An Ab-Initio Study on Conformers of Cyclohexane

Jyothy P J
Department of chemistry
Carmel college mala
Thrissur, kerala

Princy K G
Department of chemistry
Carmel college mala
Thrissur, kerala

Roshni K Thumpakara
Department of chemistry
Carmel college mala
Thrissur, kerala

Vidya Fransis
Department of chemistry
Carmel college mala
Thrissur, kerala

Abstract— **Computational chemistry uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. Ab-initio methods are based entirely on quantum mechanics and basic physical constants. The study was designed to calculate the zero point energy of the conformers of cyclohexane by using geometry optimization method. Compare the energies obtained from optimization methods with the experimental values. Then elicit the effect of different basis sets on the energies of these conformers.**

Keywords — Ab-initio, guassian03, basis sets, zero point energy.

I. INTRODUCTION

Computational chemistry simulates chemical structures and reactions numerically, based in full or in part on the fundamental laws of physics. It allows chemists to study chemical phenomena by running calculations on the computers rather than by examining reactions and compounds experimentally[1]. Computational chemistry is therefore both an independent research area and vital adjunct to experimental studies . Quantum-mechanical methods of treating molecules are classified as Ab-initio or semiempirical. The aim of Ab-initio molecular orbital theory is to predict the properties of atoms and molecules. It is based on the fundamental laws of quantum mechanics . Different mathematical transformations and approximation techniques are necessary to solve the equations that build up this theory.

II. GEOMETRICAL OPTIMIZATION OF CONFORMERS OF CYCLOHEXANE

Geometry optimization methods are used to compute the equilibrium configuration of molecules and solids. Stable states of molecular systems correspond to global and local minima on their potential energy surface[2]. Starting from a non-equilibrium molecular geometry, energy minimization employs the mathematical procedure of optimization to move atoms so as to reduce the net forces (the gradients of potential energy) on the atoms until they become negligible. A well established algorithm of energy minimization can be an efficient tool for molecular structure optimization.

A. *Guassian 03*

Starting from the basic laws of quantum mechanics, Guassian predicts the energies, molecular structures, and vibrational frequencies of molecular systems along with numerous molecular properties derived from these basic computation types. It can be used to study molecules and reactions under a wide range of conditions including both stable species and compounds which are difficult or impossible to observe experimentally such as short-lived intermediates and transition structures.[3]

B. *Basis set effects*

A basis set is the mathematical description of the orbitals within a system used to perform the theoretical calculation.[4] The basis set can be interpreted as restricting each electron to a particular region of space. The basis set is a set of atomic functions used to construct LCAO-MOs. A complete set of basis functions must be used to represent spin orbitals exactly.

C. *Preparing input for Geometry optimization*

The opt keyword in the route section requests a geometry optimization, using the basis set and level of theory specified by the other keywords. In Gaussian, the molecule specification for geometry optimization can be given in any format desired: Cartesian coordinates, z-matrix, mixed coordinates. The geometry optimization job will produce the optimized structure of the system as its output .

Here is the input file for an optimization of chair and boat conformers of cyclohexane .[5]

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Cyclohexane chair form

 # RHF/6-31G(d,p) Opt Freq T

```
X1
X2 1 r1
C5 1 r2 2 ac1
C6 2 r2 1 ac1 3 60.0
C9 1 r2 2 ac1 3 120.0
C10 2 r2 1 ac1 3 180.0
C7 1 r2 2 ac1 3 -120.0
C8 2 r2 1 ac1 3 -60.0
H3 3 r3 1 ah1 2 0.0
H3 3 r3 1 ah2 2 0.0
H5 5 r3 1 ah1 2 0.0
H5 5 r3 1 ah2 2 0.0
H7 7 r3 1 ah1 2 0.0
H7 7 r3 1 ah2 2 0.0
H4 4 r3 2 ah1 1 0.0
H4 4 r3 2 ah2 1 0.0
H6 6 r3 2 ah1 1 0.0
H6 6 r3 2 ah2 1 0.0
H8 8 r3 2 ah1 1 0.0
H8 8 r3 2 ah2 1 0.0
r1=0.5        r2=1.4        r3=1.1
ah1=170.0 ac1=90.0         ah2=90.0
```

Cyclohexane boat form

 # RHF/6-31G(d) Opt Freq T
```
X1
X2 1 1.0
X3 1 1.0 2 90.0
X4 1 1.0 3 90.0 2 180.0
C1 1 r2 2 ac1 3 0.0
C2 1 r2 2 ac2 3 60.0
C3 1 r2 2 ac2 3 120.0
C4 1 r2 2 ac1 3 180.0
C5 1 r2 2 ac2 3 -120.0
C6 1 r2 2 ac2 3 -60.0
H2 6 r3 1 ah1 4 0.0
H3 7 r3 1 ah1 4 0.0
H5 9 r3 1 ah1 4 0.0
H6 10 r3 1 ah1 4 0.0
H2 6 r3 1 ah1 2 0.0
H3 7 r3 1 ah1 2 0.0
H5 9 r3 1 ah1 2 0.0
H6 10 r3 1 ah1 2 0.0
H1 5 r3 1 ah2 2 0.0
H1 5 r3 1 ah3 4 0.0
H4 8 r3 1 ah2 2 0.0
H4 8 r3 1 ah3 4 0.0
r2=1.4     r3=1.1     ac1=60.0   ac2=90.0
ah1=110.0  ah2=110.0          ah3=140.0
```
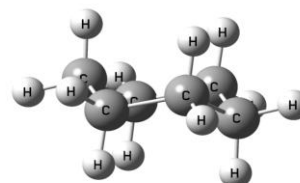
The above inputs for the optimizations of chair and boat forms were done by using the basis set 6-31G(d),it's description is that it adds polarization functions to heavy atoms:[6] use for most jobs on up to medium/large sized systems.(This basis set uses the 6-component type functions). Similarly we use the other basis sets such as 6-31G(d,p) which adds polarization functions to the hydrogen as well: use when the hydrogens are the site of interest and for final accurate energy calculations and the other basis set 6-311G(d,p) which is a triple zeta basis set and it adds extra valence functions(3 sizes of s and p functions)[7].

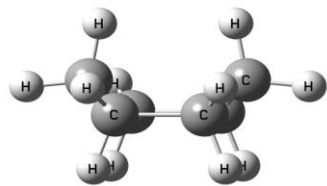## III RESULTS AND DISCUSSION

When the optimization converges, it knows that the current structure is the final one, and accordingly ends the calculation at that point. The final structure and summary of conformers of cyclohexane from the output file is given in the following pages. Summary file contains the calculation type, calculation method, basis set, imaginary frequency, dipole moment, and the processing time. Frequencies are also obtained from the output files. Frequency calculations can serve to find out the transition states. Imaginary frequencies are listed in the output of a frequency calculation as negative numbers. By definition, a structure which has n imaginary frequencies is an nth order saddle point. Thus ordinary transition structures are usually characterized by one imaginary frequency since they are first- order saddle points.

The boat conformation is a good deal less stable than the chair conformation. It is believed to lie, not at an energy minimum, but at an energy maximum; it is thus not a conformer, but a transition state between two conformers. Frequency calculations retrieve that boat conformer contains an imaginary frequency and thus it is a transition state. The final structure and summary of conformers of cyclohexane from the output file is given below.

Cyclohexane chair form

Calculation type - FREQ   **Calculation method - RHF**

Basis set - 6-31G(d)   **Imaginary frequency - 0**

Dipolemoment - 0 Debye   **Point group - D$_3$d**

Time   - 1 minutes 14 seconds

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Cyclohexane boat form

Calculation type - FREQ   **Calculation method - RHF**

Basis set – 6-31G(d)   **Imaginary frequency - 1**

Dipolemoment - 0.0272 Debye   **Point group – C₂ᵥ**

Time- 1 minutes 38 seconds

We ran geometry optimizations of cyclohexane conformers using both the 6-31G(d), 6-31G(d,p) and 6-311G(d,p) basis sets in order to determine the effects of zero point energieson the predicted structures.

Table1:- Effects of basis sets on the zero point energy of cyclohexane conformers. (Energies in hartrees/particle)

Different basis sets	Chair form	Boat form
6-31G(d)	-234.025567	-234.013298
6-31G(d,p)	-234.044890	-234.032588
6-311G(d,p)	-234.083368	-234.070943

Table 2:- Comparison of the Zero point energies with experimental values.

Different conformers of cyclohexane	6-31G(d)	6-31G(d,p)	6-311G(d,p)	Experimental value.
Chair form	0	0	0	0
Boat form	7.698Kcal/mol	7.719Kcal/mol	7.796Kcal/mol	6.8 Kcal/mol

Table 3:- Comparison of processing time in conformers of cyclohaxane using different basis sets.

Different basis sets	Chair form	Boat form
6-31G(d)	1 minutes 14 seconds	1 minutes 38 seconds
6-31G(d,p)	2 minutes 55 seconds	3 minutes 40 seconds
6-311G(d,p)	6 minutes 38 seconds	8 minutes 16 seconds

IV CONCLUSION

We conclude that our results from geometry optimizations of cyclohexane conformers agree with the following statements. "In the conformers of cyclohexane the chair being a global minimum (ground state) and the boat conformation is a transition state, allowing the inter conversion between two different twist-boat conformations. Thus the conformations involve following order of stability chair form>boat form." From the effects of basis sets on the energies of cyclohexane conformers we obtained that the minimal basis set 6-31G(d) gives the energy values which are more comparable with the experimental values. And also the other basis sets are more time consuming than 6-31G(d) basis set. 6-31G(d) thus appears to achieve the basis set limit for this model chemistry.

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