



Molecular Structure, Electrostatic Potential and HOMO, LUMO Studies of 4-Aminoaniline, 4-Nitroaniline and 4-Isopropylaniline by DFT

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ABSTRACT

This research used the method of functional density theory (DFT). The B3LYP / 6-311G (d, p) was used to determine the chemical descriptor, the ionization potential (I), the electron affinity (A), the chemical potential (μ), the chemical hardness (η); 3D maps of HOMO and LUMO orbitals were used to develop the structure and activity of quantitative relationships. The values of the energy gap showed that p-isopropylaniline is the stable molecule and p-nitroaniline is the reactive molecule. Large basis set-theoretical calculations of the dipole polarizabilities and second hyperpolarizabilities of molecules have been carried out to assess optical properties of atomic contributions to the overall molecular response tensors. The values of the dipole moment and the first-order hyperpolarizability have the same tendency because they are related to molecular symmetry. The DFT method has been used of which is to compare the angles and lengths of molecular bonds with the experimental results. This research used the electrostatic molecular potential (MEP) and electrostatic contour to understand the regions of reactivity of the three molecules. The negative molecular electrostatic potential sites intended for electrophilic attack for p-aminoaniline, p-nitroaniline and p-isopropylaniline are (C1, C2, C3, C4, C5, C6, N7, N8), (O9, O10) and (C5, C6), respectively.

Keywords: 4-Aminoaniline; 4-Nitroaniline; 4-Isopropylaniline; DFT; Chemical descriptor; NLO; Electrostatic molecular potential

1. Introduction

The density functional theory (DFT) plays an important role in studies on freezing and melting transitions [1-2]. The liquid-crystal interface [3], nucleation [4], glass transition [5] and quasi-crystals

[6] are also treated within the framework of the DFT.

Aromatic amines play an important role in the chemical and biological industries. Aniline and its derivatives are utilized in the production of pesticides,

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dyes, and antioxidants; some of the p-substituted derivatives of aniline are local anesthetics. Aniline, also known as aminobenzene, phenylamine, or benzene amine, is an aromatic organic compound with the chemical formula $C_6H_5-NH_2$ [7]. 4-Amino-aniline (Fig. 1A) represents a very interesting class of products possessing a p and r electron system and its derivatives are used in the synthesis of dyes. Its ability to donate electrons is explored in combination with an electron acceptor. It is important for us to determine the properties of its best nature as an electron donor [8]. Aromatic amines are characterized by importance in science and materials as well as in the chemical and pharmaceutical fields. Due to their high toxicity and wide uses, halogenated anilines have obtained the highest concentration of all aromatic amines. Para-nitroaniline (Fig. 1B), or 1-amino-4-nitrobenzene, is a chemical compound with the formula $C_6H_6N_2O_2$. It is an almost odorless, yellowish-orange, crystalline powder, combustible and very soluble in water, where it is very toxic to aquatic organisms [9]. Amino and methyl groups are usually called electron giving substituents to aromatic ring systems. The CH_3 group reacts with neighboring p systems via hyperconjugation, while the NH_2 group reacts with the p electrons in a ring. Both reactions involve delocalization

of electrons. Toluidine (Fig. 1C), or aminotoluene is an aromatic compound of formula C_7H_9N , consisting of a benzene ring substituted by an amine group (aniline) and a methyl group (toluene). Like all disubstituted benzenes, it exists in the form of three structural isomers, the ortho, meta and para compounds, depending on the relative position of the two substituents on the ring [10]. Charge transfer interactions form between electron donor compounds and electron acceptor compounds and result in resonance with charge transfer from the donor molecule to the acceptor molecule. Complex formation is based on the interaction of the donor's highest occupied molecular orbital with the lowest unoccupied acceptor molecular orbital [11].

This research is interested in studying the structural properties of p-aminoaniline, p-nitroaniline and 4-isopropylaniline. The DFT method was used to calculate the global descriptors (the energies and densities of the limit molecular orbitals HOMO and LUMO, the electronic chemical potential, electronegativity, chemical hardness, overall softness, overall electrophilic index, global nucleophilic index, properties non-linear magnetic optics) to compare the stability and reactivity of these molecules and determine their regions of reactivity by molecular electrostatic potential.

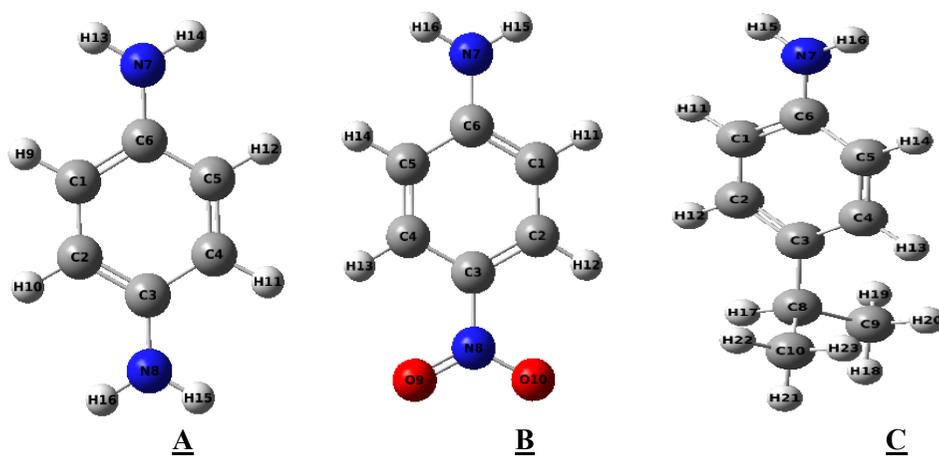


Fig. 1. Optimized molecular structure of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline.

2. Computational Method

All calculations have been carried out with the Gaussian 09 program [12] and visualized with the Gaussview software [13] on an i7 PC. The optimization was performed by density functional theory (DFT) [14] with the B3LYP functional [15-16] and the standard base 6-311G (d, p).

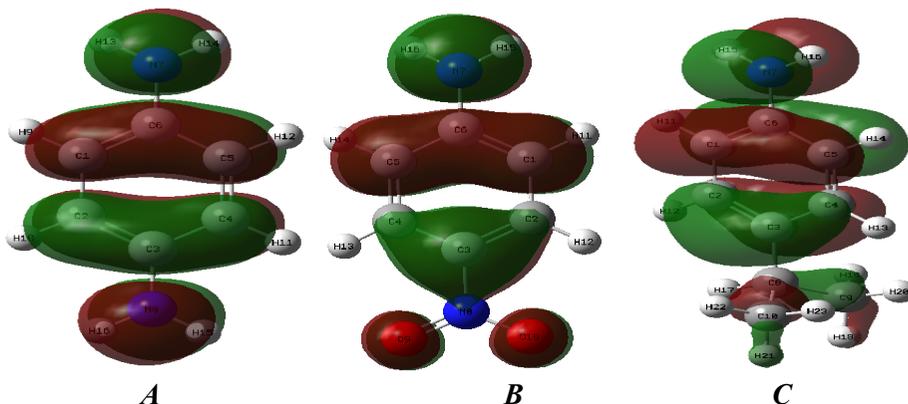
The DFT method was used to include popular local methods and gradient correction [17]. The following quantum of the chemical indices have been taken into account: the E_{HOMO} , E_{LUMO} , the energy band gap $\Delta E = E_{HOMO} - E_{LUMO}$, the quantum descriptors, the electronic affinity, the ionization potential and the atomic partial charges were calculated for the two structures from the potential electrostatic surface (ESP) according to the same theory of levels [18].

3. Results and Discussion

3.1 Quantum chemical calculation

The main orbitals involved in chemical stability are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO represents the capacity to yield an electron while the LUMO represents the capacity to gain an electron. The HOMO and LUMO energies are calculated by the B3LYP/6-311G (d, p) method. Electronic absorption corresponding to the passage of the ground to the first excited state described by an electronic excitation from the HOMO orbital to the LUMO orbital [19] with the optimized structure of molecules is illustrated in Figs. 2- 3 shows the Mulliken charge distribution for the three molecules.

HOMO



LUMO

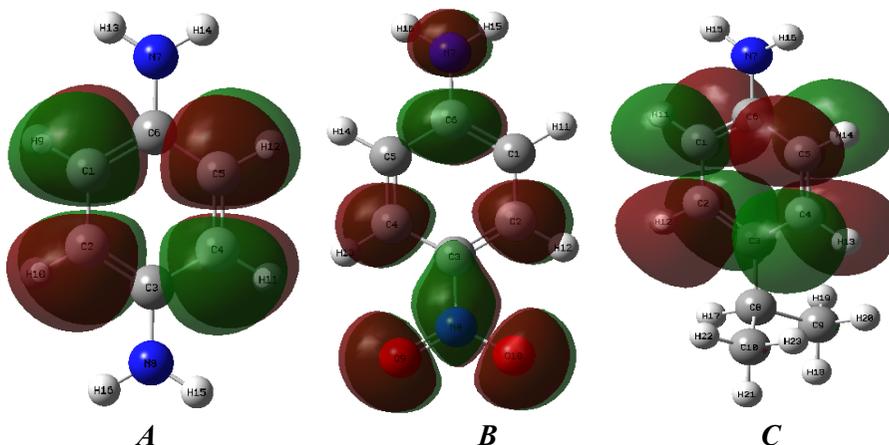


Fig. 2. HOMO and LUMO of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline.

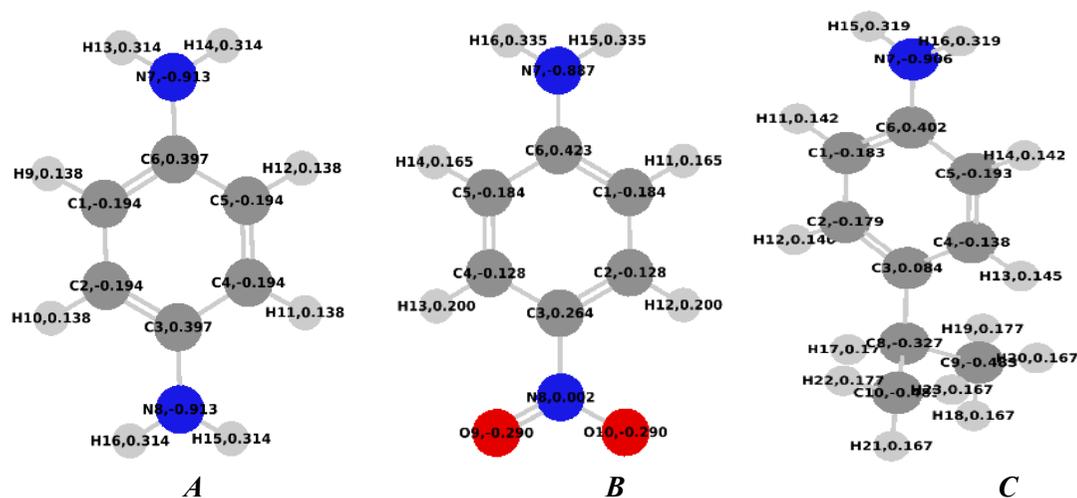


Fig. 3. Mulliken charges of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline by the B3LYP method.

Many applications are available on the utilization of the HOMO and LUMO gap as a quantum descriptor in correlates in different biochemical and chemical systems [20].

The following quantum descriptors have been calculated from the optimized structure obtained: Ionization potential:

$$I = -E_{HUMO}, \quad (3.1)$$

Electronic affinity:

$$A = -E_{LUMO}, \quad (3.2)$$

Absolute electronegativity:

$$\chi = \frac{I + A}{2}, \quad (3.3)$$

Overall hardness:

$$\eta = I - A, \quad (3.4)$$

Overall softness:

$$\sigma = \frac{1}{\eta} = \frac{1}{E_{LUMO} - E_{HOMO}}, \quad (3.5)$$

Electronic chemical potential:

$$\mu = -\frac{(I + A)}{2}, \quad (3.6)$$

Maximum charge transfer:

$$\Delta N_{\max} = \frac{\mu}{\eta}, \quad (3.7)$$

Overall electrophilicity:

$$\omega = \frac{\mu^2}{2\eta}, \quad (3.8)$$

Overall nucleophilicity N:

$$N = E_{HUMO} - E_{HOMO(TCE)}, \quad (3.9)$$

with $E_{HOMO(TCE)} = -9.3686$ eV calculated by DFT/B3LYP 6-311G (d, p).

In order to highlight the electrophilic/nucleophilic character of the molecules, we calculated the ionization potential I , the electronic affinity A , the electronic chemical potential μ , the absolute electronegativity χ , the overall hardness η , the overall softness σ , the overall electrophilicity index ω , the index of overall nucleophilicity N and the maximum charge transfer ΔN_{\max} which are shown in Table 1.

Table 1. Quantum theoretical parameters of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline, calculated by B3LYP / 6-311G (d, p).

Parameters	E _{LUMO} (eV)	E _{HOMO} (eV)	ΔE (eV)	I (eV)	A (eV)	μ (eV)
p-Aminoaniline	0.2306	-4.3713	4.6019	4.3713	-0.2306	-2.0703

Parameters	χ (eV)	η (eV)	σ (eV ⁻¹)	ω (eV)	N (eV)	ΔN _{max} (eV)
p-Aminoaniline	2.0703	4.6019	0.2173	0.6456	4.9973	0.4498

Parameters	E _{LUMO} (eV)	E _{HOMO} (eV)	ΔE (eV)	I (eV)	A (eV)	μ (eV)
p-Isopropylaniline	0.0682	-5.2286	5.2968	5.2286	-0.0682	-2.5802

Parameters	χ (eV)	η (eV)	σ (eV ⁻¹)	ω (eV)	N (eV)	ΔN _{max} (eV)
p-Isopropylaniline	2.5802	5.2968	0.1887	0.6284	4.14	0.4871

Parameters	E _{LUMO} (eV)	E _{HOMO} (eV)	ΔE (eV)	I (eV)	A (eV)	μ (eV)
p-Nitroaniline	-2.5714	-6.4621	3.8907	6.4621	2.5714	-4.5167

Parameters	χ (eV)	η (eV)	σ (eV ⁻¹)	ω (eV)	N (eV)	ΔN _{max} (eV)
p-Nitroaniline	4.5167	5.7313	0.1744	1.7797	2.9065	0.7880

The calculated energy gap values are 3.8907 eV, 5.2968 eV and 4.6019 eV for p-nitroaniline, p-isopropylaniline and p-aminoaniline, respectively. This explains why p-isopropylaniline is more stable than p-nitroaniline and p-aminoaniline.

The overall electrophilicity index values are 0.6456 eV, 0.6284 eV and 1.7797 eV for p-aminoaniline, p-isopropylaniline and p-nitroaniline, respectively. As a result, the reactivity of p-nitroaniline to a nucleophilic attack is greater than the other two molecules.

The overall nucleophilicity index values are 4.14 eV, 2.9065 eV and 4.9973 eV, for p-isopropylaniline, p-nitroaniline and p-aminoaniline. Therefore, the reactivity of p-aminoaniline to electrophilic attack is greater than that of p-nitroaniline and p-isopropylaniline.

The charge that p-nitroaniline can acquire from its environment ($\Delta N_{\max} = 0.7880$ eV) is greater than that of other molecules.

3.2 Non-linear optical properties

Intermolecular interactions such as drug-vitamin are widely understood by dipole moment and the energetic terms of hyperpolarization of the first and second-or-

der. The dipole moment (μ), the polarizability (α), the first hyperpolarizability (β) and the second hyperpolarizability (γ) are calculated using DFT on the basis B3LYP 6-311G approach (d, p). The complete equations to calculate the amplitude of the total static dipole moment (μ), the polarizability (α), the first hyperpolarizability (β) and the second hyperpolarizability (γ), by the components x, y, z of 09W the Gaussian output is as follows [21]:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}, \quad (3.10)$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}, \quad (3.11)$$

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}, \quad (3.12)$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \quad (3.13)$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}, \quad (3.14)$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}, \quad (3.15)$$

$$\langle \gamma \rangle = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2[\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{xxzz}]). \quad (3.16)$$

The results for the non-linear optical properties are tabulated in Table 2.

The dipole moment of the molecules is again calculated using DFT and method B3LYP with basic set 6-311G (d, p). The dipole moment reflects the distribution of molecular charges and is given as a three-dimensional vector. Consequently, it can be utilized as a descriptor to represent the charge movement through the molecule as a function of the negative and positive charge centers. Dipole moments are necessarily determined for neutral molecules. For charged molecules, values depend on the orientation and the choice of the origin of the molecular.

The results showed that the determined value of the dipole moment of p-nitroaniline (10.0817 D) is greater than those of p-isopropylaniline (2.4864 D) and p-aminoaniline (0.0003 D).

The results showed that the dipolar polarizability value of p-aminoaniline (-42.3552 D) was higher compared to the values of the polarizability tensors of p-nitroaniline and p-isopropylaniline.

The transitions of p-nitroaniline 125.9916 D and -0.0007 D are observed

along the x and y axes and -0.0008 D along with a negative direction, while the transitions of p-aminoaniline -0.0008 D and -0.0009 D are found along the y and z axes with a negative direction and the 0.0008 D transition is found along with a positive direction. The p-isopropylaniline transitions -0.8625 D and -1.0064 D are found along the y and z axes with a negative direction and 78.4461 D along the x-axis with a positive direction.

Dipole and first order hyperpolarizability have the same tendency because they are related to molecular symmetry.

The high and low value of β is calculated to be 135.1874 D and 0.00475 in p-nitroaniline and aminoaniline, respectively. Therefore, electron delocalization and charge transfer increase in p-nitroaniline, resulting in a greater β response of p-nitroaniline compared to p-isopropylaniline and p-aminoaniline.

The values of the second-order hyperpolarizability γ , as well as their contributing tensors, are also observed to be greater in p-aminoaniline than p-nitroaniline and p-isopropylaniline.

Table 2. Electric dipole moments (Debye) by the DFT method of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline calculated by B3LYP / 6-311G (d, p).

	Parameters	A	B	C
Dipole moment (Debye)	μ_x	0.0000	10.0817	2.4794
	μ_y	-0.0002	-0.0002	-0.1621
	μ_z	0.0002	0.0001	0.0932
	μ	0.0003	10.0817	2.4864
Polarizability (Debye)	α_{xx}	-30.5966	-56.3980	-48.7801
	α_{yy}	-42.1883	-53.5752	-58.3983
	α_{zz}	-54.2808	-60.0852	-67.1977
	α	-42.3552	-56.6861	-58.1253
First Hyperpolarizability (Debye)	β_{xxx}	-0.0008	125.9916	78.4461
	β_{xxy}	0.0002	19.8964	13.8498
	β_{xzz}	0.0004	-11.1622	-0.2943
	β_{yyy}	-0.0009	-0.0007	-0.8625
	β_{xyy}	-0.0022	-0.0001	-0.5293
	β_{yzz}	0.0000	0.0002	-0.4765
	β_{zzz}	0.0008	-0.0008	-1.0064

	β_{xxz}	0.0017	-11.1622	-0.2943
	β_{yyz}	0.0011	0.0003	1.2485
	β	0.00475	135.1878	92.0205
Second Hyperpolarizability (Debye)	γ_{xxxx}	-631.3569	-1246.4404	-1472.2424
	γ_{yyyy}	-308.6713	-370.0793	-392.4747
	γ_{zzzz}	-58.9777	-59.6126	-220.9768
	γ_{xxyy}	-145.4924	-285.8703	-326.6312
	γ_{yyzz}	-72.3390	-83.5331	-108.2036
	γ_{xxzz}	-175.3008	-253.8500	-352.9236
	γ	-357.0540	-584.5277	-732.2421

3.3 Thermodynamic parameters

This research determined for each molecule the enthalpy ΔH , the entropy ΔS , and the free energy ΔG (Table 3). The enthalpy ΔH is defined by the sum of the internal energy of a system and the product of its pressure by its volume. Entropy ΔS can be characterized by the degree of disorder or unpredictability of the information contained in a system. The ΔG is the energy relative to different reference states.

The values of ΔH and ΔS were taken directly from the Notepad file provided by the Gaussian software and ΔG was calculated by $\Delta G = \Delta H - T\Delta S$ with $T = 298K$. This ΔG amount is relative to free electrons and free nuclei. We found that the ΔG values of p-nitroaniline, p-aminoaniline and p-isopropylaniline are -1291.5×10^3 kJ/mol, -899.9×10^3 kJ/mol and -1064.3×10^3 kJ/mol, respectively.

Table 3. Thermodynamic parameters of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline.

Molecules	ΔH (Kj/mol)	ΔS (Kj/mol/K)	ΔG (Kj/mol)
A	-900×10^3	0.36024	-899.9×10^3
B	-1291.6×10^3	0.37278	-1291.5×10^3
C	-1064.2×10^3	0.41045	-1064.3×10^3

3.4 Bond length and bond angle properties

This research will deepen our knowledge of selective bond lengths (Å) and angles (θ°). The DFT level has been used with the B3LYP/6-311G (d, p) method, the utility of which is to describe the molecular physical and chemical properties [18].

Tables 4-5 were determined the comparison of the optimized bond length and the angle between experimental and calculated atomic numbered positions as shown in Fig. 1. The optimized structures using a periodic DFT calculation correspond exactly to an experimental result. The study of the geometric product, therefore, showed an excellent agreement between theoretical and experimental results.

Table 4. Bond lengths (Å) of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline.

Bond length (Å)	A	B	C	Exp [7,22]
C1-C2	1.3948	1.3948	1.3948	1.408
C2-C3	1.3949	1.3949	1.3949	1.415
C3-C4	1.3948	1.3948	1.3948	1.390
C4-C5	1.3948	1.3948	1.3948	1.395
C5-C6	1.3949	1.3949	1.3949	1.395
C6-N7	1.266	1.266	1.266	1.370
C3-N8	1.266	---	---	1.247

C3-O8	---	1.248	---	1.246
N8-O9	---	1.31	---	---
N8-O10	---	1.31	---	---
C3-C8	---	---	1.497	1.460
C8-C9	---	---	1.523	---
C8-C10	---	---	1.523	1.737

Table 5. Angles (θ°) of (A) p-aminoaniline, (B) p-nitroaniline, (C) p-isopropylaniline.

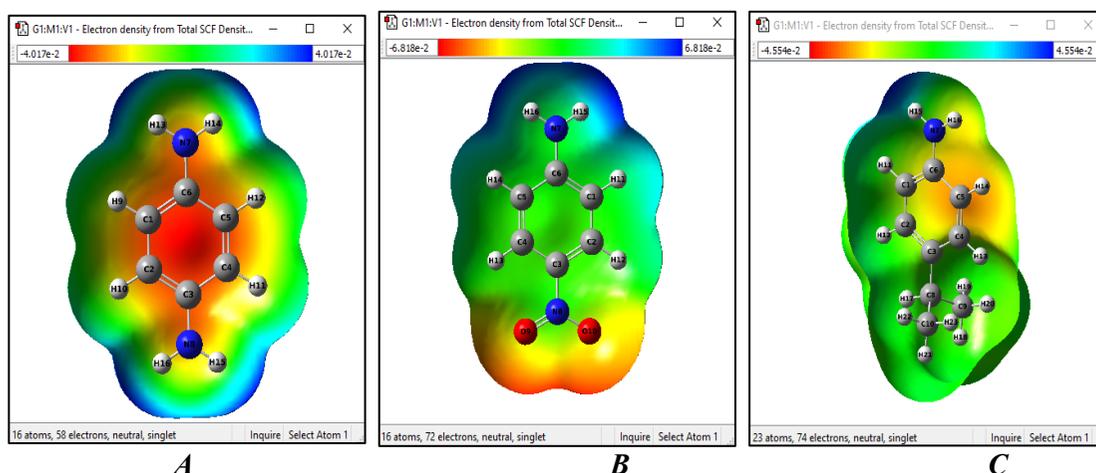
Angles (θ°)	A	B	C	Exp [7]
C1-C2-C3	119.9969	119.9969	119.9969	118.8
C2-C3-C4	120.0002	120.0002	120.0002	120.9
C3-C4-C5	120.0033	120.0033	120.0033	120.0
C5-C6-N7	119.9991	119.9991	119.9991	119.5
C2-C3-N8	120.0034	119.9973	---	120.4
O9--N8-O10	---	120.0008	---	120.8
C9--C8-C10	---	---	109.5028	120.1

3.5 Electrostatic Molecular Potential of molecules

The electrostatic molecular potential gives detailed information for the study of the biological activity and chemical reactivity of a molecule. The distribution and values of electrostatic potential determine the sites of electrophilic or nucleophilic attack in a chemical reaction [22-27]. The MEP is mainly used in the form of the reactivity map showing the most likely regions for the electrophile attack of point reagents loaded on organic compounds. It is important in the molecular modeling studies. Contour MEP, the map offers a simple tool to predict how different geometries can interact. The total electronic density and the MEP surface of the molecules studied are constructed by B3LYP / 6-311 method using

basis set G (d, p). Electrostatic potential maps and contour electrostatic potential of p-aminoaniline, p-nitroaniline and isopropylaniline are shown in Figs. 4 and 5. The color scheme for the MEP surface is red, rich in electrons, partially negative charge; blue, electron-deficient, partially positive charge; light blue, slightly electron-deficient region; yellow region, slightly rich in electrons; green, neutral, respectively. Blue represents electropositive and red the electronegative regions, respectively [28].

The negative molecular electrostatic potential sites intended for electrophilic attack for p-aminoaniline, p-nitroaniline, and p-isopropylaniline are (C1, C2, C3, C4, C5, C6, N7, N8), (O9, O10) and (C5, C6), respectively.

**Fig. 4.** Electrostatic potential maps around the molecule of p-aminoaniline, p-nitroaniline and p-isopropylaniline.

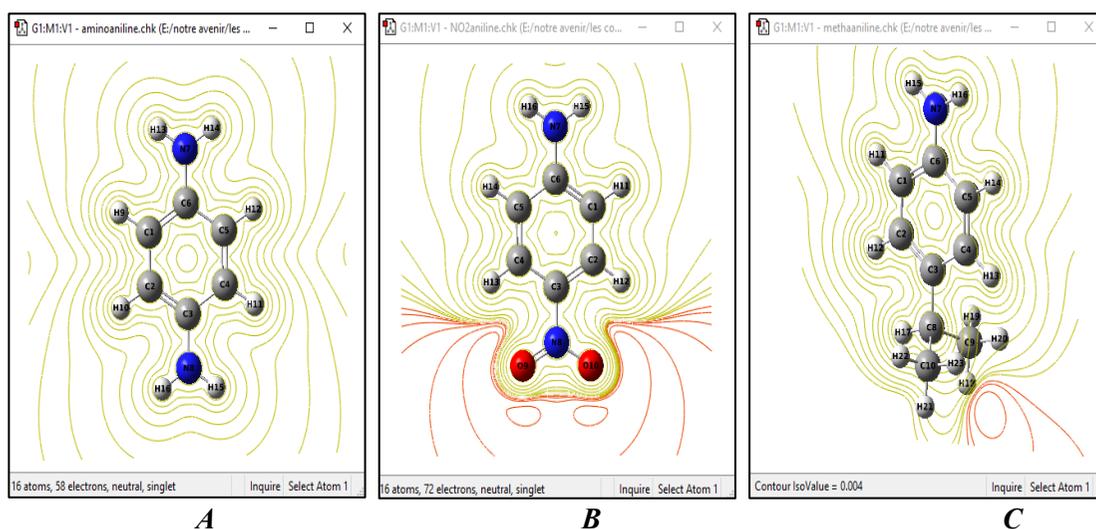


Fig. 5. Contour electrostatic potential around the molecule of p-aminoaniline, p-nitroaniline and p-isopropylaniline.

4. Conclusions

The electronic properties of the three molecules have been calculated. HOMO and LUMO energy deviations describe the possible charge, transfer interactions taking place in the molecule, and the determination of theoretical molecular structures, electrostatic potential and electrostatic potential contour maps around molecules by B3LYP / 6-311G (d, p) using the DFT method. Molecular orbitals, the MEP surface can lead to an understanding of the properties and activity of molecules. The linear polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) values of the studied molecule were calculated. DFT / B3LYP / 6-311G (d, p) has proven to be a good method of optimizing molecular geometries. The molecular electrostatic potential determined the regions rich in electrons destined for electrophilic attacks.

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