A Theoretical Study of Aniline and Nitrobenzene by Computational Overview

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ABSTRACT

Computational chemistry is used as computer programming to solve real problems in chemical, pharmaceutical, biotechnological and material science. It uses the results of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. For the calculation using molecular mechanics by Gaussian 09, two basis set such as Molecular mechanics (Mm+) and Parameterized Model number 3 (PM3) and quantum mechanics such as Density functional theory (DFT) with (WB97XD) and Hybrid functional (HF) are used to make the profile on the physical properties such as total energy, binding energy, hydration energy, dipole moment, heat of formation and energies for Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital ((LUMO). Nitrobenzene and aniline were tested in two basis set of DFT and HF to make the profile on the physical properties. These physical properties are the theoretical agreement of physical properties to safe the time and chemical in laboratory.

1. INTRODUCTION

Nitrobenzene is a water insoluble pale yellow oil or greenish-yellow crystals organic compound Which is used in the manufacture of compounds including benzidine and quinoline, soap, analgestic paracetamol, in the production of isocyanates, pesticides and pharmaceuticals drug. A vast amount of (95%) Nitrobenzene is used primarily to produce aniline, an intermediate in the production of dyestuffs and other products[1].Though nitrobenzene is occasionally used as a flavor or perfume additive, nitrobenzene is extremely toxic in large quantities which have greatly impact on human body [2]. Moreover, it seems and used as a solvent for electrophilic reagentsin the laboratory. In the laboratory experiment, it has been detected that Nitrobenzene in the air and appears to volatilize from water and soil. Environmental exposure seems to be primarily through inhalation of ambient air or through thermal exposure to products containing the chemical. It is mentionable that Nitrobenzene was nominated and designated byNational Institute of Environmental Health Sciences(NIEHS) for possible listing in the Report on Carcinogens based on the conclusions of the International Agency for Research on Cancer(IARC) working group that nitrobenzene is possibly carcinogenic to humans [3].

Regarding aniline was first obtained in1826 by the destructive distillation of indigo. It is used as organic base to make dyes, anilides, diazonium salt, drugs, explosives, plastics, antioxidants,

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activators, accelerators and photographic and rubber chemicals. Furthermore, Aniline is also used in petroleum, plastics, agricultural, explosives, and chemical industries, various fungicides and herbicides for the agricultural industry, pharmaceutical industry and other organic products. Aniline is made commercially by the catalytic hydrogenation of nitrobenzene or by the action of ammonia on chlorobenzene[4-6]. Using various oxidizing agents, aniline is converted into quinone, azobenzene, nitrosobenzene, p-aminophenol and the phenazine dye aniline black.

Waste water from manufacturing or chemical processes in industries leads to or is the source of water pollution containing specific and readily identifiable chemical compounds. During the last fifty years, the number of industries in Bangladesh has grown rapidly. But water pollution is determined within a few sub sectors, principally in the form of toxic wastes and organic pollutants. Among this huge portion can be traced to the processing of industrial chemicals and to the food production industry. In fact, a number of large- and medium-sized industries in the region covered by the Buriganga, a name of polluted river which is situated in Dhaka.[7-8].Stringent actions have been over the years but Action plan does not have adequate effluent treatment facilities. Vast majority of these defaulting industries are sugar mills, textile industries, leather processing industries, thermal power stations, chemical industries and pharmaceutical industries at where the aniline and nitrobenzene were used. Optimum number of industries have treatment facilities for industrial effluents in very small scale and even insufficient. But it is a fact that some number of trivial factories and industries cannot afford the enormous investment on pollution control equipment whereas their profit margin is extremely slender [9]. In this regard,It is very necessary to find an effective and pragmatic method of destroying the nitrobenzene and aniline in order to remove color from effluents[10-11]. A number of physical and chemical techniques has been reported for the removal of them [6, 12] such as adsorption on carbon [13], biodegradation[14], ozonation[6] and advanced oxidation processes (AOPs) [15-16] and catalytic reactions[17] which deals on photochemistry. Photochemistry, a sub-discipline of chemistry, is the study of the interactions between atoms, small molecules and light or electromagneticradiation [18]. All of these methods consume the time and chemicals so that to make a safe of time and chemicals,

computational chemistry is only an alternative way [9].

Molecular mechanics uses and practices the laws of classical physics to elucidate and interpret the structure and properties of molecules. Molecular mechanics methods are available in many computer programs, including MM3, Hyper Chem, GAUSSIAN, Quanta, Sybyl and Alchemy [19]. There are many different molecular mechanics methods. Each one is characterized as well as considered by its particular force field. It is now beingused widely in the design of new drugs and materials. Computational chemistry is capable of predicting many properties of molecules and reactions including the following; molecular energies and structures, energies and structures of transition states, bond and reaction energies, molecular orbital, vibrational frequencies, thermo-chemical properties, reaction pathways, spectroscopic quantities and numerous other molecular properties for systems in the gas phase and in solution, including the ground state and excited states [19-20]. Computational calculations provide a manageable and apt solution to this colossal task. Electronic properties such as the ionization potential (IP), electron affinity (EA) and molecular orbital (LUMO) which is directly correlated to chemical and radiation stability, can provide an information of energy gap between the uppermost occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) reliably computed using first-principles-based calculations [21]. Specifically, a large HOMO-LUMO gap implies low chemical reactivity because it hinders adding electrons to a high-lying LUMO or extracting electrons from a low-lying HOMO and prevents the formation of the activated complex of any further reaction. Thus, the HOMO-LUMO gap can be used as a simple indicator for stability in reactive environments found in all uses fields. Similarly, the ionization potential (IP) and electron affinity (EA), which measure the proclivity of compounds to lose or gain an electron, are good indicators of both of aniline and nitrobenzene of stability in extreme redox environments found near the charged electrodes of electrochemical devices. Finally, in the presence of radiation, can undergo ionization or form radicals and excited species, which lead to further degradation, and the IP can be used as metrics of stability in these environments.

2. METHODOLOGY

There are a number of different types of basis sets that are used in modern *ab initio* calculations, depending on the complexity of the problem and the desired level of accuracy [22]. Usually, a larger basis set consisting of more basis functions will yield increased accuracy. A minimal basis is one that is composed of a single basis function for each atomic orbital. A split – valence basis set treats the core and atomic orbital differently and includes more diffuse GAUSSIAN functions with a smaller orbital exponent. The geometry optimization and frequency calculations were executed simultaneously. The following route section command was used in all those calculations. Job type was WB97XD/DGTZVP optimized frequency. This process includes the performance of quantum chemical models with regard to the calculation of vibration frequencies and describes the evaluation of thermodynamic quantities resulting from vibration frequencies. In addition to their role in characterizing structures on a potential energy surface, vibration frequencies, along with molecular geometry, are the essential ingredients for calculation of thermodynamic quantities. These follow from straight forward application of statistical mechanics. Entropy is certainly the most important of these, primarily for its contribution to the free energy. Calculated vibration frequencies may be employed to yield a variety of thermodynamic quantities. This work was done in computer and software laboratory in University of Chittagong, Chittagong, Bangladesh.

2.1 Thermodynamics Quantities in GAUSSIAN 09 Output

GAUSSIAN predicts various important thermodynamic quantities at the specified temperatures and pressure, including the thermal energy correction, heat capacity and entropy. These items are broken down into their source component in the output. GAUSSIAN also predicts the zero-point energy and absolute enthalpy and Gibbs free energies. Here is the zero-point energy and thermal corrected properties output from frequency.

2.2 Examining and Interpreting the Output

The outputs were visualized using Gauss View. The relevant sections of the output file were extracted and interpreted individually as illustrated in various sections. Thermo-chemical parameters of molecules were calculated by DFT and HF methods. Thermo-chemical parameters were calculated using the following general formula.

Parameters of Reactions = (Parameters of products)-(Parameters of Reactants)

$$\Delta G = \Delta H - T\Delta S, \ \Delta E = \Delta E - P\Delta V, \ \Delta H = \Delta E + P$$

Here, G is the free energy, H is the enthalpy, S is the entropy, E is the energy, and T, P and V are the temperature, pressure and volume

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Zero-point correction=                          0.217588 (Hartree/Particle)
Thermal correction to Energy=                   0.229729
Thermal correction to Enthalpy=                 0.230674
Thermal correction to Gibbs Free Energy=        0.178505
Sum of electronic and zero-point Energies=      -442.605532
Sum of electronic and thermal Energies=         -442.593391
Sum of electronic and thermal Enthalpies=       -442.592447
Sum of electronic and thermal Free Energies=    -442.644615
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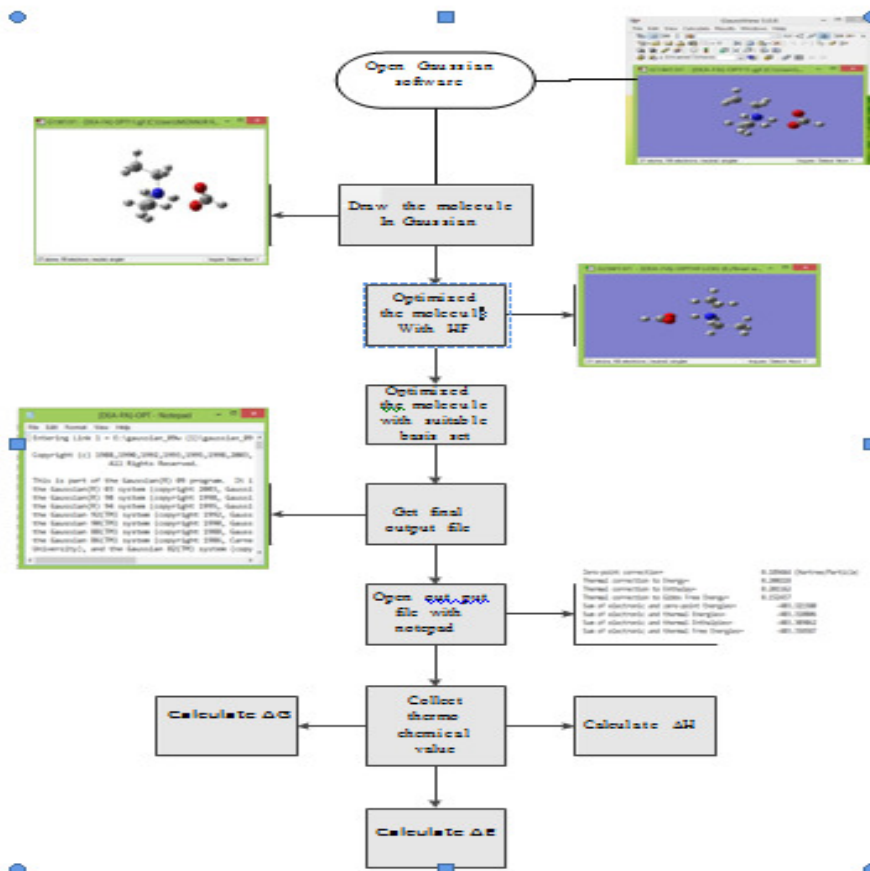
Fig. 1. Working diagram of thermodynamic result

Fig. 2. The calculated thermodynamic parameters tables were calculated as illustrate in modern *ab initio* calculation

2.3 Determination of Thermodynamic Quantities Calculation

This procedure includes the performance of quantum chemical models with regard to the calculation of the magnitudes of dipole moments. Too little experimental information is available about the sign and or direction of dipole moments or about higher moments to make comparisons of these quantities with the results of calculations of value. Models examined include Hartree-Fock (HF) models with 3-21G, 6-31G* and 6-311+G**, DFT (WB97XD) model with 3-21G, 6-31G*, DGTZVP basis sets and PM3 semi-empirical models.

```
Sum of Mulliken charges with hydrogens summed into heavy atoms =   0.00000
Electronic spatial extent (au): <R**2>=          5467.3694
Charge=          0.0000 electrons
Dipole moment (field-independent basis, Debye):
   X=          9.8381   Y=          4.0658   Z=          -0.0608 Tot=          10.6453
Quadrupole moment (field-independent basis, Debye-Ang):
   XX=          -42.4375   YY=          -89.1320   ZZ=          -89.2511
   XY=          8.8589   XZ=          -1.5874   YZ=          -0.6839
Traceless Quadrupole moment (field-independent basis, Debye-Ang):
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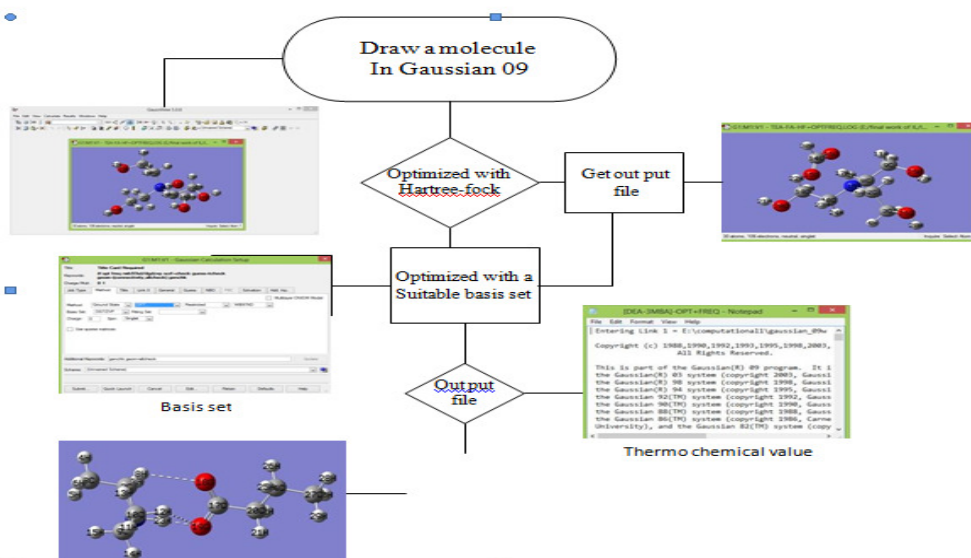
Fig. 3. Working screen shot

4

Fig. 4. Flow chart of thermodynamic quantities calculation

2.4 Frontier Molecular Orbital (FMO)

Frontier molecular orbital (FMO) has been taken from GAUSSIAN 09 by using density function theory (DFT) withWB97XD.

2.5 Molecular Orbitals and Energies in GAUSSIAN 09 Output

The Pop=Reg keyword in the route section requested data about molecular orbital is included in the output. They appear at the beginning of the population analysis section. Below is the relevant part of the output for aniline and nitrobenzene. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) may be identified by finding the point where the occupied/virtual code letter in the symmetry designation changes from O to V.

2.6 HOMO and LUMO

A qualitative indication of how a given species (atom, ion, or molecule) is polarizable can be obtained by means of the global hardness. In other words, the hardness of a species indicates the extent of its electron cloud distortion in an electric field. The global hardness (ε) and softness (σ) of a chosen molecule calculates the energy gap between the HOMO and LUMO orbitals. The mathematical expression of (h) and (s) can be written as: Energy gap $= E_{LUMO} - E_{HOMO}$
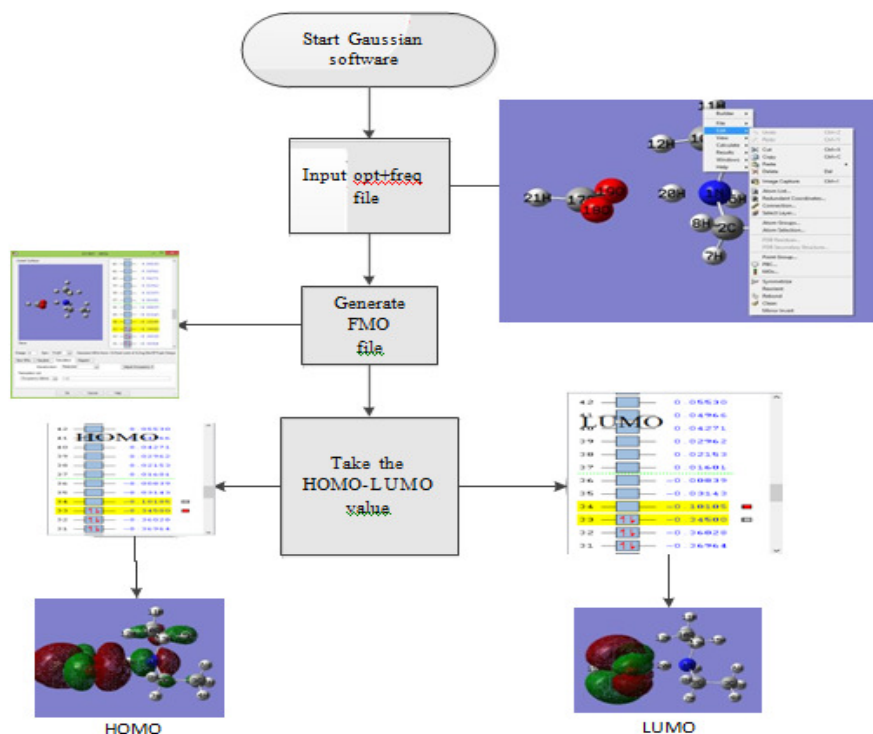
5

Fig. 5. Flow chart of calculation of HOMO-LUMO

3. RESULTS AND DISCUSSION

3.1 Optimized Structure
The following keyword input is typical for a ground state geometry optimization:
 #N B3LYP/6-31G(d) Opt Freq Test temperature=195
The level of theory in this example is the DFT method B3LYP. It is suggested over HF (Hartree Fock). The optimized structure of aniline and nitrobenze is shown in fig.7.

3.2 Bond Distance
Bond length is linked to bond order when more electrons participate in bond formation, the bond is shorter. Bond length is also inversely related to bond strength and the bond dissociation energy. All other factors being equal, a stronger bond will be shorter. The bond distance of aniline and nitrobenzene is given in table-01.

Table 2. Bond distance of aniline and nitrobenzene

Aniline			
BOND	**DISTANCE**	**BOND**	**ANGLE**
N12-H14	1.00210	H13-N12-H14	117.91902
N12-H13	1.00210	C4-N12-H13	121.03807
N12-C4	1.38637	C4-N12-H14	121.04262
C4-C5	1.40971	C3-C4-N12	120.78635
C4-C3	1.40985	C5-C4-N12	120.79980
Nitro benzene			
BOND	**DISTANCE**	**BOND**	**ANGLE**
N11-O12	1.26662	O12-N11-O13	123.62342
N11-O13	1.26662	O12-N11-C1	118.18828
N11-C1	1.46788	O13-N11-C1	118.18828
C1-C2	1.39501	N11-C1-C2	118.90105

6

C1-C6	1.39501	N11-C1-C6	118.90105

Fig. 6. working flow of HUMO-LUMO chat for optimized any molecule in Gaussian programming
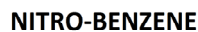

ANILINE

NITRO-BENZENE

Fig. 7. Optimized structure of aniline and nitrobenzene

3.3. HOMO and LUMO

The HOMU –LUMO grap indicates the reactivity. The higher HOMU –LUMO grap indicates the lower reactivity. Both of aniline and nitrobenzene have lower HOMU –LUMO grap such as 0.20029 and 0.1822 in HF basis set.The HOMO is the orbital of highest energy that is still occupied, so energetically it is the easiest to remove electrons from this orbital. This could be simply donating electron density to form a bond (act as a Lewis base) or it could be oxidation. The LUMO is the lowest lying orbital that is empty, so energetically it is the easiest to add more electrons into this orbital. It isn't always the HOMO and/or LUMO involved in chemical reactivity. Symmetry plays a role, too. If the HOMO or LUMO isn't of the correct symmetry, it might be the HOMO-1 or the LUMO+1 that is involved in the reaction.

Table 2. HOMO, LUMO and HOMO-LUMO GAP

COMP.	Aniline (M1)	Nitrobenzene (M2)
LUMO+2	0.03753	-0.01892
LUMO+1	0.02103	-0.04068
LUMO	0.00237	-0.11517
HOMO	-0.19792	-0.29253
HOMO-1	-0.24847	-0.29741
HOMO-2	-0.30812	-0.30130
GAP (HF)	0.20029	0.1822
GAP(ev)	5.4501711	4.957917

3.4 Electrostatic Potential

Electrostatic potential maps are exceedingly useful and valuable three dimensional diagrams of molecules. They facilitate us to visualize the charge distributions of molecules and charge related properties of molecules. They also buttress us to visualize the size and shape of molecules. An cutting-edge computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei and electrons, at a particular position. To precisely evaluate and calculate the charge dissemination of a molecule, a very enormous quantity of electrostatic potential energy values must be calculated. To make and formulate the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowermost electrostatic potential energy value and blue as the uppermost, is employed to carry the changing intensities of the electrostatic probable energy values.

3.5 Thermo-Chemistry of Aniline and Nitrobenzene

Thermo-chemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings. Using Gaussian 09, the thermo chemical properties of aniline and nitrobenzene are included in table.3.

3.6 Calculation of Steric Energy

A molecule can hold different kinds of energy such as bond and thermal energy. Molecular mechanics analyzes the steric energy of a molecule. Energy is lessened in nature and the conformation of a molecule that is favored to the bottom energy conformation. Knowledge of the conformation of a molecule is vital because the structure of a molecule often has a great consequence on its reactivity. Molecular mechanics undertakes the steric energy of a molecule to arise from a few, specific interactions within a molecule. These interactions include the extending or compacting of bonds beyond their equilibrium lengths and angles, torsional effects of twisting about single bonds, the Van der Waals attractions or repulsions of atoms that come close together, and the electrostatic interactions between partial charges in a molecule due to polar bonds.

The total steric energy of a molecule can be written as a sum of the energies of the interactions:

$$E_{steric\ energy} = E_{str} + E_{bend} + E_{str-bend} + E_{oop} + E_{tor} + E_{VdW} + E_{qq}$$

3.7 Partial Charge

A partial charge is a non-integer charge value when measured in elementary charge units. Partial charge is more commonly called net atomic charge. It is represented by the Greek lowercase letter δ, namely δ– or δ+. Partial charges are created due to the asymmetric distribution of electrons in chemical bonds. The greater partial charge indicates the lower covalency and greater ionic character in covalent compound.

3.8 Natural Bond Order (NBO)

In NBO analysis, large value shows the intensive interaction between electron donor and electron acceptors and greater the extent of conjugation of the whole system, the possible intensive interactions are given in the figure. The second

order perturbation theory analysis of Fock matrix in NBO basis shows strong intra- molecular hyper conjugative interactions of σ electrons. The nitrobenzene shows the higher positive charge of N11 atom more + 0.44 where aniline can show the positive charge in H13 and H14 atom near to +0.4. The N12 atom of nitrobenzene shows the highest electronegative charge about -0.8.
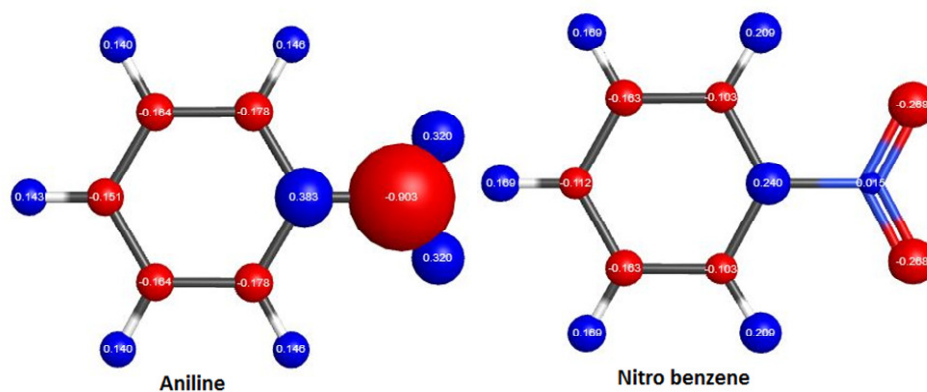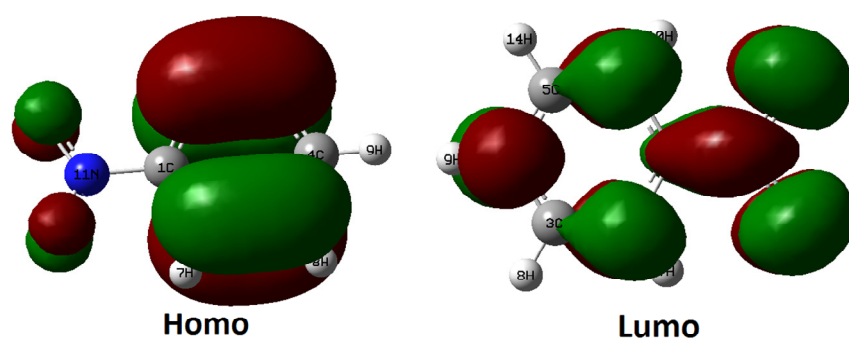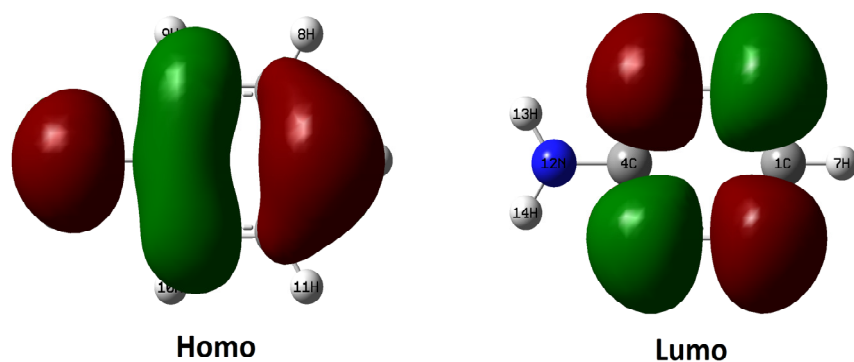

Fig. 8. HOMO and LUMO of aniline

Fig. 9. HOMO and LUMO of nitrobenzene

Fig. 10. Electrostatic potential

Table 3. Thermo-chemical properties of aniline and nitrobenzne

Compounds	Internal energy	Gibbs free energy	Enthalpy(H)	Entropy	Dipole moment
Aniline (M1)	-287.4794(H)	-287.514566(H)	-287.478(H)	75.960 cal/mol-K	1.9527 Debye
Nitrobenzene(M2)	-436.6204(H)	-436.659105(H)	-436.619(H)	83.304 cal/mol-K	5.1241Debye

Table 4. Data of total steric energy of aniline and nitrobenzene

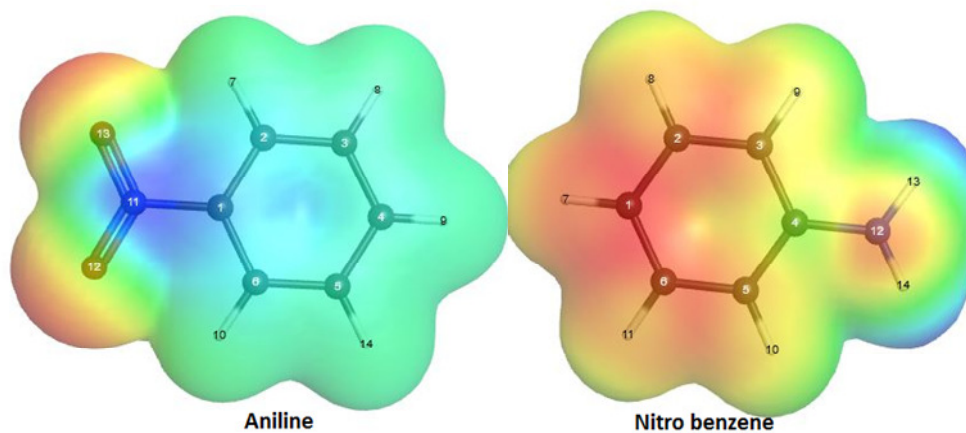| Compound	Bond stretch	Angle bend	Stretch bend	Optimized bend	Torsion	Vander Waals	Electrostatic interaction	Total steric energy in(kcal/mol)
M1	55.8670	4.7278	3.7068	0.000	0.0000	1.3224	0.0000	65.6240
M2	66.388	3.686	-1.691	0.0000	0.0000	2.5789	0.0000	70.96

Fig. 11. Partial charge particle picture

Table 5. Asymmetry and Symmetry streaching of aniline and nitrobenzene

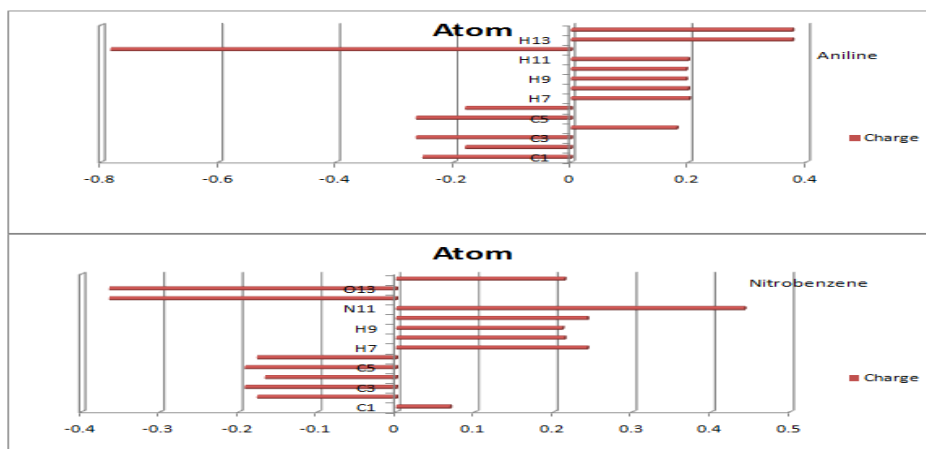| Theoretical without scaling(γ/cm^{-1})	Intensity (γ/cm^{-1})	Assignment
M1		
3754.7448	14.8295	N-H asymmetry
3625.0312	37.6120	N-H symmetry
3196.3809	22.7433	C-H symmetry
3174.8139	64.8693	C-H asymmetry
M2		
1358.1606	18.3293	N-O asymmetry
1371.2826	0.2832	N-O symmetry
3232.6691	0.0057	C-H symmetry
3231.3409	5.0068	C-H asymmetry

Fig. 12. NBO of aniline and nitrobenzene

4. CONCLUSION

Using the DFT and HF basis set, the geometry of aniline and nitrobenzene on compound incorporating transition metals and other molecules give good agreement about all atoms presence in molecule. The DFT with (WB97XD) and HF models provide good accounts of thermophysical properties study and a data base in view of computational overview. The EA, HOMO-LUMO and IP information show the scope the reactivity and degradation study of aniline and nitrobenzene in very short time without consuming money and chemicals. Thermo-chemical calculations of aniline and nitrobenzene molecules involve net bond making or breaking and absolute activation energy calculations. From the study of computational overview of aniline and nitrobenzene, it is clear that the lower HOMU –LUMO grap such as 0.20029 and 0.1822 in HF basis set indicating the lower reactivity. The total steric energy of aniline and nitrobenzene is 65.624 and 70.96 respectively. From the analysis of NBO, the nitrogen atom of nitrobenzene can show greater electro-positivity than aniline. The oxygen atom of nitrobenzene can show about -0.36 electro-negativity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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