Computational Studies On Energy Minimization Of Some Aryl Ether Based Molecules

A

Thesis submitted

In partial fulfillment of requirement for the

Degree of Master of Science in Chemistry

Submitted by

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Supervisors

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I am thankful to Miss. Karamjeet Kaur, Raman deep Kaur, and Komel Matharu, Research Scholars for their guidance and support to me.

Dated: 15th July, 2011.

Amrita Preet Joshi

Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled "**Computational Studies On Energy Minimization Of Some Aryl Ether Based Molecules**", in the partial fulfillment of the requirements for the award of the degree of Masters of Science (Chemistry), School of Chemistry and Biochemistry (SCBC), Thapar University, Patiala, is my own work during the period of January to June 2011, under the supervision of Prof. Susheel Mittal and Dr.Manmohan Chhibber. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala
Date: 15th July,2011.

Amrita Preet Joshi

This is to certify that the above statement made by candidate is correct and true to the best of our knowledge.

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Certificate

This is to certify that the project entitled "**Computational Studies On Energy Minimization Of Some Aryl Ethers Based Molecules**", being submitted by Miss. Amrita Preet Joshi in partial fulfillment of the requirement for the award of degree of Masters in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under the supervision of Prof. Susheel Mittal and Dr. Manmohan Chhibber and that no part of this project has been submitted for the award of any other degree by me.

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Certificate

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INTRODUCTION

Computational chemistry is a branch of chemistry that uses principles of computer science for solving chemical problems. It uses the results of theoretical chemistry to incorporate into efficient computer programs to calculate the structures and properties of molecules and solids. Computational chemistry results normally complement the information obtained by chemical experiments can predict unobserved chemical phenomena. Computational chemistry determine chemical structure and reactions numerically based in full or in part on fundamental laws of physics. It allows to study chemical phenomenon by running calculations on computer rather than by examining reaction and compounds experimentally. Some methods can be used to study not only stable molecules but also short lived, unstable intermediate and transition states. Computational chemistry provides information about molecules and reaction which is impossible to obtain through observation. Therefore, it is an independent research area and to experimental studies. Computational chemistry is the application of computer based models to the stimulation of chemical processes and the computation of chemical properties. It is a valuable tool for experimental chemist to bypass tedious time consuming, costly and sometimes dangerous experimental procedure.

It is now generally possible to obtaine molecular structure, reaction enthalpies, dipole moments, infrared intensities, vibrational frequencies, reaction enthalpies (with $\pm$1% accuracy) it is possible to know through geometry optimization reaction free energies and reaction rates without doing any laboratory experiments.

The process of finding the arrangement of nuclei for which the potential energy is a minimum is known as geometry optimization. Note that it takes a lot of energy to get atoms very close to each other. There is a distance with minimum energy R_o (equilibrium bond length) and it takes energy to pull the atoms apart farther than R_o. The energy approaches zero as the intermolecular distance gets very large. The lowest energy is at R_o where the gradient of the potential energy curve is zero. The geometry optimization procedure involves the calculation of gradient of the potential energy with respect to each of the nuclear coordinates.

The computing energy of a particular molecular structure and properties related to the energy is predicted by the computation methods. There are mainly two methods in computational chemistry : Molecular Mechanics Method and Electronic Method.

Molecular Mechanics Method: Large molecular systems can be simulated by Molecular Mechanics Methods and can avoid doing quantum mechanical calculations. The database of compounds used for parameterization resulting in set of parameters and functions is called the force field and is used for molecular mechanics calculations. The molecular mechanics simulation is done by using the law of classical physics to predict the structure and properties of the molecule. There are many different molecular mechanics methods each one is characterized by its particular force field. Molecular mechanics methods can be used to model very large systems such as DNA or proteins. Although DNA or protein molecules are too large for semi-empirical calculations, but they are manageable in molecular mechanics because of the approximation calculations. Molecular mechanics calculations do not explicitly treat electrons in a molecular system instead of that they perform computation based upon the interaction among the nuclei. Electronic effects are implicitly involved through parameterization. This approximation makes molecular mechanics computations quite inexpensive computationally and allows them to be used for very large systems containing many thousands of atoms.

Molecular dynamics: Molecular dynamics uses Newton's laws of motion to examine the time-dependent behavior of systems, including vibrations or brownian motion, using a classical mechanical description. Molecular dynamics combined with density functional theory. Molecular dynamics calculations are used to simulate the time-dependent behaviour known as motion, dynamics, vibrations, and trajectory of molecules. Molecular dynamics makes it possible to study the dynamic behaviour of a collection of thousands of separate molecules for example diffusion of a solute molecule through a liquid. Molecular dynamics can be used for calculations of large biomolecules in solution. This study involve results of simulations on spherands, crown ethers and hemes by use of computation studies molecular mechanics and molecular dynamics. In the spherand calculations, a combined use of distance geometry, computer graphics and molecular mechanics led to the prediction of a new spherand isomer with high Li^+ and Na^+ affinity[10]. crowns, simulated the relative cation affinities of dibenzo 18-Crown-6 and dibenzo 30-Crown-10, using molecular dynamics and free energy perturbation theory and found good agreement with the relative experimental free energies of ion binding. For the hemes, the relative free energy of association of CO and O_2 in different porphyrin using molecular dynamics.

Electronic Method: Electronic methods use the laws of quantum mechanics than classical physics as the basis for their computations. Quantum mechanics states that energy and other relative properties of a molecule may be obtained by solving schrodinger equation. For the any

smallest system however exact solution to the schrodinger equation are not computational practical. Electronic structure methods are characterized by their various mathematical approximations to its solution. The two major classes of electronic structure methods are.

Ab intio methods unlike Ab initio methods and semiempirical methods use either molecular mechanics or semiempirical methods use no experimental parameters in their computations. Instead their computations are based solely on the laws of quantum mechanics. The programs used in computational chemistry are based on many different quantum-chemical methods that solve the molecular schrodinger equation associated with the molecular Hamiltonian. Methods that do not include any empirical or semi-empirical parameters in their equations being derived directly from theoretical principles, with no inclusion of experimental data are called Ab initio method. This does not mean that the solution is an exact one that have are all approximate quantum mechanical calculations. The simplest type of ab initio electronic structure calculation is the Hartree–Fock (HF) method an extension of molecular orbital theory, in which the correlated electron–electron repulsion is not specifically taken into account, only its average effect is included in the calculation. As the basis set size is increased, the energy and wave function tend towards a limit called the Hartree–Fock limit. Many types of calculations known as post-Hartree–Fock methods begin with a Hartree–Fock calculation and subsequently correct for electron–electron repulsion, referred to as electronic correlation. As these methods are pushed to the limit, they approach the exact solution of the non-relativistic schrodinger equation. In order to obtain exact agreement with experiment, it is necessary to include relativistic and spin orbit terms, both of which are only really important for heavy atoms. In all of these approaches, in addition to the choice of method, it is necessary to choose a basis set. This is a set of functions, usually centered on the different atoms in the molecule, which are used to expand the molecular orbitals with the LCAO theory. Ab initio methods need to define a level of theory and a basis set.

The Hartree–Fock wave function is a single configuration or determinant. In some cases, particularly for bond breaking processes, this is quite inadequate, and several configurations need to be used. The coefficients of the configurations and the coefficients of the basis functions are optimized together. The total molecular energy can be evaluated as a function of the molecular geometry or potential energy surface. The stationary points of the surface lead to predictions of different isomers and the transition structures for conversion between isomers, but these can be determined without a full knowledge of the complete surface.

Semi-empirical methods: Semi-empirical methods are based on the Hartree Fock theory, but make many approximations and some parameters from empirical data. They are very important in computational chemistry for treating large molecules where the full Hartree Fock method without the approximations is too expensive.

The use of empirical parameters appears to allow some inclusion of correlation effects into the methods.

They are much faster than ab initio methods because they involve a series of approximations, restrictions and incorporation of experimental data. One of the largest simplifications is that empirical data is used for core electrons and only the valence electrons are considered explicitly. Different semi-empirical methods have been optimized for different purposes. There are many methods were designed to reproduce heat of formation and structure of a large number of organic molecules. Semi-empirical methods are specifically optimized for spectroscopy studies. ZINDO is quite good at prediction of electronic transitions in the uv-vis spectral region. Semi-empirical methods are often very good for determining structures and for calculating relative energies for molecules that are similar to experimently studied molecules.

Density functional methods: is an approximate Hamiltonian and an approximate for the total electron density. DFT methods can be very accurate for little computational cost. Some methods combine the density functional exchange functional with the Hartrees Fock exchange term and are known as hybrid functional methods.

There is need to study molecular properties of a molecule than electronic properties experimental point of view. Molecular Mechanic methods are used to study structure and properties of molecules. There are different softwares like AMBER, Cache and Gaussian etc. which are being used for the theoretical calculations.

CAChe can calculate the molecular properties like heat of formation, dipole moment, HOMO and LUMO energy, ionization potential, polarizability, λmax, UV-visible, IR spectra, free energy, transition states and activation energy, nucleophilicity and electrophilicity, bond lengths, non-bonded atom distances, bond angles and dihedral angles, bond orders and bond strain, volume and surface area, dynamic reaction coordinates.

CAChe calculate molecule size limits over 1,000 atoms.

Molecular Dynamics, which is based on the Molecular Mechanics: over 1,000 atoms and ZINDO: up to 200 atoms or up to 700 basis functions, which are smaller. The molecules which can be studied in Cache are up to Lawrencium (atomic number 103).

ZINDO has separate parameterization sets for geometry optimizations/energy calculations and for UV-visible spectral calculations.ZINDO UV-visible spectral calculations: H, Li, B, C, N, O, F, P, S, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn are possible.

Gaussian: Gaussian is a theorical calculations should be uniformly applicable to molecular systems of any size and type up to a maximum size determined only by the practical availability of computer resources. Gaussian technique provide a powerful support for experimental structural studies. Therefore molecular geometry, vibrational and some molecular properties have been studied by ab initio and DFT method most widely used program in the computation chemistry research community for performing quantum mechanics calculation on molecules. The result of many studies have indicated that DFT is powerful method for predicting the geometry and harmonic vibration of organic compounds.

Literature Review

Literature includes different software are being used for the calculations. These methods viz. Amber , Cache and most recent Gaussian. The Gaussian involves various levels viz. ground states, excited states, vibration and steady states of the molecule.

The aminonitroethane molecules as 1-amino-2-nitroethane and 1,1-diamino-2,2-dinitroethane molecules different comformational structures due to free rotation of three C-C bond. Pietsch et.al [1] performed HF/6-31(+)G*(d,p) and selected MPx (x = 2-4) calculations on these amino and nitro substituted molecules. They found optimized structures of 1-amino-2-nitroethane having amino- nitro groups in trans position and 1,1-diamino-2,2-dinitroethane having two C-H bonds in a trans position[2]. This shows that conformation structure which is sterically less hindered is more stable.

Gaussian03 using HF/3-21 calculations to study the C-C bond strengths in amino- and nitro-substituted compounds computational studies and properties of aminonitroethane molecule by Mathews et al [3].Their optimized structure had a C-C bond length of 3.187 Å and the two tri-substituted carbon structures were planar and slightly staggered with to each other as shown in **figure 6**.

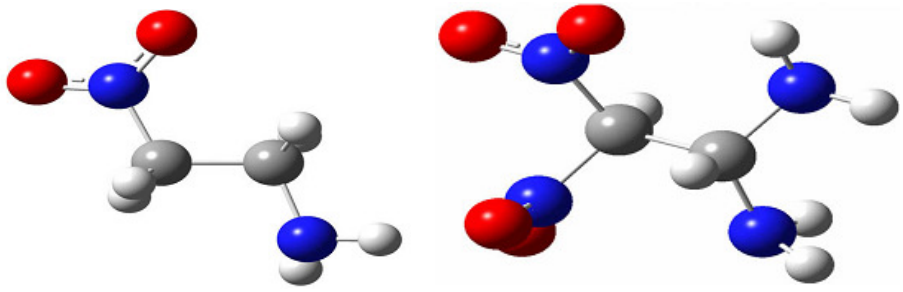


Figure 6: Optimized structures of 1-amino-2-nitroethane and 1,1-diamino-2,2- nitroethane

The ground state geometry optimization and TD-DFT the molecule spectral calculations were performed on fulvene and diphenylfulvene molecule using B3LYP/6-311+G(d,p) functional and basis set combination by R.E. Connors et.al.[4] . This along with a larger dipole moment, indicates that there is greater charge separation and π delocalization for diphenylfulvene molecule.

B3LYP/6-311+G(d,p) DFT calculations predict that diphenylfulvene molecule belongs to the C_2 point group with phenyl ring torsion angles. They had studied the structure of diphenylfulvene molecule by X-ray crystallography and have found that crystallizes with two similar molecular structures in the asymmetric unit and the angles between the fulvene ring and phenyl rings were oriented so that strain can be minimized. The inequality of phenyl rings twist angles reflect the influence of crystal packing forces on the structure of molecule. There is no experimental data is available for the geometry of diphenylfulvene molecule in an environment free of these forces. It is only computation calculations which tells the exact twisting of the molecule [5].

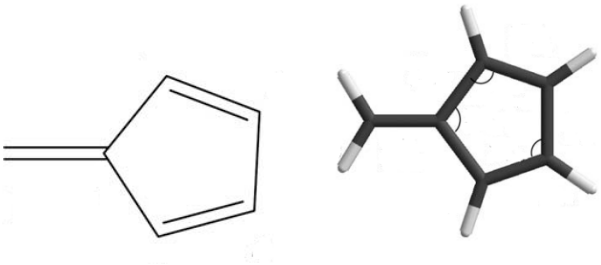


Figure 7: Molecular structure and optimized structure of fulvene

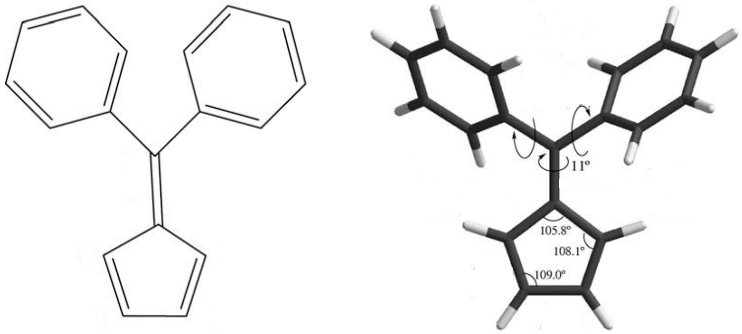


Figure 8: Molecular structure and optimized structure of diphenylfulvene

The molecular structure of 5-chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule shown in **figure 9**. Density functional theory and ab initio Hartree-Fock thory were used to optimize 5-chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule. Its optimized structure is shown in **figure 10**. The optimized structure an vibrational frequencies and IR intensities calculated by the HF and DFT theory using 3-21G, 6-31G(d), 6-311++G(d,p) and STO-3G basis sets for each methods [6].

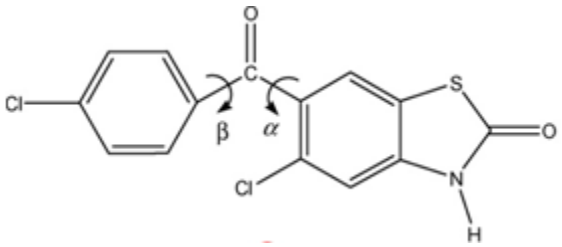


Figure 9: Molecular structure of 5-chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule

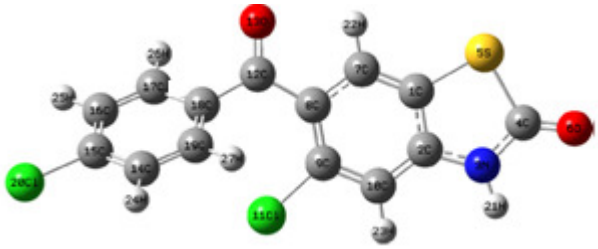


Figure 10: Optimized Structure of 5-chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule

5-chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule has three-fold rotation for one of dihedral thus one can obtain a total of $3^2 = 9$ staggered conformations. The optimized bond lengths, bond angles and dihedral angles of chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule which were calculated by using ab initio and DFT methods by using 6-311++G(d,p), 6-31G(d),3-21G and STO-3G basis sets. The conformational stability was determined to find the most stable isomer form of the 5-chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule shown in **figure 11**.

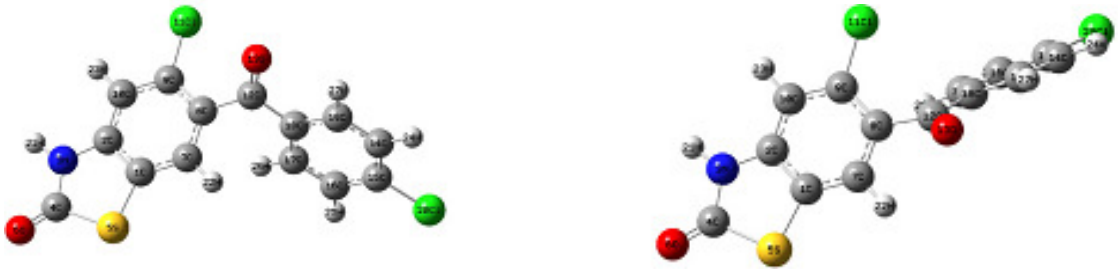


Figure 11: Conformation isomers of 5-chloro-6-(4-chlorobenzoyl)-2-benzothiazolinone molecule

The results obtained by using DFT-B3LYP are in agreement with experimental ones. The DFT-B3LYP method has better fit to experimental ones than DFT-BLYP and ab initio HF in evaluating vibrational frequencies.

DFT methods used to accurately determine atomic and molecular properties for molecules found in proteins, DNA and RNA. These properties include bond lengths, bond angles, ground-state vibrational frequencies, electron affinities, ionization potentials, heats of formation, hydrogen-bond interaction energies, conformational energies. Calculations are carried out with the 3-21G*, 6-31G*, 3-21+G*, 6-31+G* and 6-31++G* basis sets. The inclusion of diffuse functions on hydrogen atoms in the 6-31++G* basis does not generally increase the performance in terms of hydrogen-bonding interaction energies when compared to the 6-31+G* basis.

Effect of metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ni^{2+}, $Cu^{2+}$and Zn^{2+}) and water coordination on the structure and properties of L-histidine and zwitterionic L-histidine [7]. The relative stability of gas phase complexes computed with DFT methods suggest metallic complexes of the neutral L-histidine to be the most stable species[8]. Histidine coordinated by monovalent metal cations is by about more acidic than the non-coordinated histidine[9]. Divalent cations exhibit a considerably larger effect on the acidity of histidine.

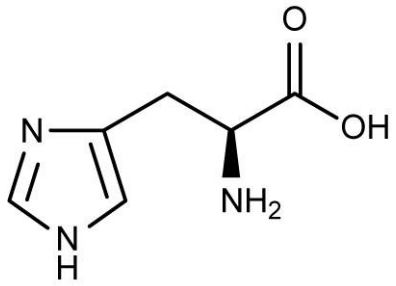


Figure 12: Molecular structure of L-histidine

A comparison of the B3LYP computed enthalpy value for the binding of sodium cation to histidine and available experimental values shows that DFT and experimental data have great agreement. Levels of theory and basis set used are MP2/6-311+G(2d,2p), MP2/6-31G(d), MP2/6-311+G(2d,2p), HF/6-31G(d) methods and are in good agreement with calculations using the B3LYP/6-31++G(d,p) method.

Gaussian Method

Gaussian is a very high end quantum chemical software package, available commercially through Gaussian, Inc. The software runs on all types of computer, including microsoft windows. Gaussian has a long list of keywords, which have additional options and extensions to a calculation. For example to determine electrons distribution throughout a molecule the computation known as a population analysis. Population analysis can specify which specific type of population analysis wish to run. Without a keyword choice entered using the advanced tab in the job configuration window, the software defaults to automatically choose mulliken population analysis.

One of advantage of Gaussian software is that the results that come from running a Gaussian calculation are automatically displayed in the view calculated quantities in the window. It is possible however to view the entire text based output file that is generated with a Gaussian calculation. Most Gaussian jobs runs to completion successfully and will not fail, assuming that the molecule being calculated is one that is reasonable in size and structure. A job will fail for no apparent reason, and can simply be restarted.

Gauss View is a graphical user interface designed to help you prepare input for submission to Gaussian and to examine graphically the output that Gaussian produces. Gaussian results that can be viewed graphically are Optimized molecular structures, molecular orbitals, electron density surfaces, electrostatic potential surfaces, surfaces for magnetic properties, surfaces viewed as contours, atomic charges and dipole moments, animation of the normal modes corresponding to vibrational frequencies, IR, Raman, NMR, and other spectra, molecular stereochemistry information, animation of geometry optimizations and potential energy surface scans.

Using Gaussian view by clicking its icon then see two windows the Gaussian Veiw control panel, which will looks like **figure 1**.

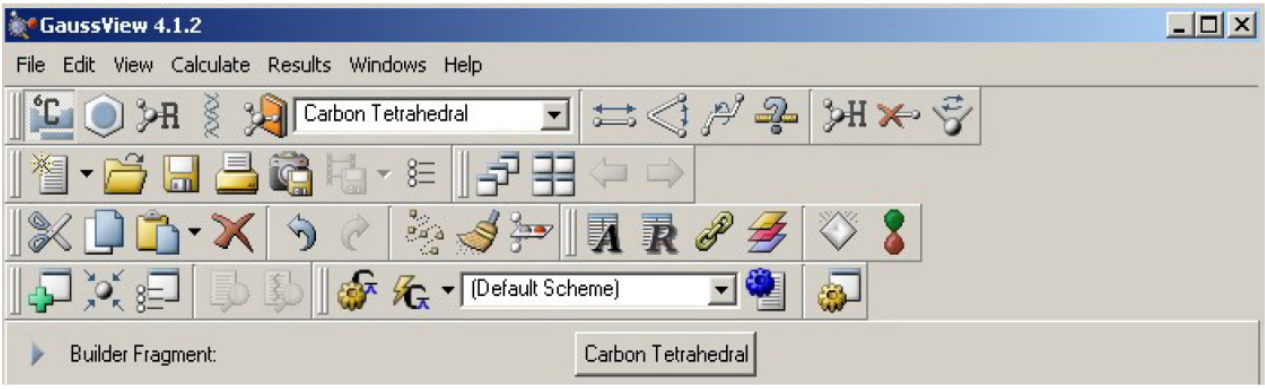


Figure 1: Gaussian view window panel

and a blank window where build molecules. Molecules are drawn using elements from the first four icons on the left side of the the control panel. Note that the default fragment is a tetrahedral carbon atom. Click on the botton labeled carbon tetrahedral and a periodic table will open. Pick an element, let us use Sulphur atom there are many choices of Sulphur atom as shown in **figure 2**.

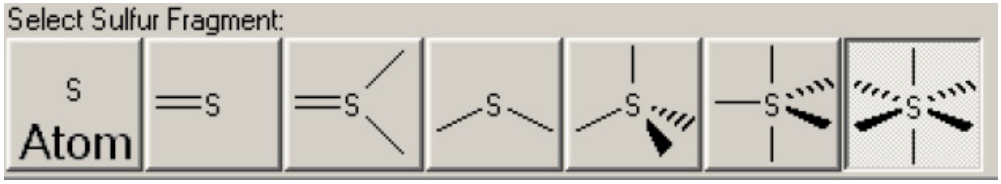


Figure 2: figure showing the different valences of atom

For giving job to a molecule following steps to be folllowed:

Step 1: Add a new folder to the desktop and give it a name.

Step 2: Using inquire tool, measure and record the preoptimization bond lengths and bond angles. On the control panel menu select gaussian calculation set up and this menu shown as **figure 3**.

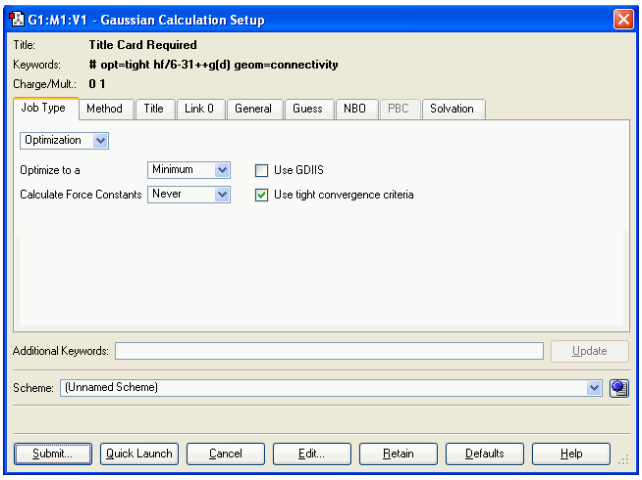


Figure 3: figure showing gaussian calculation setup

Step 3: Under the job type various calculation options like optimization, frequency, scan and energy calculations.

Step 4: Computational method provides a range of choices under the method menu as shown in **Figure 4**.

Step 5: Calculation on the ground state using functioal methods and leave the spin as default spin.

Step 6: Select a basis set from menu and go to the link0. This tells gaussian where to put files name and location in checkpoint file item as shown in **Figure 5**.

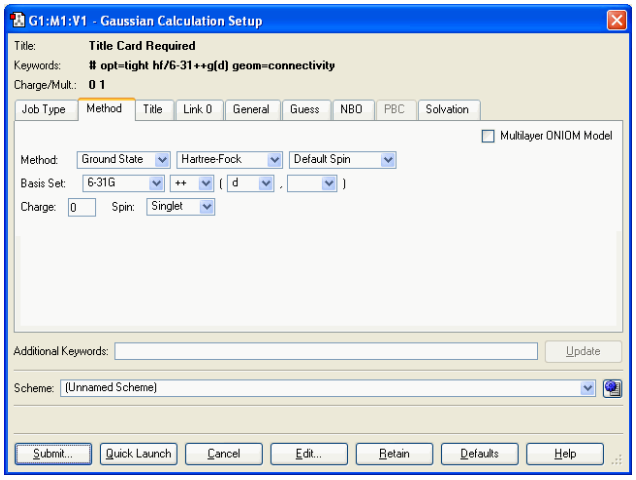


Figure 4: figure showing the gaussian calculation setup

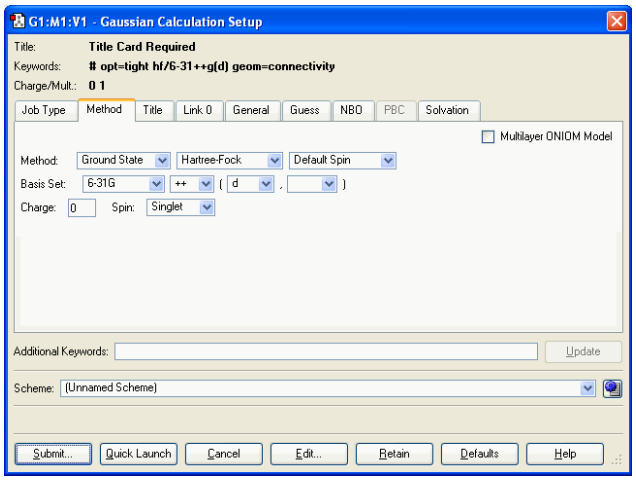


Figure 5: figure showing the gaussian calculation setup

Step 5: Calculation on the ground state using functioal methods and leave the spin as default spin.

Step 6: Select a basis set from menu and go to the link0. This tells gaussian where to put files name and location checkpoint file item as shown in **Figure 6**.

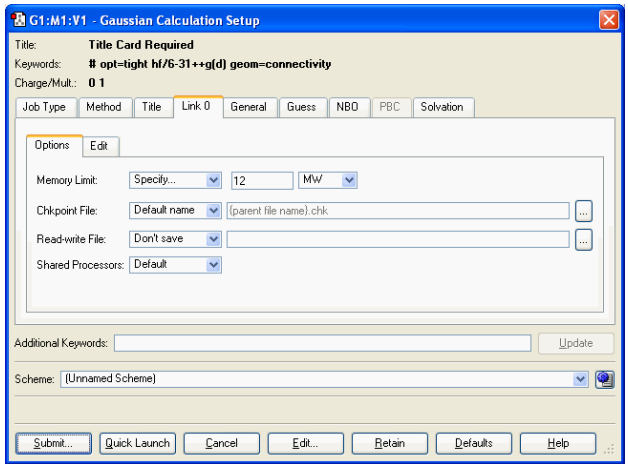


Figure 6: gaussian calculation setup memory limit

Step 7: Now submit to send the calculation from gaussian view to gaussian and save in checkpoint file.

Step 8: After job had been completed click on result tab to look at summary and other parameters in output File.

RESULT AND DISCUSSION

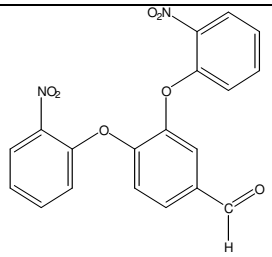
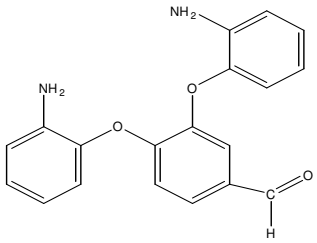
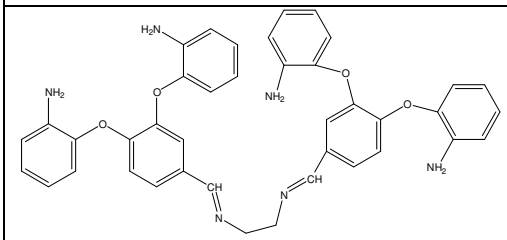
Gaussion 03 software was used to calculate optimized energies of some new molecular having triphenyl ether as basic units. Three molecules were studied to determine the optimized energies in gaseous state. Molecule 1 is a nitro derivative where as molecule 2 is a amino derivative. Molecule 3 is a dimer of the amino derivative of the triphenyl ether based molecule 2. These molecules are projected as potential ionophores for chemical sensing of metal ions. Molecule 3 is more likely to bind reversibly with the metal because of its expected geometry conversing as a cavity of sized suitable to a metal ion. Before any ionophore is put to used as a chemical sensing molecule. It needs to checked for it conformation to suitably accept the metal ion as a guest. This process is indicated by minimization of energy in the complexed form as compared to the uncomplexed and free receptor molecule.

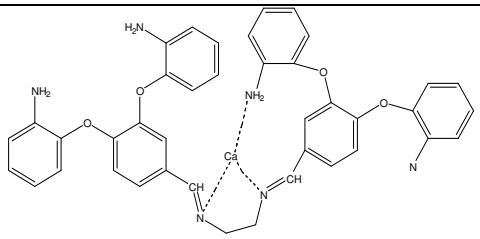
In the light of the above molecular calculation were done on the Gaussian 03 software to know if it results in decrease of energy or not.

Results of energy minimization studies on molecules 1, 2,3 and molecule 3 complex are given in **table 1**. It is seen from the table that molecule 1 is more stable than molecule 2. Where as dimer of molecule 2(molecule 3) is much more stable than molecule 1 and 2. This extra stability associated with the dimer molecule is indicative of its flexible orientation around C-C bond linking the two monomer of triphenyl ether moftifs through schiff base formation. Further minimization about 2.26 $X10^4$ Kcal/mol of energy on complexation with Ca^{2+} ion is sufficient to be recommended for its application as a calcium sensing receptor molecule.

PROJECT WORK CALCULATIONS OF MOLECULES

Table 1 Optimized energy values of triphenyl ether based molecules

Structures of molecules	Parameters used	Optimized energy Hartrees unit
 Molecule 1	Job type: Optimization Method: ground state Density function theory Default spin,B3LYP Basis set 6-311G**	-1367
 Molecule 2	Job type: Optimization Method: ground state Density function theory Default spin,B3LYP Basis set 6-311G**	-1068
 Molecule 3	Job type: Optimization Method: ground state Density function theory Default spin,B3LYP Basis set 6-311G**	-2175

 Molecule 3 interaction with Ca^{2+}	Job type: Optimization Method: ground state Density function theory Default spin,B3LYP Basis set LANL2DZ	-2211

Conversion of Energy unit

1 Hartrees = 2600 KJ/mol = 630 Kcal/mol

Table 2 Minimized energies of molecules in different units

Sr. no.	Molecules	Minimised Energy		
		Hartrees	KJ/mol	Kcal/mol
1.	Molecule 1	-1.36×10^3	-8.58×10^5	-3.59×10^5
2.	Molecule 2	-1.069×10^3	-6.70×10^5	-2.80×10^5
3.	Molecule 3	-2.175×10^3	-1.36×10^5	-5.71×10^5
4.	Molecule 3 interacted With Ca^{2+}	-2.211×10^3	-1.39×10^5	-5.80×10^5

Optimized structures of aryl ether based molecule 1 and molecule 2 are given below:

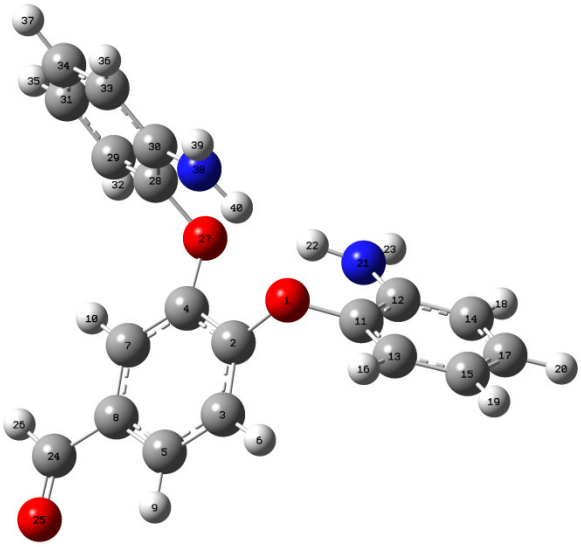


Figure 13: optimized structure of molecule 1

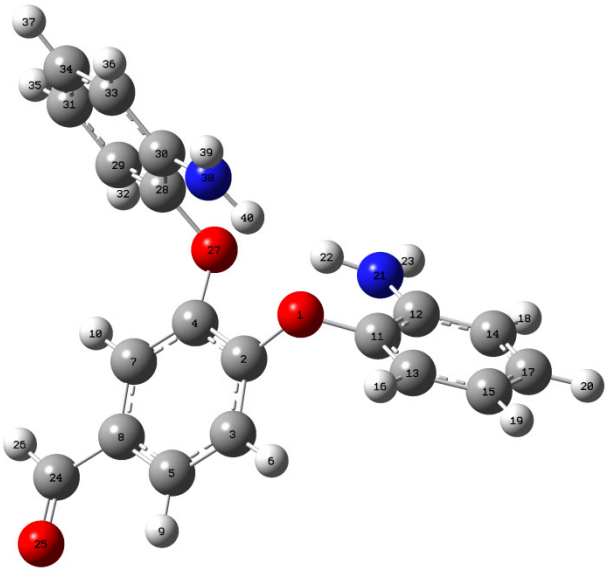


Figure 14: Optimized Structure of Molecule 2

In the purposed work molecular structural parameters like bond length and dihedral angles were also calculated for bond length of different combination of atoms were measured in Å values and are reported in **tables 3**. These values were calculated for molecule 1 and molecule 2. Bond

length values for molecule 3 are compared with corresponding values in its complexed structure with Ca^{2+} ion.

Table 3 Values of bond lengths of molecule 1 and molecule 2

Molecule 1		Molecule 2	
Bond Length	Values (Å)	Bond Length	Values (Å)
O40-N38	1.2684	O25-C24	1.24019
N38-O39	1.2651	C24-H26	1.10220
C28-O24	1.39703	C8-C24	1.47087
C16-O39	1.40321	C4-O27	1.41117
O13-N11	1.27192	C2-O1	1.49582
N11-O12	1.26132	C11-O1	1.432
O14-C5	1.39158	C21-C12	1.3750
C29-N38	1.4636	H22-N21	1.00984
O26-C25	1.2388	O27-C28	1.4312
C25-H27	1.10219	N38-C30	1.3751
C21-C25	1.4728	H39-N38	1.00257
C5-H9	1.0807	C5-H9	1.0805
C5-C8	1.4059	C5-C8	1.4059
C8-C24	1.4072	C24-H26	1.1022

Table 4 Values of bond angles of molecule 1 and molecule 2

Molecule 1		Molecule 2	
Bond angles	Values(degrees)	Bond Angles	Values(degrees)
O12-N11-O13	123.957	H39-N38-H40	118.285
O13-N11-C4	116.981	H40-N38-C30	121.551
N38-C29-C31	116.822	N38-C30-C28	120.931
C5-C15-O14	29.024	C30-C28-O27	117.782
C28-O24-C16	122.787	C28-O27-C4	119.778
O26-C25-C21	124.364	O27-C4-C2	117.396
O24-C28-C29	125.795	O1-C11-C12	117.357
C28-O24-C16	122.787	O75-C24-C8	115.514

Table 5 Values of dihedral angles of Molecule 1 and Molecule 2

Molecule 1		Molecule 2	
Dihedral Angles	Values(degrees)	Dihedral Angles	Values(degrees)
H36-C32-C30-C28	179.679	C28-O27-C4-C30	33.440
C32-C30-C28-O24	-177.204	O27-C4-C8-C7	-11.211
C30-C28-O24-C16	-124.024	C7-C28-O27-C4	-25.514
C28-O24-C16-C18	26.447	C30-C28-O24-C4	83.735
O24-C16-C18-C21	177.820	C28-O27-C4-C7	61.152
C16-C18-C21-C25	179.831	O27-C4-C7-C8	173.868
C18-C21-C25-O26	178.681	C8-C24-C5-O25	179.940
C18-C21-C19-H23	-1.255	C2-O1-C13-C11	98.385
H20-C17-C15-O14	179.357	H23-N21-C12-C14	1.162
C17-C15-O14-C5	-3.468	C12-C11-O1-C2	84.628
C15-O14-C5-C6	120.541	O1-C2-C4-O27	10.952
O14-C5-C6-C1	-20.995	C4-O29-C28-C29	-100.207
C5-C6-C1-C7	-179.435	O27-C28-C29-C31	-177.760
C1-H7-C2-H8	179.341	C30-N38-C28-O27	178.481
C1-C2-C3-H9	-179.750	C28-O27-C4-C30	-33.440
C3-H9-C4-N11	-179.163	C4-C8-C7-C24	179.791
C4-N11-O12-C3	178.466	C8-C7-C24-O25	-1.208
C3-O13-C4-N11	27.165	C5-C8-C7-O25	0.072
O12-N11-C4-C5	152.340	C3-C5-C8-C24	-179.441
N11-C4-C5-C6	33.513	C8-C24-C7-C4	0.372

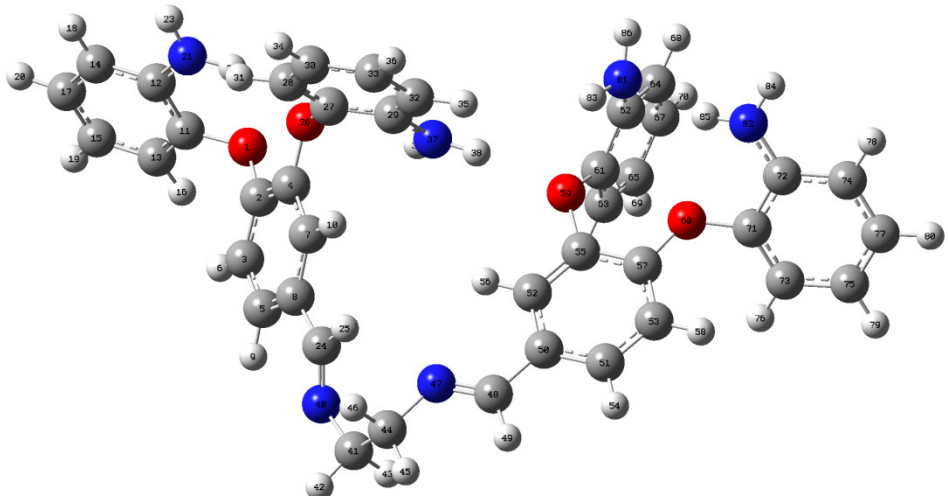


Figure 14: Optimized structure of molecule 3

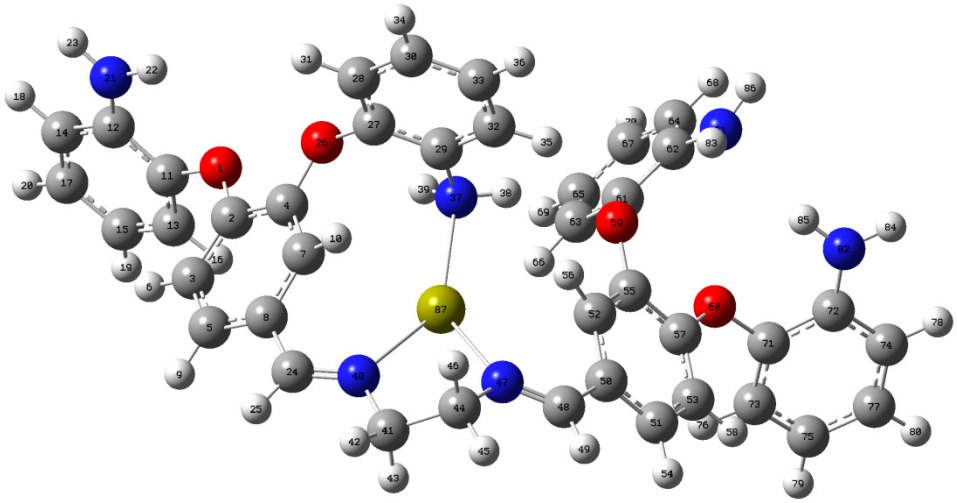


Figure 15: Optimized structure of molecule 3 interacted wih Ca^{2+}

From **table 4** very interesting observation about changes in bond lengths of bonds involving atoms that are participated in the complexation with metal ion is noticed.

Table 5 Values of bond length of optimized structure of molecule 3 and molecule 3 interacted with Ca^{2+}

Bond Lengths	Molecule 3	Molecule 3 interacted with Ca^{2+}
	Values (Å)	Values(Å)
C50-C48	1.4691	1.4643
C48-N47	**1.2817**	**1.3094**
N47-C44	1.4660	1.4860
C44-C41	1.5444	1.5474
N37-C29	**1.3764**	**1.4624**
C41-N40	1.4712	1.4872
N40-C24	1.2840	1.3085
C24-C8	1.4691	1.4680
C8-C7	1.4032	1.4288
C7-H10	1.0798	1.1090
H9-C5	1.0811	1.0869
C24-H25	1.0882	1.0957
C41-H42	1.0939	1.0981
C41-H43	1.0938	1.1000
C44-H45	1.1010	1.0990
C48-H49	1.0826	1.0959
C51-H54	1.0826	1.0870
C8-C5	1.4031	1.4086
C44-C46	1.0940	1.0984
C52-H56	1.0796	1.0911
N47-Ca87	-	2.4549
N37-Ca87	-	2.5539
N40-Ca87	-	2.4655

There is a sharp increase in the bond length between C48-N47 from 1.2817Å to 1.3094Å i.e. 0.0277Å .This sharp raise in the bond length is due to coordination of lone pair on nitrogen toward calcium atom resulting in attraction of electrons of C=N double bond and hence a increase in bond length.

Another a major change in bond length is noticed in N37-C29 bond length is increase from 1.3764 Å to1.4624 Å which is about 0.086Å. The elongation of the bond in the complex molecule is due to the participation of lone pair on N37 in the complexation with calcium. Since this C-N bond is not conjugated with the benzene ring hence the effect of lone pair of nitrogen is seen only in terms of little weaking of C-N bond.

In the purposed work dihedral angles of various combinations were measured for molecule 3 and compared with the complexed molecules.

Table 5 Values of bond angles of molecule 3 and molecule 3 interacted with Ca^{2+}

Bond angles	Molecule 3	Molecule 3 with Ca^{2+}
	Values(degree)	Values(degree)
C48-N47-C50	31.295	122.657
C48-N47-C44	121.021	121.171
C44-C41-N40	109.982	119.363
N40-C24-C8	119.277	123.309
C24-C8-C7	119.011	116.999
C24-C8-C4	121.987	123.603
C24-N40-C41	121.701	121.172
C41-C44-N47	110.507	111.835
C44-N47-C48	121.021	121.171
N47-C48-C50	121.029	122.657
C48-C50-C52	120.555	121.239
N47-C48-C50	140.305	-
C48-C50-C52	69.851	-
N37-N47-Ca87	143.337	-

N40-N47-Ca87	140.305	-
C48-N47-Ca87	123.298	-
C24-N40-Ca87	120.955	-
C29-N37-Ca87	98.721	-
C44-N47-Ca87	114.636	-

Table 6 Values of dihedral angles of molecule 3 and molecule 3 interacted with Ca^{2+} ion

Dihedral angles	Values (degree)	
	Molecule 3	Molecule 3 interacted with Ca^{2+} ion
C52-C50-C48-N47	-2.233	23.405
C50-C48-C44-C44	179.31	-179.198
C48-C47-C44-C41	-120.78	-127.280
C47-C44-C41-N40	-59.963	-48.228
C41-N40-C24-C8	1.555	-158.506
C44-C41-N40-C24	173.812	-179.844
N40-C24-C8-C5	5.635	145.044
N40-C24-C8-C7	-169.530	28.844
N40-C24-C8-C4	172.856	169.454
C8-C7-C4-C5	1.280	0.858
C5-C3-C8-C7	-178.734	4.293
H9-C5-C8-C24	4.567	8.170
H25-C5-C8-C24	-179.222	-32.409
H42-C41-N40-C24	125.006	36.613
H43-C41-N40-C24	-121.778	82.081
C44-C41-N40-H45	176.045	171.958
N40-C41-C44-H46	59.269	70.309
C44-N47-C48-C49	-0.736	3.221
H45-C44-C41-H43	-61.825	131.086
H45-C44-C41-H42	53.059	-52.937

C48-C47-Ca87-N37	-	-55.798
C24-N40-Ca87-N37	-	30.803
C29-N37-Ca87-N37	-	57.908
C41-N40-Ca87-N37	-	-160.712
C44-N47-Ca87-N37	-	-17.787
H38-N37-Ca87-N47	-	38.599
H56-C44-N47-Ca87	-	-78.020

The values of bond angles and dihedral angles are reported in **table 5 and 6** respectively. A number of new orientations of bond angles can be seen in the complexed molecular structure as compared to the free dimer molecules 3. It is really difficult to explain the change through discussion but can be justified from the three dimensional view of the molecular structure.

Conclusion

1. Density Functional Theory based calculations indicate that molecule 3 which is a dimer of molecule 2 is possessing the least energy among the nitro substituted triphenyl ether (molecule 1), amino substituted triphenyl ether (molecule 2) and the dimer of molecule 2 (molecule 3) joined through Schiff base reaction.
2. Molecule 3 is more stable than molecule 2 by 2.91×10^4 Kcal/mol.
3. Complexation of molecule 3 with calcium result in further stabilization by 2.26×10^4 Kcal/mol energy.
4. Change in bond lengths of molecule 3 on complexation with Ca^{2+} ion and explain easily by the fundamental principles of Chemistry.
5. Molecule 3 is purposed as suitable receptor for chemical sensing of Ca^{2+} ion.

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