

# First principles study of structural equilibrium configuration of Ortho-, Meta-, and Para-chloroaniline molecules

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**Abstract:** This work has studied the ground state energy, binding energy, equilibrium geometry, charge distribution, and dipole moment of ortho-, meta-, and para-chloroanilines using a wide range of advanced theoretical methods including first-principles Hartree-Fock (HF), Møller-Plesset (MP) perturbation theory, Configuration Interaction (CI) and Density Functional Theory [DFT (B3LYP)] with basis sets 3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*, 6-311G, 6-311G\*, and 6-311G\*\*. The trend in ground state energy is obtained in  $E_{\text{DFT}} < E_{\text{HF+MP3}} < E_{\text{HF+MP2}} < E_{\text{CISD}} < E_{\text{HF}}$ . The calculated binding energies for these molecules in DFT calculations using the 6-311G\*\* basis set are determined to be 7590.61 KJ/mol, 7589.14 KJ/mol, and 7586.73 KJ/mol respectively. The positive binding energy values occur in all these molecules indicate the stability of the molecule. The bond length between carbon (C) and chlorine (Cl) in ortho, meta and para chloroaniline is determined to be 1.769 Å, 1.765 Å, and 1.765 Å respectively. In calculation at the HF+MP2 level, the C-Cl bond length for ortho, meta, and para chloroaniline molecules are determined to be 1.742 Å, 1.741 Å, and 1.740 Å respectively. There is a reduction in the C-Cl bond length when the chlorine atom's position in chloroaniline changes from ortho to meta and then to para positions. The values of bond angle and dihedral angle for these molecules at the HF, HF+MP2, and DFT (B3LYP) levels of calculation are nearly equal. The distribution of charges in each molecule results in a net sum of Mulliken charges equal to zero. The calculated dipole moments for ortho, meta, and para chloroaniline molecules are 2.1194 Debye, 3.5398 Debye, and 4.1385 Debye, respectively.

**Keywords:** Equilibrium configuration; Chloroaniline; First principles; Ground state energy; Charge distribution; Dipole moment.

## Introduction

Aniline and its derivatives are versatile mediators widely employed across various domains including the synthesis of dyes, plasticizers, pharmaceuticals, pesticides, polymers, rubber additives, photographic chemicals, varnishes and as essential precursors for amino aromatic derivatives<sup>1</sup>. Chloroaniline is a flat molecule and it serves as a vital organic starting material with broad utility in various industries including plastics, pharmaceuticals, pesticides and the production of everyday consumer chemical products<sup>2,3</sup>. Ortho-chloroaniline (also called 2-Chloroanili-

ne) is an organic compound classified as an aniline derivative. It is composed of a benzene ring with a chlorine atom and an amino group (-NH<sub>2</sub>) attached to it. It exhibits limited solubility in water but readily dissolves in various organic solvents like ethanol and diethyl ether<sup>4, 5</sup>. Meta-chloroaniline is also known as 3-Chloroaniline or 3-Chlorobenzeneamine, presents as a colorless to light amber liquid with a sweet aroma. It remains insoluble in water but readily dissolves in ethanol and ether. It is also soluble either in organic acids like formic, acetic acid or in both the organic or inorganic acid. It serves as an intermediate

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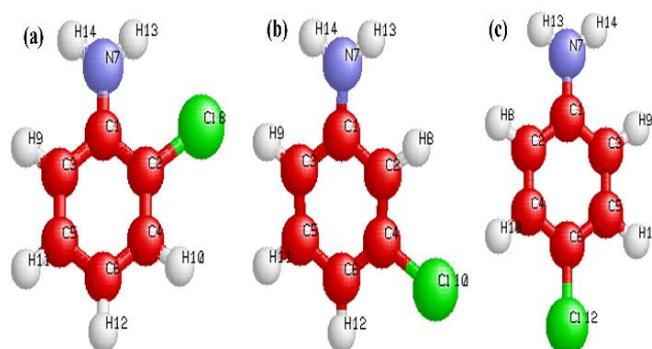
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compound in the production of the herbicide chloraniline and the pharmaceutical diuretic and antihypertensive drug hydrochlorothiazide<sup>4,6</sup>. Para-chloroaniline (PCA, also known as 4-chloroaniline) appears as a white or pale yellow solid. It serves as a critical intermediate in the production of over ten dyes and pigments, textile and rubber sectors and has been identified as a degradation byproduct in certain pharmaceutical formulations<sup>7</sup>. The invention provides a kind of ammonia<sup>8</sup> and prepare application in the Ortho-Chloro aniline. P-chloroaniline's adsorption geometries are displayed by the DFT calculations on a series of Pd substrates, such as stepped surfaces [Pd(221) and Pd(211)], flat surfaces [Pd(111) and Pd(100)], and clusters [Pd13 and Pd55]. The p-chloroaniline's adsorption energies on these models [Pd(221), Pd(211), Pd(111), Pd(100), Pd13-icosahedral, Pd13-cubo-octahedron, and Pd55] were 21.90, 22.13 21.70, 22.11, 22.53, 22.65, and 22.23 eV, respectively<sup>9</sup>. The success of density function theoretical results provide a way to use a force field and an appropriate procedure for the aniline family spectroscopic property assignments<sup>10</sup>. It is found that the DFT approach provides more precise results for a range of computations. It is thus because of the exchange-correlation potential term that give wholesome interaction for each quantity of electrons with the help of density functional<sup>11</sup>. Figures 1(a) (b) and (c) show the optimized structure of ortho-chloroaniline (o-chloroaniline), meta-chloroaniline (m-chloroaniline) and para-chloroaniline (p-chloroaniline) using basis set 6-311G\*\* in the DFT level of calculation. In the Figure 1(a), the position of two adjacent carbon-atoms like 1, 2 or 1, 3 of the benzene molecule is known as ortho-position. The structure of o-chloroaniline (Figure 1(a)) had a hydrogen atom in ortho position and it has been replaced by chlorine hence became o-chloroaniline. In the context of the benzene molecule, the m-position refers to the locations of carbon atoms at positions 1 and 4 or 1 and 5 as shown in Figure 1(b). In this specific structure of m-chloroaniline depicted in Figure 1(b), the hydrogen atom originally in the meta position has been substituted with a chlorine atom. In the context of the benzene molecule, the term para-position designates the arrangement of carbon atoms at positions 1 and 6 (Figure 1(c)), which are diagonally across from each

other. The particular structure of p-chloroaniline depicted in Figure 1(c) initially contained a hydrogen atom located in the para position, but this hydrogen atom has been replaced with a chlorine atom.



**Figure 1: Optimized configuration of (a) o-chloroaniline (b) m-chloroaniline (c) p-chloroaniline molecule.**

Efficiently modifying non-activated aromatic C-H bonds has become a highly valuable synthetic technique due to its remarkable versatility. Achieving precise positional control has mainly relied on directing-group strategies. Selectively functionalizing distant C-H bonds, especially those far from the active functional or directing group, has remained a formidable task in the realm of synthetic organic chemistry<sup>12, 13</sup>. The first-principles approaches are widely used to study the electronic structure and to determine various properties<sup>11, 14</sup>. The understanding of the chemical, physical and spectral properties of substituted benzenes heavily rely on knowledge of their electronic structure<sup>15,16</sup>. However, a comprehensive *ab initio* calculation to determine fundamental properties such as the ground state energy, bond length, binding energy, equilibrium geometry, dipole moment and charge distribution of aromatic compounds like o-chloroaniline, m-chloroaniline and p-chloroaniline has not been conducted. Therefore, this study aims to address the above mentioned gap using the first-principles calculations using the Gaussian 98 set of program.

### Computational details

In this work, the first principles Hartree-Fock (HF), Møller-Plesset (MP) perturbation theory, Configuration Interaction (CI) and Density Functional Theory (DFT) with Becke's three parameter (local, non-local, Hartree-Fock) hybrid

exchange functional with Lee–Yang–Parr correlation functional (B3LYP) were employed using the Gaussian 98 program to perform the calculations for finding the ground state energy, binding energy (B. E.), equilibrium geometry, bond lengths, dipole moment and charge distribution of ortho, meta and para chloroaniline molecules. Gaussian calculations were best prepared using the GaussView interface. The basis sets used in these calculations were encompassed by a variety of options, including 3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*, 6-311G, 6-311G\*, and 6-311G\*\*, with the starred sets incorporating polarization functions. Among these basis sets, those like 3-21G, 4-31G, and 6-31G contain three, four and six Gaussian-type functions specifically designed for inner core electrons along with two different sizes of Gaussian-type basis functions tailored for each valence orbital. In a similar way, the 6-311G basis set features six Gaussian-type functions for inner core electrons and three distinct sizes of Gaussian-type basis functions for each valence orbital. The remaining basis sets, namely 6-31G\*, 6-31G\*\*, 6-311G\*, and 6-311G\*\*, introduces the influences of polarization functions into the 6-31G and 6-311G basis sets respectively. To ensure the reliability and consistency of our results, a rigorous examination was conducted to assess their convergence concerning the increasing size and complexity of the basis sets employed. Gaussian is a general-purpose *ab initio* electronic structure package which can predict many properties of molecules and reaction pathways based on various uncorrelated and correlated wave function.

## Result and discussions

In this section, we discuss the results of the ground state energy, binding energy, equilibrium geometry, charge distribution and dipole moment of o-chloroaniline, m-chloroaniline and p-chloroaniline molecule.

### (i) Ground state energy, binding energy and equilibrium geometry of the o-chloroaniline molecule

#### (a) Ground state energy and binding energy of o-chloroaniline molecule

Figure 2 depicts ground state energy levels of o-chloroaniline using HF, HF+MP2, HF+MP3, CISD and DFT calculation methods with 3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*, 6-311G, 6-311G\* and 6-311G\*\* basis sets. It reveals that increasing the basis set size and complexity consistently lowers the molecule's ground state energy across all calculation levels. The energy reduction when transitioning from 3-21G to 4-31G is smaller than that when shifting from 4-31G to 6-31G. The addition of d-type and p-type Gaussian polarization functions (i.e. \* and \*\*) to the 6-31G and 6-311G basis sets lowers the ground state energy compared to their corresponding un-starred basis sets. The lowering in energy when changing from 6-31G to 6-31G\* is comparable to the lowering when changing from 6-311G to 6-311G\*. Similarly, the reduction in energy when switching from 6-31G\* to 6-31G\*\* closely remains same with the energy decrease observed when changing from 6-311G\* to 6-311G\*\*. The changing basis set from 6-31G\* to 6-311G\* makes the decrease in energy approximately 0.01% at the HF calculation level. The inclusion of p-type polarization (double starred) in the 6-31G and 6-311G basis sets also leads to a 0.01% reduction in energy at the HF calculation level. As the basis set size and complexity increase, the calculated ground state energy approaches the experimental value<sup>17</sup>, indicating basis set convergence.

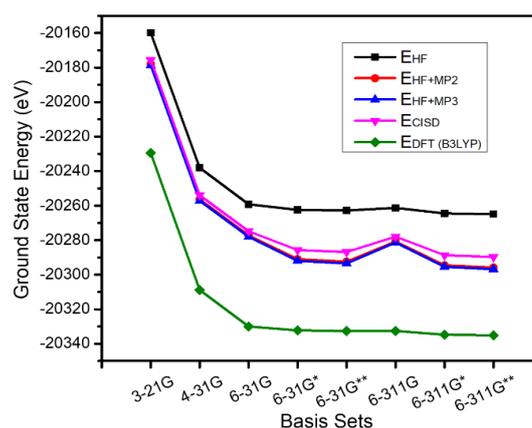


Figure 2: Ground state energy of the o-chloroaniline molecule.

Figure 2 also illustrates that the HF+MP2 ground state energy decreases relative to HF as the basis set size increases. The difference  $\delta E_{MP2} = E_{HF+MP2} - E_{HF}$  represents the many-body contributions to the ground state energy of o-chloroaniline. DFT ground state energy values are

notably lower compared to HF+MP3 values, following the trend  $E_{DFT} < E_{HF+MP3} < E_{HF+MP2} < E_{CISD} < E_{HF}$ .

Table 1 presents the binding energy values for the o-chloroaniline molecule computed using the HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP) methods with the 6-311G\*\* basis set. These positive binding energy values indicate the molecule's stability. The binding energy is 6288.53 KJ/mol at the HF level with the highest value

observed in the HF+MP2 method. Compared to HF, there is an approximately 21.4% increase in binding energy at HF+MP2, a 16.7% increase at HF+MP3, a 3% increase at CISD, and a 20.7% increase at DFT (B3LYP). This demonstrates the significant role of correlation effects in binding atoms within the o-chloroaniline molecule at HF+MP2, HF+MP3, and DFT (B3LYP) levels. The exception is observed at the CISD level of calculation.

**Table 1: Binding energy of o-chloroaniline molecule.**

Basis set	Binding Energy (KJ/mol.)				
	HF	HF+MP2	HF+MP3	CISD	DFT (B3LYP)
6-311G**	6288.53	7631.52	7338.91	6476.12	7590.61

### b) Equilibrium geometry of o-chloroaniline molecule

Table 2 provides optimized values for bond length, bond angle and dihedral angle in the o-chloroaniline molecule computed using HF, HF+MP2, and DFT (B3LYP) methods with the 6-311G\*\* basis set. The bond lengths of C<sub>4</sub>-H<sub>10</sub> and C<sub>6</sub>-H<sub>12</sub> are identical at the HF, HF+MP2 and DFT levels measuring 1.074 Å, 1.085 Å and 1.083 Å respectively. Similarly, N<sub>7</sub>-H<sub>13</sub> and N<sub>7</sub>-H<sub>14</sub> exhibit equal bond lengths at HF, HF+MP2 and DFT levels measuring 0.989 Å, 1.003 Å

and 1.003 Å respectively. Figure 1(a) shows the attachment of the chlorine atom to the second carbon atom with distances of 1.755 Å, 1.742 Å, and 1.769 Å at the HF, HF+MP2 and DFT levels of calculation respectively. Table 2 also shows that the slight variations in bond angles are observed among different atom at the HF, HF+MP2 and DFT levels of calculation. Furthermore, the dihedral angle remains constant at 180° for all calculation levels, indicating that the o-chloroaniline molecule maintains a planar structure.

**Table 2: Optimized parameters of o-chloroaniline molecule.**

Methods	Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
HF	R(C <sub>1</sub> ,C <sub>2</sub> )=1.394	A(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> )=116.93	D(C <sub>3</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=0
	R(C <sub>1</sub> ,C <sub>3</sub> )=1.399	A(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=121.83	D(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=0
	R(C <sub>2</sub> ,C <sub>4</sub> )=1.381	A(C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=121.26	D(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=0
	R(C <sub>3</sub> ,C <sub>5</sub> )=1.377	A(C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=120.41	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=180
	R(C <sub>4</sub> ,C <sub>6</sub> )=1.381	A(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> )=122.34	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=0
	R(C <sub>1</sub> ,N <sub>7</sub> )=1.366	A(C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=119.50	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=0
	R(C <sub>2</sub> ,Cl <sub>8</sub> )=1.755	A(C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=118.69	D(H <sub>8</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=0
	R(C <sub>3</sub> ,H <sub>9</sub> )=1.076	A(C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=118.85	D(H <sub>9</sub> ,C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=0
	R(C <sub>4</sub> ,H <sub>10</sub> )=1.074	A(C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=119.11	D(H <sub>10</sub> ,C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=0
	R(C <sub>5</sub> ,H <sub>11</sub> )=1.076	A(C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=120.28	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=0
	R(C <sub>6</sub> ,H <sub>12</sub> )=1.074	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=121.22	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=180
	R(N <sub>7</sub> ,H <sub>13</sub> )=0.989	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=120.20	
	R(N <sub>7</sub> ,H <sub>14</sub> )=0.989		
HF+MP2	R(C <sub>1</sub> ,C <sub>2</sub> )=1.410	A(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> )=117.02	D(C <sub>3</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=0
	R(C <sub>1</sub> ,C <sub>3</sub> )=1.409	A(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=121.78	D(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=0
	R(C <sub>2</sub> ,C <sub>4</sub> )=1.394	A(C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=121.51	D(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=0
	R(C <sub>3</sub> ,C <sub>5</sub> )=1.394	A(C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=20.11	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=180
	R(C <sub>4</sub> ,C <sub>6</sub> )=1.396	A(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> )=121.82	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=0
	R(C <sub>1</sub> ,N <sub>7</sub> )=1.372	A(C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=118.99	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=0
	R(C <sub>2</sub> ,Cl <sub>8</sub> )=1.742	A(C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=118.46	D(H <sub>8</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=0
	R(C <sub>3</sub> ,H <sub>9</sub> )=1.088	A(C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=118.77	D(H <sub>9</sub> ,C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=0
	R(C <sub>4</sub> ,H <sub>10</sub> )=1.085	A(C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=119.29	D(H <sub>10</sub> ,C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=0
	R(C <sub>5</sub> ,H <sub>11</sub> )=1.086	A(C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=119.97	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=0
	R(C <sub>6</sub> ,H <sub>12</sub> )=1.085	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=120.69	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=180
	R(N <sub>7</sub> ,H <sub>13</sub> )=1.003	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=120.33	
	R(N <sub>7</sub> ,H <sub>14</sub> )=1.003		

DFT (B3LYP)	R(C <sub>1</sub> ,C <sub>2</sub> )=1.407	A(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> )=116.67	D(C <sub>3</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=0
	R(C <sub>1</sub> ,C <sub>3</sub> )=1.408	A(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=122.12	D(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=0
	R(C <sub>2</sub> ,C <sub>4</sub> )=1.388	A(C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=121.38	D(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=0
	R(C <sub>3</sub> ,C <sub>5</sub> )=1.387	A(C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=120.08	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=180
	R(C <sub>4</sub> ,C <sub>6</sub> )=1.391	A(C <sub>2</sub> ,C <sub>1</sub> ,H <sub>7</sub> )=122.03	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=0
	R(C <sub>1</sub> ,N <sub>7</sub> )=1.370	A(C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=118.86	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=0
	R(C <sub>2</sub> ,Cl <sub>8</sub> )=1.769	A(C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=118.58	D(H <sub>8</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=0
	R(C <sub>3</sub> ,H <sub>9</sub> )=1.085	A(C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=118.98	D(H <sub>9</sub> ,C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=0
	R(C <sub>4</sub> ,H <sub>10</sub> )=1.083	A(C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=119.19	D(H <sub>10</sub> ,C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=0
	R(C <sub>5</sub> ,H <sub>11</sub> )=1.084	A(C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=120.08	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=0
	R(C <sub>6</sub> ,H <sub>12</sub> )=1.083	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=120.73	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=180
	R(N <sub>7</sub> ,H <sub>13</sub> )=1.003	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=120.46	
	R(N <sub>7</sub> ,H <sub>14</sub> )=1.003		

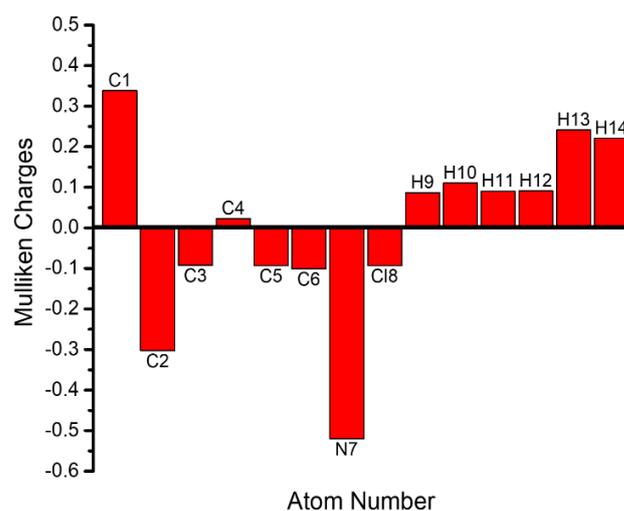
Table 3 compares the calculated carbon-chlorine (C-Cl) bond lengths for the o-chloroaniline molecule using the 6-311G\*\* basis set with experimental measurements. The calculated C-Cl bond lengths ( $R_{C-Cl}$ ) are nearly in good

agreement with the experimental values<sup>17</sup> and deviating takes place by less than 5% for all methods. The HF+MP2 method yields a value of 1.742 Å for the C-Cl bond length, which closely matches the experimental value of 1.70 Å.

**Table 3: Comparison between the calculated and experimentally observed values of the carbon-chlorine bond length for o-chloroaniline molecule.**

Parameter	Levels of calculation	Calculated value	Experimental value <sup>17</sup>
Bond length (in Å)	HF	1.755	1.70 ± 0.01
	HF+MP2	1.742	
	DFT	1.769	

Figure 3 and Table 4 present the charge distribution and dipole moment respectively for the o-chloroaniline molecule using the 6-311G\*\* basis set at the DFT (B3LYP) level. Charge distribution reveals how charge is distributed among the molecule's atoms, while the dipole moment indicates that whether the molecule is polar or nonpolar. In figure 3, positive charges are concentrated on the first and fourth carbon atoms as well as all hydrogen atoms in the o-chloroaniline molecule, each having a small positive charge. Negative charges are centered on the nitrogen atom, chlorine atom and the remaining carbon atoms, resulting in a net Mulliken charge of zero.



**Figure 3: Charge distribution of o-chloroaniline molecule.**

**Table 4: Dipole moment of o-chloroaniline molecule.**

Dipole moment (Debye)			
X= -0.9322	Y= -1.9033	Z= 0.0000	Total = 2.1194

Table 4 shows that the breakdown of dipole moment into X, Y and Z components. The dipole moments have magnitudes of 0.9322 debye and 1.9033 debye along the X and Y axes respectively. The total dipole moment of the o-chloroaniline molecule measures 2.1194 debye, primarily in the negative

Y-direction. This dipole moment is stronger than that of aniline<sup>15, 16</sup>, indicating that the positive and negative charge centers are relatively distant from each other in o-chloroaniline. Consequently, o-chloroaniline is more

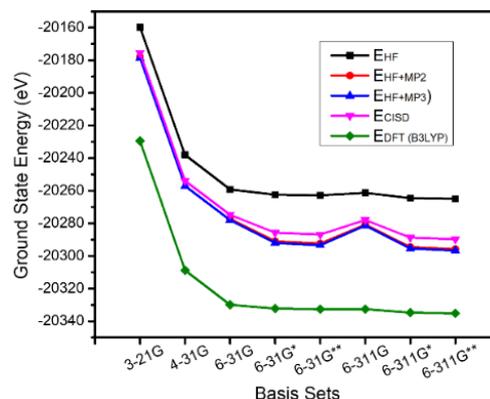
polarized than aniline, confirming its status as a polar molecule.

**(ii) Ground state energy, binding energy and equilibrium geometry of m-chloroaniline molecule**

**(a) Ground state energy and binding energy of m-chloroaniline molecule**

Figure 4 corresponds to the calculated ground state energy for m-chloroaniline molecule using HF, HF+MP2, HF+MP3, CISD and DFT levels of calculation with 3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*, 6-311G, 6-311G\* and 6-311G\*\* basis sets. It is seen that the ground state energy are lowered with increasing size and complexity of the basis sets in all levels of calculation. The lowering in the energy values on changing the basis sets from 3-21G to 4-31G is much less than the corresponding lowering in the energy values on changing the basis sets from 4-31G to 6-31G. The values of ground state energy of m-chloroaniline molecule get lowered with the addition of d-type and p-type Gaussian polarization functions to 6-31G and 6-311G basis set as compared to the energy values obtained with the corresponding unstarred basis sets. The lowering in the energy values on changing the basis set from 6-31G to 6-31G\* is almost similar to the corresponding lowering in the energy values on changing the basis set from 6-311G to 6-311G\*. Similarly, the lowering in the energy values on changing the basis set from 6-31G\* to 6-31G\*\* is almost similar to the corresponding lowering in the energy values on changing the basis set from 6-311G\* to 6-311G\*\*. The lowering in the value of energy when the basis set is changed from 6-31G\* to 6-311G\* is found to be around 0.01% at HF level of calculation. However by the inclusion of the p-type polarization (double starred) in the basis sets

6-31G and 6-311G, the lowering in the value of energy is also found to be around 0.01% at HF level of calculation. Calculated ground state energy approaches to



**Figure 4: Ground state energy of the m-chloroaniline molecule.**

the basis set of larger size and higher complexity as demanded by the variational method. From the above analysis, it is clearly seen that the results for the ground state energy of m-chloroaniline molecule are basis set convergent. Figure 4 shows that the lowering in the HF+MP2 value of the ground state energy of m-chloroaniline molecule as compared to the corresponding HF value increases as the size of the basis set increases. The difference in ground state energy values  $\delta E_{MP2} = E_{HF+MP2} - E_{HF}$  gives the value of many body contributions to the ground state energy of the m-chloroaniline molecule. Furthermore, it is also seen that the DFT ground state energy of m-chloroaniline molecule are considerably lower as compared to the corresponding HF+MP3 values. The trend in energy is  $E_{DFT} < E_{HF+MP3} < E_{HF+MP2} < E_{CISD} < E_{HF}$ . Table 5 shows the values of the binding energy for m-chloroaniline molecule calculated in the HF, HF+MP2, HF+MP3, CISD and DFT (B3LYP) with the basis set 6-311G\*\* and these values of the binding energy are positive indicating the stability of this molecule.

**Table 5: Binding energy of m-chloroaniline molecule.**

Basis set	Binding Energy (KJ/mol.)				
	HF	HF+MP2	HF+MP3	CISD	DFT (B3LYP)
6-311G**	6289.24	7630.21	7338.28	6476.12	7589.14

It is seen that the binding energy at HF level of calculation is found to 6289.24 KJ/mol. The maximum value of binding energy is obtained at HF+MP2. Furthermore, the increase

in the binding energy at HF+MP2, HF+MP3, CISD and DFT (B3LYP) levels of calculation takes place by 21.3%, 16.7%, 3% and 20.7% respectively than that of the HF. This

shows that correlation effect for binding of atoms in m-chloroaniline molecule play important role at HF+MP2, HF+MP3 and DFT (B3LYP) levels of calculation. The CISD level of calculation yields an exception.

**(b) Equilibrium geometry of m-chloroaniline molecule**

Table 6 shows the calculated optimized values of the bond length, bond angle and dihedral angle of m-chloroaniline molecule using the HF, HF+MP2 and DFT (B3LYP) with

the basis set 6-311G\*\*. The bond length of N7-H13 and N7-H14 are found to be equal with 0.989 Å, 1.003 Å and 1.003 Å at HF, HF+MP2 and DFT levels of calculation respectively. The distance of the chlorine atom from the fourth carbon atom is found to be 1.748 Å, 1.741 Å and 1.765 Å in HF, HF+MP2 and DFT levels of calculation respectively.

**Table 6: Optimized parameters of m-chloroaniline molecule.**

Methods	Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
HF	R(C1,C2)=1.395	A(C2,C1,C3)=118.75	D(C3,C1,C2,C4)=0
	R(C1,C3)=1.396	A(C1,C2,C4)=119.50	D(C2,C1,C3,C5)=0
	R(C2,C4)=1.378	A(C1,C3,C5)=120.18	D(C1,C2,C4,C6)=0
	R(C3,C5)=1.379	A(C2,C4,C6)=122.50	D(N7,C1,C2,C4)=180
	R(C4,C6)=1.380	A(C2,C1,N7)=120.38	D(N7,C1,C2,H8)=0
	R(C1,N7)=1.370	A(C1,C2,H8)=120.48	D(N7,C1,C3,H9)=0
	R(C2,H8)=1.074	A(C1,C3,H9)=119.69	D(H8,C2,C4,H10)=0
	R(C3,H9)=1.076	A(C2,C4,H10)=118.41	D(H9,C3,C5,H11)=0
	R(C4,Cl10)=1.748	A(C3,C5,H11)=119.16	D(H10,C4,C6,H12)=0
	R(C5,H11)=1.076	A(C4,C6,H12)=120.86	D(C2,C1,N7,H13)=0
	R(C6,H12)=1.072	A(C1,N7,H13)=121.02	D(C2,C1,N7,H14)=180
	R(N7,H13)=0.989	A(C1,N7,H14)=120.84	
	R(N7,H14)=0.989		
HF+MP2	R(C1,C2)=1.407	A(C2,C1,C3)=118.70	D(C3,C1,C2,C4)=0
	R(C1,C3)=1.408	A(C1,C2,C4)=119.78	D(C2,C1,C3,C5)=0
	R(C2,C4)=1.393	A(C1,C3,C5)=120.35	D(C1,C2,C4,C6)=0
	R(C3,C5)=1.394	A(C2,C4,C6)=122.01	D(N7,C1,C2,C4)=180
	R(C4,C6)=1.395	A(C2,C1,N7)=120.42	D(N7,C1,C2,H8)=0
	R(C1,N7)=1.376	A(C1,C2,H8)=120.42	D(N7,C1,C3,H9)=0
	R(C2,H8)=1.086	A(C1,C3,H9)=119.49	D(H8,C2,C4,H10)=0
	R(C3,H9)=1.087	A(C2,C4,H10)=118.54	D(H9,C3,C5,H11)=0
	R(C4,Cl10)=1.741	A(C3,C5,H11)=119.28	D(H10,C4,C6,H12)=0
	R(C5,H11)=1.087	A(C4,C6,H12)=120.47	D(C2,C1,N7,H13)=0
	R(C6,H12)=1.084	A(C1,N7,H13)=120.94	D(C2,C1,N7,H14)=180
	R(N7,H13)=1.003	A(C1,N7,H14)=120.77	
	R(N7,H14)=1.003		
DFT (B3LYP)	R(C1,C2)=1.406	A(C2,C1,C3)=118.58	D(C3,C1,C2,C4)=0
	R(C1,C3)=1.407	A(C1,C2,C4)=119.54	D(C2,C1,C3,C5)=0
	R(C2,C4)=1.387	A(C1,C3,C5)=120.33	D(C1,C2,C4,C6)=0
	R(C3,C5)=1.388	A(C2,C4,C6)=122.50	D(N7,C1,C2,C4)=180
	R(C4,C6)=1.390	A(C2,C1,H7)=120.46	D(N7,C1,C2,H8)=0
	R(C1,N7)=1.375	A(C1,C2,H8)=120.44	D(N7,C1,C3,H9)=0
	R(C2,H8)=1.083	A(C1,C3,H9)=119.53	D(H8,C2,C4,H10)=0
	R(C3,H9)=1.085	A(C2,C4,H10)=118.41	D(H9,C3,C5,H11)=0
	R(C4,Cl10)=1.765	A(C3,C5,H11)=119.27	D(H10,C4,C6,H12)=0
	R(C5,H11)=1.084	A(C4,C6,H12)=120.78	D(C2,C1,N7,H13)=0
	R(C6,H12)=1.081	A(C1,N7,H13)=121.11	D(C2,C1,N7,H14)=180
	R(N7,H13)=1.003	A(C1,N7,H14)=120.86	
	R(N7,H14)=1.003		

On observing the bond angle from the Table 6, it is found that the angle between different atoms are slightly different in HF, HF+MP2 and DFT levels of calculation. Table 6 also

shows the dihedral angle of different atoms in m-chloroaniline molecule and it is found to be 180° for all

levels of calculation. This means that the m-chloroaniline molecule is a planar molecule.

Table 7 shows the comparison of calculated and experimentally observed values of the carbon-chlorine bond length for m-chloroaniline molecule with respect to the basis set 6-311G\*\*. It is seen that the carbon-chlorine bond length ( $R_{C-Cl}$ ) is close to the experimentally observed value

for all methods within 4%. It is seen from Table 7 that the HF, HF+MP2 and DFT values for the carbon-chlorine bond length of m-chloroaniline molecule agree to each other within 2%. The HF+MP2 value of 1.741 Å for the carbon-chlorine bond length of m-chloroaniline molecule is the closest to the experimental value 1.70 Å.

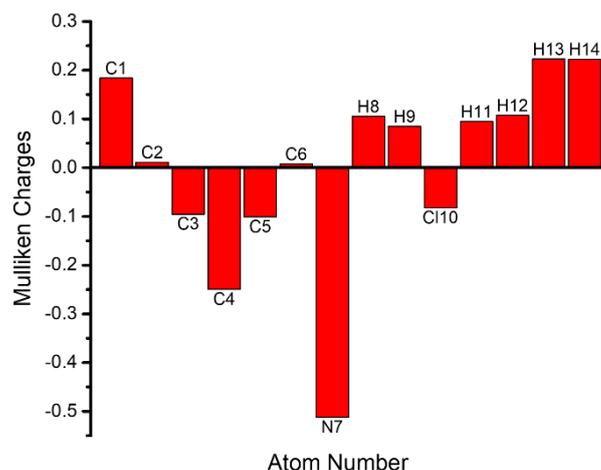
**Table 7: Comparison between the calculated and experimentally observed values of the carbon-chlorine bond length for m-chloroaniline molecule.**

Parameter	Levels of calculation	Calculated value	<sup>[17]</sup> Experimental value
Bond length (in Å) $R_{C-Cl}$	HF	1.748	1.70 ± 0.01
	HF+MP2	1.741	
	DFT	1.765	

Figure 5 shows the calculated value of charge distribution of m-chloroaniline molecule using basis set 6-311G\*\* at DFT (B3LYP) level of calculation. When tenth hydrogen [Figure 1(b)] of aniline molecule is replaced by chlorine atom, it is observed that the positive charges are confined to the first carbon atom, second carbon atom sixth carbon atom and all the hydrogen atoms of m-chloroaniline molecule. Each hydrogen atom has a small positive charge. The negative charges are confined to the nitrogen atom, chlorine atom and all the remaining carbon atoms of m-chloroaniline molecule so that sum of Mulliken charges is zero.

Table 8 shows dipole moment of m-chloroaniline molecule using basis set 6-311G\*\* at DFT (B3LYP) level of calculation. It is obtained that the dipole moment of m-chloroaniline molecule is broken down into X, Y and Z components with magnitude of 0.5028 debye and 3.5039 debye along the X and Y axis respectively. The total dipole moment of m-chloroaniline molecule has a magnitude of

3.5398 debye, mostly in the negative Y- direction. This is a strong dipole moment than that of o-chloroaniline molecule indicating that the centers of positive and negative charge are relatively far away from each other in this molecule than that of o-chloroaniline molecule. This shows that m-chloroaniline molecule is a polar molecule.



**Figure 5: Charge distribution of m-chloroaniline molecule.**

**Table 8: Dipole moment of m-chloroaniline molecule.**

Dipole moment (Debye)			
X= -0.5028	Y= -3.5039	Z= 0.0000	Total = 3.5398

(iii) **Ground state energy, binding energy and equilibrium geometry of the p-chloroaniline molecule**

(a) **Ground state energy and binding energy of p-chloroaniline molecule**

Figure 6 illustrates ground state energy variations in the p-chloroaniline molecule across different levels of calculation (HF, HF+MP2, HF+MP3, CISD, and DFT) using various basis sets (3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*, 6-311G, 6-311G\*, and 6-311G\*\*). In general, as basis set size

and complexity increase, the ground state energy of the p-chloroaniline molecule decreases. The reduction in energy when transitioning from 3-21G to 4-31G is smaller than the reduction when switching from 4-31G to 6-31G. Incorporating d-type and p-type Gaussian polarization functions to the 6-31G and 6-311G basis sets further lowers the ground state energy of the p-chloroaniline molecule compared to their non-starred basis sets counterparts. The decrease in energy when changing from 6-31G to 6-31G\* is similar to the decrease when transitioning from 6-311G to 6-311G\*. Similarly, the reduction in energy when going from 6-31G\* to 6-31G\*\* is almost identical to the decrease when shifting from 6-311G\* to 6-311G\*\*. The change in energy on shifting from 6-31G\* to 6-311G\* is approximately 0.01% at the HF level of calculation. This percentage remains consistent with the inclusion of p-type polarization (double-starred) in the 6-31G and 6-311G basis sets at the HF level. As basis sets become larger and more complex, the calculated ground state energy approaches the experimental value<sup>17</sup>, demonstrating basis set convergence. Figure 6 also highlights that the difference between HF+MP2 and HF ground state energy increases with larger basis sets, providing insights into many-body contributions<sup>18</sup>. Additionally, DFT ground state energy values for p-chloroaniline are notably lower compared to their HF+MP3 counterparts, following the trend  $E_{\text{DFT}} < E_{\text{HF+MP3}} < E_{\text{HF+MP2}} < E_{\text{CISD}} < E_{\text{HF}}$ .

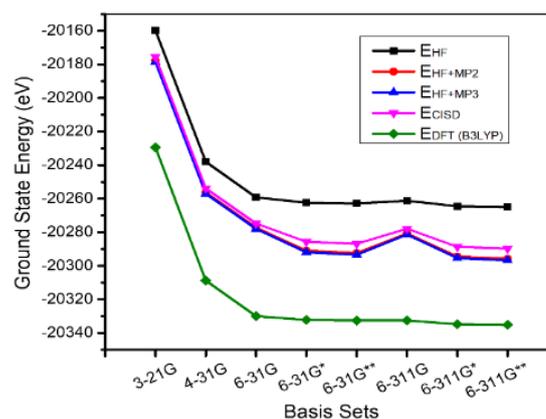


Figure 6: Ground state energy of the p-chloroaniline molecule.

Table 9 exhibits the binding energy values for the p-chloroaniline molecule, computed at various calculation levels (HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP)), using the 6-311G\*\* basis set. These positive binding energy values confirm the molecule's stability<sup>19</sup>, with the HF level registering a binding energy of 6286.51 KJ/mol. The highest value is observed at the HF+MP2 level, highlighting the significant role of correlation effects in maintaining stability. Moreover, there is observed an increase in binding energy at the HF+MP2, HF+MP3, CISD, and DFT (B3LYP) levels, exceeding the HF level by 21.3%, 16.7%, 3%, and 20.7%, respectively. This emphasizes the substantial impact of correlation effects<sup>20</sup> on the molecular binding<sup>21</sup> in p-chloroaniline, with the exception being the CISD level.

Table 9: Binding energy of p-chloroaniline molecule.

Basis set	Binding Energy (KJ/mol.)				
	HF	HF+MP2	HF+MP3	CISD	DFT (B3LYP)
6-311G**	6286.51	7626.25	7334.64	6472.71	7586.73

### (b) Equilibrium geometry of p-chloroaniline molecule

Table 10 presents optimized values for bond length, bond angle and dihedral angle characteristics in the p-chloroaniline molecule using HF, HF+MP2, and DFT (B3LYP) calculations with the 6-311G\*\* basis set. The bond lengths of N<sub>7</sub>-H<sub>13</sub> and N<sub>7</sub>-H<sub>14</sub> are determined as 0.989 Å, 1.003 Å, and 1.003 Å for HF, HF+MP2, and DFT, respectively. Additionally, the chlorine atom's distance

from the sixth carbon atom is found to be 1.751 Å, 1.740 Å, and 1.765 Å at HF, HF+MP2, and DFT levels. An examination of bond angles in Table 10 reveals slight variations between different atom combinations in the HF, HF+MP2 and DFT calculations. Moreover, the dihedral angle among various atoms consistently measures 180° across all calculation levels. This observation confirms the planar structure of the p-chloroaniline molecule.

**Table 10: Optimized parameters of p-chloroaniline molecule.**

Methods	Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
HF	R(C <sub>1</sub> ,C <sub>2</sub> )=1.395	A(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> )=118.28	D(C <sub>3</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=0
	R(C <sub>1</sub> ,C <sub>3</sub> )=1.395	A(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=120.78	D(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=0
	R(C <sub>2</sub> ,C <sub>4</sub> )=1.381	A(C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=120.78	D(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=0
	R(C <sub>3</sub> ,C <sub>5</sub> )=1.381	A(C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=120.10	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=180
	R(C <sub>4</sub> ,C <sub>6</sub> )=1.380	A(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> )=120.86	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=0
	R(C <sub>1</sub> ,N <sub>7</sub> )=1.372	A(C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=119.79	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=0
	R(C <sub>2</sub> ,H <sub>8</sub> )=1.076	A(C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=119.79	D(H <sub>8</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=0
	R(C <sub>3</sub> ,H <sub>9</sub> )=1.076	A(C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=119.91	D(H <sub>9</sub> ,C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=0
	R(C <sub>4</sub> ,H <sub>10</sub> )=1.074	A(C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=119.91	D(H <sub>10</sub> ,C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=0
	R(C <sub>5</sub> ,H <sub>11</sub> )=1.074	A(C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=120.02	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=0
	R(C <sub>6</sub> ,Cl <sub>12</sub> )=1.751	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=120.94	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=180
	R(N <sub>7</sub> ,H <sub>13</sub> )=0.989	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=120.94	
R(N <sub>7</sub> ,H <sub>14</sub> )=0.989			
HF+MP2	R(C <sub>1</sub> ,C <sub>2</sub> )=1.407	A(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> )=118.14	D(C <sub>3</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=0
	R(C <sub>1</sub> ,C <sub>3</sub> )=1.407	A(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=121.03	D(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=0
	R(C <sub>2</sub> ,C <sub>4</sub> )=1.395	A(C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=121.03	D(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=0
	R(C <sub>3</sub> ,C <sub>5</sub> )=1.395	A(C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=119.81	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=180
	R(C <sub>4</sub> ,C <sub>6</sub> )=1.396	A(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> )=120.93	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=0
	R(C <sub>1</sub> ,N <sub>7</sub> )=1.378	A(C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=119.56	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=0
	R(C <sub>2</sub> ,H <sub>8</sub> )=1.088	A(C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=119.56	D(H <sub>8</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=0
	R(C <sub>3</sub> ,H <sub>9</sub> )=1.088	A(C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=120.19	D(H <sub>9</sub> ,C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=0
	R(C <sub>4</sub> ,H <sub>10</sub> )=1.085	A(C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=120.19	D(H <sub>10</sub> ,C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=0
	R(C <sub>5</sub> ,H <sub>11</sub> )=1.085	A(C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=119.91	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=0
	R(C <sub>6</sub> ,Cl <sub>12</sub> )=1.740	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=120.88	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=180
	R(N <sub>7</sub> ,H <sub>13</sub> )=1.003	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=120.88	
R(N <sub>7</sub> ,H <sub>14</sub> )=1.003			
DFT (B3LYP)	R(C <sub>1</sub> ,C <sub>2</sub> )=1.406	A(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> )=118.08	D(C <sub>3</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=0
	R(C <sub>1</sub> ,C <sub>3</sub> )=1.406	A(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=120.97	D(C <sub>2</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=0
	R(C <sub>2</sub> ,C <sub>4</sub> )=1.389	A(C <sub>1</sub> ,C <sub>3</sub> ,C <sub>5</sub> )=120.97	D(C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=0
	R(C <sub>3</sub> ,C <sub>5</sub> )=1.389	A(C <sub>2</sub> ,C <sub>4</sub> ,C <sub>6</sub> )=119.86	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,C <sub>4</sub> )=180
	R(C <sub>4</sub> ,C <sub>6</sub> )=1.390	A(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> )=120.96	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=0
	R(C <sub>1</sub> ,N <sub>7</sub> )=1.376	A(C <sub>1</sub> ,C <sub>2</sub> ,H <sub>8</sub> )=119.66	D(N <sub>7</sub> ,C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=0
	R(C <sub>2</sub> ,H <sub>8</sub> )=1.085	A(C <sub>1</sub> ,C <sub>3</sub> ,H <sub>9</sub> )=119.66	D(H <sub>8</sub> ,C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=0
	R(C <sub>3</sub> ,H <sub>9</sub> )=1.085	A(C <sub>2</sub> ,C <sub>4</sub> ,H <sub>10</sub> )=120.11	D(H <sub>9</sub> ,C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=0
	R(C <sub>4</sub> ,H <sub>10</sub> )=1.083	A(C <sub>3</sub> ,C <sub>5</sub> ,H <sub>11</sub> )=120.11	D(H <sub>10</sub> ,C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=0
	R(C <sub>5</sub> ,H <sub>11</sub> )=1.083	A(C <sub>4</sub> ,C <sub>6</sub> ,H <sub>12</sub> )=119.86	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=0
	R(C <sub>6</sub> ,Cl <sub>12</sub> )=1.765	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>13</sub> )=121.01	D(C <sub>2</sub> ,C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=180
	R(N <sub>7</sub> ,H <sub>13</sub> )=1.003	A(C <sub>1</sub> ,N <sub>7</sub> ,H <sub>14</sub> )=121.01	
R(N <sub>7</sub> ,H <sub>14</sub> )=1.003			

Table 11 displays carbon-chlorine bond lengths in the p-chloroaniline molecule obtained through different computational methods with the 6-311G\*\* basis set. Impressively, the calculated bond lengths ( $R_{C-Cl}$ ) are in close agreement with experimental data, with discrepancies

of less than 4% across all methods. The HF+MP2 calculation provides the closest match, yielding a carbon-chlorine bond length of 1.740 Å, which is just 0.04 Å longer than the experimentally measured value of 1.70 Å<sup>17</sup>.

**Table 11: Comparison between the calculated and experimentally observed values of the carbon-chlorine bond length for p-chloroaniline molecule.**

Parameter	Levels of calculation	Calculated value	Experimental value <sup>17</sup>
Bond length (in Å)	HF	1.751	1.70 ± 0.01
	HF+MP2	1.740	
	DFT	1.765	

In figure 7, the charge distribution within the p-chloroaniline molecule has been shown using the DFT (B3LYP) method and the 6-311G\*\* basis set. The outcomes show that positive charges are primarily centered

on the first, fourth and fifth carbon atoms as well as all hydrogen atoms in the p-chloroaniline molecule bearing a small positive charge. In contrast, negative charges are concentrated on the nitrogen and chlorine atoms, as well as

the remaining carbon atoms. This distribution results in a net sum of Mulliken charges equaling zero.

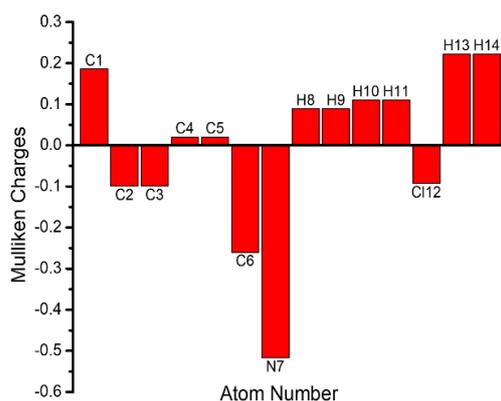


Figure 7: Charge distribution of p-chloroaniline molecule.

Table 12: Dipole moment of p-chloroaniline molecule.

Dipole moment (Debye)			
X= 0.0000	Y= 0.0000	Z= -4.1385	Total = 4.1385

Table 12 provides a breakdown of the dipole moment of the p-chloroaniline molecule into its X, Y, and Z components. The total dipole moment has a magnitude of 4.1385 debye and is oriented entirely in the negative Z-direction. This dipole moment is stronger than that of the m-chloroaniline molecule, signifying that the positive and negative charge centers are relatively more separated in the p-chloroaniline molecule compared to the m-chloroaniline molecule. This suggests that the p-chloroaniline molecule is a polar molecule. Since the p-chloroaniline molecule is planar, the dipole moment is aligned along the Z-axis due to the interchange of X and Z coordinates.

## Conclusion

The first-principles calculations i.e. HF, HF+MP2, HF+MP3, CISD and DFT were used to study the structural equilibrium configuration of chloroaniline (ortho, meta and para) molecule using the basis set 3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*, 6-311G, 6-311G\* and 6-311G\*\*. The ground state energy is determined in the following order i.e.  $E_{DFT} < E_{HF+MP3} < E_{HF+MP2} < E_{CISD} < E_{HF}$  when employing various basis sets. Utilizing the 6-311G\*\* basis set in DFT calculations, the computed binding energy values for these molecules are 7590.61 KJ/mol, 7589.14 KJ/mol, and

7586.73 KJ/mol, respectively. The binding energy increases at higher calculation levels, with the largest increase observed at the HF+MP2 level. The calculation of bond length, bond angle and dihedral angle for chloroaniline molecules (ortho, meta and para) are carried out at HF, HF+MP2 and DFT (B3LYP) level of calculation and the values of these parameters are found to be approximately same. The C-Cl bond length in ortho, meta and para chloroaniline is found to be 1.769Å, 1.765Å and 1.765Å respectively at DFT level of calculation. The experimental values of C-Cl bond length in ortho, meta and para chloroaniline molecules are same which is 1.70Å. During the HF+MP2 calculation, the C-Cl bond lengths for ortho, meta, and para chloroaniline molecules are determined 1.742 Å, 1.741 Å, and 1.740 Å, respectively.. Clearly, a reduction in the C-Cl bond length is observed as the chlorine atom's position in chloroaniline shifts from ortho to meta and then to para positions. The charge distribution within each molecule leads to a net sum of Mulliken charges equating to zero. The dipole moment values for the ortho, meta, and para chloroaniline molecules are computed as 2.1194 Debye, 3.5398 Debye, and 4.1385 Debye, respectively in which dipole moment of p-chloroaniline is stronger than dipole moment of m- chloroaniline structure and the dipole moment of it is stronger than o-chloroaniline. Moreover, within ortho, meta and para chloroaniline, polarization is in increasing order as we go from ortho to meta and meta to para chloroaniline. So degree of polarization in para-chloroaniline is the highest out of three.

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