

# Chemical Reactivity of Atrazine Employing the Fukui Function

Luis Humberto Mendoza-Huizar and Clara Hilda Rios-Reyes

Universidad Autónoma del Estado de Hidalgo. Centro de Investigaciones Químicas. Carretera Pachuca-Tulancingo km. 4.5 Mineral de la Reforma, Hidalgo, México. hhuizar@uaeh.edu.mx

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**Abstract.** In the present work we calculated reactivity descriptors for atrazine at MP2/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level in order to analyze its reactivity. Reactivity descriptors such as ionization energy, molecular hardness, electrophilicity, condensed Fukui function and total energies were determined to identify changes in the reactivity of atrazine in the gas and aqueous phases. The influence of the solvent was taken into account with the PCM model. The values of the reactivity descriptors indicated that the interaction of atrazine with water diminished its reactivity in comparison with the exhibited in gas phase. Also, it was found that the electrophilic and free radical attacks were equivalent and they were located on all the cases in the ethylamine and isopropylamine groups.

**Keywords:** Atrazine, reactivity, Fukui, B3LYP, MP2, PCM.

**Resumen.** En el presente trabajo calculamos descriptores de reactividad para la atrazina, en el nivel de teoría MP2/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p), con la intención de analizar su reactividad. Se calcularon descriptores tales como energía de ionización, dureza, electrofilicidad, funciones de Fukui y diferencias de energías para identificar los cambios de reactividad de la atrazina en fase gas y en fase acuosa. La influencia del disolvente se tomó en cuenta empleando el modelo PCM. Los descriptores de reactividad calculados sugieren que en agua la reactividad de la atrazina disminuye en comparación con la atrazina en fase gas. Se encontró que las reactividades, electrofílica y por radicales libres, en la atrazina son equivalentes y localizadas en todos los casos en los grupos etilamina e isopropilamina.

**Palabras clave:** Atrazina, reactividad, Fukui, B3LYP, MP2, PCM.

## Introduction

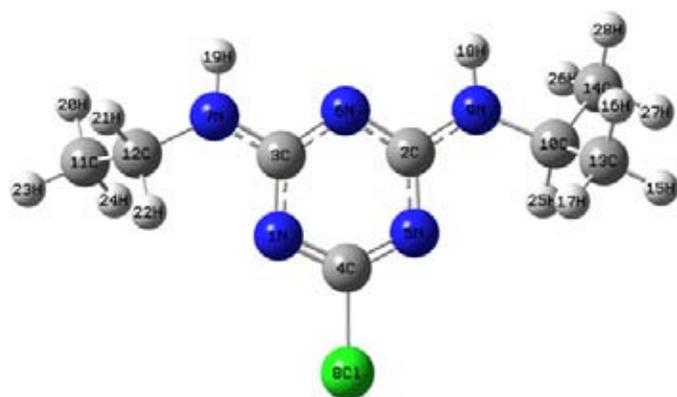
Atrazine (2-chloro-4-ethylamino-6-isopropyl-amine-s-triazine), see Figure 1, is one of the most widely used herbicides in the world [1]. Its half-life degradation in soil ranges from 1.5 months to 5 years [2, 3] and its intensive use in agriculture has led to the accumulation of atrazine, polluting the soil and the water at levels exceeding the permissible limits. Moreover, the resistance of atrazine to microbial degradation, and its slow hydrolysis, low vapor pressure, and moderate aqueous solubility enhance its presence as groundwater contaminant [4]. It has recently been reported that atrazine can induce hermaphroditism and demasculinization in African frogs, while in humans; the effects in this sense are not clear yet [5]. Considering these facts, it is not surprising that many efforts have been focused in developing efficient remediation treatments to clean atrazine from groundwater [6-20]. Some enzymes like the Glutathione

S-transferase from maize have been employed to enclose this herbicide without cause its degradation [21]. Advanced oxidation processes (AOPs), photochemical degradation, chemical oxidation via O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and Fenton reactions are among the most cited in the literature for atrazine degradation [6-20]. Chan and Chu [21] and Gallard and De Laat [22] studied the mechanisms involved in the atrazine oxidation by Fenton reactions and they observed that the presence of free radicals (•OH) initiates the degradation of atrazine through an alkylic-oxidation (alkylamino side-chain oxidation), dealkylation (alkylic sidechain cleavage), and/or dechlorination (hydroxylation at the chlorine site). However, a consensus on the mechanism of this process does not exist [23]. In this sense, a detailed study of the reactivity exhibited by atrazine may become fundamental to understand its degradation mechanism. Although, it has been reported an evaluation of the reactivity of atrazine employing frontier molecular orbitals, such study was used to determine predictors related with its ozonation rate constant [26]. To our knowledge, a quantum mechanical study of atrazine to evaluate global and local reactivity descriptors is still missing. Therefore, we consider that this kind of study will contribute to get a better understanding of the chemical behavior, in the gas and solution phases, of this important herbicide.

## Theory

From density functional theory (DFT) it is possible to define and justify concepts of chemical reactivity such as the electronic chemical potential ( $\mu$ ), the absolute hardness ( $\eta$ ), and the global electrophilicity ( $\omega$ ) [27, 28]. The electronic chemical potential  $\mu$  was defined by Parr and Pearson [29] as

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



**Figure 1.** Atrazine (2-chloro-4-ethylamino-6-isopropyl-amine-s-triazine).

which is the negative of the electronegativity introduced by Mulliken. The global hardness can be calculated from [29-32]:

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

where  $I$  is the vertical ionization energy and stands for the vertical electron affinity, and the global electrophilicity index was introduced by Parr [33] and is given by:

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

According to its definition, this index measures the propensity of chemical species to accept electrons. Thus, a good nucleophile is characterized by low values of  $\mu$  and  $\omega$ ; and, otherwise, a good electrophile is characterized by high values of  $\mu$  and  $\omega$ . On the other hand, the hard and soft acids and bases (HSAB) principle has been very useful to predict the reactivity of chemical systems [34-36]. The HSAB principle has been used in a local sense in terms of DFT concepts such as the Fukui function  $f(r)$  [34]. Parr and Yang showed that sites in chemical species with the largest values of Fukui Function ( $f(r)$ ) are those with higher reactivity. The Fukui function is defined as [34]:

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

where  $\rho(r)$  is the electronic density,  $N$  is the number of electrons and  $r$  is the external potential exerted by the nucleus. 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. Therefore, it indicates the propensity of the electronic density to deform at a given position upon accepting or donating electrons [34-36]. Also, it is possible to define the corresponding condensed or atomic Fukui functions on the  $j$ th atom site as,

$$f_j^- = q_j(N) - q_j(N - 1), \quad (5)$$

$$f_j^+ = q_j(N + 1) - q_j(N), \quad (6)$$

$$f_j^0 = \frac{1}{2} q_j [(N + 1) - q_j (N - 1)] \quad (7)$$

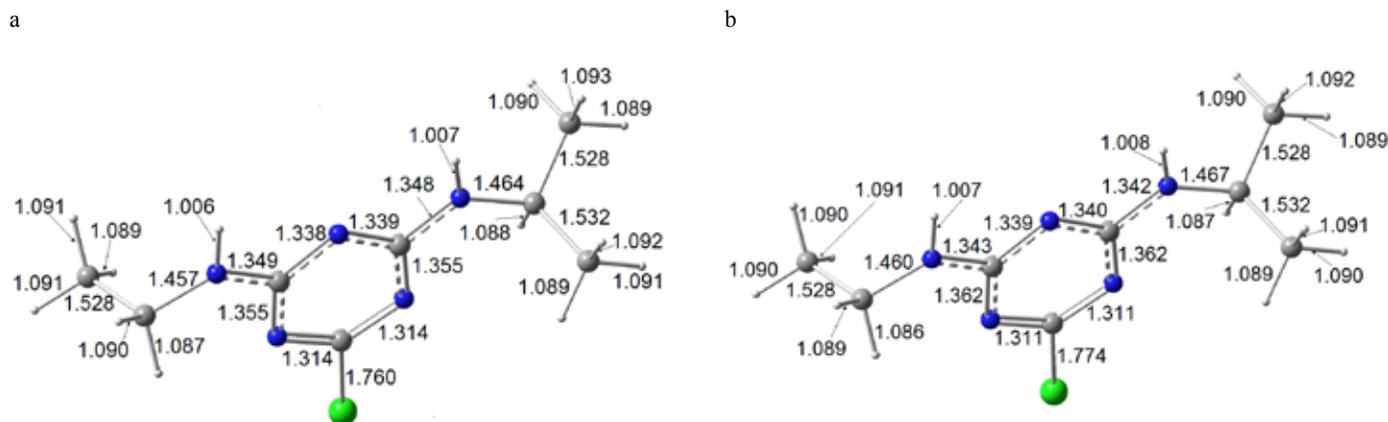
for an electrophilic  $f_j^-(r)$ , nucleophilic or free radical attack  $f_j^+(r)$ , on the reference molecule, respectively. In these equations,  $q_j$  is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the  $j$ th atomic site in the neutral ( $N$ ), anionic ( $N + 1$ ) or cationic ( $N - 1$ ) chemical species. Here, it is important to mention that independently of the approximations used to calculate the Fukui function, all of them follow the exact equation:

$$\int f(r) dr = 1 \quad (8)$$

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

## Results and Discussion

Figure 2a shows the optimized structure of atrazine at B3LYP/6-311++G(2d,2p) level in gas phase. The total energy calculated was -1047.5021 hartrees, while the HOMO-LUMO gap obtained was 5.91 eV. In order to analyze the effect of water in the electronic properties of atrazine, the optimized structure in gas phase was used as starting point at the B3LYP/6-311++G(2d,2p) level without any symmetry constraints employing the PCM solvation model. In this model, the solvent is treated as an unstructured continuum outside the solvent-accessible surface of the solute and it is characterized only by its dielectric constant which is 78.5 for water at 25 °C. The optimized structure, in aqueous phase, is depicted in Figure 2b. The total energy for atrazine calculated under this condition was -1047.5121 hartrees while the energy gap is 5.78 eV. The energy difference between the gas phase and the structure in aqueous phase is 6.3 kcal-mol<sup>-1</sup>, suggesting that atrazine



**Figure 2.** Optimized structures of atrazine in a) Gas phase and b) water phase. In both cases the bond distances are labeled in each Figure. The dihedral angle 3C-7N-12C-11C, 2C-9N-10C-14C and 2C-9N-10C-13C were -87.21, 150.71 and -84.87 in gas phase. For aqueous phase the values were -89.20, 147.24 and -88.55 respectively. See Figure 1 for atomic labels.

in water is slightly more stable than in gas phase. It is important to mention that were not obtained significant differences, neither in distances nor angles, when the solvent effect was considered. Moreover, the bond distances were very similar to those obtained by the experimental and theoretical techniques [37]. The geometries showed in Figure 2 were reoptimized at B3LYP/6-311++G(3df,3dp) level (results not shown), however the bond distances and angles were practically the same that the calculated at B3LYP/6-311++G(2d,2p) level. From the values of the frequencies calculated at B3LYP/6-311++G(2d,2p) level for atrazine, it could be identified a stretching triazine ring vibration on  $1624\text{ cm}^{-1}$ , a N-H deformation on  $1530\text{ cm}^{-1}$ , a C=N bending on  $1449\text{ cm}^{-1}$  and an Aryl-N on  $1346\text{ cm}^{-1}$ . For aqueous atrazine the vibrations above mentioned were shifted to a lower frequencies of  $1620$ ,  $1526$ ,  $1443$  and  $1343\text{ cm}^{-1}$ . These values compare favorably with the experimental vibrations detected for pure atrazine at  $1618$ ,  $1548$ ,  $1448$  and  $1348\text{ cm}^{-1}$  respectively [38, 39]. Last results suggest that the level of theory is adequate to analyze the electronic properties of atrazine.

Reactivity descriptors were obtained by single point calculations employing the MP2/6-311++G(2d,2p) level of theory and using the B3LYP/6-311++G(2d,2p) geometries. In table 1, it is reported the values of the electronic energies calculated for atrazine with the charges +1, 0 and -1, which corresponds to the cationic, neutral and anionic species, respectively. From table 1, it can be observed that the energy difference at the MP2/6-311++G(2d,2p) level indicates that water stabilizes the atrazine by  $5.94\text{ kcal}\cdot\text{mol}^{-1}$ . Same tendency was obtained from DFT calculations.

From the values reported in table 1, it was possible to calculate the value of vertical ionization energy 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. In a similar way, the ionization potential was 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).

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

Fase	Charge +1 (multiplicity = 2)	Charge 0 (multiplicity = 1)	Charge -1 (multiplicity = 2)
Gas	-1045.026181	-1045.361961	-1045.316048
Water	-1045.088768	-1045.371427	-1045.402399

From the results reported in Table 2, it may be observed that the global hardness decreases when solvent was taken into account. Note that the values of  $\mu$  and  $\omega$  are bigger in solution than in gas phase where the rise in  $\mu$  and  $\omega$  suggested that the electrophilic behavior increases on atrazine in presence of water.

### Local reactivity descriptors

Experimental reports have indicated that the more reactive sites for the atrazine degradation are located on the isopropylamine and ethylamine groups [40]. In some cases a dechlorination-hydroxylation is possible, however it is produced only in small quantities [21,22]. Thus, in general, the degradation mechanism for atrazine involves either an oxidation or a hydroxylation of the lateral chains rather than the open of the heteroatom ring [40]. Here, it is important to mention that this situation is based on experiments where a free radical attack is predominant and other kinds of techniques have been scarcely investigated [41]. Thus, a calculation of the local reactivity descriptors would allow identifying the kind of process to make efficiently the atrazine degradation. Although, the Fukui function allows determining the pin point distribution of the active sites on a molecule, the value of this function is completely dependent of the kind of charges used. A variety of forms to calculate the charges has been reported. Most of them are based in some sort 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 [42]. It has been reported that the charges obtained from electrostatic potentials are better than those obtained from Mulliken Population analysis to estimate the condensed reactivity indexes [43, 44]. Also, the NBO charges have found a good acceptance to calculate the Fukui function [45]. Due to the sensitivity of the Fukui function with the type of population analysis to be performed, in the present work we calculated the values of the Fukui function by employing the Mulliken, MEP and NBO populations charges. In table 3 it is reported the values of the Fukui function calculated from the NBO charges. The values of Fukui function obtained employing MEP were very similar to those obtained from the NBO charges, while the values obtained from the Mulliken charges (not reported) suggested a predominant reactivity in the ring which does not corresponds with the experimental reports for the degradation of atrazine [21, 22]. From Table 3, note the presence of negative values of the Fukui function. Recently it was reported that a negative Fukui function value means that when adding an electron to

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

Fase	I /eV	A /eV	HOMO /eV	LUMO /eV	$\Delta(H-L)$ /eV	$\eta$ /eV	$\mu$ /eV	$\omega$ /eV
Gas	9.133	-1.249	-0.359	0.038	10.791	5.191	-3.942	1.497
Agua	7.688	0.842	-0.366	0.043	11.120	3.423	-4.265	2.658

**Table 3.** Values of the Fukui function considering NBO charges according with equations (5-7).

	$f_j^-(r)$		$f_j^+(r)$		$f_j^0(r)$	
	Gas	Aqueous	Gas	Aqueous	Gas	Aqueous
1N	-0.295	-0.253	-0.051	-0.077	-0.173	-0.165
2C	<b>0.194</b>	<b>0.191</b>	-0.065	-0.054	<b>0.064</b>	<b>0.069</b>
3C	<b>0.110</b>	<b>0.113</b>	-0.061	-0.054	<b>0.024</b>	<b>0.029</b>
4C	<b>0.136</b>	<b>0.107</b>	-0.265	-0.284	-0.065	-0.089
5N	-0.246	-0.230	-0.047	-0.077	-0.146	-0.154
6N	-0.158	-0.223	-0.157	-0.146	-0.157	-0.185
7N	-0.028	-0.012	-0.034	-0.037	-0.031	-0.025
8Cl	-0.062	-0.031	-0.145	-0.140	-0.104	-0.086
9N	-0.476	-0.518	-0.033	-0.036	-0.255	-0.277
10C	<b>0.050</b>	<b>0.052</b>	<b>0.000</b>	<b>0.002</b>	<b>0.025</b>	<b>0.027</b>
11C	<b>0.003</b>	<b>0.001</b>	<b>0.004</b>	<b>0.001</b>	<b>0.004</b>	<b>0.001</b>
12C	<b>0.008</b>	<b>0.002</b>	<b>0.008</b>	<b>0.005</b>	<b>0.008</b>	<b>0.003</b>
13C	<b>0.006</b>	<b>0.002</b>	<b>0.004</b>	<b>0.001</b>	<b>0.005</b>	<b>0.002</b>
14C	<b>0.017</b>	<b>0.010</b>	<b>0.006</b>	<b>0.002</b>	<b>0.012</b>	<b>0.006</b>
15H	-0.045	-0.032	-0.023	-0.008	-0.034	-0.020
16H	-0.021	-0.019	-0.015	-0.005	-0.018	-0.012
17H	-0.008	-0.014	<b>0.011</b>	-0.001	<b>0.001</b>	-0.008
18H	-0.032	-0.037	-0.021	-0.018	-0.026	-0.028
19H	-0.012	-0.007	-0.021	-0.018	-0.016	-0.013
20H	-0.011	-0.003	-0.015	-0.006	-0.013	-0.004
21H	-0.022	-0.007	-0.027	-0.013	-0.024	-0.010
22H	<b>0.004</b>	<b>0.001</b>	<b>0.001</b>	-0.005	<b>0.002</b>	-0.002
23H	-0.020	-0.004	-0.025	-0.008	-0.022	-0.006
24H	<b>0.008</b>	<b>0.000</b>	<b>0.007</b>	-0.002	<b>0.008</b>	-0.001
25H	-0.029	-0.034	0.001	-0.005	-0.014	-0.020
26H	-0.013	-0.014	-0.005	-0.004	-0.009	-0.009
27H	-0.038	-0.025	-0.020	-0.007	-0.029	-0.016
28H	-0.018	-0.015	-0.012	-0.005	-0.015	-0.010

the molecule, in some spots, the electron density is reduced; alternatively when removing an electron from the molecule, in some spots, the electron density is increased. Ayres et al, has related this behavior with the reduction and oxidation of atomic centers into the molecule [46]

From the values reported in Table 3, the reactivity order for the electrophilic case was C2>C4>C3>C10>C14>C12=H24>C13>H22>C11 in gas phase while in aqueous phase was C2>C3>C4>C10>C14>C12=C13>H22. Note that the position of reactive electrophilic sites are similar in both cases and they are mainly located on the ethylamine and isopropylamine groups and in the ring, however, due to steric effects the reactivity in the ring might be difficult. Here, it is interesting to observe that the atrazine degradation employing electrophilic agents would be equivalent in the gas and water phases. On the other hand, for nucleophilic attack, the reactivity was found

exclusively on the ethylamine and isopropylamine groups with a lost of reactivity on the hydrogens 17, 22, 24 and 25 in the water phase, in comparison with gas phase. The nucleophilic reactivity order was H17>C12>H24>C14>C13>H25>2H22 and C12>C14>C10=C11=C13 for gas and water phases, respectively. Note that it was observed a less reactivity for this kind of attack in comparison with the electrophilic attack. The attack for free radicals was C2>C10>C3>C14>C12>H25>C13>H22>H17 for the gas and C2>C3>C10>C14>C12>C11 for the water phase. It is evident that in the water phase the reactivity diminishes in comparison with the gas phase, which suggests that in aqueous conditions the atrazine is more stable than in the gas phase. If one compares the three kinds of attacks it is possible to observe that in gas phase the electrophilic and free radical attacks are equivalent and it shows a bigger reactivity in comparison with the nucleophilic case. Also, note that under aqueous conditions, the reactivity is slightly favored to an electrophilic attack. However, it is important to mention that in both, the phases and the attacks, the reactivity is remaining on the ethylamine and isopropylamine groups. Last results suggest that the degradation of atrazine can be performed by employing either free radical agents or electrophilic agents in order to attack the lateral chains. Therefore, the use of a specific attack will depend on the experimental conditions where the atrazine is present. These results are consistent with recent experimental results where electrophilic agents were employed to get a full mineralization of atrazine via electrochemical route by using electrophilic agents, however in such study an explanation about the electrochemical reactivity exhibited for the atrazine it was not reported [47-49].

## Conclusions

In the present work reactivity descriptors for atrazine were calculated employing DFT theory in the gas and aqueous phases. The results suggested that the interaction of atrazine with water diminished its reactivity in comparison with the reactivity exhibited in the gas phase. It was possible to observe that the main attacks to degrade the atrazine can be performed by employing either electrophilic or free radical attacks. In both cases, the reactive sites are located predominantly on the ethylamine and isopropylamine groups. Last results suggested that the techniques based on electrophilic attack can be employed to carry out the degradation of atrazine.

## Methodology

A starting geometry was generated using the PM3 method [50] implemented in Spartan02 [51]. The optimal conformation was subjected to full geometry optimization in gas phase employing the hybrid functional B3LYP [52-54] and the basis set 6-311++G(2d,2p) [55, 56]. The optimized atrazine in gas phase was reoptimized at the B3LYP/6-311++G(2d,2p) level employing the PCM solvation model [57, 58]. The vibrational frequencies for all cases were computed to make sure

that the stationary points were minima. In our calculations a Møller-Plesset correction energy correlation was performed employing the second order Moller Plesset's theory [59] and the basis set 6-311++G(2d,2p) level of theory using the B3LYP/6-311++G(2d,2p) geometries.

### Computational resources

All the calculations reported here were performed with the package Gaussian 03 [60] and visualized with the GaussView V. 2.08 [61] and Gabedit [62] packages, using a cluster with 14 Xeon 3.0 GHZ cores and 7 GB of memory.

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