113.590 | -2.737 | 5.015 | 0.199 | -4.265 | 4.265 | 0.273 |
| **QLDA** | -9.42 | -0.29 | 9.13 | 3.438 | 126.618 | -3.432 | 4.565 | 0.219 | -4.855 | 4.855 | 0.235 |
| | | | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | | |
| **QL** | -9.33 | 0.99 | 10.32 | 5.108 | 119.635 | -1.639 | 5.160 | 0.194 | -4.170 | 4.170 | 0.274 |
| **QLD** | -9.33 | 1.11 | 10.44 | 3.935 | 129.998 | -2.068 | 5.220 | 0.192 | -4.110 | 4.110 | 0.277 |
| **QLDA** | -9.46 | 0.31 | 9.77 | 3.104 | 134.173 | -2.746 | 5.885 | 0.205 | -4.575 | 4.575 | 0.248 |
| | | | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | | |
| **QL** | -7.20 | -2.74 | 4.46 | 4.651 | 93.002 | -1.097 | 2.230 | 0.448 | -4.970 | 4.970 | 0.455 |
| **QLD** | -7.36 | -2.82 | 4.51 | 6.487 | 123.068 | -1.562 | 2.270 | 0.441 | -5.090 | 5.490 | 0.421 |
| **QLDA** | -7.33 | -3.30 | 4.03 | 3.401 | 131.698 | -2.098 | 2.015 | 0.496 | -5.315 | 5.315 | 0.418 |
| | | | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | | |
| **QL** | -7.35 | -2.93 | 4.42 | 4.776 | 79.355 | -2.783 | 2.210 | 0.452 | -5.140 | 5.140 | 0.421 |
| **QLD** | -7.33 | -2.82 | 4.51 | 3.748 | 114.015 | -3.097 | 2.255 | 0.443 | -5.075 | 5.075 | 0.427 |
| **QLDA** | -7.50 | -3.53 | 3.97 | 3.672 | 122.182 | -3.717 | 1.985 | 0.504 | -5.515 | 5.515 | 0.374 |
| | | | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | | | |
| **QL** | -6.57 | -3.60 | 2.97 | 4.642 | 104.412 | -2.298 | 1.485 | 0.673 | -5.085 | 5.085 | 0.645 |
| **QLD** | -6.54 | -3.48 | 3.06 | 3.681 | 140.928 | -2.246 | 1.530 | 0.654 | -5.010 | 5.010 | 0.650 |
| **QLDA** | -6.71 | -4.14 | 2.57 | 3.774 | 125.006 | -2.272 | 1.285 | 0.778 | -5.425 | 5.425 | 0.613 |

[a] μ is the dipole moment, MV is the Molecular Volume, TNC is the sum of the total negative charge, η is the global hardness, σ is the global softness, π is the chemical potential, χ is the electronegativity and ΔN is the fraction of the electrons transferred

**Table 13**. The calculated condensed Fukui functions for electrophilic attack ($f^-$) for the non-protonated species in water solution.

| method and molecule | Atom of interest | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C2 | N3 | C4 | C5 | C6 | C7 | C8 | C9 | **C10** |
| **MP2/3-21G** | | | | | | | | | |
| **QL** | | 12.10 | 3.02 | 8.77 | 10.99 | 22.72 | 10.16 | 7.90 | **23.41** |
| **QLD** | 1.16 | 12.80 | 4.34 | 6.26 | 10.19 | 22.24 | 12.51 | 5.88 | **23.51** |
| **QLDA** | | 10.42 | 2.13 | 10.78 | 10.91 | 23.37 | 8.47 | 9.38 | **23.21** |
| | | | | | | | | | |
| **MP2/6-31G** | | | | | | | | | |
| **QL** | | 11.91 | 2.48 | 8.85 | 10.43 | 23.10 | 10.31 | 7.93 | **23.77** |
| **QLD** | 2.16 | 12.61 | 3.78 | 6.17 | 9.61 | 22.60 | 12.88 | 5.75 | **23.89** |
| **QLDA** | | 10.14 | 1.80 | 10.77 | 10.44 | 23.78 | 8.63 | 9.38 | **23.45** |
| | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | |
| **QL** | 1.52 | 10.06 | 2.56 | 8.23 | 9.56 | 23.49 | 11.40 | 8.32 | **24.20** |
| **QLD** | 3.88 | 10.59 | 4.65 | 4.42 | 8.33 | 22.67 | 15.62 | 4.84 | **23.79** |
| **QLDA** | | 8.82 | 1.75 | 10.16 | 9.62 | 23.90 | 9.56 | 10.02 | **23.91** |
| | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | |
| **QL** | 1.29 | 10.49 | 2.65 | 8.45 | 10.15 | 23.86 | 9.85 | 8.33 | **24.07** |
| **QLD** | 2.19 | 11.35 | 3.86 | 6.04 | 9.56 | 23.14 | 11.91 | 6.45 | **24.25** |
| **QLDA** | 1.19 | 9.22 | 2.15 | 9.53 | 9.72 | 24.35 | 9.09 | 8.99 | **24.13** |
| | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | |
| **QL** | 1.26 | 10.30 | 2.29 | 8.64 | 10.01 | 24.07 | 9.83 | 8.29 | **24.42** |
| **QLD** | 2.25 | 11.12 | 3.29 | 6.45 | 9.39 | 23.40 | 11.87 | 6.46 | **24.51** |
| **QLDA** | 1.17 | 8.88 | 1.68 | 9.95 | 9.60 | 24.58 | 8.94 | 9.08 | **24.38** |
| | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | |
| **QL** | 1.33 | 9.97 | 2.39 | 8.74 | 9.63 | 24.31 | 9.56 | 8.47 | **24.56** |
| **QLD** | 2.07 | 10.88 | 3.49 | 6.51 | 9.10 | 23.58 | 11.44 | 6.75 | **24.81** |
| **QLDA** | 1.24 | 8.58 | 1.85 | 10.04 | 9.06 | 24.78 | 8.70 | 9.18 | **24.61** |

**Table 14**. The calculated condensed Fukui functions for nucleophilic attack ($f^{+}$) for the non-protonated species in water solution.

| **Method and molecule** | **Atom of interest** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | N3 | C4 | C5 | C6 | C7 | C8 | C9 | C10 | C11 | O12 | **O13** |
| **MP2/3-21G** | | | | | | | | | | | |
| **QL** | 15.92 | 10.39 | 8.03 | 22.94 | 14.56 | 5.34 | 8.70 | 13.73 | | | |
| **QLD** | 14.48 | 9.18 | 9.46 | 22.59 | 15.21 | 4.70 | 9.47 | 13.91 | | | |
| **QLDA** | 20.37 | 16.00 | | 14.97 | 7.02 | 8.99 | 2.06 | 9.97 | 8.82 | 6.41 | **1.52** |
| | | | | | | | | | | | |
| **MP2/6-31G** | | | | | | | | | | | |
| **QL** | 15.87 | 11.89 | 7.58 | 23.85 | 13.81 | 5.01 | 8.51 | 12.70 | | | |
| **QLD** | 14.28 | 10.33 | 9.25 | 23.62 | 14.54 | 4.27 | 9.46 | 12.87 | | | |
| **QLDA** | 20.12 | 16.30 | | 13.13 | 5.39 | 8.54 | 1.54 | 8.43 | 13.06 | 7.21 | **1.60** |
| | | | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | | |
| **QL** | 13.65 | 11.52 | 8.83 | 22.69 | 13.84 | 5.49 | 9.07 | 13.04 | | | |
| **QLD** | 12.01 | 9.70 | 10.78 | 22.31 | 14.57 | 4.56 | 10.20 | 13.31 | | | |
| **QLDA** | 17.58 | 17.92 | | 15.44 | 7.69 | 9.39 | 2.48 | 9.55 | 8.83 | 4.75 | **1.12** |
| | | | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | | |
| **QL** | 16.37 | 12.23 | 7.56 | 22.82 | 13.03 | 5.81 | 7.77 | 12.47 | | | |
| **QLD** | 14.88 | 10.75 | 9.22 | 22.34 | 13.78 | 5.23 | 8.44 | 12.74 | | | |
| **QLDA** | 19.28 | 15.73 | | 14.26 | 6.11 | 8.48 | 2.43 | 9.29 | 9.66 | 7.61 | **2.34** |
| | | | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | | |
| **QL** | 14.96 | 13.36 | 8.89 | 22.15 | 12.43 | 5.99 | 7.91 | 12.60 | | | |
| **QLD** | 13.85 | 11.01 | 10.02 | 22.43 | 13.40 | 5.29 | 8.88 | 12.67 | | | |
| **QLDA** | 18.35 | 16.30 | | 13.83 | 5.11 | 8.66 | 2.15 | 9.14 | 11.66 | 7.84 | **2.47** |
| | | | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | | | |
| **QL** | 16.06 | 12.51 | 7.56 | 23.08 | 12.75 | 5.82 | 7.68 | 12.46 | | | |
| **QLD** | 14.40 | 10.54 | 9.64 | 22.57 | 13.74 | 5.02 | 8.59 | 12.73 | | | |
| **QLDA** | 18.88 | 15.35 | | 13.68 | 5.34 | 8.37 | 2.36 | 9.22 | 10.45 | 8.49 | **2.83** |
| | | | | | | | | | | | |

**Table 15**. The calculated condensed Fukui functions for electrophilic attack ($f^{-}$) for the protonated species in water solution.

| **Method and molecule** | **Atom of interest** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C1 | C2 | N3 | C5 | C6 | C7 | C8 | C9 | C10 |
| **MP2/3-21G(d,p)** | | | | | | | | | |
| **QL** | 1.20 | 3.20 | 7.95 | 9.50 | 5.12 | 26.51 | 12.07 | 6.54 | 27.75 |
| **QLD** | 1.18 | 3.80 | 7.91 | 8.71 | 4.79 | 26.74 | 12.85 | 5.95 | 27.96 |
| **QLDA** | 1.17 | 3.65 | 7.73 | 9.08 | 5.14 | 26.90 | 12.74 | 6.04 | 27.47 |
| | | | | | | | | | |
| **MP2/6-31G** | | | | | | | | | |
| **QL** | 1.43 | 3.50 | 7.72 | 9.59 | 5.01 | 26.48 | 12.07 | 6.51 | 27.67 |
| **QLD** | 1.64 | 3.76 | 7.44 | 9.37 | 4.61 | 26.72 | 12.00 | 6.44 | 27.98 |
| **QLDA** | 1.08 | 4.19 | 7.54 | 8.80 | 5.04 | 27.01 | 13.24 | 5.75 | 27.28 |
| | | | | | | | | | |
| **RHF/ 6-31G(d.p)** | | | | | | | | | |
| **QL** | 2.17 | 2.85 | 6.89 | 10.14 | 4.73 | 26.01 | 10.90 | 8.20 | 27.67 |
| **QLD** | 3.95 | 2.44 | 6.22 | 11.03 | 4.29 | 25.88 | 9.11 | 9.25 | 27.92 |
| **QLDA** | 1.55 | 3.27 | 7.05 | 9.29 | 4.72 | 26.35 | 12.35 | 7.52 | 27.40 |
| | | | | | | | | | |
| **B3LYP/6-31G(d.p)** | | | | | | | | | |
| **QL** | 2.01 | 3.52 | 7.37 | 9.23 | 5.24 | 27.29 | 10.77 | 7.01 | 27.00 |
| **QLD** | 16.46 | 12.94 | | 22.21 | 1.16 | 1.67 | 9.19 | 15.99 | |
| **QLDA** | 2.07 | 3.76 | 7.07 | 9.09 | 5.00 | 27.47 | 10.99 | 6.89 | 26.90 |
| | | | | | | | | | |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | |
| **QL** | 1.95 | 3.41 | 7.28 | 9.47 | 5.34 | 27.29 | 10.70 | 7.06 | 27.08 |
| **QLD** | 2.16 | 3.53 | 7.12 | 9.47 | 5.04 | 27.43 | 10.47 | 7.13 | 27.21 |
| **QLDA** | 2.02 | 3.70 | 6.95 | 9.27 | 5.06 | 27.54 | 10.96 | 6.92 | 27.06 |
| | | | | | | | | | |
| **BP86/CEP-31G** | | | | | | | | | |
| **QL** | 2.14 | 3.70 | 7.02 | 9.34 | 5.11 | 27.54 | 10.52 | 6.97 | 27.04 |
| **QLD** | 2.20 | 3.83 | 6.97 | 9.17 | 4.88 | 27.67 | 10.54 | 6.87 | 27.16 |
| **QLDA** | 2.33 | 3.93 | 6.63 | 9.30 | 4.78 | 27.67 | 10.58 | 6.91 | 27.08 |

**Table 16**. The calculated condensed Fukui functions for nucleophilic attack ($f^{+}$) for the protonated species in water solution.

| **Method and molecule** | **Atom of interest** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C1 | C2 | N3 | C4 | C5 | C6 | C7 | C8 | C9 | C10 |
| **MP2/3-21G** | | | | | | | | | | |
| **QL** | | 3.73 | 13.37 | 20.62 | 3.52 | 30.18 | 10.01 | 2.50 | 9.53 | 6.27 |
| **QLD** | | 3.84 | 12.46 | 19.52 | 3.89 | 30.12 | 9.92 | 2.16 | 9.55 | 5.86 |
| **QLDA** | 2.69 | 2.29 | 15.28 | 23.24 | | 22.77 | 5.76 | 4.06 | 5.02 | 4.81 |
| **MP2/6-31G** | | | | | | | | | | |
| **QL** | | 4.34 | 12.40 | | 3.20 | 30.39 | 9.84 | 2.42 | 9.38 | 5.82 |
| **QLD** | | 4.31 | 11.56 | 21.05 | 3.93 | 30.24 | 9.92 | 2.03 | 9.53 | 5.61 |
| **QLDA** | 3.23 | 2.77 | 14.16 | 23.39 | | 20.92 | 4.95 | 4.10 | 4.49 | 4.14 |
| **RHF/ 6-31G(d.p)** | | | | | | | | | | |
| **QL** | | 4.40 | 11.84 | 21.21 | 4.32 | 29.78 | 9.27 | 2.72 | 9.37 | 5.94 |
| **QLD** | | 4.03 | 11.07 | 20.90 | 5.32 | 29.42 | 9.51 | 2.33 | 9.42 | 5.96 |
| **QLDA** | 2.78 | 3.50 | 13.43 | 23.36 | | 24.21 | 6.05 | 4.10 | 5.42 | 4.61 |
| **B3LYP/6-31G(d.p)** | | | | | | | | | | |
| **QL** | 1.22 | 4.36 | 15.22 | 21.59 | 3.33 | 28.15 | 8.43 | 3.37 | 8.26 | 5.60 |
| **QLD** | | 2.05 | 16.26 | 4.32 | 4.58 | 12.94 | 17.96 | 13.61 | 3.70 | 21.90 |
| **QLDA** | 3.42 | 3.58 | 16.13 | 21.56 | | 20.66 | 4.82 | 4.59 | 5.09 | 4.48 |
| **B3LYP/6-31G ++(d.p)** | | | | | | | | | | |
| **QL** | 1.36 | 4.20 | 13.83 | 22.30 | 4.06 | 28.06 | 8.18 | 3.50 | 8.31 | 5.71 |
| **QLD** | | 4.12 | 13.47 | 21.20 | 4.22 | 28.28 | 8.41 | 3.15 | 8.40 | 5.58 |
| **QLDA** | 3.64 | 3.27 | 15.30 | 21.80 | | 20.41 | 4.33 | 4.81 | 4.84 | 4.46 |
| **BP86/CEP-31G** | | | | | | | | | | |
| **QL** | 1.46 | 4.24 | 15.10 | 21.69 | 3.43 | 27.97 | 8.22 | 3.57 | 8.11 | 5.63 |
| **QLD** | 1.05 | 4.07 | 14.22 | 20.75 | 4.33 | 27.56 | 8.56 | 3.17 | 8.29 | 5.63 |
| **QLDA** | 3.82 | 3.56 | 16.01 | 21.19 | | 19.57 | 4.23 | 4.88 | 4.85 | 4.45 |

**Table 17.** The calculated quantum chemical parameters for the Fe- inhibitor complexes (DFT/B3LYP/6-31G ++(d, p) results *in vacuo*).

| **Quantum parameters** | **Molecules** | | |
|---|---|---|---|
| | QL | QLD | QLDA |
| Interaction energy (eV) | -1.653 | -1.529 | -2.211 |
| $E_{HOMO}$ (eV) | -4.03 | -3.85 | -4.42 |
| $E_{LUMO}$ (eV) | -2.21 | -2.06 | -2.29 |
| ΔE (eV) | 1.82 | 1.79 | 2.13 |
| dipole moment, μ (D) | 4.530 | 4.287 | 1.911 |
| molecular volume ,MV ($cm^3$/mol) | 95.4 | 138.7 | 167.9 |
| sum of the total negative charge, TNC (e) | -3.130 | -4.227 | -3.744 |
| global hardness, η (eV) | 0.910 | 0.895 | 1.065 |
| global softness, σ ($eV^{-1}$) | 1.099 | 1.117 | 0.939 |
| chemical potential, Pi (eV) | -3.120 | -2.955 | -3.355 |
| electronegativity, χ (eV) | 3.120 | 2.955 | 3.355 |
| fraction of electrons transferred, ΔN (e) | 2.132 | 2.260 | 1.711 |