

Research Article

Chemical Reactivity of Isoproturon, Diuron, Linuron, and Chlorotoluron Herbicides in Aqueous Phase: A Theoretical Quantum Study Employing Global and Local Reactivity Descriptors

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We have calculated global and local DFT reactivity descriptors for isoproturon, diuron, linuron, and chlorotoluron herbicides at the MP2/6-311++G(2d,2p) level of theory. The results suggest that, in aqueous conditions, chlorotoluron, linuron, and diuron herbicides may be degraded by elimination of urea moiety through electrophilic attacks. On the other hand, electrophilic, nucleophilic, and free radical attacks on isoproturon may cause the elimination of isopropyl fragment.

1. Introduction

Phenylurea herbicides (PUHs) are an important group of pesticides which have been broadly used in agriculture. These herbicides have been used for selective pre- and postemergence weed control on crops such as asparagus, beans, cotton, maize, fruit, and wheat [1–3]. Recently, PUHs have received particular attention because of their high biotoxicity and possible carcinogenic properties [4]. Also, it is important to mention that because of their low volatility, slow biodegradation, and low sorption in soils, PHUs have been frequently detected in surface, ground, and even drinking water [5], by which they have the potential to impact ground water quality [6]. Moreover, this kind of compounds requires several weeks to months for their removal from the environment [7], and they have been considered as priority hazardous substances [8].

Specifically, the PUHs 3-(4-isopropylphenyl)-1,1-dimethyl urea (isoproturon), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), 3-(3,4-diclorofenil)-1-metoxi-1-metilurea (linuron), and 3-(3-chloro-p-tolyl)-1,1-dimethylurea (chlorotoluron) are slowly degraded in water and are quite

persistent [8, 9], and it is increasingly common to find their parent compounds and metabolites in groundwater in concentrations exceeding the drinking water threshold limit of $0.1 \mu\text{g L}^{-1}$ [10, 11]. In animals, a long term exposure to large amounts of these PHUs has shown to cause tumors in kidneys, decreased red blood cells, liver enlargement, growth retardation, increased mortality, enlarged spleens, splenic hemosiderosis, and chronic methemoglobinemia, among others [12]. Although, there are so far no reported incidences of human poisoning, based on effects seen in animals, acute exposure to PHUs would be expected to cause mild skin irritation and headaches, drowsiness, and lack of coordination [13]. Thus, the efforts of many researchers have been focused on developing new and efficient remediation treatments to clean these phenylurea herbicides from the environment. Probably, Advanced Oxidation Processes (AOPs) [11, 14–22] and microbial [23–26] degradation methods are the preferred techniques to degrade this group of herbicides along with fungal degradation techniques [10, 27–29]. However, it has been reported that AOPs may produce harmful intermediates [30–32], while microbial and fungal degradation methods are

unable to degrade completely these PHUs [29, 33]. In soils, it has been observed that these herbicides may be degraded through demethylation at the urea nitrogen by mean enzymatic and microbial activity [34]. However, in aqueous conditions, the molecular basis for the initial degradation of these phenylurea herbicides remains unknown [35, 36].

Therefore, there is great interest in understanding the initial degradation pathways of this set of herbicides in order to develop new methods for degrading phenylurea herbicides in water. In this sense a detailed knowledge of the reactivity exhibited by isoproturon, diuron, linuron, and chlorotoluron at the molecular level may become fundamental to recognize their degradation mechanism in aqueous conditions. However, a study of the pinpoint distribution of the reactivity of these PHUs requires making precise measurements at the molecular level which may become experimentally complicated. In this sense, an advantage of the theoretical quantum methods resides in the fact that the electronic properties of the molecules may be calculated with enough accuracy, at the molecular level, to explain adequately the experimental behavior. Nevertheless, only few theoretical studies have analyzed the electronic properties of isoproturon, diuron, linuron, and chlorotoluron. Worrall and Thomsen calculated quantum and topological descriptors for linuron and diuron which were related to their biological activity [37]. In other study, the fragmentation pathways of the anionic forms of diuron were investigated employing the Density Functional Theory (DFT) [38] while the structure and vibrational spectrum of chlorotoluron and isoproturon were analyzed by Q. Wang and H. L. Wang [39] and Vrielynck et al. [40], respectively. However, to the best of our knowledge, isoproturon, diuron, linuron, and chlorotoluron reactivity, at the molecular level, has not been analyzed yet. Therefore, in this work we have analyzed the molecular reactivity of isoproturon, diuron, linuron, and chlorotoluron employing the global and local reactivity descriptors derived from DFT. We consider that this kind of study will contribute to get a better understanding of the chemical behavior in aqueous media of these PHUs herbicides.

2. Theory

The general behavior of a molecular system may be analyzed employing the global reactivity parameters derived from the Density Functional Theory. The typical parameters employed are the electronic chemical potential (μ), the electronegativity (χ), and hardness (η), which are defined through the following equations [41–47]:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{\nu(r)} = -\frac{1}{2}(I - A), \quad (1)$$

$$\chi = -\mu, \quad (2)$$

$$\eta = \left(\frac{\partial \mu}{\partial N} \right)_{\nu(r)} = \left(\frac{\partial^2 E}{\partial N^2} \right)_{\nu(r)} = (I - A). \quad (3)$$

In these equations, E , N , and $\nu(r)$ are the energy, number of electrons, and the external potential of the system, respectively. The energy value of the vertical electronic affinity (A) can be calculated as $A = E(N) - E(N + 1)$, where $E(N)$ and $E(N + 1)$ are the total ground-state energies in the neutral N and singly charged ($N + 1$) configurations. On the other hand, the ionization potential (I) can be calculated as $I = E(N - 1) - E(N)$. The chemical potential can be related to the escaping tendency of an electron and is characteristic of the molecular electronegativity [48], while η has been related to the polarizability of the molecular system [49, 50]. Additional to μ , χ , and η , the global electrophilicity index ω can be written as [51]

$$\omega = \frac{\mu^2}{2\eta}. \quad (4)$$

This index measures the susceptibility of chemical species to accept electrons, by which, low values of ω indicate the presence of good nucleophiles, while good electrophiles are characterized by higher values of ω [51].

Additional to the global reactivity parameters, it has been possible to define local reactivity parameters [52, 53], such as the Fukui Function ($f(\vec{r})$) [54, 55]. The Fukui function can be written as [56]

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_{\nu(r)} = \left(\frac{\partial \mu(\vec{r})}{\partial \nu(r)} \right), \quad (5)$$

where $\rho(\vec{r})$ is the electronic density. The Fukui function, equation (5), can be evaluated by using a finite difference approximation. However, due to the discontinuity of the electron density with respect to the number of electrons (N), this approximation leads to three types of Fukui Function for a system, namely, $f^+(\vec{r})$, $f^-(\vec{r})$, and $f^0(\vec{r})$ for nucleophilic, electrophilic, and free radical attacks, respectively [52]. These condensed functions can be written as [52]

$$\begin{aligned} f^+(\vec{r}) &= \rho_{N+1}(\vec{r}) - \rho_N(\vec{r}), \\ f^-(\vec{r}) &= \rho_N(\vec{r}) - \rho_{N-1}(\vec{r}), \end{aligned} \quad (6)$$

$$f^0(\vec{r}) = \frac{1}{2} [\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r})].$$

However, for studying the reactivity at the atomic level, a more convenient way of calculating the Fukui function is through the condensed forms of Fukui functions for an atom j in a molecule which are expressed as [52]

$$\begin{aligned} f_j^+(\vec{r}) &= q_{j(N)} - q_{j(N+1)}, \\ f_j^-(\vec{r}) &= q_{j(N-1)} - q_{j(N)}, \\ f_j^0(\vec{r}) &= \frac{1}{2} \{q_{j(N-1)} - q_{j(N+1)}\}. \end{aligned} \quad (7)$$

In these equations, q_j is the atomic charge (evaluated from Mulliken population, electrostatic derived charge, etc.) at the j th atomic site in the neutral (N), anionic ($N + 1$), or cationic ($N - 1$) chemical species.

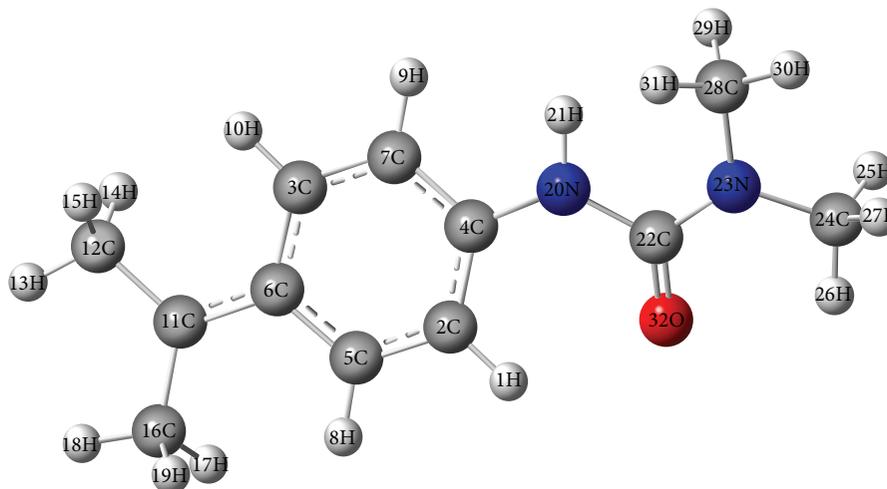


FIGURE 1: Optimized structure of isotroturon at the MP2/6-311++G(2d,2p) level of theory. Bond distances: 2C-4C = 1.39, 2C-5C = 1.37, 3C-6C = 1.40, 3C-7C = 1.36, 4C-7C = 1.39, 5C-6C = 1.40, 6C-11C = 1.43, 11C-12C = 1.50, 11C-16C = 1.50, 4C-20N = 1.40, 20N-22C = 1.39, 22C-23N = 1.37, 22C-32O = 1.24, 23N-28C = 1.46, 23N-24C = 1.46, N-H = 1.00, C-H = 1.09 in methyl groups, and C-H = 1.08 in the ring. Dihedral angle 12C-11C-6C-3C = -0.2 , 2C-4C-20N-22C = 22.03 .

3. Methodology

The optimal conformations of isotroturon, chlorotoluron, diuron, and linuron were subjected to full geometry optimization in the gas phase employing the hybrid functional B3LYP [57–59] and the basis set 6-311++G(2d,2p) [60, 61]. The optimized molecules in the gas phase were further reoptimized at the B3LYP/6-311++G(2d,2p) level employing the PCM solvation model [62, 63], with the dielectric constant 78.5 for water at 25°C. The vibrational frequencies were computed to make sure that the stationary points were minima in the potential energy surface. Finally, the optimized B3LYP/6-311++G(2d,2p) geometries were reoptimized employing the second order Møller Plesset theory (MP2) [64] with the basis set 6-311++G(2d,2p) in the aqueous phase. The final atomic charges for isotroturon, chlorotoluron, diuron, and linuron were obtained in the framework of MP2 theory; in all calculations of these atomic charges, the option DENSITY = MP2 was used. All the calculations here reported were performed with the package Gaussian 09 [65] and visualized with GaussView V. 2.08 [66].

4. Results and Discussion

The isotroturon, diuron, linuron, and chlorotoluron structures were optimized at the B3LYP/6-311++G(2d,2p) level in the gas phase. In order to take into account the effect of solvation on the electronic properties of isotroturon, diuron, linuron, and chlorotoluron, 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 all cases a frequency analysis was applied to the optimized geometries to verify the stability criterion and in all cases the frequency values were positive. Thus, it could be identified stretching N-H vibrations at 3639, 3644, 3593, and 3645 cm^{-1} , strong

TABLE 1: Electronic energies calculated at the MP2/6-311++G(2d,2p) level of theory.

	Cation/ E_h	Neutral/ E_h	Anion/ E_h
Isotroturon	-650.482060	-650.608629	-650.728242
Chlorotoluron	-1031.69563	-1031.95653	-1031.97778
Diuron	-1451.54737	-1451.81897	-1451.84796
Linuron	-1526.57888	-1526.85348	-1526.88449

stretching vibrations of the carbonyl bond at 1663, 1675, 1688, and 1670 cm^{-1} , while N-C-N symmetric stretching vibrations were observed at 1032, 1043, 1039, and 1039 cm^{-1} , for isotroturon, diuron, linuron, and chlorotoluron, respectively. These values compare favorably with those values reported in the literature for phenylurea compounds [67, 68]. Also, the structures optimized at the B3LYP/6-311++G(2d,2p) level were further reoptimized at the MP2/6-311++G(2d,2p) level in the aqueous phase; see Figures 1, 2, 3, and 4. The bond distances and angles obtained at the MP2/6-311++G(2d,2p) levels are comparable with those reported in the literature [68, 69].

5. Global Reactivity Descriptors

The global reactivity descriptors in the aqueous phase for isotroturon, chlorotoluron, diuron, and linuron were obtained at the MP2/6-311++G(2d,2p) level of theory. In Table 1, the values of the electronic energies calculated for these herbicides with the charges +1, 0, and -1 are reported, which correspond to the cationic, neutral, and anionic species, respectively. The values reported in Table 1 were used to calculate the global reactivity descriptors (μ , η , and ω) through (1), (3), and (4); see Table 2. Note that the values of hardness and chemical potential are following

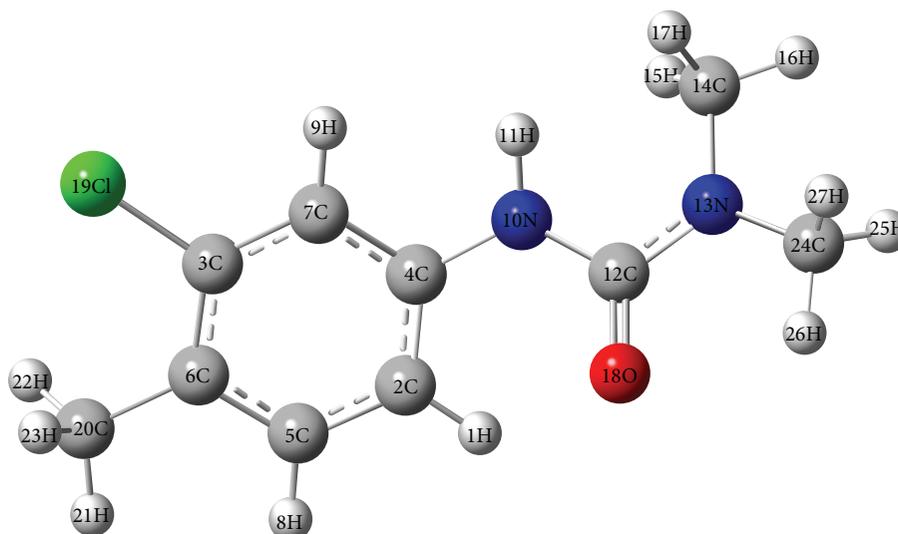


FIGURE 2: Optimized structure of chlorotoluron at the MP2/6-311++G(2d,2p) level of theory. Bond distances: 2C-4C = 1.40, 2C-5C = 1.39, 3C-6C = 1.40, 3C-7C = 1.39, 4C-7C = 1.40, 5C-6C = 1.40, 6C-20C = 1.50, 3C-19Cl = 1.76, 4C-10N = 1.41, 10N-12C = 1.39, 12C-18O = 1.24, 12C-13N = 1.36, 13N-24C = 1.45, 13N-14C = 1.46, N-H = 1.00, C-H = 1.09 in methyl groups, and C-H = 1.08 in the ring. Dihedral angle 2C-4C-10N-12C = -17.53, 10N-12C-13N-21O = 18.34.

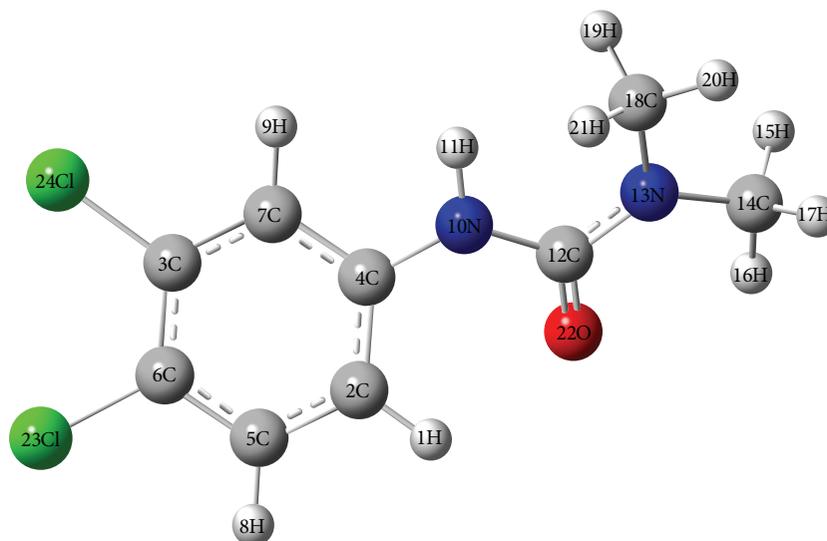


FIGURE 3: Optimized structure of diuron at the MP2/6-311++G(2d,2p) level of theory. Bond distances: 2C-4C = 1.40, 2C-5C = 1.39, 3C-6C = 1.40, 3C-7C = 1.39, 4C-7C = 1.40, 5C-6C = 1.39, 6C-23Cl = 1.74, 3C-24Cl = 1.74, 4C-10N = 1.40, 10N-12C = 1.40, 12C-22O = 1.24, 12C-13N = 1.36, 13N-18C = 1.46, 13N-14C = 1.46, N-H = 1.00, C-H = 1.09 in methyl groups, and C-H = 1.08 in the ring. Dihedral angle 2C-4C-10N-12C = 40.3.

the order: linuron > diuron > chlorotoluron > isoproturon. Last result suggests that linuron is the most stable specie of this set of herbicides, while isoproturon result to be the most reactive. Also, note that chlorotoluron exhibits the lower value of ω which indicates that it is better nucleophile in comparison to isoproturon, diuron, and linuron. Note that μ , η , and ω are global type response functions that characterize the molecule as a whole which allow us to characterize global reactivity trends [41]. However, it is important to evaluate local reactivity descriptors as the condensed Fukui function to analyze the pinpoint distribution of the reactivity

in the molecule in order to propose specific degradation mechanisms.

6. Local Reactivity Descriptors for Neutral CPAs

For the PHUs analyzed in the present work, the values of the condensed Fukui function for electrophilic, nucleophilic, and free radical attacks were evaluated through (7). It is important to mention that the values of the Fukui function are dependent on the scheme of charges used. Thus, it is

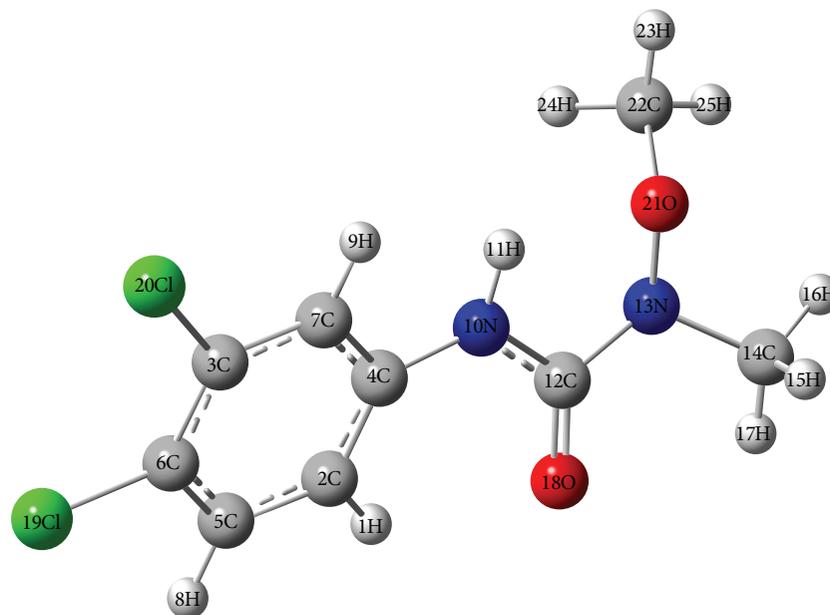


FIGURE 4: Optimized structure of linuron at the MP2/6-311++G(2d,2p) level of theory. Bond distances: 2C-4C = 1.40, 2C-5C = 1.39, 3C-6C = 1.40, 3C-7C = 1.39, 4C-7C = 1.40, 5C-6C = 1.39, 6C-19Cl = 1.74, 3C-20Cl = 1.74, 4C-10N = 1.40, 10N-12C = 1.37, 12C-18O = 1.23, 12C-13N = 1.40, 13N-21O = 1.42, 13N-14C = 1.46, 21O-22C = 1.44, N-H = 1.00, C-H = 1.09 in methyl groups, and C-H = 1.08 in the ring. Dihedral angle 2C-4C-10N-12C = -17.53, 10N-12C-13N-21O = 18.34.

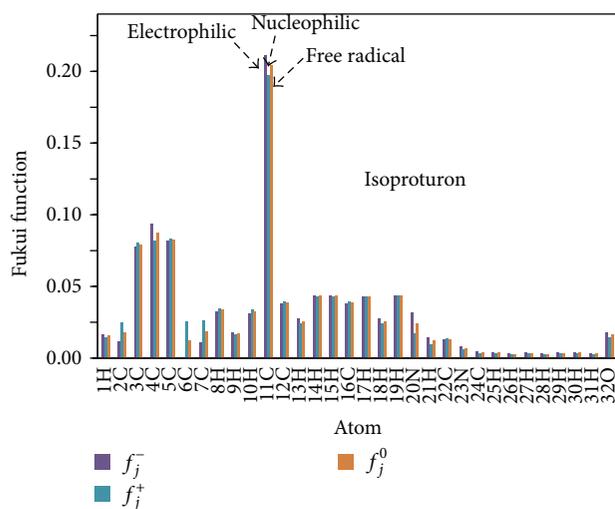


FIGURE 5: Values of the Fukui function for isoprotruron considering Hirshfeld charges according to (7).

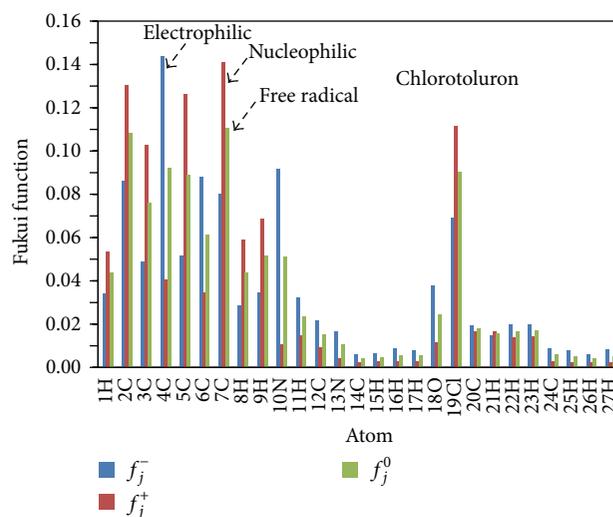


FIGURE 6: Values of the Fukui function for chlorotoluron considering Hirshfeld charges according to (7).

well known that the Fukui function values obtained from various population schemes may provide negative values; however, the Hirshfeld Stockholder population scheme [70] yields positive values [71]. Therefore, Hirshfeld partitioning scheme was used to derive the atomic charges at the MP2/6-311++G(2d,2p) level. In Figures 5, 6, 7, and 8 the values of the condensed Fukui function for isoprotruron, chlorotoluron, diuron, and linuron are reported, respectively. From Figure 5, observe that for isoprotruron the more reactive sites to electrophilic, nucleophilic, or free radical attacks are located

interchangeably on 11C. Last result suggests that chemical attacks on 11C would cause the elimination of the isopropyl moiety. The Fukui function values for chlorotoluron are reported in Figure 6; note that the distribution of the more reactive sites for this herbicide are located on 4C, 7C, and 7C atoms for electrophilic, nucleophilic, and free radical attacks, respectively. Also, it is possible to deduce that electrophilic attacks on 4C would cause the elimination of the metoxi-1-metilurea moiety. On the other hand, the atom 7C is susceptible to either nucleophilic or free radical substitutions.

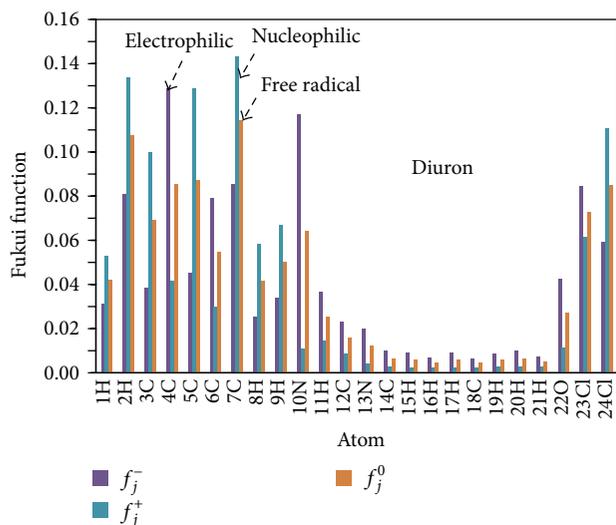


FIGURE 7: Values of the Fukui function for diuron considering Hirshfeld charges according to (7).

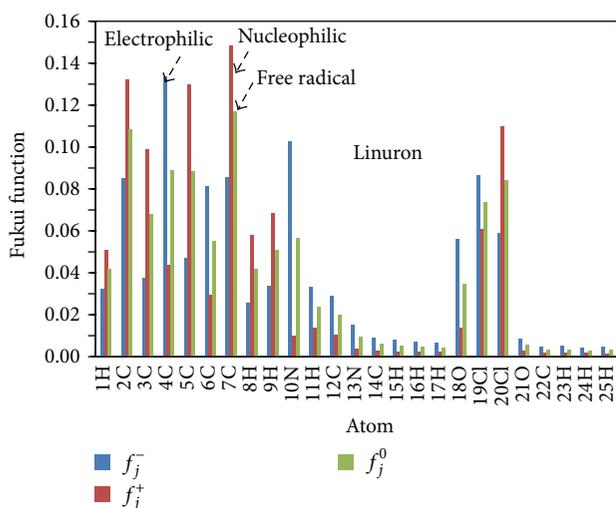


FIGURE 8: Values of the Fukui function for linuron considering Hirshfeld charges according to (7).

Here, it is interesting to highlight that the values of the Fukui Function found for diuron (see Figure 7) and linuron (see Figure 8) indicate that the more reactive sites are located on 4C, 7C, and 7C. Thus, nucleophilic and free radical attacks on diuron and linuron would cause a substitution of the hydrogen atom on 7C, while electrophilic attacks on diuron and chlorotoluron would cause the elimination of the dimethylurea fragment.

7. Conclusions

In the present work, we have analyzed the chemical reactivity of isotoproturon, chlorotoluron, diuron, and linuron herbicides in the aqueous phase employing global and local reactivity

TABLE 2: Global reactivity descriptors for isotoproturon, chlorotoluron, diuron, and linuron at the MP2/6-311++G(2d,2p) level of theory, in the aqueous phase.

	I/eV	A/eV	η/eV	μ/eV	ω/eV
Isotoproturon	-3.44	-3.25	0.19	3.35	29.62
Chlorotoluron	-7.10	-0.58	6.52	3.84	1.13
Diuron	-7.39	-0.79	6.60	4.09	1.27
Linuron	-7.47	-0.84	6.63	4.16	1.30

parameters derived from the Density Functional Theory. Global reactivity parameters indicate that isotoproturon is the most reactive while linuron is the most stable. The Fukui function values suggest that electrophilic attacks on chlorotoluron, linuron, and diuron herbicides would cause the elimination of the urea moiety while electrophilic, nucleophilic, or free radical attacks on isotoproturon would eliminate the isopropyl moiety in aqueous conditions.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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