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Research Article

# Quantum Chemical Studies On Reactivity of Some Amino Acids towards Electrophilic and Nucleophilic Attack with Iron

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**Abstract**: Semiemperical and density functional methods (DFT) have been used to predict the reactivity of some amino acids (alanine, glycine and leucine) towards electrophilic and nucleophilic attacks with iron (Fe). Both methods revealed that the reactivity of the three amino acids studied decreases in the order leucine> alanine > glycine. The sites for nucleophilic attack are the carbon atom (C-7), the nitrogen atom (N-5) and the nitrogen atom (N-5) for leucine, alanine and glycine respectively, while the sites for electrophilic attack are the carboxyl functional group for leucine, alanine and glycine respectively. Molecular orbital diagrams have been used to represent the information obtained from DFT study. The results obtained from the study indicated that DFT and quantum chemical principles can be used to predict the reactivity of leucine, alanine and glycine towards electrophilic and neuclophilic attacks**.**

**Keywords:** Aminoacids, Electrophilic, Nucleophilic, Reactivity, Iron

## INTRODUCTION

Amino acids are molecules having amino and carboxylic acid functional groups[1-2]. They are essential in biological systems but before they can be useful, they have to react with other constituents within the same biological systems[3]. Such reactions may involve the transfer and acceptance of electrons. Quanta chemical principles have been discovered to be of immerse use in the modelling of the expected reactivity of amino acids. In this paper, the electrophilic and nucleophilic reactions involving some amino acids (alanine, glycine and leucine) with Fe using quantum chemical principles was considered. Attempts shall be made at establishing the order for the reactivity of the molecules and from DFT study, the possible sites for electrophilic and nucleophilic attacks shall be highlighted. The chemical and optimised structures of glycine, alanine and leucine are presented in **Fig. No.1.**

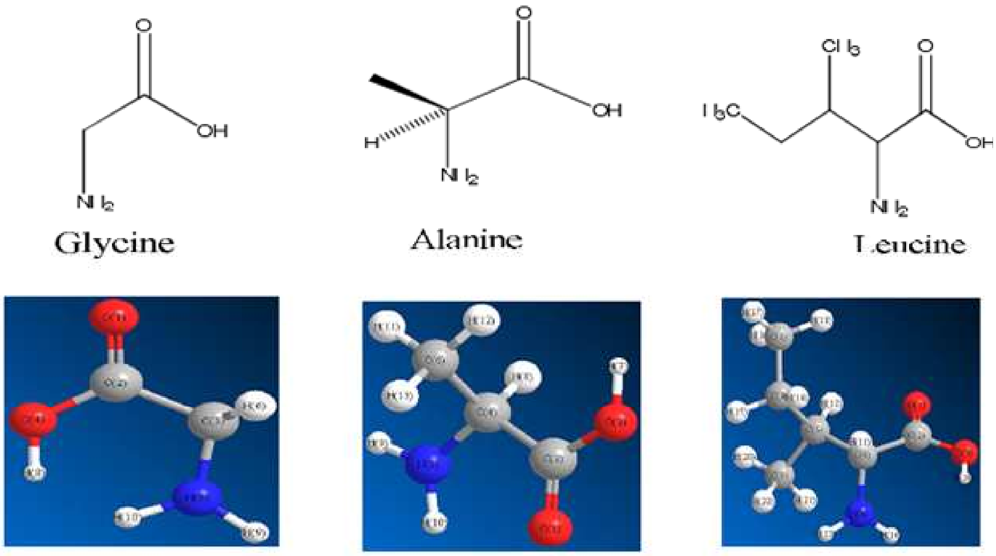



Fig.No.1: Chemical and optimised structures of glycine, alanine and leucine

## COMPUTATIONAL PROCEDURE

Quantum chemical calculations were carried out using Parametric method number 6 (PM6), Parametric method number 3 (PM3), Austin model 1 (AM1), Recife model (RM1), and Modified neglect of diatomic overlap (MNDO) and Hamiltonians in the MOPAC 2008 program[4]. Calculations were performed on a high power (HP) compatible Pentium V (2.0 GHz and 4GB RAM) computer. The quantum chemical indices calculated included, the energy of the highest occupied molecular orbital ($E_{HOMO}$), the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), the dipole moment ($\mu$), the total energy (TE), the electronic energy (EE) and ionization potential (IP). *Ab initio* parameters were computed using the GAMES programme[5]. The parameters calculated were, total charge of the molecules, electron density and Milliken charge on the atom. The programme setting of the Games were DFT (correlation type), B3LYP (correlation method) and 631-G (Baisis set).

## RESULTS AND DISCUSSION

**Global reactivity: Tables 1, 2 and 3** present values of some quantum chemical parameters using, PM6, PM3, AM1, RM1 and MNDO models for alanine, glycine and leucine respectively. The results obtained indicate that the energy of the highest occupied molecular orbital ($E_{HOMO}$) is highest for leucine and follows the order: leucine> alanine > glycine. This indicates that leucine should be more reactive than alanine while glycine should be the least reactive molecule[6]. On the other hand, values of $E_{LUMO}$ tend to decrease with increasing reactivity. From literature, most reactions involving amino acids can be viewed on the basis of donor-acceptor interaction between the $\pi$-electron of the amino acid molecule and the d-orbital of the atom. $E_{HOMO}$ is associated with the electron donating ability of the molecule[7].

Therefore, increasing value of $E_{HOMO}$, suggests better inhibition efficiency because the adsorption and electron donating ability of the compound would be enhanced. On the other hand, $E_{LUMO}$ is associated with the tendency of the inhibitor to accept electrons. Therefore, lower values of $E_{LUMO}$ suggest significant potentials for the acceptance of the transferred electrons. The results obtained also reveal that the energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) for these amino acids decreases in the order similar to that obtained for the $E_{LUMO}$. This indicates that leucine is the most reactive. Larger values of the $\Delta E$ suggest low reactivity of a chemical species while lower value of the energy gap suggests better reactivity because the energy to remove electron from the last occupied orbital will be low.

**Table 1: Calculated quantum chemical parameters for alanine**

| Models | PM6 | PM3 | AMI | RM1 | MNDO |
|---|---|---|---|---|---|
| $E_{HOMO}$ (eV) | -9.011 | -8.765 | -9.387 | -9.357 | -9.799 |
| $E_{LUMO}$ (eV) | 0.494 | 1.074 | 1.245 | 1.213 | 1.076 |
| $E_{L-H}$ (eV) | 9.505 | 9.839 | 10.632 | 10.57 | 10.875 |
| Total energy(eV) | -1225.13 | -1213.08 | -1328.54 | -1318.41 | -1334.46 |
| Electronic energy (eV) | -4547.25 | -4534.48 | -4676.3 | -4676.51 | -4689.94 |
| Core-core repulsion (eV) | 3322.119 | 3321.405 | 3347.76 | 3358.097 | 3355.482 |
| Cosmo area ($Å^2$) | 121.37 | 121.37 | 121.37 | 121.37 | 121.37 |
| Cosmo volume ($Å^3$) | 108.9 | 108.9 | 108.9 | 108.9 | 108.9 |
| IP (eV) | 9.011 | 8.765 | 9.387 | 9.357 | 9.799 |
| Dipole (Debye) | 4.478 | 3.2 | 3.9 | 3.939 | 3.777 |
| $E_{exp}$ (%) | 76.03 | | | | |

**Table 2: Calculated quantum chemical parameters for glycine**

| Models | PM6 | PM3 | AMI | RM1 | MNDO |
|---|---|---|---|---|---|
| $E_{HOMO}$ (eV) | -8.939 | -8.714 | -9.378 | -9.298 | -9.847 |
| $E_{LUMO}$ (eV) | 0.472 | 1.048 | 1.201 | 1.167 | 1.038 |
| $E_{L-H}$ (eV) | 9.411 | 9.762 | 10.579 | 10.465 | 10.885 |
| Total energy(eV) | -1075.19 | -1063.54 | -1172.84 | -1164.38 | -1178.23 |
| Electronic energy (eV) | -3425.08 | -3430.66 | -3559.42 | -3552.5 | -3570.92 |
| Core-core repulsion (eV) | 2349.888 | 2367.113 | 2386.57 | 2388.118 | 2392.692 |
| Cosmo area ($Å^2$) | 104.81 | 104.81 | 104.81 | 104.81 | 104.81 |
| Cosmo volume ($Å^3$) | 89.01 | 89.01 | 89.01 | 89.01 | 89.01 |
| IP (eV) | 8.939 | 8.714 | 9.378 | 9.298 | 9.847 |
| Dipole (Debye) | 4.415 | 3.793 | 3.864 | 3.885 | 3.735 |
| $E_{exp}$ (%) | 65.91 | | | | |

The adsorption power and the reactivity of compounds such as amino acids increase with decreasing value of the dipole moment ($\mu$). However, the possibilities of irregularities for correlation between reactivity and dipole moment have been established. The results obtained, indicate that the order for the decrease in reactivity with dipole moment is similar to the order obtained from $E_{LUMO}$ and $E_{HOMO}$. On the contrary, the core core repulsion energy (C-C), cosmo area (CosAr), cosmo volume (CosVol) and ionization potentials (IP) increased in the same order.

From the values of the ground state energy of the systems, the ionization energy (IE) and the electron affinity (EA) of these amino acids were calculated using the following equations[8],

$$IE = E_{(N-1)} - E_{(N)} \qquad ...(1)$$

$$EA = E_{(N)} - E_{(N+!)} \qquad ...(2)$$

**Table 3: Calculated quantum chemical parameters for leucine**

| Models | PM6 | PM3 | AMI | RM1 | MNDO |
|---|---|---|---|---|---|
| $E_{HOMO}$ (eV) | -9.179 | -9.085 | -9.535 | -9.485 | -10.026 |
| $E_{LUMO}$ (eV) | 0.488 | 0.867 | 1.142 | 1.092 | 0.913 |
| $E_{L-H}$ (eV) | 9.667 | 9.952 | 10.677 | 10.577 | 10.939 |
| Total energy(eV) | -1672.96 | -659.64 | -1793.46 | -1778.13 | -1800.23 |
| Electronic energy (eV) | -8484.94 | -8411.39 | -8590.87 | -8617.41 | -8610.81 |
| Core-core repulsion (eV) | 6811.987 | 6751.745 | 6797.411 | 6839.282 | 6810.586 |
| Cosmo area (Å$^2$) | 166.86 | 166.86 | 166.86 | 166.86 | 166.86 |
| Cosmo volume (Å$^3$) | 167.2 | 167.2 | 167.2 | 167.2 | 167.2 |
| IP (eV) | 9.179 | 9.085 | 9.535 | 9.485 | 10.026 |
| Dipole (Debye) | 4.006 | 3.649 | 3.713 | 1.092 | 3.754 |
| $E_{exp}$ (%) | 88.06 | | | | |

where $E_{(N-1)}$, $E_{(N)}$ and $E_{(N+1)}$ are the ground state energies of the system with N-1, N and N+1 electrons respectively. Calculated values of IE and EA are presented in Tables 4, 5 and 6 for alanine, glycine and leucine respectively. IE values are comparable to values of IP obtained through semi-empirical calculations. Ionization energy measures the tendency towards loss of electron while electron affinity measures the tendency toward the acceptance of electron indicating that IE is closely related to $E_{HOMO}$ while EA is related to $E_{LUMO}$. In this case, two systems, that is Fe and these amino acids are brought together hence electrons will flow from the lower system (having lower electronegativity) to the system with higher electronegativity until the chemical potential becomes equal.

Global softness (S) of these amino acids was evaluated using the finite difference approximation which can be expressed as follows[8].

$$S = 1/[(E_{(N-1)}-E_{(N)}) - (E_{(N)}-E_{(N+!)})] \qquad \ldots (3)$$

Similarly, the global hardness ($\eta$) which is the inverse of global softness was calculated using the relation, $\eta$=1/S. The electronegativity ($\chi$) of these amino acids were also estimated using equation 4,

$$\chi = ½(\delta^2E/\delta N^2)_\upsilon = (IP - EA)/2 \qquad \ldots (4)$$

where E, N and $\upsilon$ are the ground state energy, the number of electrons and the external potential due to the nuclei. Table 4, 5 and 6 also present values of IP, EA, S, $\chi$ and $\eta$ obtained from PM6, PM3, AM1, RM1 and MNDO calculations for alanine, glycine and leucine respectively. The parameters $\eta$ and S are related to the energy gap ($\Delta$E) of the inhibitors. A hard molecule has a large energy gap while a soft molecule has small energy gap implying that a soft molecule is more reactive than a hard molecule.

**Table 4: Quantum chemical descriptors for alanine**

| Models | PM6 | PM3 | AMI | RM1 | MNDO |
|---|---|---|---|---|---|
| $E_N$ (eV) | -1672.9570 | -1659.6440 | -1793.4570 | -1778.1270 | -1800.2260 |
| $E_{N-1}$ (eV0 | -1664.4381 | -1651.1802 | -1784.6655 | -1769.4848 | -1790.9357 |
| $E_{N+1}$ (eV0 | -1673.0161 | -1659.1948 | -1792.8958 | -1777.6020 | -1799.8668 |
| IE (eV) | 8.5190 | 8.4638 | 8.7915 | 8.6422 | 9.2903 |
| EA (Ev) | -0.0591 | -0.4492 | -0.5612 | -0.5250 | -0.3592 |
| $\chi$(eV) | 4.2890 | 4.0073 | 4.1152 | 4.0586 | 4.4655 |
| S(/eV) | 0.1182 | 0.1122 | 0.1069 | 0.1091 | 0.1036 |
| $\eta$ (eV) | 8.4598 | 8.9130 | 9.3527 | 9.1672 | 9.6495 |
| $\delta$ | 0.1602 | 0.1679 | 0.1542 | 0.1604 | 0.1313 |

**Table 5: Quantum chemical descriptors for glycine**

| Models | PM6 | PM3 | AMI | RM1 | MNDO |
|---|---|---|---|---|---|
| $E_N$ (eV) | -1225.1330 | -1213.0750 | -1328.5380 | -1318.4140 | -1334.4560 |
| $E_{N-1}$ (eV0 | -1216.7339 | -1204.8652 | -1319.9030 | -1309.9224 | -1325.3800 |
| $E_{N+1}$ (eV0 | -1225.0865 | -1212.3702 | -1327.7638 | -1317.6771 | -1332.2348 |
| IE (eV) | 8.3991 | 8.2098 | 8.6350 | 8.4916 | 9.0760 |
| EA (Ev) | -0.0465 | -0.7048 | -0.7742 | -0.7369 | -2.2212 |
| $\chi$(eV) | 4.1763 | 3.7525 | 3.9304 | 3.8774 | 3.4274 |
| S(/eV) | 0.1184 | 0.1122 | 0.1063 | 0.1084 | 0.0885 |
| $\eta$ (eV) | 8.4456 | 8.9146 | 9.4092 | 9.2285 | 11.2972 |
| $\delta$ | 0.1672 | 0.1821 | 0.1631 | 0.1692 | 0.1581 |

**Table 6: Quantum chemical descriptors for leucine**

| Models | PM6 | PM3 | AMI | RM1 | MNDO |
|---|---|---|---|---|---|
| $E_N$ (eV) | -1075.1920 | -1063.5431 | -1172.8443 | -1164.3812 | -1178.2324 |
| $E_{N-1}$ (eV0 | -1066.7876 | -1055.3136 | -1164.1373 | -1155.8618 | -1169.0440 |
| $E_{N+1}$ (eV0 | -1074.6061 | -1062.1237 | -1171.4667 | -1163.0186 | -1175.8843 |
| IE (eV) | 8.4044 | 8.2295 | 8.7070 | 8.5194 | 9.1884 |
| EA (Ev) | -0.5859 | -1.4194 | -1.3776 | -1.3626 | -2.3481 |
| $\chi$(eV) | 3.9092 | 3.4051 | 3.6647 | 3.5784 | 3.4201 |
| S(/eV) | 0.1112 | 0.1036 | 0.0992 | 0.1012 | 0.0867 |
| $\eta$ (eV) | 8.9903 | 9.6489 | 10.0846 | 9.8820 | 11.5365 |
| $\delta$ | 0.1719 | 0.1863 | 0.1654 | 0.1731 | 0.1552 |

From the results presented in **Table 7, 8 and 9** which is the Fukui and global softness indices for electrophilic andnucleophilic attacks in Pen G calculated from Mulliken (Lowdin) charges (calculated from B3YLP**/631G) for alanine, glycine and leucine respectively $\eta$ values are relatively lower for leucine and higher for glycine which indicates that leucine should be most reactive while glycine should be least reactive. The fraction of electron transferred, $\delta$ can be calculated using equation (5)

$$\delta = (\chi_{Fe} - \chi_{inh})/2(\eta_{Fe} + \eta_{inh}) \qquad \ldots(5)$$

where$\chi_{Fe}$ and $\chi_{inh}$ are the electronegativity of Fe and the amino acids respectively. $\chi = (IP + EA)/2$. $\eta_{Fe}$ and $\eta_{inh}$ are the global hardness of Fe and the amino acids respectively. In order to validate equation (5) for this study, the theoretical values of $\chi_{Fe}$ = 7ev and $\eta_{Fe}$ = 0 were used for the computation of $\delta$ values for various models. Calculated values of $\delta$ for the amino acids were comparable (≈ 0.2). This can be explained in terms of similarity in the amino acids' parent structure.

**Table 7: Fukui and global softness indices for electrophilic andnucleophilic attacks in Pen G calculated from Mulliken (Lowdin) charges (calculated from B3YLP**/631G) for alanine**

| Atom No | f+ (\|e\|) | f - (\|e\|) | S+ (eV\|e\|) | S- (eV\|e\|) |
|---|---|---|---|---|
| 1 O | -0.148(-0.161) | -0.126(-0.137) | -0.017(-0.019) | -0.015(-0.016) |
| 2 C | -0.109(-0.128) | -0.052(-0.006) | -0.013(-0.015) | -0.006(-0.001) |
| 3 O | -0.024(-0.102) | -0.064(-0.063) | -0.003(-0.012) | -0.008(-0.007) |
| 4 C | 0.047(0.006) | 0.124(0.014) | 0.006(0.001) | 0.015(0.002) |
| 5 N | 0.058(0.067) | -0.291(-0.408) | 0.007(-0.008) | -0.034(-0.048) |
| 6 C | 0.055(-0.024) | 0.025(-0.029) | 0.006(-0.003) | 0.003(-0.003) |

**Table 8: Fukui and global softness indices for electrophilic andnucleophilic attacks in Pen G calculated from Mulliken (Lowdin) charges (calculated from B3YLP**/631G) for glycine**

| Atom No | $f^+$ (\|e\|) | $f^-$ (\|e\|) | $S^+$ (eV\|e\|) | $S^-$ (eV\|e\|) |
|---|---|---|---|---|
| 1 O | -6.649(-6.384) | 1.292(1.078) | -0.665(-0.638) | 0.129(0.108) |
| 2 C | -3.478(-3.156) | 0.667(0.782) | -0.348(-0.316) | 0.067(0.078) |
| 3 O | -4.997(-5.099) | 0.076(0.041) | -0.500(-0.510) | 0.008(0.004) |
| 4 C | 2.348(2.308) | -0.183(-0.538) | 0.235(0.231) | -0.018(-0.054) |
| 5 N | 8.149(7.787) | -1.570(-1.160) | 0.815(0.779) | -0.157(-0.116) |

**Table 9: Fukui and global softness indices for electrophilic and nucleophilic attacks in Pen G calculated from Mulliken (Lowdin) charges (calculated from B3YLP**/631G) for leucine**

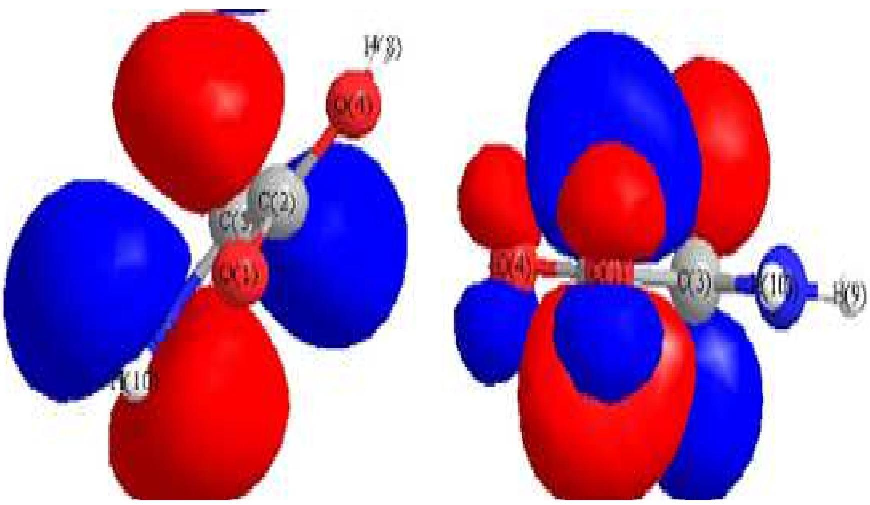
| Atom No | $f^+$ (\|e\|) | $f^-$ (\|e\|) | $S^+$ (eV\|e\|) | $S^-$ (eV\|e\|) |
|---|---|---|---|---|
| 1 O | 0.000(0.000) | 14.749(13.604 | 0.000(0.000) | 1.622(1.496) |
| 2 C | 0.000(0.000) | 14.967(13.898) | 0.000(0.000) | 1.646(1.529) |
| 3 O | 0.000(0.000) | 10.646(10.935) | 0.000(0.000) | 1.171(1.203) |
| 4 C | -0.010(0.001) | 8.801(8.507) | -0.001(0.000) | 0.968(0.936) |
| 5 C | 0.048(0.060) | -2.322(-1.306) | 0.005(0.007) | -0.255(-0.144) |
| 6 N | -0.001(0.000) | 7.651(7.906) | 0.000(0.000) | 0.842(0.870) |
| 7 C | 0.116(0.029) | -14.113(-12.022) | 0.013(0.003) | -1.552(-1.322) |
| 8 C | -0.004(-0.029) | 6.193(5.311) | 0.000(0.000) | 0.681(0.584) |
| 9 C | 0.091(0.002) | -18.417(-17.355) | 0.010(-0.006) | -2.026(-1.909) |
| 10 C | 0.154(-0.093) | -20.224(-17.246) | 0.017(-0.010) | -2.225(-1.897) |

**Local selectivity**: The local selectivity of the amino acids can be analyzed using condensed Fukui and condensed softness functions. The condensed Fukui function and condensed softness are indices which allow for the distinction of each part of a molecule on the basis of its chemical behavior due to different substituent's functional groups. The Fukui function is motivated by the fact that if an electron (δ) is transferred to an N electron molecule, it will tend to distribute so as to minimize the energy of the resulting N + δelectron system. The resulting change in electron density is the nucleophilic ($f^+$) and electrophilic ($f^-$) Fukui functions which can be calculated using the finite difference approximation as follows[9],

$$f^+ = (\delta\rho(r)/\delta N)^+_{\upsilon} = q_{(N+1)} - q_{(N)} \qquad ...(6)$$

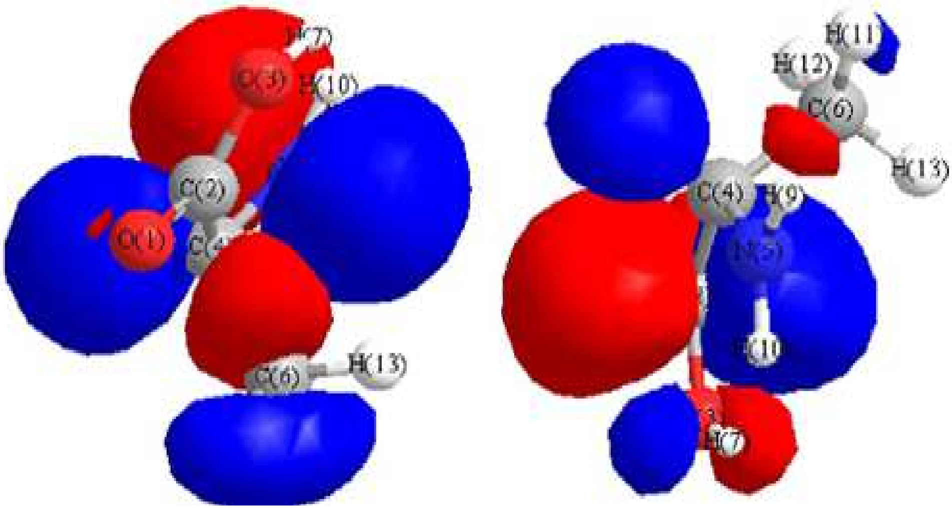
$$f^- = (\delta\rho(r)/\delta N)^-_{\upsilon} = q_{(N)} - q_{(N-1)} \qquad ...(7)$$

where ρ, $q_{(N+1)}$, $q_{(N)}$ and $q_{(N-1)}$ are the density of electron and the Mulliken charge of the atom with N+1, N and N-1 electrons. Calculated values of $f^+$ and $f^-$ for the carbon, nitrogen and oxygen atoms in alanine, glycine and leucine molecules are presented in Table 7, 8 and 9 respectively. It is expected that the site for nucleophilic attack is the site where the value of $f^+$ is maximum while the site for electrophilic attack is controlled by $f^-$. If it is assumed that the protonated forms of the inhibitors' molecules have a net positive charge, it can be deduced that the sites for nucleophilic attack are the carbon atom (C-7), the nitrogen atom (N-5) and the nitrogen atom (N-5) for leucine, alanine and glycine respectively while the sites for electrophilic attack are the carboxyl functional group for alanine, glycine and leucine respectively. This information can also be seen in the molecular orbital of the inhibitors showing the LUMO and HOMO energies of alanine, glycine and leucine respectively **(Fig. No.2, 3 and 4).**



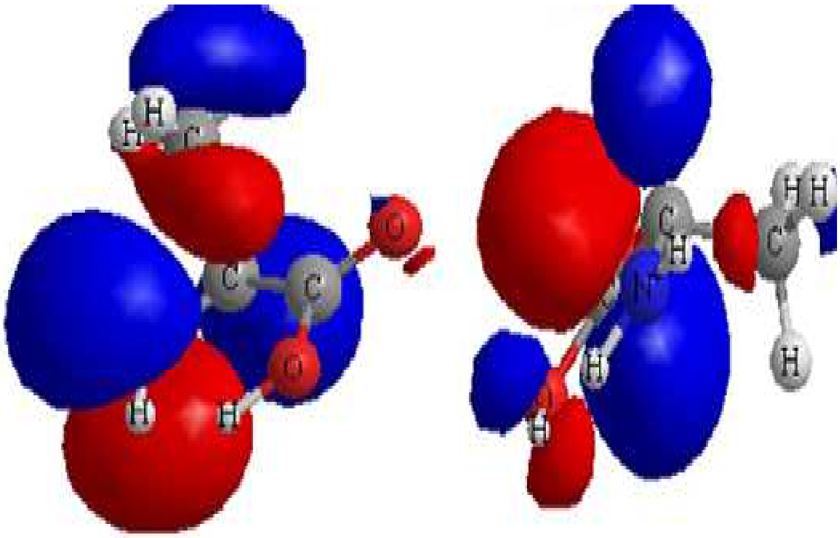
HOMO LUMO

Fig.No.2: Molecular orbital of glycine showing the LUMO and HOMO energies




HOMO LUMO

Fig.No.3: Molecular orbital of alanine showing the LUMO and HOMO energies



HOMO LUMO

Fig.No.4: Molecular orbital of leucine showing the LUMO and HOMO energies

The local softness, S for an atom is the product of the condensed Fukui function (f) and the global softness (S), as shown in equations 8 and 9 [10]

$$S^{+}=(f^{+}) \quad \ldots(8)$$

$$S^{-}=(f^{-})S \quad \ldots(9)$$

The local softness contains the same information as the condensed Fukui function plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner. The relative nucleophilicity and electrophilicity are defined as ($S^{+}/S^{-}$) and ($S^{-}/S^{+}$), respectively. These functions have been successfully applied for the prediction of reactivity sequences of carbonyl compounds towards a nucleophilic attack. It was observed that the atoms with highest value of relative nucleophilicity and electrophilicity are similar to those obtained for the Fukui functions.

## CONCLUSION

Quantum chemical principles could be used to study the reactivity of alanine, glycine and leucine towards electrophilic or nucleophilic attacks. Results obtained indicate that Leucine is most reactive while glycine is least reactive. Result obtained from PM6, PM3, AM1, RM1 and MNDO Hailtonians are comparable. The authors recommend the matching of experimental and theoretical data for future research.

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