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RESEARCH ARTICLE

Structural Equilibrium Configuration of Benzene and Aniline: A First-Principles Study

Krishna Bahadur Rai[1], Rishi Ram Ghimire[1], Chandra Dhakal[2],
Kiran Pudasainee[3], Bijay Siwakoti[4,*]
[1]Department of Physics, Patan Multiple Campus, Tribhuvan University, Nepal
[2]Department of Physics, Florida International University, USA
[3]Department of Physics, St. Xavier's College, Maitighar, Katmandu, Nepal
[4]Department of Mathematics and Physics, Southern University and A & M College, LA, USA
[*]corresponding author: siwakoti.bijay@gmail.com

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Abstract

The present work describes the equilibrium configuration of aromatic compounds like benzene and aniline molecules using the first principle *(ab initio)* calculation method implemented by the Gaussian 98 set of programs. The ground state energy for benzene and aniline molecules obtained using the DFT (B3LYP) calculation is lower than that obtained with the HF+MP2 method which, in turn, is lower than that obtained with the HF calculation. The calculated values of bond length, bond angle, and dihedral angle for these molecules with HF, HF+MP2, and DFT (B3LYP) levels of calculation agree with each other within 2%. The calculated C-C and C-H bond lengths of the benzene molecule are 1.394 Å and 1.084 Å at DFT (B3LYP) calculation and these values agree well with the experimental value of 1.395 Å and 1.084 Å for C-C and C-H bond. Also, the calculated value of bond angles and dihedral angles for benzene molecule are 120^{o} and 180^{o} respectively. For aniline molecule, the C-N and N-H bond lengths are found 1.378 Å and 1.003 Å respectively at DFT (B3LYP) calculation, which agrees with the experimental value of C-N and N-H bond lengths with values of 1.475 Å and 1.008 Å within 7% respectively. For the benzene molecule, there is a symmetrical charge distribution. The total dipole moment of the benzene molecule is zero, indicating that the centers of positive and negative charge coincide with each other such that the benzene molecule is non-polar whereas aniline is a polar molecule with a dipole moment of 1.9828 Debye.

Keywords: *Benzene, Aniline, DFT calculation, Hartree-Fock method, Basis set*

Introduction

Benzene is a flat molecule with every carbon and every hydrogen lying in the same plane. Each carbon is bonded to three other atoms and it uses sp^2 orbitals [1]. It is a symmetrical molecule with each carbon atom lying at the apex of a regular hexagon and every bond angle is 120º. Each bond orbital is cylindrically symmetrical about the line joining the atomic nuclei and hence these bonds are designated as sigma bonds. All carbon-carbon bonds are equal (C-C = 1.39 Å) and intermediate in length of single and double bonds along with all carbon-hydrogen bonds of equal length (C-H = 1.10 Å) [2, 3]. Aniline is also a flat molecule, with every carbon, hydrogen, and nitrogen lying in the same plane. The carbon-nitrogen (C-N) and nitrogen-hydrogen (N-H) bond lengths in aniline molecule are 1.386 Å and 1.013 Å respectively and H-N-H bond angle is 119º [4, 5]. The atomic structures in complex molecules such as benzene help in identifying various atomic parameters [1, 2]. As a whole having defined the parameters like bond lengths, binding energies, and electron density, the molecular structure of any molecules can be well described. In principle, the required values of parameters are assigned based on molecular orbital calculations. Furthermore, the study of molecular physics demands the calculation of bond length and binding energies. Bond lengths in any molecule between its different atoms are used to analyze its molecular structure. Binding energies bind the molecule by bringing its constituents within a boundary to give a particular structure to any molecule [6]. The first-principles approaches are widely used to study the electronic structure and to determine various properties such as ground state energy, dipole moment, atomic charges, ionization potential, electron affinities, vibrational frequencies, polarizability and nuclear quadrupole moment and electronic structure of solids, surfaces, and clusters of many-electron systems [7, 8]. They are based on the fundamental laws of quantum mechanics and use a variety of mathematical transformations and approximation techniques to solve the basic equations. The concept of bond order indices and valence indices, calculated from the semiempirical bond order matrix, are of direct chemical significance because they can be well correlated with the corresponding chemical notions [9, 10, 11]. They may be useful both in studying the links between quantum mechanics and ordinary chemistry in general and in giving better interpretations and getting a deeper understanding of the results of the actual chemical calculations for systems in particular. The first-principles (or *ab initio*) self-consistent theory has been incorporated into the semi-empirical MINDO/3 method to calculate bond order indices in some substituted benzenes involving $-NH_2$ and -Cl as substituent [12, 13]. Knowledge of the electronic structure of substituted benzenes (i.e. aniline) is of basic importance for a deeper understanding of their chemical and spectral properties. Therefore, the study of their electronic structure has received much attention at every stage of the development of the molecular orbital theory [14, 15, 16]. In the present work, we deal with the first-principles calculations of the equilibrium configuration of benzene and aniline molecules, ground state energy, binding energy (B. E.), equilibrium geometry, bond lengths, dipole moment, charge distribution on each atom of benzene and aniline molecules using the Gaussian 98 set of programs.

Computational details

In this study, we have investigated the equilibrium configuration, structure, and electronic properties of benzene and its derivatives using the first principles Hartree-Fock (HF), Moller-Plesset (MP) perturbation theory, Configuration Interaction (CI) and Density Functional Theory (DFT (B3LYP)) methods. These first principles calculations from the Gaussian 98 set of programs were used to find the ground state energy, B. E., equilibrium geometry, bond lengths, dipole moment, and charge distribution of aromatic compounds benzene and aniline molecules. The basis set used in the calculation were 3-21G, 4-31G, 6-31G, 6-31G*, 6-31G**, 6-311G, 6-311G*, and 6-311G** where the starred sets include polarization functions. Basis sets like 3-21G, 4-31G, and 6-31G use three, four, and six Gaussian-type functions for inner core electrons and two sizes of Gaussian type of basis function for each valence orbital. Similarly, a basis set like 6-311G uses six Gaussian types of function for inner core electrons and three sizes of Gaussian type of basis function for each valence orbital. The remaining basis sets 6-31G*, 6-31G**, 6-311G*, and 6-311G** include the effect of polarization functions in 6-31G and 6-311G basis sets respectively. The consistency of the results obtained has been tested by convergence concerning the use of a basis set of increasing size and complexity.

Results and discussion

The results thus obtained are given and analyzed in this result and discussion section.

(a) Ground state energy and binding energy of benzene molecule

Figure 1 gives the ground state energy of the benzene molecule using different bases set in different levels of calculation. From Figure 1, it is seen that the ground state energy of the benzene molecule calculated using the basis sets 3-21G, 4-31G, 6-31G, 6-31G* (i.e. * means d-type polarization function), 6-31G** (i.e. ** means d-type and p-type Gaussian polarization function), 6-311G, 6-311G* and 6-311G** are lowered with increasing size and complexity of the basis set in all the levels of calculation i.e. HF, HF+MP2, HF+MP3, CISD and DFT (B3LYP). 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. With the addition of d-type and p-type Gaussian polarization functions (i.e. * and **) to 6-31G and 6-311G basis set, it is seen that the ground state energy of benzene molecule gets lowered as compared to the 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 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 0.02% at HF level of calculation. By inclusion of the p-type polarization in the basis sets 6-31G* and 6-311G* such that forming basis sets 6-31G** and 6-311G**, the lowering in the value of energy is also found to be around 0.02% at HF level of calculation. Calculated ground state energy approaches to the experimental value [17] as we go to the basis set of larger size and higher complexity as demanded by the variational method. From the above analysis, it is clearly seen that our results for the ground state energy of benzene molecule are basis set convergent.

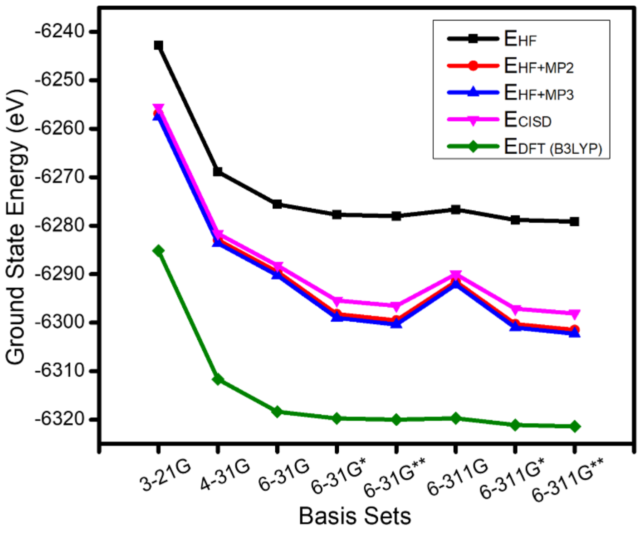

***Figure 1**: Ground state energy of the benzene molecule using HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP) methods using different basis sets*

It is also seen from Figure 1 that the HF+MP2 ground state energy of the benzene molecule gets lowered as compared to the corresponding HF values. Furthermore, it is also seen that the DFT ground state energy of the benzene molecule is considerably lower as compared to the corresponding HF+MP3 values. The trend in energy is $E_{DFT} < E_{HF+MP3} < E_{HF+MP2} < E_{CISD} < E_{HF}$. This is because in the HF+MP2 (MP2 - Moller-Plesset second-order perturbation approximation) level of calculation the second-order interaction energy due to electron correlation reduces the total energy. On adding the third-order correction to interaction energy to the HF+MP2 level of calculation further energy reduction is expected which is seen in Figure 1. The DFT level of calculation includes the dynamic correlation effect of the electron's motion. The presence of the quantity of motion in one electron affects the motion of other electrons. The interaction energy of the system has a negative value, which further reduces the total energy. Similarly, in CISD calculation energy is expected to be less than in HF calculation because CISD calculation adds the effects due to the empty excited level on HF calculation. The basis set 6-311G** gives the minimum ground state energy among all the basis sets chosen. Therefore, the basis set 6-311G** has been chosen for our calculation.

Table 1 indicates the binding energy (B. E.) of a benzene molecule and is obtained using the equation: B.E. = 6 E(C) + 6 E(H) - E(C_6H_6). It is seen that the calculated values of B. E. of a benzene molecule with HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP) levels of calculation are positive with basis set 6-311G** indicating the stability of this molecule.

Table 1: *Binding energy of benzene molecule using HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP) methods concerning the basis set 6-311G***

Basis set	Binding Energy (KJ/mol.)				
	HF	HF+MP2	HF+MP3	CISD	DFT
6-311G**	5671.66	6717.51	6522.04	5928.79	6716.28

Here, Table 1 shows that the B. E. is 5671.66 KJ/mol and 6717.51 KJ/mol at HF and HF+MP2 levels of calculation respectively. It is observed that there is an increase in the B. E. at HF+MP2 level of calculation by 18.4% than that of HF level of calculation. The B. E. is highest for HF+MP2 level of calculation. It is also seen that there is an increase in the B. E. at HF+MP3, CISD, and DFT (B3LYP) levels of calculation by 15%, 4.5%, and 18.4% respectively than that of the HF level of calculation. This shows that the correlation effect for binding of atoms in benzene molecule plays an important role at HF+MP3 and DFT (B3LYP) levels of calculation. The exception is obtained for the CISD level of calculation.

Table 2: *Optimized parameters of benzene molecule using the basis set 6-311G** at HF, HF+MP2 and DFT level of calculation*

Levels of calculation	Bond length (in Å)				Bond angle (°)		Dihedral angle (°)	
	C-H		C-C		Calculated	[a]Expt.	Calculated	[a]Expt.
	Calculated	[a]Expt.	Calculated	[a]Expt.				
HF	1.076	1.084 ± 0.006	1.386	1.395 ± 0.003	120	120	180	180
HF+MP2	1.086		1.399		120		180	
DFT	1.084		1.394		120		180	

[a] *The experimental values of the bond length, bond angle, and dihedral angle are from Weast [17].*

Table 2 gives the optimized parameters of benzene molecules. From this Table, it is seen that the bond length between carbon and hydrogen atom, i.e. C-H, is found to be 1.076 Å in HF level of calculation whereas this distance is found to be increased by around 0.9% in HF+MP2 level of calculation than in HF level of calculation. In the DFT level of calculation the increase in bond length, C-H, is found by around 0.7% than in HF level of calculation. The distance between two carbon atoms C-C in benzene molecule is found to be 1.386 Å in the HF level of calculation and increases by around 0.9% and 0.6% in HF+MP2 and DFT levels of calculation respectively in the HF level of calculation. Table 2 also shows the values of bond angle and dihedral angle and they are 120° and 180° respectively for all levels of calculation. This shows that the benzene molecule is planar. The DFT (B3LYP) value of 1.084 Å for the carbon-hydrogen bond length of the benzene molecule is the closest to the experimental value of 1.084 Å. The DFT value of 1.394 Å for the carbon-carbon bond length of the benzene molecule is the closest to the experimental value of 1.395 Å. The calculated value of bond angles and dihedral angles at HF, HF+MP2, and DFT (B3LYP) levels of calculation are in excellent agreement with experimental values.

(b) Equilibrium geometry of benzene molecule

Figure 2 shows the equilibrium geometry configuration of the benzene molecule obtained with the DFT (B3LYP) level of calculation using the basis set 6-311G**. Since the DFT (B3LYP) level of calculation with the basis set 6-311G** adds the dynamic correction effects of electron's motions on the HF level of calculation. This increases the accuracy of calculation as the technique approaches the phenomena in an electronic state very closely. With this configuration, we have studied the variation of energy concerning bond lengths, bond angle, and dihedral angle and they are shown in Figures 3, 4, 5, and 6 respectively.

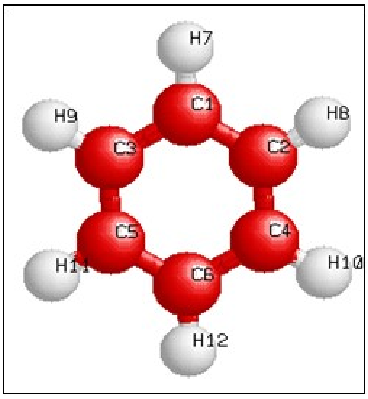

***Figure 2**: Equilibrium configuration of benzene molecule using a basis set 6-311G** in the DFT level of calculation*

Figure 3 shows that the ground state energy of the benzene molecule is minimum corresponding to the carbon-carbon bond length 1.395 Å. Figure 4 indicates that the ground state energy of the benzene molecule is minimum corresponding to the carbon-hydrogen bond length 1.085 Å. Both bond lengths i.e. 1.395 Å and 1.085 Å for C-C and C-H respectively agree well with the experimental value 1.395 Å and 1.084 Å [17]. Figure 5 informs that the ground state energy of the benzene molecule is minimum corresponding to the bond angle 120°. Figure 6 shows the variation of energy of the benzene molecule with a dihedral angle. The minimum energy occurs corresponding to the dihedral angle of 180°.

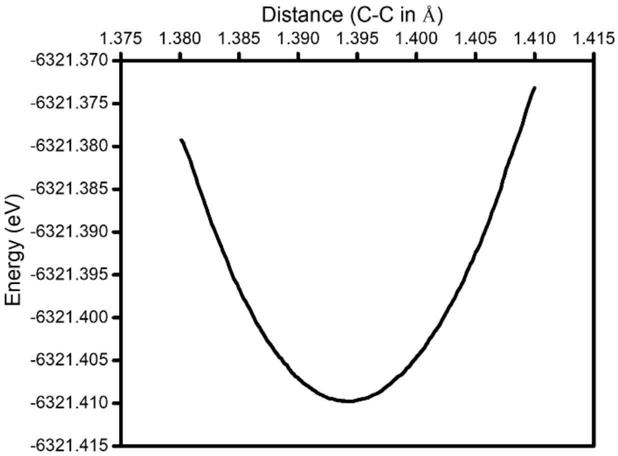

***Figure 3:** Variation of energy of benzene molecule with bond length of C-C with respect to basis set 6-311G** in the DFT calculation*

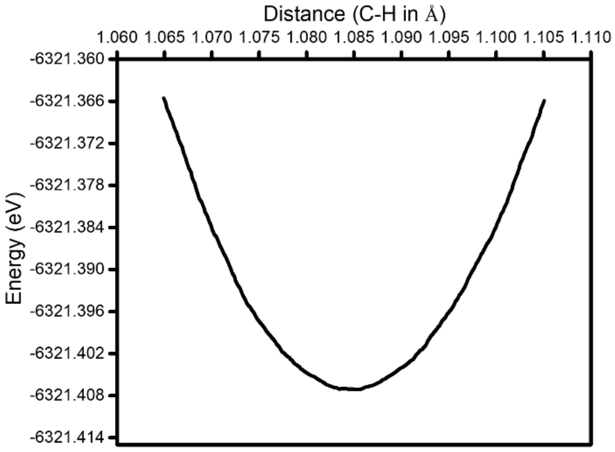

***Figure 4:** Variation of energy of benzene molecule with bond length of C-H with respect to basis set 6-311G** in the DFT calculation*

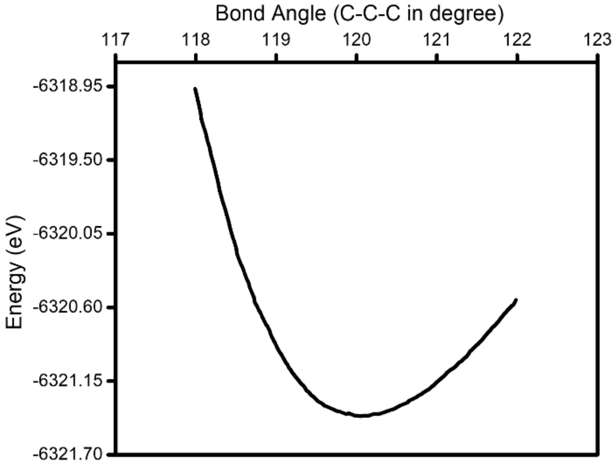

***Figure** 5: Variation of energy of benzene molecule with bond angle of C-C-C with respect to basis set 6-311G** in the DFT calculation*

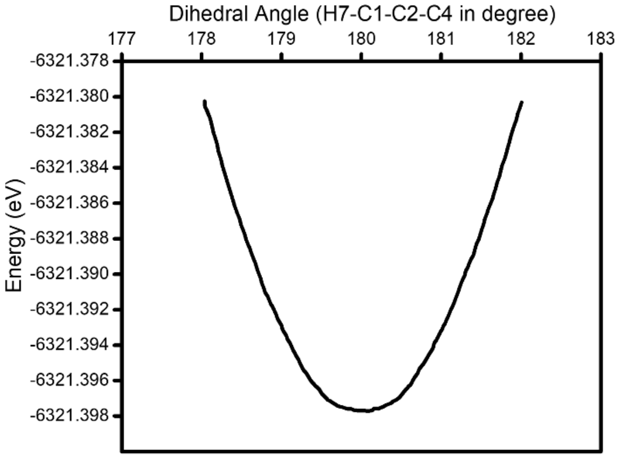

***Figure 6:** Variation of energy of benzene molecule with dihedral angle of H7-C1-C2-C4 with respect to basis set 6-311G** in the DFT calculation*

Figure 7 shows the calculated value of Mulliken charges distributions of benzene molecule using a basis set 6-311G** at the DFT (B3LYP) level of calculation. The charge distribution information reveals how the charge is distributed among the various atoms in the molecule. From Figure 7, it is seen that each carbon has a small negative charge and each hydrogen has a small positive charge. The charge distribution (i.e. Mulliken charges) takes an equal negative charge on each carbon atom and is equal to that of the carbon atom but positive charge on each hydrogen atom. Therefore, the sum of Mulliken charges = 0.000. This shows that there is a symmetrical charge distribution in the benzene molecule.

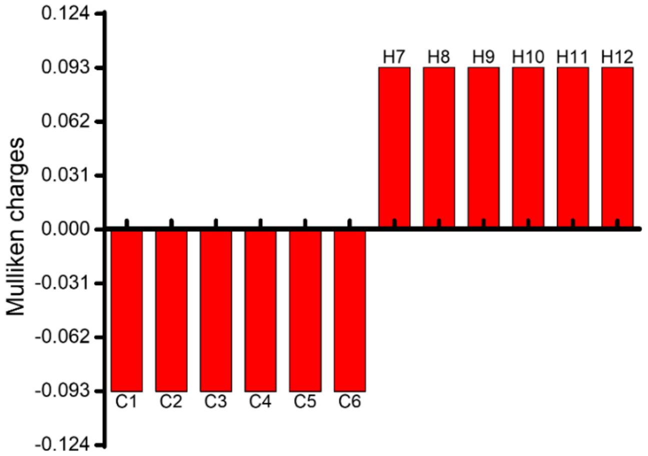

***Figure 7:** Mulliken charges distributions of benzene molecule using a basis set 6-311G** at DFT (B3LYP) level of calculation*

Table 3 shows the calculated value of the dipole moment of the benzene molecule using a basis set 6-311G** at the DFT (B3LYP) level of calculation. The dipole moment measurement gives that whether the molecule is polar or nonpolar.

***Table 3:** Dipole moment of benzene molecule using a basis set 6-311G** at DFT (B3LYP) level of calculation*

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

From Table 3, it is also observed that the dipole moment of the benzene molecule is broken down into X, Y, and Z components with their respective values X= 0.0000, Y= 0.0000, and Z= 0.0000. The total dipole moment of the benzene molecule is zero, indicating that the centers of positive and negative charge coincide with each other and this informs that the benzene molecule is non-polar.

(c) Ground state energy and binding energy of aniline molecule

We have calculated the ground state energy and binding energy for aniline molecule using different basis sets in different levels of calculation.

Figure 8 gives the ground state energy for aniline molecule at HF, HF+MP2, HF+MP3, CISD, and DFT levels of calculation using different basis sets i.e. 3-21G, 4-31G, 6-31G, 6-31G*, 6-31G**, 6-311G, 6-311G*, and 6-311G**. In all levels of calculation, it is observed that the energy values decrease as the size and complexity of the basis set increases. The decrease in energy values when changing from the 3-21G to 4-31G basis set is much smaller compared to the decrease when changing from the 4-31G to 6-31G basis set. When d-type and p-type Gaussian polarization functions are added to the 6-31G and 6-311G basis sets, it is found that the ground state energy of the aniline molecule decreases compared to the values obtained with the corresponding unstarred basis sets (without (d,p)). The decrease in energy values when transitioning from 6-31G to 6-31G* is almost similar to the decrease when transitioning from 6-311G to 6-311G*. Similarly, the decrease in energy when changing from 6-31G* to 6-31G** is almost similar to the decrease when changing from 6-311G* to 6-311G**. The decrease in energy values when transitioning from 6-31G* to 6-311G* is approximately 0.02% at the HF level of calculation. Additionally, by including p-type polarization (double starred) in the 6-31G and 6-311G basis sets, resulting in the 6-31G** and 6-311G** basis sets, the decrease in energy values is also around 0.02% at the HF level of calculation. This indicates that the calculated ground state energy approaches the experimental value as the basis set size and complexity increase, as expected by the variational method. Based on the analysis presented above, it is evident that the results obtained for the ground state energy of the aniline molecule are convergent concerning the basis set used.

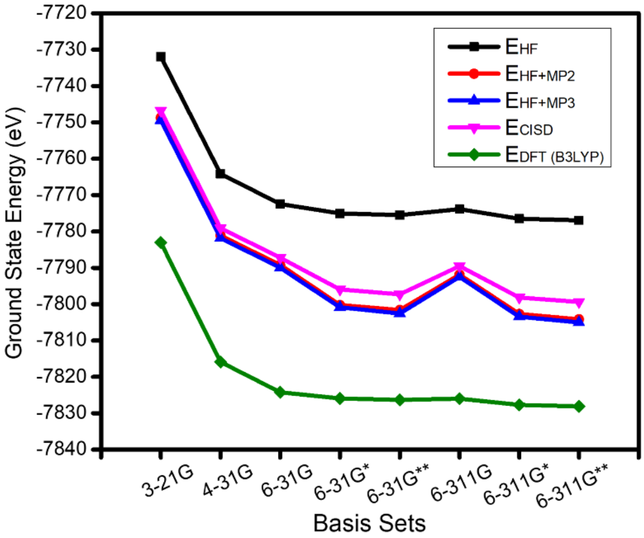

Figure 8: *Ground state energy of the aniline molecule using HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP) methods using different basis sets*

From Figure 8, it can be observed that the ground state energy of the aniline molecule calculated using the HF+MP2 method is lower compared to the corresponding HF values. Additionally, the DFT ground state energy values for aniline molecules are significantly lower than the corresponding HF+MP3 values. The trend in energy, from lowest to highest, is $E_{DFT} < E_{HF+MP3} < E_{HF+MP2} < E_{CISD} < E_{HF}$. It is seen from Figure 8 that a lowering in the HF+MP2 ground state energy value of aniline molecule as compared to the corresponding HF takes place 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 aniline molecule. In our calculation, this is found to be -16.80298 eV, -16.94992 eV, -16.79481 eV, -25.20038 eV, -26.11468 eV, -18.01932 eV, -26.18271 eV, and -27.23579 eV for 3-21G, 4-31G, 6-31G, 6-31G*, 6-31G**, 6-311G, 6-311G* and 6-311G** basis sets respectively.

Table 4 shows the calculated values of the binding energy of aniline molecule using HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP) methods concerning the basis set 6-311G**.

Table 4: *Binding energy of aniline molecule using HF, HF+MP2, HF+MP3, CISD, and DFT (B3LYP) methods with respect to the basis set 6-311G***

Basis set	Binding Energy (KJ/mol.)				
	HF	HF+MP2	HF+MP3	CISD	DFT(B3LYP)
6-311G**	6420.14	7700.15	7438.61	6706.23	7696.54

Table 4 shows the values of the binding energy for aniline molecule calculated in the HF, HF+MP2, HF+MP3, CISD, and DFT(B3LYP) levels of calculation with the basis set 6-311G** and they are positive. This positive binding energy signifies the stability of the aniline molecule. The highest binding energy value is observed at the HF+MP2 level of calculation. This indicates that the correlation effect significantly contributes to the stability of the aniline molecule. Additionally, there is an increase in the binding energy at the HF+MP2, HF+MP3, CISD, and DFT (B3LYP) levels of calculation by approximately 19.9%, 15.9%, 4.5%, and 19.9% respectively compared to the HF level of calculation. This demonstrates that the correlation effect plays an important role in the binding of atoms in the aniline molecule, particularly at the HF+MP3 and DFT (B3LYP) levels of calculation. However, an exception is observed for the CISD level of calculation.

Table 5 gives the calculated optimized values of the bond length, bond angle, and dihedral angle of aniline molecule for HF, HF+MP2, and DFT levels of calculation. From Table 5, it is seen that the HF level of calculation gives an equal bond length (i.e. 1.395 Å) between the first and second carbon atoms (C1 and C2) and the first and third carbon atoms (C1 and C3). The bond length between the second and fourth carbon atoms (C2 and C4) and third and fifth carbon atoms (C3 and C5) are also equal i.e. 1.382 Å at the HF level of a calculation. Similarly, the bond length between the fourth and sixth carbon atoms (C4 and C6) is found to be equal to the bond length between the fifth and sixth carbon atoms (C5 and C6). The magnitude of these bond lengths (i.e. C4 and C6; C5 and C6) is found to be 1.385 Å, 1.399 Å, and 1.394 Å at HF, HF+MP2, and DFT levels of calculation respectively. Figure 9 shows that the NH_2 group is attached to the first carbon atom and it lies in the same plane in which the ring of benzene lies. The distance of the nitrogen atom in NH_2 from the first carbon is found to be 1.374 Å, 1.379 Å, and 1.378 Å in HF, HF+MP2, and DFT levels of calculation respectively. The distance of the hydrogen atom from the nitrogen atom in NH_2 is found to be 0.989Å in the HF level of calculation. This distance is increased by 1.4% in

Table 5: *Optimized parameters of aniline molecule using the basis set 6-311G** at HF, HF+MP2 and DFT (B3LYP) levels of calculation*

Methods	Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
HF	C1-C2 =1.395	C2-C1-C3 =118.49	C3-C1-C2-C4 =0
	C1-C3 =1.395	C1-C2-C4 =120.39	C2-C1-C3-C5 =0
	C2-C4 =1.382	C1-C3-C5 =120.39	C1-C2-C4-C6 =0
	C3-C5 =1.382	C2-C4-C6 =121.12	N7-C1-C2-C4 =180
	C4-C6 =1.385	C2-C1-N7 =120.76	N7-C1-C2-H8 =0
	C1-N7 =1.374	C1-C2-H8 =119.59	N7-C1-C3-H9 =0
	C2-H8 =1.077	C1-C3-H9 =119.59	H8-C2-C4-H10 =0
	C3-H9 =1.077	C2-C4-H10 =119.00	H9-C3-C5-H11 =0
	C4-H10 =1.076	C3-C5-H11 =119.00	H10-C4-C6-H12 =0
	C5-H11 =1.076	C4-C6-H12 =120.76	C2-C1-N7-H13 =0
	C6-H12 =1.075	C1-N7-H13 =120.91	C2-C1-N7-H14 =180
	N7-H13 =0.989	C1-N7-H14 =120.91	
	N7-H14 =0.989		
HF+MP2	C1-C2 =1.408	C2-C1,C3 =118.42	C3-C1-C2-C4 =0
	C1-C3 =1.408	C1-C2-C4 =120.60	C2-C1-C3-C5 =0
	C2-C4 =1.396	C1-C3-C5 =120.60	C1-C2-C4-C6 =0
	C3-C5 =1.396	C2-C4-C6 =120.75	N7-C1-C2-C4 =180
	C4-C6 =1.399	C2-C1-N7 =120.79	N7-C1-C2-H8 =0
	C1-N7 =1.379	C1-C2-H8 =119.37	N7-C1-C3-H9 =0
	C2-H8 =1.088	C1-C3-H9 =119.37	H8-C2-C4-H10 =0
	C3-H9 =1.088	C2-C4-H10 =119.13	H9-C3-C5-H11 =0
	C4-H10 =1.087	C3-C5,H11 =119.13	H10-C4-C6-H12 =0
	C5-H11 =1.087	C4-C6-H12 =120.56	C2-C1-N7-H13 =0
	C6-H12 =1.085	C1-N7-H13 =120.85	C2-C1-N7-H14 =180
	N7-H13 =1.003	C1-N7-H14 =120.85	
	N7-H14 =1.003		
DFT(B3LYP)	C1-C2 =1.406	C2-C1-C3 =118.31	C3-C1-C2-C4 =0
	C1-C3 =1.406	C1-C2-C4 =120.53	C2-C1-C3-C5 =0
	C2-C4 =1.390	C1-C3-C5 =120.53	C1-C2-C4-C6 =0
	C3-C5 =1.390	C2-C4-C6 =120.96	N7-C1-C2-C4 =180
	C4-C6 =1.394	C2-C1-H7 =120.85	N7-C1-C2-H8 =0
	C1-N7 =1.378	C1-C2-H8 =119.45	N7-C1-C3-H9 =0
	C2-H8 =1.086	C1-C3-H9 =119.45	H8-C2-C4-H10 =0
	C3-H9 =1.086	C2-C4-H10 =119.07	H9-C3-C5-H11=0
	C4-H10 =1.085	C3-C5-H11 =119.07	H10-C4-C6-H12 =0
	C5-H11 =1.085	C4-C6-H12 =120.65	C2-C1-N7-H13 =0
	C6-H12 =1.083	C1-N7-H13 =120.95	C2-C1-N7-H14 =180
	N7-H13 =1.003	C1-N7-H14 =120.95	
	N7-H14 =1.003		

HF+MP2 and DFT levels of calculation. The hydrogen atoms attached to the second and third carbon atoms are found to lie at equal distances. Similarly, the hydrogen atoms attached to the fourth and fifth carbon atoms lie at the same distances. These are obtained for all levels of calculation used. The hydrogen atom attached to the sixth carbon atom lies at a distance of 1.075 Å in the HF level of calculation. On observing the bond angle, from Table 5, it is seen that all the bond angles formed by C1-C2-C4, C1-C3-C5, C1-C2-C8, C1-C3-C9, C2-C4-C10, C3-C5-C11, C1-C7-C13, C1-C7-C14 are close to 120°. Table 5 also shows the dihedral angle of different atoms in aniline molecules for HF, HF+MP2, and DFT levels of calculation. This means that the aniline molecule is planar.

(d) Equilibrium geometry of aniline molecule

Figure 9 shows the equilibrium geometry configuration of the aniline molecule obtained with the DFT (B3LYP) level of calculation using the basis set 6-311G**. With this configuration, we have also studied the variation of energy concerning bond length, bond angle, and dihedral angle as shown in Figures 10, 11, 12, and 13 respectively.

Figure 10 informs that the ground state energy of the aniline molecule is minimal corresponding to the carbon-nitrogen bond length of 1.378 Å, which agrees to the experimental value of 1.475 Å [17] within 7%. It is also seen from Figure 11 that the ground state energy of the aniline molecule is minimal corresponding to the nitrogen-hydrogen bond length of 1.000 Å and it agrees to the experimental value of 1.008 Å [17] within 1%. Figure 12 shows that the energy of the aniline molecule is minimum corresponding to the C-N-H bond angle 120º. Figure 13 gives the variation of energy of aniline molecule with dihedral angle N7-C1-C2-C4. The minimum energy occurs corresponding to the dihedral angle of 180º.

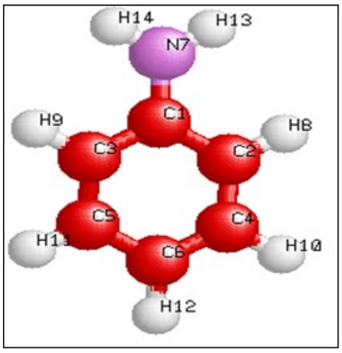

***Figure 9**: Equilibrium configuration of aniline molecule using a basis set 6-311G** in the DFT level of calculation*

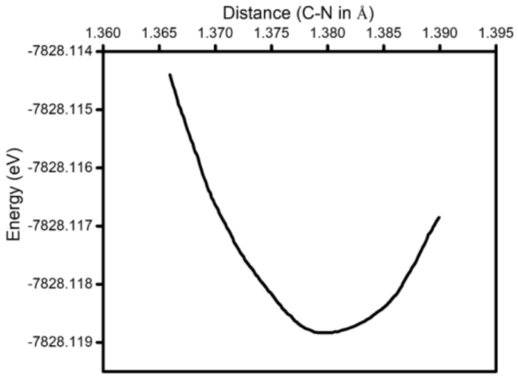

***Figure 10:** Variation of energy of aniline molecule with C-N bond length concerning basis set 6-311G** in the DFT calculation*

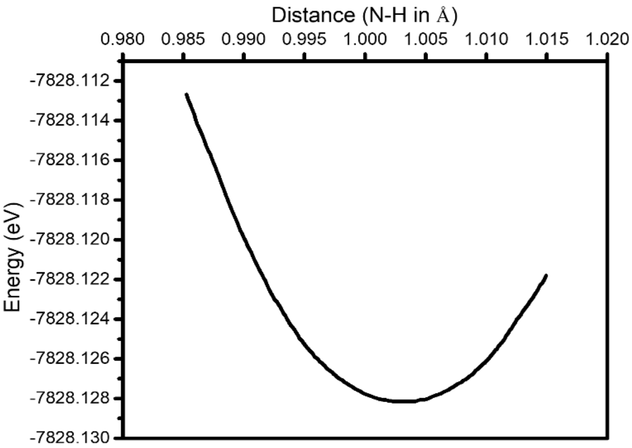

***Figure 11**: Variation of energy of aniline molecule with N-H bond length with respect to basis set 6-311G** in the DFT calculation*

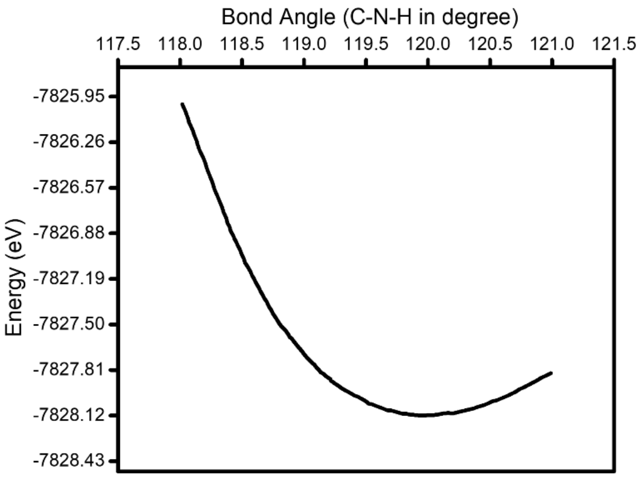

***Figure 12**: Variation of energy of aniline molecule with bond angle of C-N-H with respect to basis set 6-311G** in the DFT calculation*

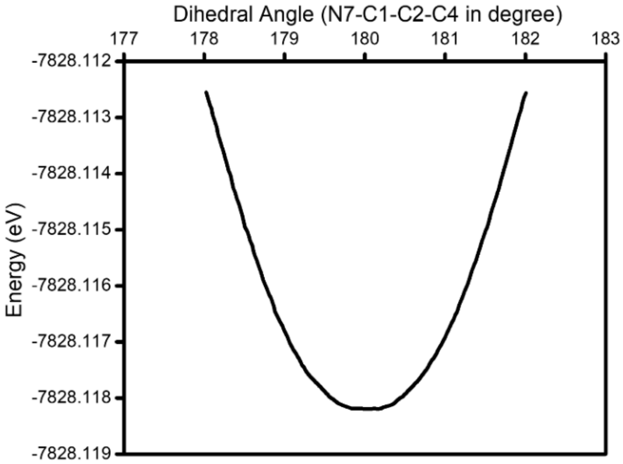

***Figure 13**: Variation of energy of aniline molecule with a dihedral angle of N7-C1-C2-C4 concerning basis set 6-311G** in the DFT calculation*

Figure 14 displays the calculated values of Mulliken charge distributions for the aniline molecule using the 6-311G** basis set at the DFT (B3LYP) level of calculation. When the seventh hydrogen (Figure 9) of the benzene molecule is replaced by the NH_2 group, the first carbon atom acquires a slightly positive charge whereas the nitrogen atom acquires a negative charge. From Figure 14, it is seen that the positive charges are confined to the first carbon atom and all the hydrogen atoms of the aniline molecule. Each hydrogen atom has a small positive charge. The negative charges are confined to the nitrogen atom and all the remaining carbon atoms of the aniline molecule so that the sum of Mulliken charges is zero.

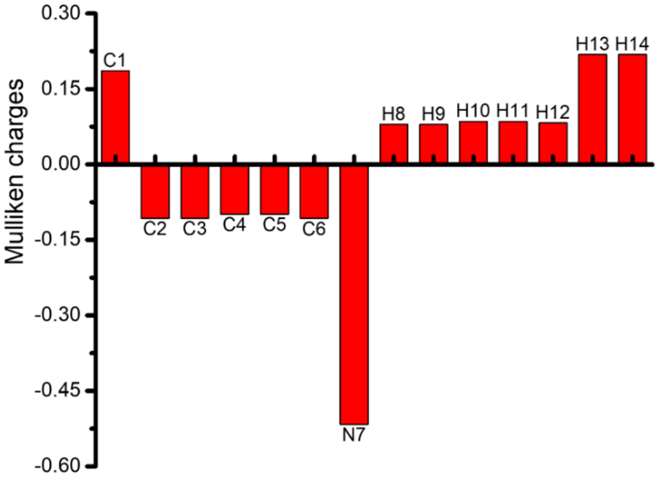

***Figure 14:** Mulliken charges distributions of aniline molecule using basis set 6-311G** at DFT (B3LYP) level of calculation*

Table 6 displays the calculated values of dipole moment for the aniline molecule using the 6-311G** basis set at the DFT (B3LYP) level of calculation.

***Table 6:** Dipole moment of benzene molecule using a basis set 6-311G** at DFT (B3LYP) level of calculation*

Dipole moment (Debye)			
X= 0.0000	Y=1.9828	Z= 0.0000	Total = 1.9828

Table 6 provides a breakdown of the dipole moment of the aniline molecule into its X, Y, and Z components. The total dipole moment of the aniline molecule has a magnitude of 1.9828 Debye, with the direction exclusively along the Y-axis. This dipole moment is relatively weak, suggesting that the positive and negative charge centers within the molecule are relatively close to each other. Consequently, the aniline molecule can be characterized as a polar molecule.

Conclusion

The first Principles study was conducted to analyze the equilibrium configurations of benzene and aniline aromatic compounds using various levels of calculation: HF, HF+MP2, and DFT, employing the 6-311G** basis set. The results were compared with experimental data. For benzene, the C-C bond length was calculated as 1.386 Å, 1.399 Å, and 1.394 Å for HF, HF+MP2, and DFT, respectively. The C-H bond length was determined to be 1.076 Å, 1.086 Å, and 1.084 Å for the same calculation levels. These values closely matched the corresponding experimental values (1.395 Å and 1.084 Å) within a 1% margin. The binding energy of benzene was calculated as 5671.66 KJ/mol, 6717.51 KJ/mol, and 6716.28 KJ/mol for HF, HF+MP2, and DFT, respectively. The bond angles and dihedral angles were consistent with the experimental values of 120° and 180°, confirming that benzene is a planar, non-polar molecule. For aniline, at the DFT level, the C-N and N-H bond lengths were found to be 1.378 Å and 1.003 Å, respectively. These values agreed with experimental values (1.475 Å and 1.008 Å) within a 7% difference. At the HF+MP2 level, the C-N and N-H bond lengths were 1.379 Å and 1.003 Å. The binding energies for aniline were 6420.14 KJ/mol, 7700.15 KJ/mol, and 7696.54 KJ/mol for HF, HF+MP2, and DFT, respectively. The study indicated that when a hydrogen atom in benzene was replaced by an amine group to form aniline, there was a slight change in the bond length between consecutive carbon atoms in the ring. The calculated bond angles and dihedral angles confirmed that aniline, like benzene, is a planar molecule. However, the dipole moment of aniline was determined to be 1.9828 Debye, suggesting that aniline is a polar molecule, unlike the non-polar benzene molecule.

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