Original Research Article

A theoretical study of aniline and nitrobenzene by computational overview

Abstract: Computational chemistry is used as computers programming to solve real problems in chemical, pharmaceutical, biotechnology 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 9.8, nitrobenzene and aniline were tested in two basis set such as Mm+ and PM3 to make the profile on the physical properties, such as, total energy, binding energy, hydration energy, dipole moment, heat of formation and energies for HOMO and LUMO. These physical properties are the theoretical agreement of physical properties to safe the time and chemical in laboratory.

Keywords: Gaussian 9.8, HOMU, LUMO, MP2 and MP3

1.0 INTRODUCTION:

Nitrobenzene is a water insoluble pale yellow oil or greenish-yellow crystals organic compound. Nitrobenzene is used in the manufacture of compounds including benzidine and quinoline, soap, analgestic paracelamol, in the production of isocyanates, pesticides and pharmaceuticals drug. Nitrobenzene is used primarily 95% to produce aniline, an intermediate in the production of dyestuffs and other products[1]. Although occasionally used as a flavoring or perfume additive, nitrobenzene is highly toxic in large quantities[2]. In the laboratory, it is occasionally used as a solvent, especially for electrophilic reagents. Nitrobenzene has been detected in air and appears to volatilize from water and soil. Environmental exposure appears to be primarily through inhalation of ambient air or through dermal exposure to products containing the chemical. Nitrobenzene was nominated by National Institute of Environmental Health Sciences(NIEHS) for possible listing in the Report on Carcinogens based on the conclusions of an the International Agency for Research on Cancer(IARC) working group that nitrobenzene is possibly carcinogenic to humans [3].

Aniline first obtained in1826 by the destructive distillation of indigo, an organic base used to make dyes, anilides, diazonium salt, drugs, explosives, plastics, antioxidants, activators, accelerators,and photographic and rubber chemicals. It is also used in petroleum, plastics, agricultural, explosives, and chemical industries,Various fungacides and herbicides for the agricultural industry, Pharmaceutical, organic chemical, and other products. Aniline is prepared commercially by the catalytic hydrogenation of nitrobenzene or by the action of ammonia on chlorobenzene. Using various oxidizing agents, aniline is converted into quinone, azobenzene, nitrosobenzene, p-aminophenol,and the phenazine dye aniline black.Photochemistry, a sub-discipline of chemistry, is the study of the interactions between atoms, small molecules, and light (or electromagnetic radiation).

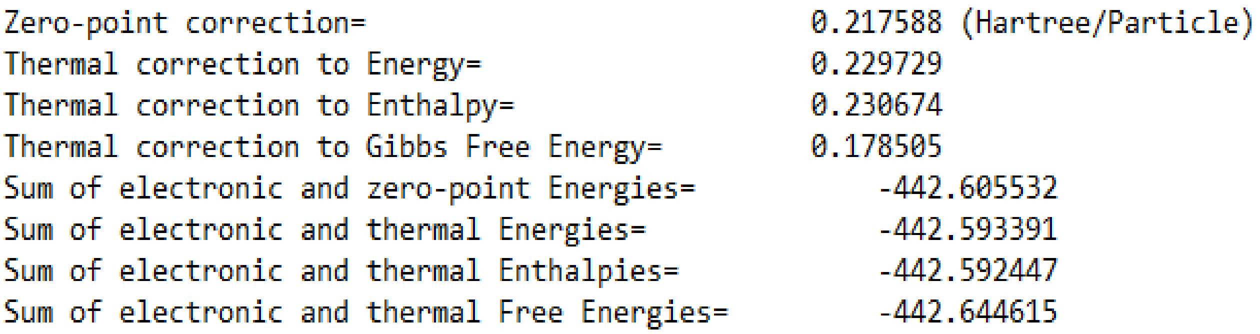
Waste water from manufacturing or chemical processes in industries contributes to water pollution containing specific and readily identifiable chemical compounds. During the last fifty years, the number of industries in Bangladesh has grown rapidly. But water pollution is concentrated within a few sub sectors, mainly in the form of toxic wastes and organic pollutants. Out of this a large portion can be traced to the processing of industrial chemicals and to the food products industry. In fact, a number of large- and medium-sized industries in the region covered by the Buriganga[4-5]. Action Plan does not have adequate effluent treatment facilities. Most of these defaulting industries are sugar mills, textile industries, distilleries, leather processing industries, and thermal power stations, chemical industries pharmaceutical industries due to use the aniline and nitrobenzene. Most major industries have treatment facilities for industrial effluents. But this is not the case with small-scale industries, which cannot afford enormous investments in pollution control equipment as their profit margin is very slender. [6]. It is necessary to find an effective method of destroying the nitrobenzene and aniline in order to remove color from effluents[7-8]. A number of physical and chemical techniques has been reported for the removal of them [9-10] such as adsorption on carbon [11], biodegradation[12], ozonation[10] and advanced oxidation processes (AOPs) [13-14] and catalytic reactions[15].All of these method consume the time and chemicals so that to make a safe of time and chemicals, computational chemistry is only an alternative way.

Molecular mechanics uses the laws of classical physics to explain and interpret the structure and properties of molecules. Molecular mechanics methods are available in many computer programs, including MM3, HyperChem, GAUSSIAN, Quanta, Sybyl and Alchemy [16]. There are many different molecular mechanics methods. Each one is characterized by its particular force field. It is widely used 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 orbitals, 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 [16-17]. Computational calculations provide a manageable 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 be energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied reliably computed using first-principles-based calculations [18]. 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 batteries and super capacitors. 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.

2.0 METHADOLOGY

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 [19]. 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 orbitals 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:-WB97XD/DGTZVP opt freq.This process include the performance of quantum chemical models with regard to the calculation of vibrational frequencies, and describes the evaluation of thermodynamic quantities resulting from vibrational frequencies. In addition to their role in characterizing structures on a potential energy surface, vibrational frequencies, along with molecular geometry, are the essential ingredients for calculation of thermodynamic quantities. These follow from straightforward application of statistical mechanics. Entropy is certainly the most important of these, primarily for its contribution to the free energy. Calculated vibrational frequencies may be employed to yield a variety of thermodynamic quantities. This work was done in computer and software laboratory in European University of Bangladesh, Dhaka, Bangladesh.

2.1 Thermodynamics Quantities in GAUSSIAN 09 Output



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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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Figure 1: Working diagram of thermodynamic result

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. Computing Thermo-chemical Parameters of Reactions

Thermo-chemical Parameters were calculated using the following general formula.

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

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

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

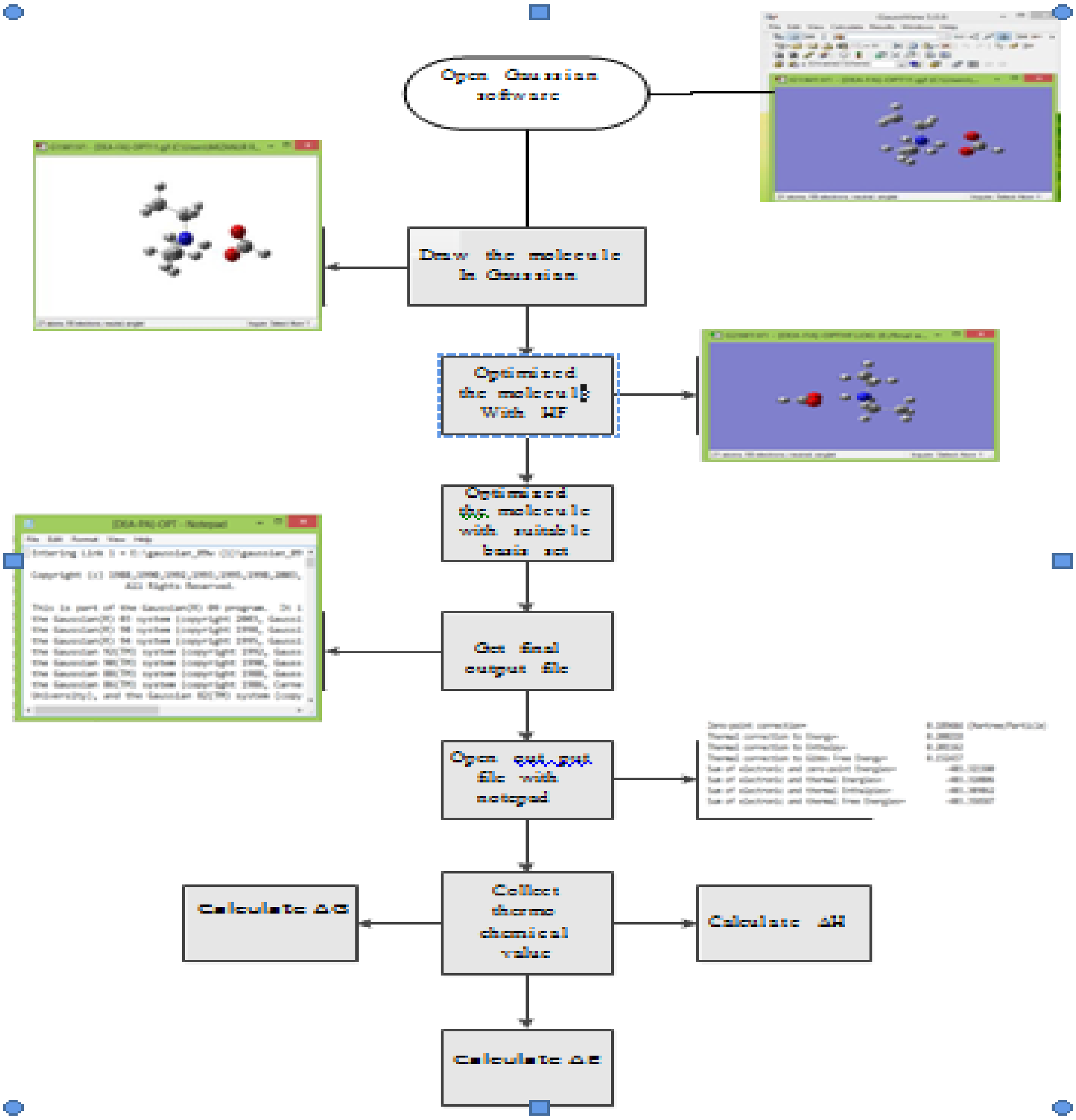


Figure 1: The calculated thermodynamic parameters tables presented in chapter four were calculated as illustrate above

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 models with 3-21G, 6-31G* and 6-311+G** and DFT (WB97XD) model with 3-21G, 6-31G*, DGTZVP basis sets and AM1 and PM3 semi-empirical models.

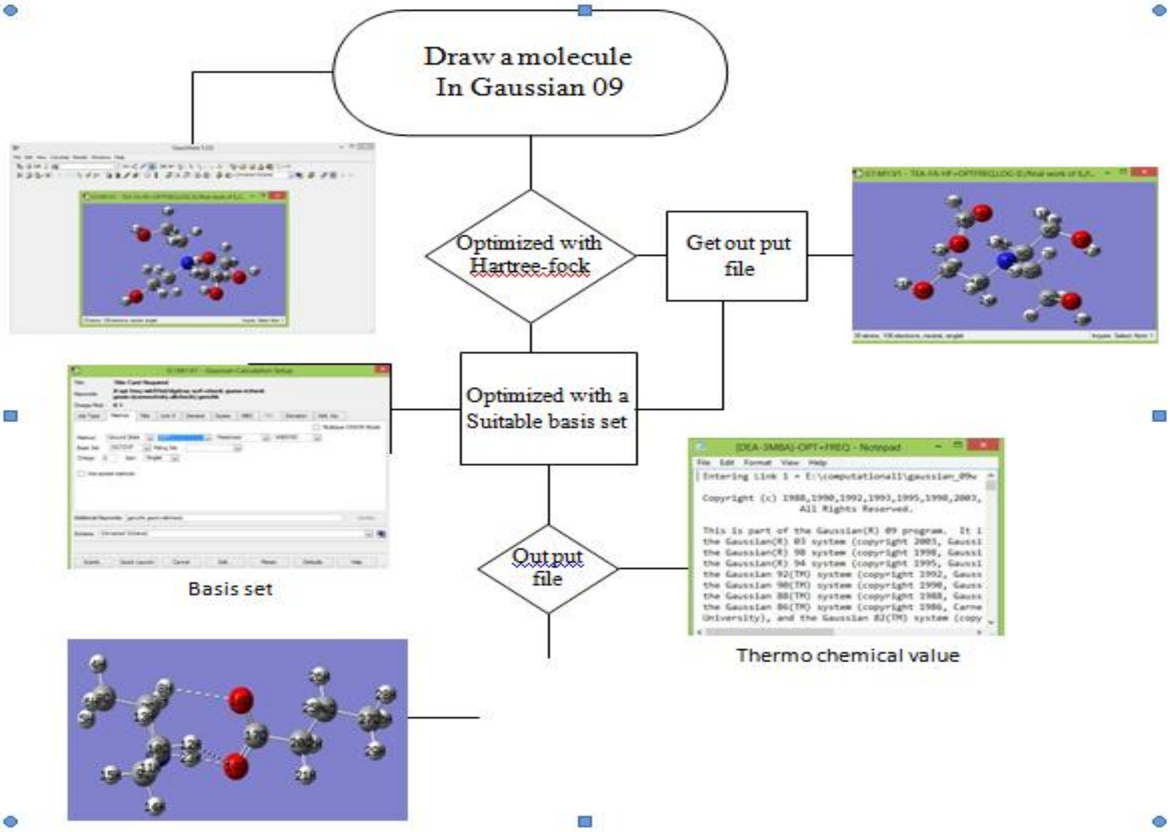
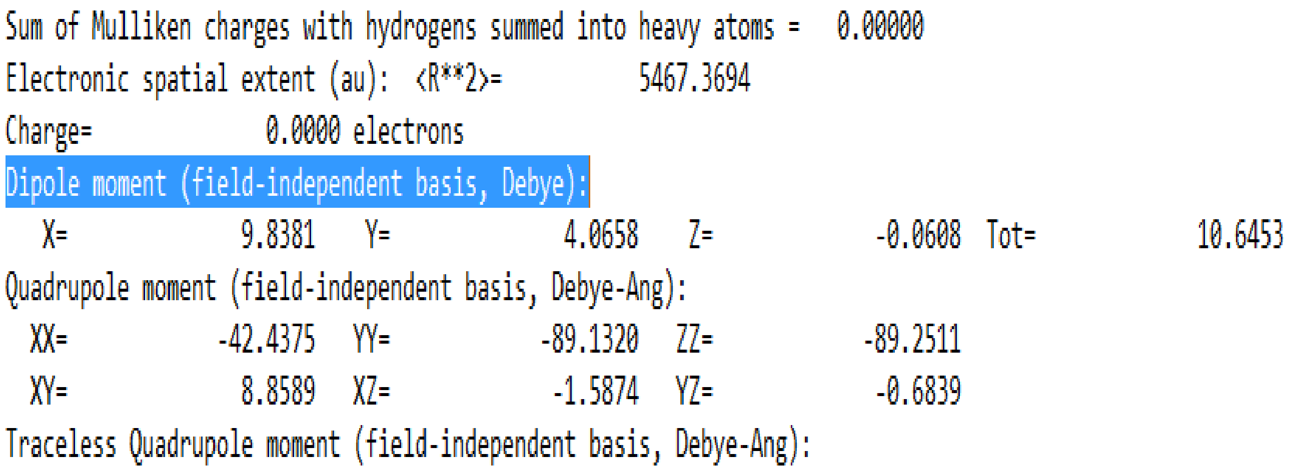


Figure 3:Flow chart of thermodynamic quantities calculatio



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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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Figure 2: working screen shot.

2.4 Frontier Molecular Orbital(FMO)

This method assesses the performance of quantum chemical models with regard to the calculation of the magnitudes of HOMO-LUMO gaps. Too little experimental information is available about the sign and or direction of HOMO-LUMO gaps or about higher moments to make comparisons of these quantities with the results of calculations of value. Frontier molecular has been taken from GAUSSIAN 09 by using density function theory (DFT) and WB97XD.

2.5 Molecular orbitals and energies in GAUSSIAN 09 output

The Pop=Reg keyword in the route section requested data about molecular orbitals be included in the output. They appear at the beginning of the population analysis section. Below is the relevant part of the output for ammonium based ionic liquid. 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 with Global Hardness and softness

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 $=E_{LUMO}-E_{HOMO}$

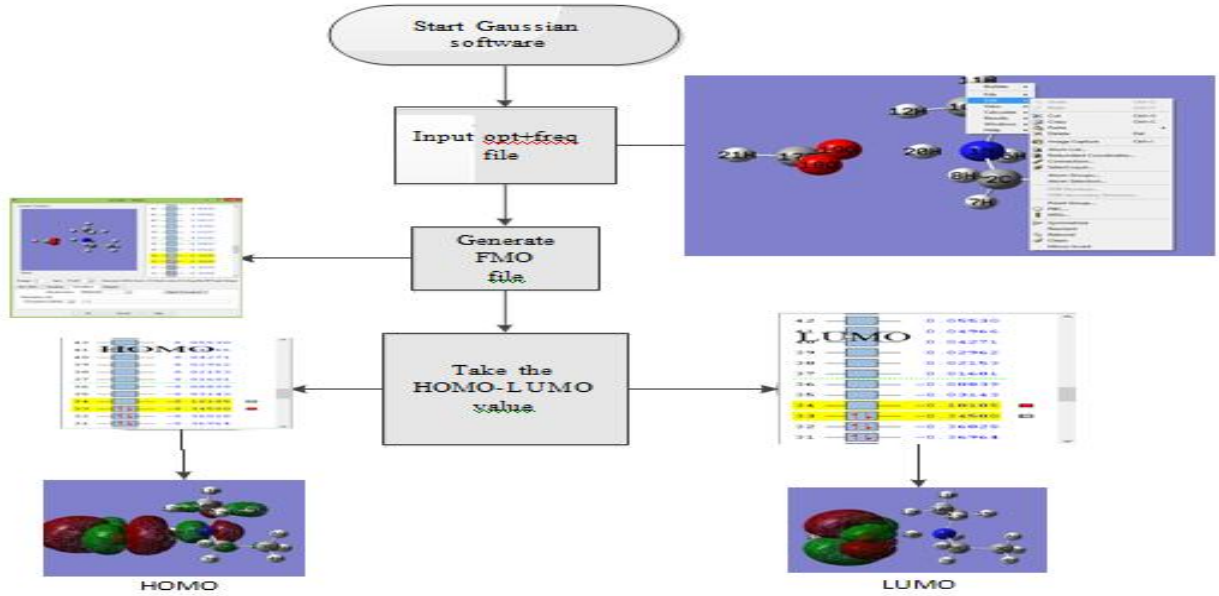


Figure 4: Flow chart of calculation of HOMO-LUMO

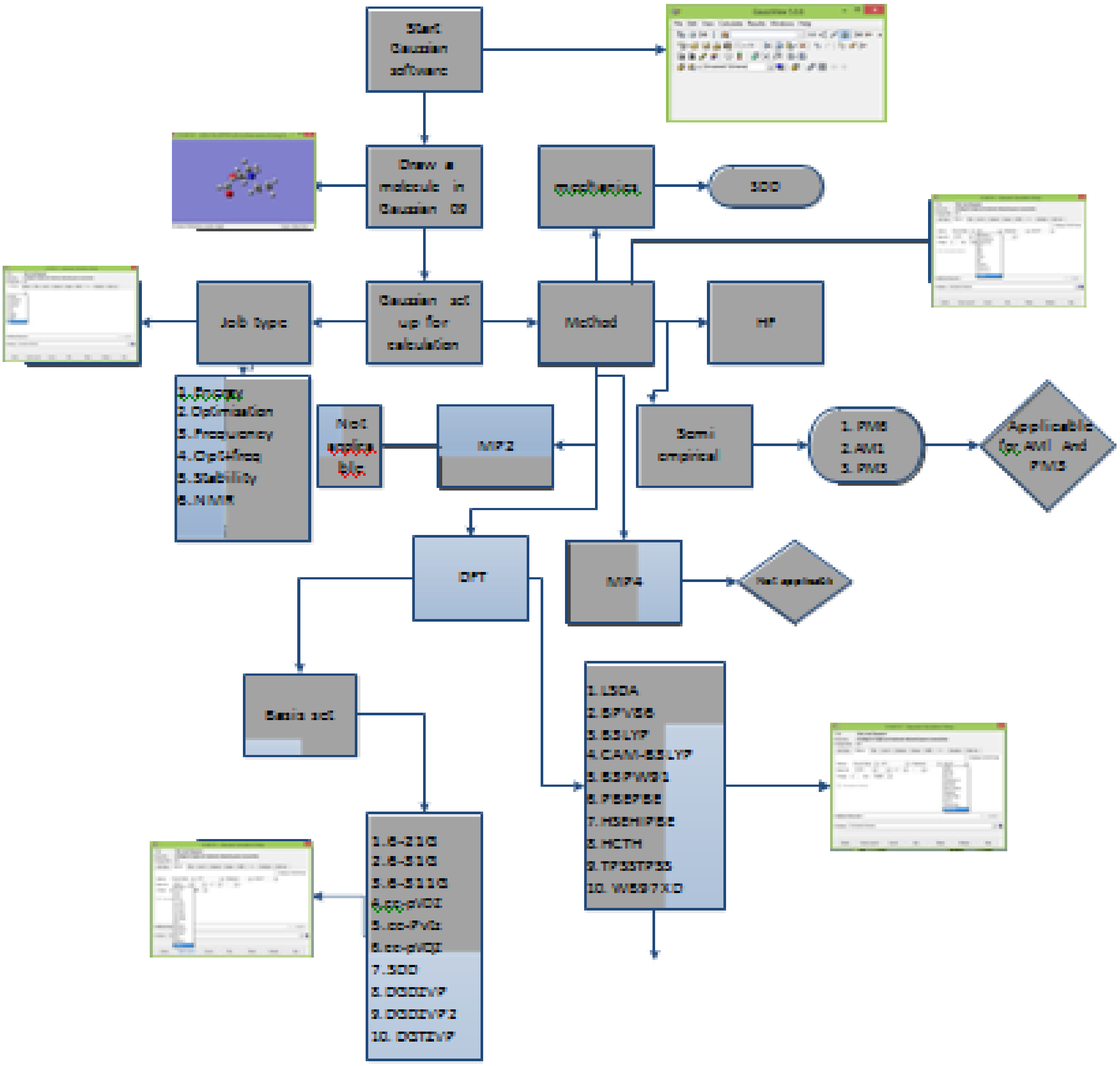
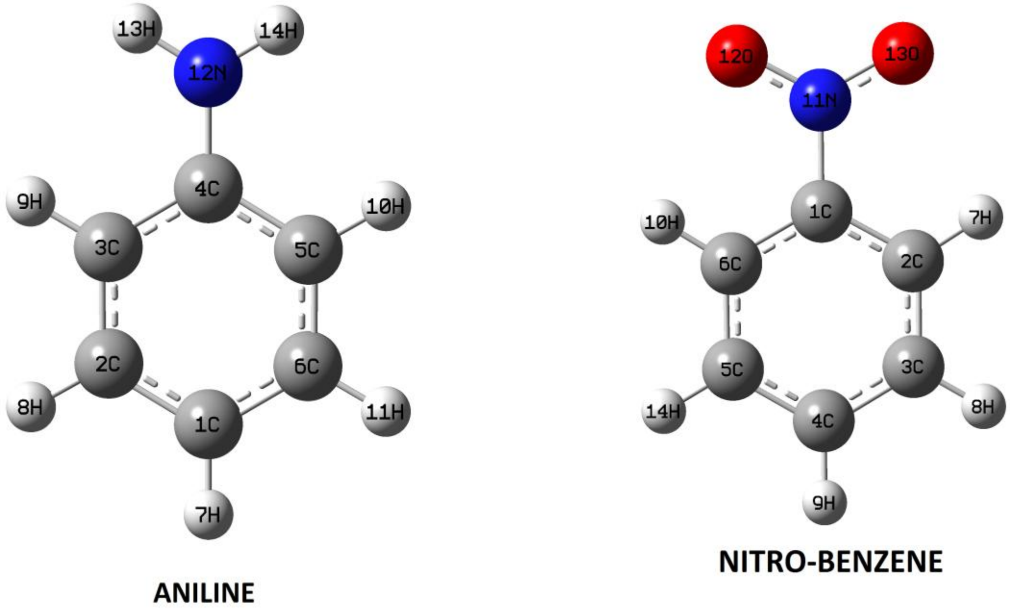


Figure 5: working flow chat

3.0 RESULT AND DISCUSSION

3.1 Optimized Structure



ANILINE

NITRO-BENZENE

Figure 6: Optimized structure

3.2: Bond distance:

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
C1-C6	1.39501	N11-C1-C6	118.90105

3.4: 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.

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

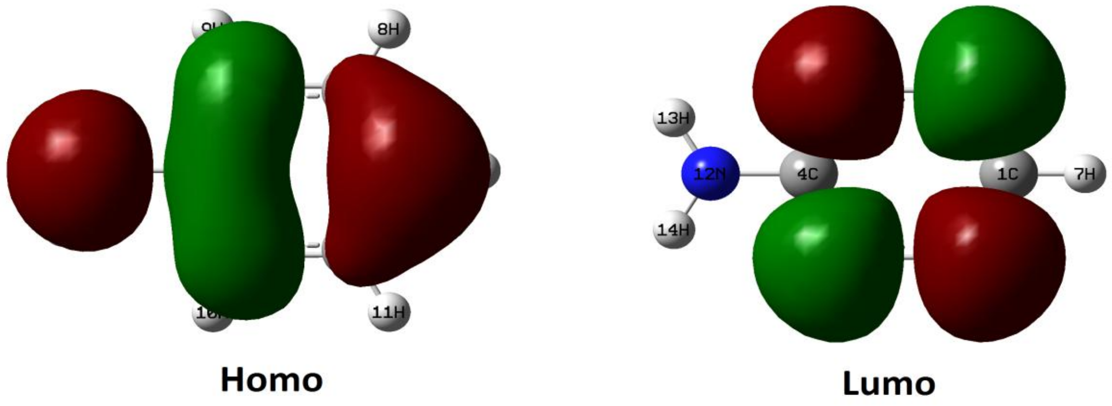


Figure 7: HOMO LUMO of Aniline

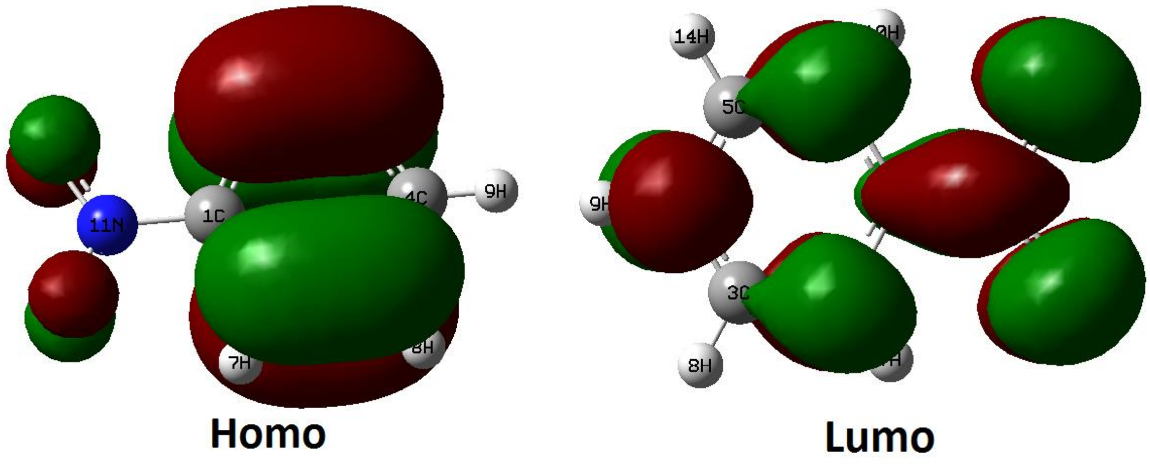
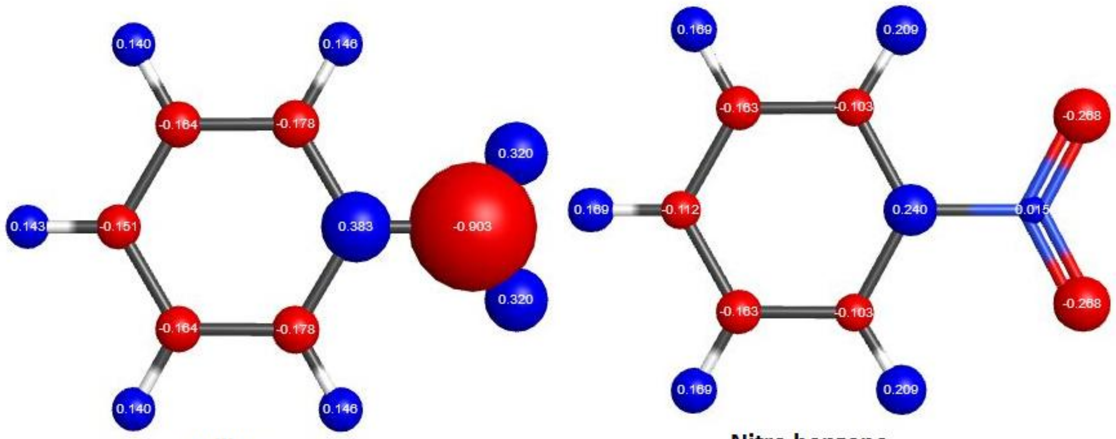


Figure 8: HOMO LUMO of nitrobenzene

3.5 Electrostatic potential

Electrostatic potential maps are very useful three dimensional diagrams of molecules. They enable us to visualize the charge distributions of molecules and charge related properties of molecules. They also allow us to visualize the size and shape of molecules. An advanced 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 accurately analyze the charge distribution of a molecule, a very large quantity of electrostatic potential energy values must be calculated. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values.



Aniline **Nitro benzene**

Figure 9: Electrostatic potential

3.6:Thermo-chemistry

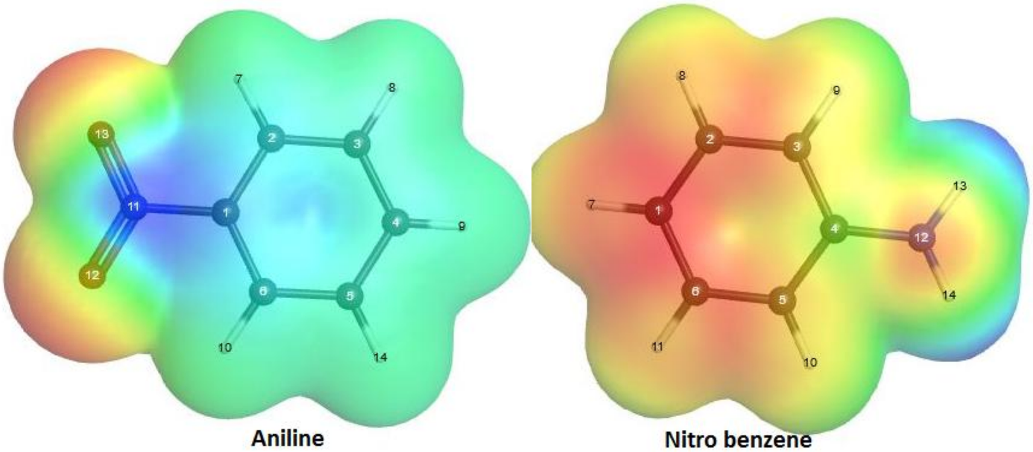
compounds	Enternal energy	Gibbs free energy	Enthalpy(H)	Entropy	Dipole moment
Aniline (M1)	-287.4794(H)	-287.514566(H)	-287.478(H)	75.960 cal/mol-K	1.9527 Debye
Nitrobenzene(M2)	-436.6204(H)	-436.659105(H)	-436.619(H)	83.304 cal/mol-K	5.1241Debye

Compound	Bond stretch	Angle bend	Stretch bend	Op bend	Torsion	Vander Waals	Electrostatic	Total
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

Experimental(γ/cm-1)	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

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.



Aniline Nitro benzene

Figure 10: Partial charge particle picture

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. In nitrobenzene show the higher positive charge of C1 and N11 atom where aniline can show the positive charge in C4 atom.

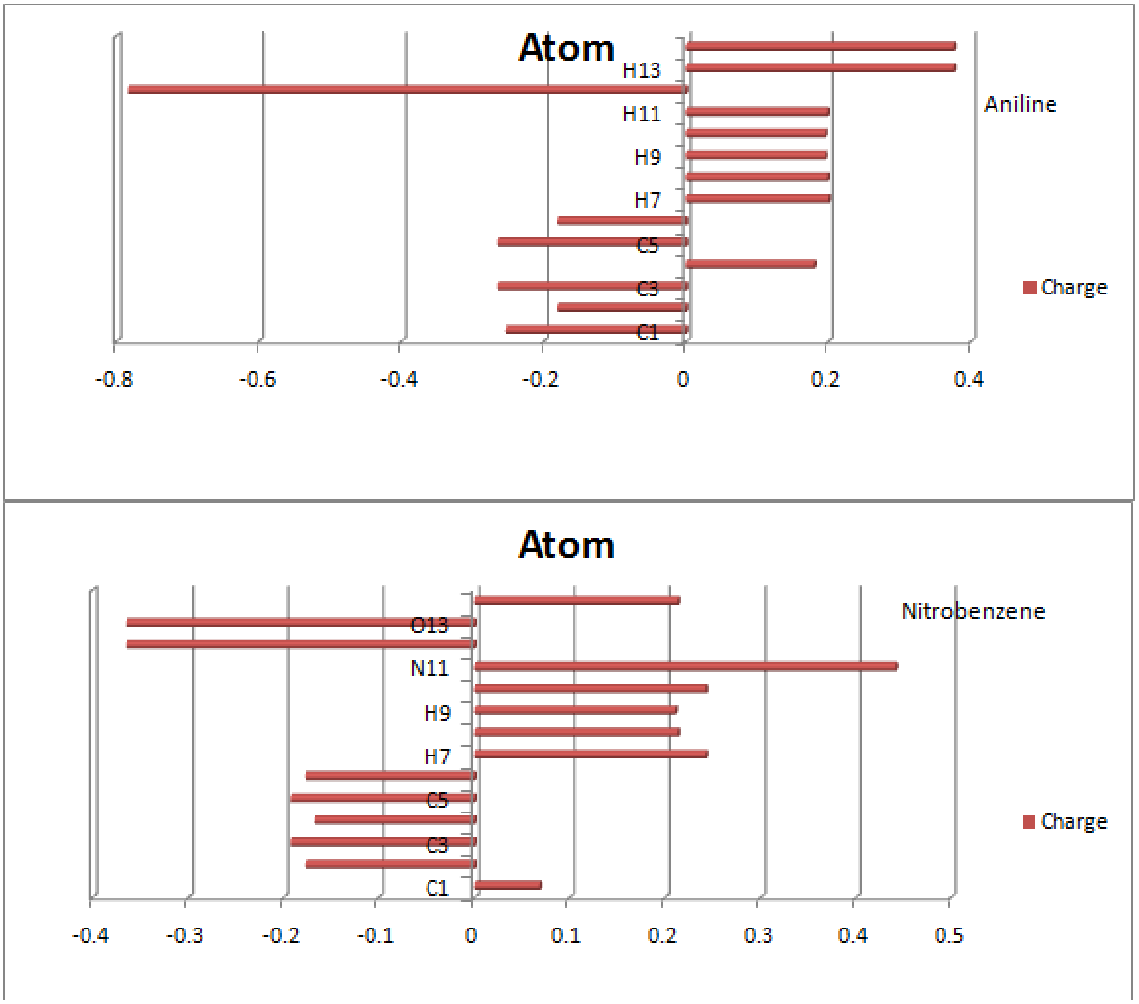


Figure 11: NBO of aniline and nitrobenzene

4.0 Conclusion

Using the Hartree-Fock models, the geometry calculations on compounds incorporating transition metals give good agreement, but the PM2 and PM3 semi-empirical model and density functional, thermo physical properties, models provide good accounts. 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. The cost of MP2 and MP3 models may be prohibitive. Thermo-chemical calculations in particular those organic and inorganic molecules, which involve net bond making or breaking, and absolute activation energy calculations.

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