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Evaluation by NMR spectroscopy and global descriptors of the para substituents of aniline by the DFT method

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1. Introduction

Abstract

Classical physics perfectly describes our daily environment but becomes inoperative at the microscopic scale of atoms and particles. Quantum mechanics is the fundamental theory of the particles of matter constituting the objects of the universe and the forces animating these objects. This study was designed to calculate the structural and spectroscopic properties of the p-chloroaniline, p-fluoroaniline, and p-bromoaniline molecules. The theoretical approach to the functional density of NMR spectrophotometry is estimated by DFT. The molecules are optimized by the theoretical level B3LYP/6-311G (d, p), the ionization potential, electronic affinity, the chemical potential electronics, chemical hardness. Nonlinear optical descriptors (NLO) such as dipole moment and polarizability are also determined. We also report with what precision the HOMO-LUMO deviations of this method predict the lowest excitation energies using DFT. The atomic partial charges were also calculated for the three structures from the potential electrostatic surface (ESP) according to the same level theory.

p-Chloroaniline is an organochlorine compound with the formula ClC₆H₄NH₂ (Figure 1A). This pale yellow solid is one of the three isomers of chloroaniline. The interest of p-chloroaniline in the environment is due to its recognized toxicity associated with its ubiquitous diffusion. Can be present in industrial effluents, sludge and agricultural soils; they are produced in biodegradation processes of acylanilide, and phenyl carbamate, can be derived from the synthesis of azo dyes and industrial application and are important intermediaries in the production of polymers, rubber additives, 2 dyes, and pharmaceutical products. Due to the high persistence in the environment and low natural biodegradability, sanitation strategies have been developed for their destruction, based on different processes and reagents [1]. p-Chloroaniline is used as an intermediate in the production of several products. Thus, releases of p-chloroaniline into the environment may occur from some of the industrial sources (production, processing, dyeing/printing industry) [2]. Thus, its monitoring and control of exposure, in both industrial and residential environments, are of special interest. Researchers have been looking for good materials as gas sensors with high sensitivity for a long time [3]. Due to their high

toxicity, large diffusion, and low biodegradability, p-chloroaniline have been listed as important persistent toxic organic pollutants in many countries. The presence of p-chloroaniline could produce obvious toxicity to organisms, such as phaeodactylum tricornutum, oreochromis niloticus, photobacteria phosphoreum, and Comamonas testosterone. The wastewater containing p-chloroaniline eventually enter biological wastewater treatment systems [4]. Aromatic amines are of great importance in the and materials sciences as well as in the pharmaceutical and chemical industries. Halogenated anilines gained the most concentration of all aromatic amines, due to their high toxicity and wide uses. For example, they can be used as reagents or precursors for the synthesis of organic dyes, in pigments, in agricultural agents, in pharmaceuticals, and rubber Industries. p-Bromoaniline (Figure 1B) is a compound in which an aniline molecule is substituted by a bromine atom in the para position. p-bromoaniline can be made by reacting aniline with bromine with protection with acetyl chloride [5]. Commercially available, this compound can be used as a constituent element [6], p-Fluoroaniline (Figure 1C) are an important class of fluorine compounds, because they exhibit interesting biological activities and, therefore, are widely used as key intermediates in the manufacturing of leading pharmaceutical and agrochemicals (pesticides, herbicides, and fungicides). p-Fluoroaniline isomers are used in the synthesis of fluorobenzofuroxanes. In general, benzofuroxane derivatives exhibit remarkable biological activities, such as antimicrobial, fungicide, algaecide, herbicide, nematocidal activity [7]. The characterization of intermolecular interactions and the nature of molecular geometry has been carried out. Using a quantum chemical approach, using a functional density theory (DFT) method. This approach made it possible to have a detailed image of the chemical descriptor of the molecule [8]. Since the ascent of DFT initiated by the Hohenberg–Kohn theorem, it has become the most widely used quantum chemical method in chemistry and physics. Although no systematic way of improving DFT is known, important progress has been achieved over the years in finding helpful functional descriptions [9].

In this paper, we are interested in the study of the structural properties of the p-chloroaniline, pfluoroaniline, and p-bromoaniline. We used the quantum density functional theory (DFT) method to calculate thermochemical descriptors (the optimization of the geometries, lengths and bond angles of molecules, the energies and densities of HOMO boundary molecular orbitals and LUMO, electronic chemical potential, electronegativity, chemical hardness, overall softness, overall electrophilic index, global nucleophilic index, non-linear magnetic optical properties) to compare the stability and reactivity of these molecules and to study their biological activities by electrostatic potential molecular.



Figure 1: Optimized molecular structure of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline.

2. Computational method

All calculations have been performed using the GAUSSIAN 09 program [10]. The geometry for all structures and the RMN spectra was optimized at the DFT/B3LYP level of theory with a 6-311G (d, p)

basis set [11]. The latter one contains diffuse and polarization functions, as well as effective core potentials. The most stable structures of the investigated compounds were obtained by full optimization without any geometrical constraints and no imaginary frequencies were presented. The mentioned theoretical model was chosen to optimize the geometries of the investigated compounds, as it is recommended for the determination of the geometry of similar coumarin derivatives. For the simulation of the ¹H and ¹³C NMR spectra of the studied compounds, the GIAO (Gauge Independent Atomic Orbital) approach was used. For this purpose, the geometry of TMS (internal standard) in the same solvents was optimized at the same level of theory.

In order to obtain values for the chemical shifts of the hydrogen and carbon atoms, it is necessary to subtract the calculated values for TMS from corresponding values of investigated compounds [12]. The FMOs (HOMO and LUMO) are very important for describing chemical reactivity. The HOMO that has no electrons, represents the ability of (E_{HOMO}) to donate an electron, whereas, the LUMO haven't electrons represent the ability of (E_{LUMO}) to accept or gain an electron. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability, and chemical hardness the softness of compounds and the atomic partial charges were also calculated for the three structures from the potential electrostatic surface (ESP) according to the same theory of levels [13].

3. Results and discussion

3.1. Theoretical chemical displacements ¹H and ¹³C NMR of the molecules

The entire calculations were performed at the density functional (DFT) level on a computer using the Gaussian 09 program package, invoking gradient geometry optimization. The geometry of the title the compound, together with that of tetramethylsilane (TMS) is fully optimized. ¹H and ¹³C NMR chemical shifts are calculated with the GIAO approach by applying the B3LYP method [14]. Then, GIAO ¹³C and ¹H calculations of the titer the molecules are calculated and compared to the experimental data are presented in table 1. The result shows that in the NMR range, the chemical shift of typical organic molecules is generally > 100 ppm for ¹³C and < 10 ppm for and ¹H, the accuracy ensures reliable interpretation of spectroscopy parameters. it seems that the chemical shifts calculated for the carbon and hydrogen atoms are in good agreement with the experimental results.

	Α	В	С	
Nuclei	δ_{GIAO}	δ_{GIAO}	δ_{GIAO}	δ_{Exp}
C ₁	115.6	116.6	114.2	117.34
C ₂	129.6	132.4	116.3	133.09
C ₃	127.7	116.7	157.3	119.97
C ₄	129.6	132.4	116.3	126.96
C ₅	155.6	116.6	114.2	129.22
C ₆	146.5	147.4	144.0	144.82
H9	6.75	6.52	6.61	7.15
H_{10}	7.24	7.35	6.99	6.52
H_{11}	7.24	7.35	6.99	6.51
H_{12}	6.75	6.52	6.61	6.00
H_{13}	6.27	6.27	6.27	7.14
H_{14}	6.27	6.27	6.27	7.15

Table 1: The theoretical ¹H and ¹³C NMR chemical shifts of the molecules calculated using GIAO / B3LYP(6-311G (d, p)), (Experimental values for the p-chloroaniline crystal structure [15-17]).

3.2. 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 and LUMO energies are calculated by the B3LYP / 6-311G (d, p) method. Electronic absorption corresponds to the transition from the ground to the first excited state described by an electronic excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) with the optimized structure of molecules is illustrated in figure 2. The Mulliken charges of the three molecules are given in figure 3.

HOMO



LUMO



Figure 2: HOMO and LUMO of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline.



Figure 3: Mulliken charges of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline 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 [18, 19]. The following quantum descriptors have been calculated from the optimized structure obtained:

Ionization potential:	$I = -E_{HOMO}$
Electronic affinity:	$A = -E_{LUMO}$
Absolute electronega	tivity: $\chi = \frac{I+A}{2}$
Overall hardness:	$\eta = I - A$
Overall softness:	$\sigma = \frac{1}{\eta} = \frac{1}{E_{\text{LUMO}} - E_{\text{HOMO}}}$
Electronic chemical]	potential: $\mu = -\frac{(I+A)}{2}$
Maximum charge tra	nsfer: $\Delta Nmax = -\frac{\mu}{\eta}$
Overall electrophilic	ity: $\omega = \frac{\mu^2}{2\eta}$
Overall nucleophilia	N: N = $E_{HOMO} - E_{HOMO(TCE)}$ with $E_{HOMO(TCE)}$ = -9.3686 eV calculated by
DFT/B3LYP 6-311G	b (d, p).

In order to highlight the electrophilic/nucleophilic character of p-chloroaniline, p-bromoaniline and p-fluoroaniline, 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 nucleophilic N and the maximum charge transfer ΔN_{max} (Table 2).

Parameters	E _{LUMO} (eV)	E _{HOMO} (eV)	$\Delta E (eV)$	I (eV)	A (eV)	μ (eV)
p-Chloroaniline	-0.4762	-5.7147	5.2385	5.7147	0.4762	-3.0954
Parameters	χ (eV)	η (eV)	σ (eV ⁻¹)	ω (eV)	N (eV)	$\Delta N_{max}(eV)$
p-Chloroaniline	3.0954	5.2385	2.6492	0.9145	3.6539	0.5908
Parameters	E _{LUMO} (eV)	E _{HOMO} (eV)	ΔE (eV)	I (eV)	A (eV)	μ (eV)
p-Bromoaniline	-0.3919	-5.6225	5.2306	5.6225	0.3919	-3.0072
Parameters	χ (eV)	η (eV)	σ (eV ⁻¹)	ω (eV)	N (eV)	$\Delta N_{max}(eV)$
Parameters p-Bromoaniline	χ (eV) 3.0072	η (eV) 5.2306	σ (eV⁻¹) 0.1911	ω (eV) 0.8644	N (eV) 3.7461	ΔN _{max} (eV) 0.5749
Parameters p-Bromoaniline	χ (eV) 3.0072	η (eV) 5.2306	σ (eV⁻¹) 0.1911	ω (eV) 0.8644	N (eV) 3.7461	$\frac{\Delta N_{max}(eV)}{0.5749}$
Parameters p-Bromoaniline Parameters	χ (eV) 3.0072 Ε _{LUMO} (eV)	η (eV) 5.2306 Ε _{HOMO} (eV)	σ (eV ⁻¹) 0.1911 ΔΕ (eV)	<u>ω (eV)</u> 0.8644 I (eV)	N (eV) 3.7461 A (eV)	ΔN _{max} (eV) 0.5749 μ (eV)
Parameters p-Bromoaniline Parameters p-Fluoroaniline	χ (eV) 3.0072 E _{LUMO} (eV) -0.4044	η (eV) 5.2306 Ε_{HOMO} (eV) -5.5806	σ (eV ⁻¹) 0.1911 ΔE (eV) 5.1762	ω (eV) 0.8644 I (eV) 5.5806	N (eV) 3.7461 A (eV) 0.4044	ΔN _{max} (eV) 0.5749 μ (eV) -2.9925
Parametersp-BromoanilineParametersp-Fluoroaniline	χ (eV) 3.0072 E _{LUMO} (eV) -0.4044	η (eV) 5.2306 Ε _{HOMO} (eV) -5.5806	σ (eV ⁻¹) 0.1911 ΔE (eV) 5.1762	ω (eV) 0.8644 I (eV) 5.5806	N (eV) 3.7461 A (eV) 0.4044	ΔN _{max} (eV) 0.5749 μ (eV) -2.9925
Parametersp-BromoanilineParametersp-FluoroanilineParameters	<u>χ (eV)</u> 3.0072 <u>E_{LUMO} (eV)</u> -0.4044 <u>χ (eV)</u>	η (eV) 5.2306 Ε _{HOMO} (eV) -5.5806 η (eV)	σ (eV ⁻¹) 0.1911 ΔE (eV) 5.1762 σ (eV ⁻¹)	ω (eV) 0.8644 I (eV) 5.5806 ω (eV)	N (eV) 3.7461 A (eV) 0.4044 N (eV)	ΔN _{max} (eV) 0.5749 μ (eV) -2.9925 ΔN _{max} (eV)

 Table 2: Quantum theoretical parameters of the (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline, calculated by B3LYP / 6-311G (d, p).

The energy gap of p-fluoroaniline (5.1762 eV) is slightly lower than the energy gaps corresponding to p-chloroaniline (5.2385 eV) and p-bromoaniline (5.2306 eV), therefore p-fluoroaniline is the slightly reactive molecule given its low energy gap value and p-chloroaniline and p-bromoaniline are slightly stable molecules. Hardness gives an idea of the relative duration of a molecule to store electrons in its environment. According to the table, we have almost the same value of the chemical hardness of the three molecules, therefore they contain more electrons in their environment which reflects their close stabilities between them.

The electrophilicity index of p-chloroaniline ($\omega = 0.9145 \text{ eV}$) is higher than that of p-bromoaniline ($\omega = 0.8644 \text{ eV}$) and p-fluoroaniline ($\omega = 0.8650 \text{ eV}$) which shows that the reactivity of p-chloroaniline visa-vis nucleophilic attack is greater than that of p-bromoaniline and p-fluoroaniline.

The nucleophilicity index of p-fluoroaniline (N = 4.198 eV) is higher than that of p-bromoaniline (N = 3.7461 eV) and p-chloroaniline (N = 3.6539 eV), which shows that the reactivity of p-fluoroaniline visà-vis electrophilic attack is greater than that of p-bromoaniline and p-chloroaniline.

3.3. Non-linear optical properties

The dipole moment is an important parameter that describes the interaction among atoms. It is the product of the magnitude of charges and distance between them [20]. The values for the distribution of charges in x, y, and z-directions are listed in table 3. The NLO behavior of molecules has been theoretically deduced by the calculated value of the first and second order hyperpolarization. The first geometry of molecules was optimized using the Gaussian 09 package program using a basic set 6-311G (d, p) and a functional hybrid exchange with the Lee-Yang - Parr correlation functional (B3LYP), and the energy terms the first and second-order hyperpolarization. The first hyperpolarization (β), the second hyperpolarization (γ), the dipole moment (μ) and the polarizability (α) are calculated using a basic set of DFT. Complete equations to calculate the amplitude of the total static dipole moment (μ), the average polarizability (α), the anisotropy of the polarizability and the first average hyperpolarization (β), using the x, y, z components of 09 the Gaussian output is the next one [21] :

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

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

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

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

$$\langle \Upsilon \rangle = \frac{1}{5} (\Upsilon_{xxx} + \Upsilon_{yyy} + \Upsilon_{zzz} + 2[\Upsilon_{xxy} + \Upsilon_{yyz} + \Upsilon_{xxz}])$$

The dipole moment of the molecule is also calculated by DFT of Method B3LYP with basic set 6-311G (d, p). The dipole moment reflects the distribution of molecular charges and is given as a threedimensional vector. Therefore, it can be used as a descriptor to represent the charge movement through the molecule as a function of the positive and negative charge centers. Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. The results show that the determined value of the dipole moment of pchloroaniline (4.6195 D) is greater than those of p-bromoaniline (4.2169 D) and p-fluoroaniline (2.4452 D), which reflects the stability of p-chloroaniline with respect to other molecules. The results revealed that the value of the dipolar polarizability tensors of p-bromoaniline and p-fluoroaniline was high in all three directions compared to the values of the polarizability tensors of p-chloroaniline. The high values of the calculated dipole polarization are -53.9761 D and -43.9220 D for p-bromoaniline and pfluoroaniline, respectively, while the low value of dipolar polarization (-54.1892 D) is observed in pchloroaniline. So p-bromoaniline and p-fluoroaniline are slightly polarizable and are mildly chemically active. The transitions 21.8103 D and 0.0004 D of p-chloroaniline are observed along the x and y axes with a positive direction and -0.0013 D along the z-axis with a negative direction, while the transitions 12.6105 D and 0.0134 D of p-bromoaniline are found along the x and z axes with a positive direction

and the transition -1.4354 D is found along with a negative direction along the y-axis and the transitions 44.5293 D and 0.0007 D of p-fluoroaniline are found along x and z axes with a positive direction and - 0.0005 D along the y-axis with a negative direction. The high and low β is calculated to be 38.0802 D and 12.8405 in p-fluoroaniline and p-chloroaniline, respectively. Therefore, electron delocalization and charge transfer increase in p-fluoroaniline, resulting in a greater β response compared to p-chloroaniline. The values of the second-order hyperpolarizability γ , as well as their contributing tensors, are also observed to be greater in p-bromoaniline and p-fluoroaniline compared to p-chloroaniline.

	Parameters	Α	В	С
	μ_{x}	4.6195	4.2169	1.9768
	μ_{y}	0.000	0.000	-1.4392
Dipole moment (Debye)	μ_z	-0.0001	-0.0001	0.0014
	μ	4.6195	4.2169	2.4452
	α_{xx}	-44.0577	-56.7313	-41.2435
Polarizability	$\alpha_{\rm vv}$	-53.5928	-49.2506	-39.9238
(Debye)	α_{zz}	-64.9173	-55.9466	-50.5989
	α	-54.1892	-53.9761	-43.9220
	β_{xxx}	21.8103	12.6105	44.5293
	β_{xyy}	-7.3249	-1.4354	1.2645
	β_{xzz}	-27.3259	5.0124	-7.7136
First	β_{yyy}	0.0004	-1.4354	-0.0005
Hyperpolarizability	β_{xxy}	0.0015	-23.8981	0.0008
(Debye)	β_{yzz}	-0.0002	-1.0365	0.0000
	β_{zzz}	-0.0013	0.0134	0.0007
	β_{xxz}	-0.0033	0.0090	0.0009
	β_{yyz}	0.0003	-0.0004	0.0003
	β	12.8405	30.9420	38.0802
	$\gamma_{\rm xxxx}$	-1202.96	-1327.3572	-700.53
	γ_{yyyy}	-304.22	-286.3175	-285.74
Second	γ_{zzzz}	-74.17	-67.4348	-53.22
Hyperpolarizability	$\gamma_{ m xxyy}$	-275.09	-276.4502	-146.07
(Debye)	$\gamma_{ m yyzz}$	-74.72	-70.4772	-68.39
	$\gamma_{\rm xxzz}$	-309.52	-219.0555	-147.77
	γ	-580.00	-562.614	-352.79

Table 3: Electric dipole moments (in Debye) by method DFT of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline calculated using B3LYP / 6-311G (d, p).

3.4. Thermodynamic parameters

We determined for each molecule the enthalpy ΔH , the entropy ΔS , and the free enthalpy ΔG (Table 4). The enthalpy ΔH is the sum of the internal energy of a system and the product of its pressure by its volume. Entropy ΔS , it characterizes by the degree of disorder or unpredictability of the information contained in a system. We have found that p-chloroaniline has a lower ΔG energy. This result means that p-chloroaniline is thermodynamically more stable.

Table 4: Thermodynamic parameters of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline.

Molecules	∆H (Kcal/mol)	∆S (Kcal/mol/K)	$\Delta \mathbf{G}$ (Kcal/mol)
А	-1807734.12	0.0846	-1807759.21
В	-255144.88	0.0792	-255168.48
С	-242673.07	0.0808	-242697.14

3.5. Bond length and angle properties

In this article, we will deepen our studies on selective bond lengths (Å) and angles (degrees). 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 [22]. Tables 5 and 6 show the comparison of the optimized bond length and the angle between experimental and calculated atomic numbered positions as (Figure 1) the optimized structure using a periodic DFT calculation corresponds exactly to an experimental result. The DFT results were very similar and in good condition according to the experimental structure. The study of the geometric product, therefore, showed an excellent agreement between theoretical and experimental results.

Parameters	А	В	С	Exp
C ₁ -C ₂	1.3952	1.3948	1.3948	1.398
C ₂ -C ₃	1.3947	1.3949	1.3949	1.380
C ₃ -C ₄	1.3954	1.3948	1.3948	1.404
C ₄ -C ₅	1.3948	1.3948	1.3948	1.386
C ₅ -C ₆	1.3951	1.3949	1.3949	1.380
C ₃ -N ₁₁	1.4700	1.266	1.266	1.404
C ₆ -Cl ₁₄	1.0100			1.03
C ₃ -Br ₈		1.881		1.89
C ₃ -F ₈			1.32	1.33
C_1 - C_2 - C_3	120.00	120.01	119.99	122.0
C_2 - C_3 - C_4	119.99	120.00	120.00	119.0
C ₃ -C ₄ -C ₅	119.99	119.99	120.00	119.0
C_1 - C_6 - N_7	119.98	120.00	120.01	117.0
$C_{5}-C_{6}-Cl_{14}$	120.01			119.0
C_6 - Cl_{14} - C_1	120.00			119.0
C ₄ -C ₃ -Br ₈		120.00		120.08
C_2 - C_3 - F_8			120.02	119.9
$C_2-C_1-C_6-N_7$	179.96	179.96	179.99	180.0
C_4 - C_5 - C_6 - Cl_{14}	179.98			178.2
C ₁ -C ₂ -C ₃ -Br ₈		179.99		179.8
$C_1 - C_2 - C_3 - F_8$			179.99	179.8

Table 5: Bond lengths (Å), Angles (θ°) and dihedral angles (θ°) of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline (Experimental values [16], [23] and [17].

3.6. Molecular electrostatic potential

Molecular electrostatic potential (MEP) gives detailed information for studies on chemical reactivity or the biological activity of a compound. The spatial distribution and the values of the electrostatic potential determine the attack of an electrophilic or of a nucleophilic agent as the primary event of a chemical reaction. Furthermore, the three-dimensional distribution of the electrostatic potential is largely responsible for the binding of a substrate at the active site of a receptor [24]. The molecular electrostatic potential 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 molecules. It is very important in 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 / 6-311G (d, p) method. Total electronic density mapped with the electrostatic potential surface, the electrostatic contour map potential of p-chloroaniline, p-bromoaniline and p-fluoroaniline are shown in figures 4 and 5.

The color scheme for the MESP surface is red, rich in electrons, partially negative charge; blue, electrondeficient, 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 [25]. Electrophilic attack sites are Cl14, Br8, and F8 for p-chloroaniline, pbromoaniline and p-fluoroaniline.



Figure 4: Electrostatic potential maps around the molecule of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline.



Figure 5. Contour electrostatic potential around the molecule of (A) p-chloroaniline, (B) p-bromoaniline, (C) p-fluoroaniline.

Conclusion

In this work, the structural and spectroscopic data of the molecules in the ground state were calculated using the functional density method using a basic set 6-311G (d, p). The results of the ¹³C and ¹H NMR chemical shifts have been given and are in agreement with the corresponding experimental values. In addition, the electronic properties of the compound were calculated. The HOMO and LUMO energy gaps explain the possible charge, the transfer interactions taking place within the molecules, and the determination of the theoretical molecular structures of three molecules by B3LYP / 6-311G (d, p) with the DFT method, and the electrostatic potential contour and the electrostatic potential mapped around the molecules. The linear polarizability (α), the first-order hyperpolarizability (β) and the second-order hyperpolarizability (γ) values of the investigated molecules have been computed.

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