

Scientific paper

# Chemical Reactivity of Quinmerac Herbicide Through the Fukui Function

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## Abstract

In the present work we have calculated DFT reactivity descriptors for quinmerac (7-chloro-3-methylquinoline-8-carboxylic acid) at the MP2/6-311++G(d,p)//B3LYP/6-311++G(2d,2p) level of theory to analyze its reactivity. Reactivity descriptors such as ionization energy, molecular hardness, electrophilicity, condensed Fukui function and total energies were calculated to predict changes in its reactivity. The Fukui function values predict that electrophilic and free radical attacks on quinmerac might cause aromatic substitutions, while nucleophilic attacks would cause cleavage of the C=N bond.

**Keywords:** quinmerac, Fukui function, DFT, MP2, PCM.

## 1. Introduction

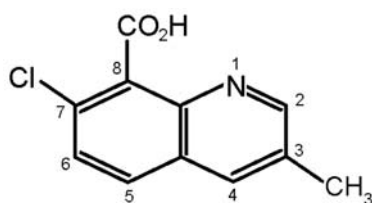
Nowadays, the use of herbicides is the cheapest and most reliable way of chemical control of weeds. Although there are different kinds of herbicides according to their action mode, auxinic herbicides are the most widely used because they were the first selective herbicides developed.<sup>1,2</sup> Quinmerac, 7-chloro-3-methylquinoline-8-carboxylic acid (see Figure 1), is a herbicide with auxinic activity. It is used for the postemergence control of cleavers, speedwells and other broad-leaved weeds in cereals, oil-seed rape and sugar beet.<sup>3</sup> Quinmerac has shown positive effects to increase fruit set in tomatoes (*Lycopersicon esculentum*),<sup>4</sup> to improve fruit size and quality in several citrus species,<sup>5</sup> olives, and peaches.<sup>6</sup> Moreover, because of its effectiveness to control weeds, quinmerac is being considered to increase yield in crops such as coffee (*Coffea arabica*).<sup>7</sup>

Some reports suggest that quinmerac is absorbed primarily via the root system but it can also be absorbed from the foliage too.<sup>3,9,10</sup> Thus, its mode of action has been proposed as a root growth inhibition.<sup>3,9,10</sup> In other reports it has been suggested that quinmerac stimulates H<sub>2</sub>O<sub>2</sub> generation which contributes to the induction of cell

death in Galium leaves. This overproduction of H<sub>2</sub>O<sub>2</sub> could be triggered by the decline of photosynthetic activity due to ABA-mediated stomatal closure.<sup>1</sup> Additionally, it has been reported that quinmerac stimulates the ethylene biosynthesis causing the growth inhibition in sensitive weeds.<sup>11</sup> However, the molecular basis of its mode of action are still unknown.<sup>2,8</sup>

In recent years, there have been major concerns about quinmerac herbicide residues and associated food safety issues, their negative impacts on the environment and the increasing occurrence of herbicide resistance in weed populations.<sup>12,13</sup> A recent study suggests that a combination of metamitron and quinmerac is toxic to algae, aquatic invertebrates and higher aquatic plants.<sup>14</sup> Thus, this herbicide is prohibited to be used in or near to surface waters or coastal waters.<sup>14</sup> Also, a combination of quinmerac with chloridazon may cause sensitization by skin contact toxic to aquatic organisms and it may cause long-term adverse effects in aquatic environments.<sup>15</sup> It is also important to mention here that quinmerac has been found in groundwater, surface water, and drinking water<sup>16</sup> and it is considered as an emerging water contaminant.<sup>17–21</sup> Recently, it was reported that quinmerac is stable to hydrolysis at pH 5 to 9 and a direct aqueous photolysis under artificial light simulating summer sunlight at 54

°C showed that quinmerac is slowly degraded.<sup>22</sup> Also, the efficiency of the photocatalytic degradation of quinmerac in aqueous TiO<sub>2</sub> suspensions was studied as a function of the light source, TiO<sub>2</sub> loading, pH, temperature, electron acceptors, and hydroxyl radical (•OH) scavenger.<sup>21</sup> The results indicated that quinmerac degradation led to the formation of organic intermediates and ionic subproducts and the rate of its degradation increases with the amount of free radicals •OH in solution.<sup>21</sup> In addition, it was found that UV light is effective for quinmerac degradation through a decarboxylation reaction in presence of titanium oxide, however this reaction leads to the formation of subproducts whose environmental dangerousness is still not well known.<sup>23</sup> Unfortunately, information on degradation and metabolic pathways of quinmerac in water is limited, since the main information is related to its absorption in soils and plant metabolism.<sup>1</sup> Therefore, there is an urgent need to understand the quinmerac reactivity for developing new methods for its removal from water. To our knowledge, a quantum chemical study of quinmerac to evaluate the global and local reactivity descriptors of this herbicide is still missing. Thus, in the present work we have analyzed the molecular reactivity of quinmerac through global reactivity descriptors and the Fukui Function derived from the Density Functional Theory (DFT). We consider that this study will contribute to get a better understanding of its chemical behavior, in the gas and solution phases of this important chemical herbicide.



**Figure 1.** 7-chloro-3-methylquinoline-8-carboxylic acid. IUPAC name of quinmerac.

## 2. Theory

From DFT it is possible to define molecular stability and reactivity descriptors such as the electronic chemical potential ( $\mu$ ), absolute hardness ( $\eta$ ), and global electrophilicity index ( $\omega$ ).<sup>24–30</sup> The electronic chemical potential  $\mu$  was originally defined by Parr and Pearson as:<sup>31</sup>

$$\mu = -\frac{1}{2}(I + A) \quad (1)$$

where,  $\mu$  is defined as the negative of the electronegativity of atoms and molecules,  $I$  and  $A$  are the vertical ionization potential energy and the vertical electron affinity respecti-

vely. On the other hand, the absolute hardness can be evaluated through the following equation:<sup>24–30</sup>

$$\eta = I - A \quad (2)$$

Also, the global electrophilicity index  $\omega$  introduced by Parr et al. can be calculated using the electronic chemical potential  $\mu$  and the chemical hardness  $\eta$ .<sup>32</sup>

$$\omega = \frac{\mu^2}{2\eta} \quad (3)$$

According to the equation (3)  $\omega$  measures the tendency of chemical species to accept electrons. Thus, a good nucleophile is characterized by low values of  $\mu$  and  $\omega$  while a good electrophile has high values of  $\mu$  and  $\omega$ .<sup>33</sup> On the other hand, the hard and soft acids and bases principle (HSAB) has been useful to predict the reactivity of some chemical systems.<sup>34–41</sup> The HSAB principle has been used in a local sense in terms of DFT local properties such as the Fukui function  $f(\vec{r})$ .<sup>42,43</sup> Gázquez and Méndez proved that sites in chemical species with the largest values of the Fukui Function  $f(\vec{r})$  are those with higher reactivity.<sup>42,43</sup> According to Parr and Yang, the Fukui function can be written as:<sup>44</sup>

$$f(\vec{r}) = \left( \frac{\partial \rho(\vec{r})}{\partial N} \right)_v, \quad (4)$$

where  $\rho(\vec{r})$  is the electronic density,  $N$  is the number of electrons and  $n$  is the external potential exerted by the nuclei. The Fukui function is a local reactivity descriptor that indicates the preferred regions where a chemical species will change its density when the number of electrons is modified.<sup>45–50</sup> Different procedures have been reported in the literature to calculate the change in the electronic density on each atom.<sup>46–53</sup> Bultinck et al. proposed that the density of an atom may be evaluated as:

$$\rho_A(\vec{r}, N) = w_A(\vec{r}, N) \rho(\vec{r}, N) \quad (7)$$

Where  $w_A(\vec{r}, N)$  is a weight function dependent on the number of electrons contained in the molecule. Thus, this weight function will be different whether the molecule has  $N$ ,  $N-dN$  or  $N+dN$  electrons even if the geometry is the same. Also, it is important to mention that the weight functions for all atoms always sum to the unity, and that usually a positive definite weight function is used.<sup>54,55</sup>

$$\sum_A^M w_A(\vec{r}, N) = 1 \quad (8)$$

Also, Bultinck *et al.* have proposed that the condensed Fukui function can be computed using either the *fragment of molecular response* (FMR) approach or the *res-*

ponse of molecular fragment (RMF) approach.<sup>55</sup> In the Mulliken approach, the weight factor proposed from Bultinck et al is not dependent on the number of electrons and the two approaches lead to same expressions to evaluate the condensed Fukui function. Here it is convenient to remember that Mulliken charges and Natural charges are both based on orbital occupancies and similar expressions may be used to evaluate the condensed Fukui function. Thus, under these conditions, it is possible to define the corresponding condensed or atomic Fukui function on the atom A for an electrophilic attack as:<sup>55</sup>

$$\begin{aligned} f_A^-(\bar{r}) &= \int w_A^M(\bar{r}) [\rho(\bar{r}, N) - \rho(\bar{r}, N-1)] d\bar{r} = \\ &= \int [\rho_A(\bar{r}, N) - \rho_A(\bar{r}, N-1)] d\bar{r} = \\ &= P_A(\bar{r}, N) - P_A(\bar{r}, N-1) = \\ &= q_A(\bar{r}, N-1) - q_A(\bar{r}, N) \end{aligned} \quad (9)$$

Where  $P_A(\bar{r}, N)$  is the population on the atom A in the molecule with  $N$  electrons, and it can be evaluated through

$$P_A(\bar{r}, N) = \int \rho_A(\bar{r}, N) d\bar{r}, \quad (10)$$

and  $q_A(\bar{r}, N)$  is the atomic charge on the atom A for the molecule with  $N$  electrons. Note that the equation (9) is the atom condensed Fukui function introduced by Yang and Mortier.<sup>47</sup> The nucleophilic attack is given by:

$$f_A^+(\bar{r}) = q_A(\bar{r}, N) - q_A(\bar{r}, N+1), \quad (11)$$

For a free radical attack the expression is given by:

$$f_A^0(\bar{r}) = \frac{1}{2} (q_A(\bar{r}, N-1) - q_A(\bar{r}, N+1)) \quad (12)$$

It is important to mention that independently of the approximations used to calculate the Fukui function, all of them follow the exact closure equation:<sup>34</sup>

$$\int f(r) dr = 1 \quad (13)$$

which is important for the use of the Fukui function as an intramolecular reactivity index.

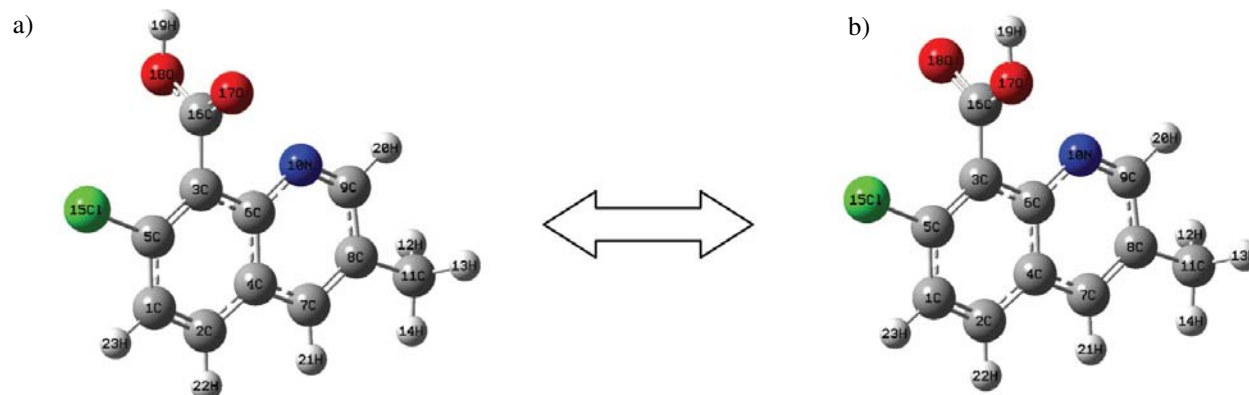
### 3. Methodology

A starting geometry was generated using the PM6 method<sup>56</sup> implemented in Mopac2012.<sup>57</sup> The optimal conformation was subjected to full geometry reoptimization in the gas phase employing the hybrid functional B3LYP<sup>58–60</sup> and the basis set 6-311++G(2d,2p).<sup>61,62</sup> The optimized herbicides in the gas phase were further reoptimized at the B3LYP/6-311++G(2d,2p) level employing the PCM solvation model.<sup>63,64</sup> The vibrational frequencies were computed to make sure that the stationary points were minima in the potential energy surface. In our calculations a Møller-Plesset correction energy correlation was performed employing the second order Moller Plesset's theory (MP2)<sup>65</sup> with the basis set 6-311++G(d,p) level of theory using the optimized B3LYP/6311++G(2d,2p) geometries. All the calculations here reported were done with the package Gaussian 03<sup>66</sup> and visualized with the GaussView V. 2.08<sup>67</sup> and Gabedit<sup>68</sup> packages, using a cluster with 13 Xeon 3.0 GHZ cores and 7 GB of memory.

## 4. Results and Discussion

### 4.1. Geometry Optimization

Quinmerac was first optimized at the B3LYP/6-311++G(2d,2p) level in the gas phase. Note that this mo-



**Figure 2.** Optimized structures of quinmerac in the gas phase, a) conformer I with the bond distances in Angstroms of 1C-2C = 1.37, 2C-4C=1.42, 4C-6C=1.42, 6C-3C=1.42, 3C-5C=1.37, 5C-15Cl=1.75, 3C-16C=1.50, 6C-10N=1.36, 10N-9C=1.31, 9C-8C=1.42, 8C-7C=1.37, 1C-23H=1.08, 2C-22H=1.08, 7C-21H=1.08, 8C-11C=1.05, 11C-12H=1.09, 11C-13H=1.09, 11C-14H=1.09, 3C-16Cl=1.50, 16C-18O=1.35, 18O-19H=0.97, angles 5C-3C-16C=122.28, 9C-8C-11C=120.02, dihedral angles 5C-3C-16C-17O=85.46 and 5C-3C-16C-18O=–93.90. b) structure of conformer II, all bond lengths and angles are similar to those obtained for the conformer I.

lecule can show two possible conformers as shown in Figure 2a and 2b. The total energy calculated for the conformer I depicted in Figure 2a, was  $-1089.62841514$  hartrees, while its HOMO-LUMO gap was 4.68 eV. The energy for conformer II was  $-1089.62841514$  hartrees and its HOMO-LUMO gap is 4.68 eV predicting that both structures are equivalent.

In order to analyze the effect of water on the electronic properties of quinmerac, the optimized structures in the gas phase were used as starting point to reoptimize them at the B3LYP/6-311++G(2d,2p) level without any symmetry constraints employing the PCM solvation model. In this model, the solvent is considered as an unstructured polarizable continuum characterized by its dielectric constant (78.5 for water at 25 °C). The total energy and gap values for conformer I are  $-1089.65308821$  and 4.72 eV respectively. No differences in total energy and in the gap values were obtained for second conformer in comparison to the conformer I. The energy difference between the conformers in the gas and aqueous phases is  $15.48 \text{ kcal mol}^{-1}$  which corresponds to the solvation energy of quinmerac. It is important to mention that there were not obtained significant differences, neither in distances nor angles, when the solvent effect was considered. Moreover, the bond distances were similar to those measured by experimental techniques for similar quinolic compounds.<sup>69</sup> Unfortunately, up to our knowledge, the experimental geometry of quinmerac has not been reported. In all the cases a frequency analysis was carried out to verify that the optimized geometry is a minimum. The frequency values obtained are positive and they are coincident with those reported in the literature for quinolinic molecules.<sup>70</sup>

In Table 1, we report the values of the electronic energies calculated for quinmerac with the charges +1, 0 and -1 at the MP2/6-311++G(d,p)//B3LYP/6-311++G(2d,2p) level of theory. MP2 calculations were carried out to improve the evaluation of the energy correlation calcu-

lated at the B3LYP/6-311++G(2d,2p) level. From the values calculated at the MP2 level, it can be observed that there is not energy difference between the conformer I and II in the gas or aqueous phase. However the energy difference between the conformers in the gas and aqueous phases is  $15.43 \text{ kcal mol}^{-1}$ .

The global reactivity descriptors for quinmerac were calculated from the values reported in Table 1. The value of the vertical electron affinity energy is calculated as  $A = E(N + 1) - E(N)$  where  $E(N)$  and  $E(N + 1)$  are the total ground-state energies in the neutral  $N$  and singly charged ( $N + 1$ ) configurations while the vertical ionization potential can be calculated as  $I = E(N - 1) - E(N)$ . The values of  $\mu$ ,  $\eta$ ,  $\omega$  were calculated employing the equations 1, 2 and 3 respectively, see Table 2. From the values reported in this table, it may be observed that the value of the global hardness decreases when the solvent effect is taken into account. Although this result may suggest a bigger stability of quinmerac in aqueous phase, it has to be considered that the value of the hardness must be evaluated at the same phase to be compared. Thus, a direct comparison of the values of  $\mu$  at different phases is not an absolute criterion of chemical stability. Note that the value of  $\mu$  is bigger in solution in comparison to the gas phase suggesting that the electrophilic behavior increases on quinmerac in presence of water.

## 4. 2. Condensed Fukui Function

Reactivity indexes derived from DFT theory have been successfully applied in describing and understanding chemical reactivity by defining atomic reactivity indexes, such as the condensed Fukui function which works even when FMO theory sometimes fails in its predictions.<sup>46</sup> We employed the equations 9–12 to calculate the values of the Fukui function atom by atom for electrophilic, nucleophilic and free radical attacks. However, it is important to mention that the value of this function is dependent on the

**Table 1.** Electronic energies in hartrees for quinmerac at the MP2/6-311++G(d,p)//B3LYP/6-311++G(2d,2p) level.

Phase	Charge +1 (multiplicity=2)	Charge 0 (multiplicity =1)	Charge -1 (multiplicity =2)
Gas (Conformer I)	-1086.929807	-1087.284046	-1087.2687
Gas (Conformer II)	-1086.929811	-1087.284047	-1087.2687
Water (Conformer I)	-1087.010759	-1087.308639	-1087.3478
Water (Conformer II)	-1087.010756	-1087.308635	-1087.3478

**Table 2.** Reactivity descriptors for quinmerac at the level MP2/6-311++G(d,p)//B3LYP/6-311++G(2d,2p).

	I /eV	A /eV	HOMO /eV	LUMO /eV	$\Delta(H-L)$ /eV	$\eta$ /eV	$\mu$ /eV	$\omega$ /eV
Gas	9.64	0.42	-8.89	0.82	9.71	9.22	-5.03	1.37
Water	8.10	-1.06	-8.84	1.13	9.98	9.17	-3.52	0.68

scheme of charges used. A variety of schemes to evaluate atomic charges has been reported.<sup>46</sup> Most of them are based on some kind of population analysis. The arbitrariness in the way of choosing the charges has been one of the principal criticisms to the condensed Fukui function approximation.<sup>55,71</sup> Recently NBO charges have found good acceptance to calculate the condensed Fukui function and good agreement with the experimental results has been obtained as compared to electrostatic potentials and Hirshfeld charges.<sup>72–74</sup> In Table 3 we report the values of the condensed Fukui function obtained from NBO charges in the gas and aqueous phases and at the B3LYP/6-311++G(2d,2p) level of theory. From Table 3 it is possible to observe that at the DFT level in the gas phase the most electrophilic active site is located on C115. In the case of nucleophilic attacks, the most active site is on C7. For free radical attacks the most reactive site is on C16. In the aqueous phase C2, C7 and C2 are the more reactive sites for electrophilic, nucleophilic and free radical attacks, respectively. Additionally, we evaluated the Fukui function values at the MP2/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory. We carried out these calculations in order to compare the results provided by the B3LYP hybrid functional with those given by more sophisticated level of calculation as MP2 theory.<sup>65</sup> From the Fukui function values obtained at the MP2 level, see Table 4, it is possible to note some differences in comparison to those values obtained at the DFT level. Thus, in the gas phase C2, N10 and C3 are the more reactive sites for elec-

trophilic, nucleophilic and free radical attacks, respectively. In the aqueous phase the more reactive sites are located on C2, N10 and C2 atoms. Note that these results are different to those predicted from B3LYP calculations.

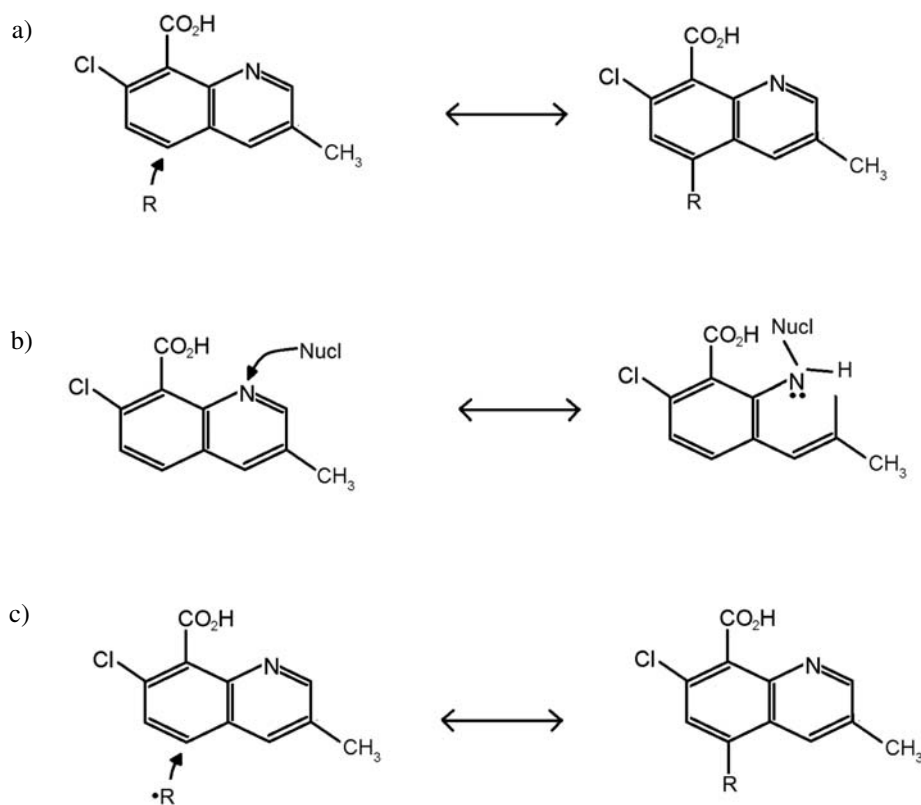
Last results indicate a strong influence of water on the reactivity showed by quinmerac. Additionally, we analyzed the influence of the chosen charge during the evaluation of the Fukui Function and we calculated it employing MEP and Mulliken charges, not shown. At the MP2 level the values of Fukui Function evaluated through MEP charges were similar to those calculated from NBO charges. The Fukui Function values calculated through Mulliken charges were not consistent with the tendencies reported by MEP and NBO charges. In summary, from MP2 calculations it is possible to predict that the most electrophilic site is located on C2. Under these conditions an electrophile would attack this position to make aromatic substitutions (Figure 3a). Consequently, dechlorination might not be the first step in this pathway reaction. A similar situation may be inferred for a free radical attack on C2 (Figure 3c). Although the N atom in the ring has been related to an electrophilic attack our studies suggest that this atom is a good site for a nucleophilic attack (see Figure 3b). This result agrees with some reports in the literature which indicate that a nucleophilic attack is possible on the heterocyclic nitrogen.<sup>75,76</sup> This is probably caused because the lone pair of electrons on nitrogen cannot be delocalized around the ring. It is interesting to highlight that nucleophilic attacks might cause the opening of the pyri-

**Table 3.** Values of the condensed Fukui Function in quinmerac computed from NBO charges according to equations (9, 11, 12) and at the level B3LYP/6-311++G(2d,2p).

ATOM	Gas			Aqueous		
	f <sup>-</sup>	f <sup>+</sup>	f <sup>0</sup>	f <sup>-</sup>	f <sup>+</sup>	f <sup>0</sup>
C1	0.000	0.054	0.027	-0.026	0.055	0.015
C2	0.125	0.115	0.120	<b>0.221</b>	0.109	<b>0.165</b>
C3	0.118	0.115	0.117	0.141	0.107	0.124
C4	0.005	-0.02	-0.008	-0.008	-0.008	-0.008
C5	0.06	0.034	0.047	0.071	0.055	0.063
C6	-0.022	-0.018	-0.02	-0.013	0.005	-0.004
C7	0.059	<b>0.134</b>	0.097	0.063	<b>0.153</b>	0.108
C8	0.116	0.045	0.08	0.128	0.028	0.078
C9	0.007	0.089	0.048	-0.003	0.122	0.06
N10	0.076	0.111	0.094	0.094	0.128	0.111
C11	-0.021	-0.015	-0.018	-0.019	-0.007	-0.013
H12	0.036	0.026	0.031	0.028	0.014	0.021
H13	0.036	0.026	0.031	0.028	0.015	0.021
H14	0.02	0.021	0.02	0.013	0.012	0.013
C115	<b>0.159</b>	0.086	<b>0.122</b>	0.134	0.056	0.095
C16	-0.021	-0.021	-0.021	-0.024	-0.013	-0.018
O17	0.086	0.044	0.065	0.06	0.031	0.046
O18	0.022	0.009	0.015	0.015	0.009	0.012
H19	0.024	0.028	0.026	0.013	0.012	0.012
H20	0.031	0.037	0.034	0.023	0.031	0.027
H21	0.027	0.033	0.03	0.025	0.031	0.028
H22	0.027	0.032	0.029	0.007	0.029	0.018

**Table 4.** Values of the condensed Fukui Function in quinmerac computed from NBO charges according to equations (9, 11, 12) and at the level B3LYP/6-311++G(2d,2p).

ATOM	Gas			Aqueous		
	$f^-$	$f^+$	$f^0$	$f^-$	$f^+$	$f^0$
C1	-0.080	0.061	-0.009	0.056	0.033	0.045
C2	<b>0.215</b>	0.085	0.150	<b>0.326</b>	0.065	<b>0.196</b>
C3	0.179	0.161	<b>0.170</b>	0.181	0.139	0.160
C4	0.024	-0.038	-0.007	-0.038	-0.025	-0.031
C5	0.151	0.019	0.085	0.041	0.031	0.036
C6	-0.065	-0.081	-0.073	-0.034	-0.054	-0.044
C7	0.035	0.147	0.091	0.079	0.163	0.121
C8	0.131	0.037	0.084	0.094	0.020	0.057
C9	-0.036	0.111	0.037	-0.032	0.147	0.058
N10	0.115	<b>0.195</b>	0.155	0.119	<b>0.238</b>	0.179
C11	-0.032	-0.016	-0.024	-0.019	-0.009	-0.014
H12	0.030	0.022	0.026	0.015	0.015	0.015
H13	0.030	0.023	0.026	0.016	0.015	0.015
H14	0.017	0.022	0.019	0.008	0.015	0.012
C115	0.128	0.073	0.101	0.070	0.050	0.060
C16	-0.044	-0.030	-0.037	-0.029	-0.018	-0.024
O17	0.056	0.047	0.052	0.035	0.031	0.033
O18	0.008	0.005	0.007	0.007	0.007	0.007
H19	0.024	0.023	0.023	0.012	0.011	0.011
H20	0.027	0.037	0.032	0.013	0.041	0.027
H21	0.025	0.035	0.030	0.021	0.036	0.029
H22	0.027	0.030	0.029	0.028	0.025	0.027
H23	0.036	0.031	0.034	0.030	0.023	0.027

**Figure 3.** Proposed mechanisms for a) electrophilic, b) nucleophilic and free radical attacks, according to the Fukui Function values reported in Table 3 obtained at the MP2/6-311++G(d,p)/B3LYP/6-311++G(2d,2p) level.

dine ring by cleavage of the C=N bond, see Figure 3b–c. This result is coincident with the reported by Pareja et al for quinclorac case since quinclorac has a similar structure to quinmerac.<sup>77</sup> Theoretical analyses of the proposed mechanisms are beyond of the scope of this paper; however they will be studied in future works.

## 5. Conclusions

In this work we have studied the quinmerac reactivity through reactivity descriptors at the MP2/6-311++G(d,p)//B3LYP/6-311++G(2d,2p) level of theory. The results indicate that the solvation modifies the values of the reactivity descriptors of quinmerac. Also, the electrophilic behavior of quinmerac increases in the aqueous phase. The values of the Fukui function indicated that the more reactive sites are located on C2, N10 and C2 for electrophilic, nucleophilic and free radical attacks, respectively and in aqueous conditions. These results indicated that an electrophilic or free radical attack on quinmerac might cause an aromatic substitution on 2C, while a nucleophilic attack would cause the cleavage of the C=N bond. The FF values predicted by NBO and MEP charges were equivalent while those obtained through Mulliken population did not show any tendency. The B3LYP functional fails to reproduce the values of the FF at the MP2 level. Last result indicates the evaluation of the energy correlation is an important factor to predict adequately the local reactivity of quinmerac herbicide.

## 6. Acknowledgments

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## Povzetek

Za quinmerac (7-kloro-3-metilkinolin-8-karboksilno kislino) smo izračunali DFT deskriptorje reaktivnosti, kot so ionizacijska energija, molekularna trdnost, elektrofilnost, Fukui funkcija in celokupna energija. Reaktivnost smo analizirali na MP2/6-311++G(d,p)//B3LYP/6-311++G(2d,2p) nivoju teorije. Vrednosti deskriptorjev reaktivnosti kažejo, da interakcija quinmeraca z vodo zmanjšuje njegovo reaktivnost. Velikost Fukui funkcije napoveduje, da napad elektrofilnih in prostih radikalov na quinmerac lahko povzroči aromatsko substitucijo, medtem ko nukleofilni napad napoveduje razcep C=N vezi.