

Stability due to π -Conjugation

Abstract—Computationally confirming that π -conjugation generally leads to a stable molecule

I. INTRODUCTION

IN the following project we are going to run an optimization on two similar molecules to confirm whether conjugation in the π bonds makes an actual difference in the energies of the two molecules.

II. METHODOLOGY

To check if a molecule is more stable in a π -conjugated system, we need two similar molecules only differing in the aspect of having a π -conjugation. Then the difference in their energies, in principle, should validate if the following hypothesis is true or not.

III. CONSTRUCTION

The following experiment requires two similar molecules with difference in the position of the π bonds. For the following experiment, the chosen molecule is a cyclohexadiene, the isomers being cyclohex-3-diene and cyclohex-4-diene.

Construct the following molecules in a z-matrix or via Gaussian View. After constructing them run an optimization and frequency calculation on it via Gaussian.

After formation of the log file, extract the value of the energies of the molecules from it.

IV. RESULTS & ANALYSIS

These are the results of the following experiment :

- Cyclohex-3-diene

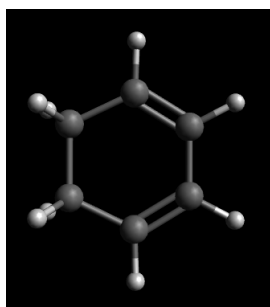


Fig. 1. π -conjugated

$$\Delta E_{\pi-conj} = -230.543581880$$

In the following molecule, there is a conjugation between the π bonds between Carbons 1-2 and Carbons 3-4.

- Cyclohex-4-diene

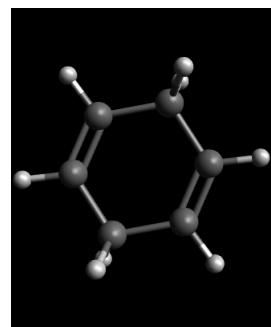


Fig. 2. Not π -conjugated

$$\Delta E_{non\pi-conj} = -230.539671058$$

In the following molecule, there is a no conjugation between the π bonds between Carbons 1-2 and Carbons 4-5, as conjugation occurs on alternate π bonds.

Hence the difference in the energies is :

$$\Delta E_{\pi-conj} - E_{non\pi-conj} = -0.003910822$$

which is a negative quantity, thus confirming that the conjugated molecule is more stable than a non conjugated molecule.

V. CONCLUSION

From the experiment, (by comparing the values of energies) it was computationally verified that a π -conjugated molecule is more stable than a non π -conjugated molecule.

Analyzing SN_2 Reaction

Abstract—Explaining why, in a SN_2 reaction, the energy of the transition state is more than that of the sum of the energies of the reactant or the products.

I. INTRODUCTION

IN the following project, we will analyze, why in SN_2 reaction of $Cl + CH_3$, the energy of transition state is less than the sum of the energies of the reactants or the products.

II. CONSTRUCTION

To analyze the energies of the molecules, energies of the transition state, individual molecules CH_3Cl , Cl , I , and CH_3I will be required. Construct the above mentioned molecules, run an optimization and frequency calculation, and extract their energies from the log files created.

III. RESULTS

The energies of the following molecules id :

- Transition State

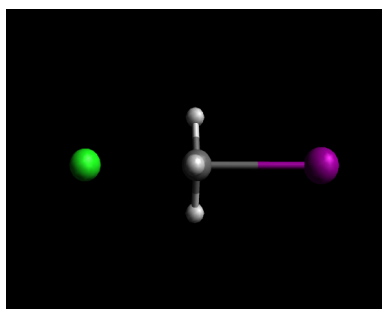


Fig. 1. Transition State

$$\Delta E_{ts} = -7344.30800534$$

- Chloromethane

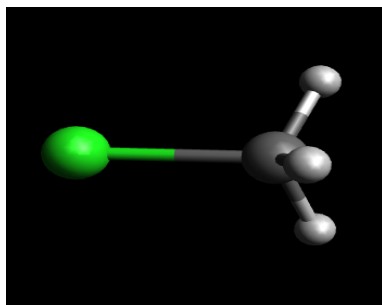


Fig. 2. Chloromethane

$$\Delta E_{CH_3Cl} = -496.572131399$$

- Iodine

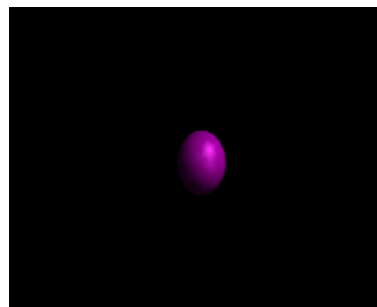


Fig. 3. Iodine

$$\Delta E_I = -6877.31428064$$

- Iodomethane

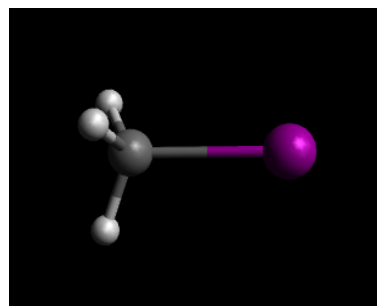


Fig. 4. Iodomethane

$$\Delta E_{CH_3I} = -6916.82057526$$

- Chlorine

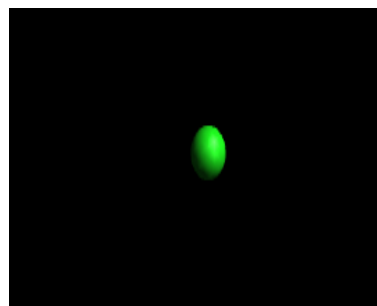


Fig. 5. Chlorine

$$\Delta E_{Cl} = -457.052022181$$

Sum of the reactants :

$$\Delta E_{Reactant} = 7373.886412039$$

Sum of the products :

$$\Delta E_{Product} = 7373.872597441$$

Hence, it can be seen that the reactant and the products have more energy than the transition state. But the sum of energies of the reactants and the products is more stable than that of the transition state. Hence the reactants and products are more stable than the transition state.

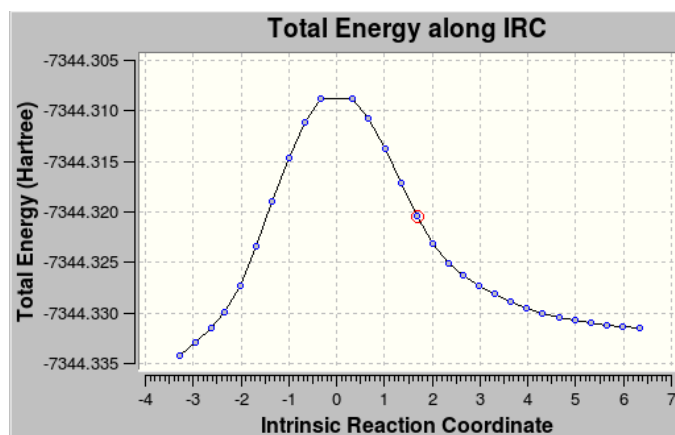


Fig. 6. IRC Graph

IV. ANALYSIS

In the results it can be seen that the reactants and the products are more stable than the transition state itself thus proving our hypothesis wrong.

V. CONCLUSION

This project concludes that individually the reactants and the products are more unstable than the transition state but is not more stable than when they are able to interact with each other.

Hence it is not an abnormality of the SN_2 reaction.

Surface Energy Graph

Abstract—Making a molecule and plotting its surface energy by rotating it about two bonds.

I. INTRODUCTION

IN the following project we are going to make the pentane molecule and compute the energy while rotating it about two central bonds, and plot them in a graph, identifying all the unique minimum energies.

II. CONSTRUCTION

Construct the pentane molecule using any of the methods and add two lines of code at the end to specify that you want the molecule to rotate, mentioning the bond, its rotation degrees and also the number of rotations you want it to make.

For example in the pentane molecule, you want it to rotate by the central two bonds. So to do it, you add the following lines to the end of the code :

```
1 2 3 4 S 18 20.0
2 3 4 5 S 18 20.0
```

Where the first four numbers specify the bond, the second last representing the number of steps, and the last representing the angle to rotate for every step.

III. RESULTS

To get the energy surface graph, open the file in Gaussian and go to Results and go to scans to find the surface energy scans. It should look something like this :

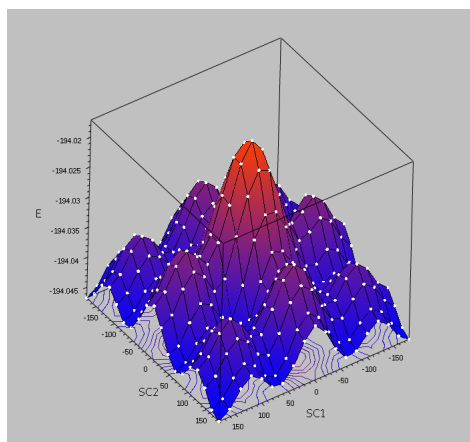


Fig. 1. Surface Energy

IV. ANALYSIS

This is the 3-d graph of energy, the two axes representing the two bonds and the z axis representing the energy. The following graph can be thought of as two 2-d graphs of bond vs energy, having different conformers. So it can be assumed that at a particular conformer of one bond, the other bond can have all the conformers for it. This can also be visualized by the graph.

Hence to find the minimas, it can be seen that minimas occur at conformers when both the bonds have low energy. Thus the minimas will occur at Anti-Anti, Gauche-Gauche and Anti-Gauche conformers.

- Anti - Anti Conformer

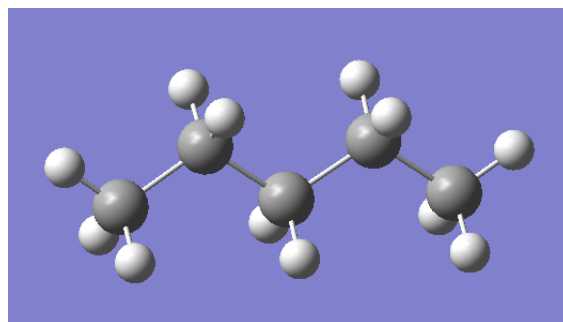


Fig. 2. Anti-Anti Conformer

$$\Delta E_{Anti-Anti} = -194.04493$$

- Anti - Gauche Conformer

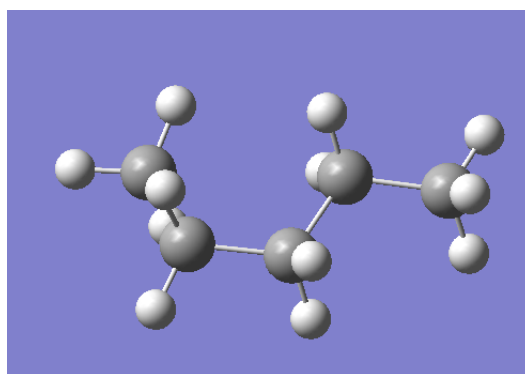


Fig. 3. Anti-Gauche Conformer

$$\Delta E_{Anti-Gauche} = -194.04342$$

- Gauche - Gauche Conformer

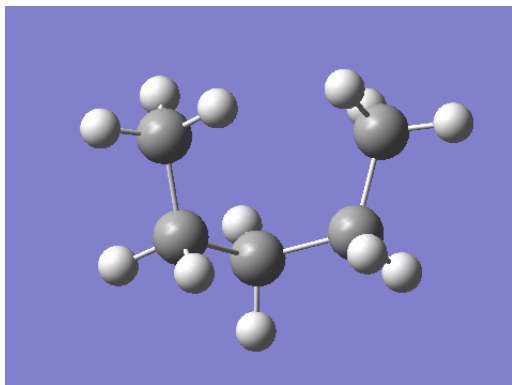


Fig. 4. Gauche-Gauche Conformer

$$\Delta E_{Gauche-Gauche} = -194.04342$$

It is known that Anti is more stable than Gauche conformer, thus if the following data is extrapolated the trend expected is that Anti-Anti conformer will be the most stable with Anti-Gauche following it and finally Gauche-Gauche conformer.

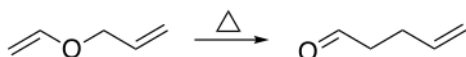
Thus, the energy availed is as expected.

V. CONCLUSION

Minimas of a molecule when it rotates from two bonds can be considered as a set of rotations of a single bond about different conformers of the other bond.

Following such analogy, it can be predicted that minimas will be availed when both the bonds are in their minimum energies. This fact is proven in the following experiment.

Claisen Reaction



• Product

Fig. 1. Reaction to be modelled

Abstract—Modelling the reaction given and finding out its properties.

I. INTRODUCTION

IN the following project we are going to model the reaction given from the transition state via an IRC calculation.

II. CONSTRUCTION

Find the transition state of the reaction and model it using Gaussian. It should look something like this :

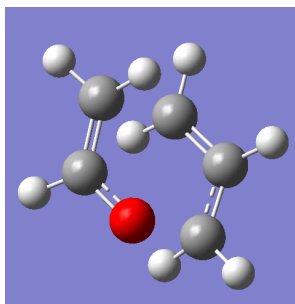


Fig. 2. Reaction to be modelled

In this construction, the bonds between oxygen and the carbon bond is a partial bond similarly with the carbon carbon bond.

Then construct an IRC file and run it to get a reactants and product.

III. RESULT

• Reactants

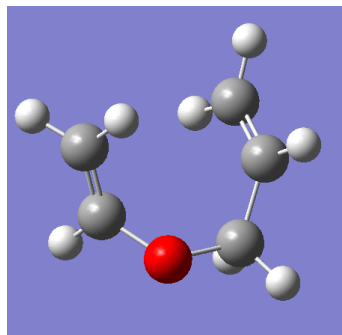


Fig. 3. Reactants

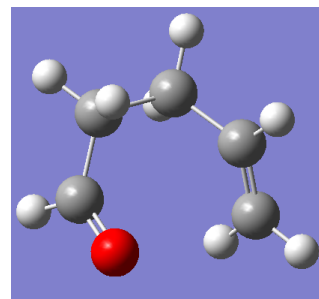


Fig. 4. Product

The IRC graph of the reaction looks like this :

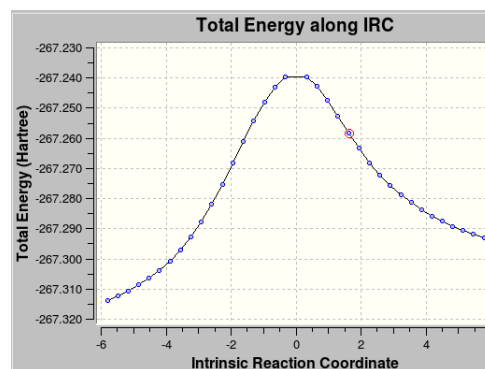


Fig. 5. IRC Graph

IV. ANALYSIS

The following reaction is a Claisen reaction following a pericyclic transition state, in which all the double bonds shift from the current bond to next one, thus forming a domino effect which shifts all the bonds to the next one as carbon cannot have more than one bond. It would be something like this :



Fig. 6. Starting of Formation of Transition State

The question arises as to why will the following bonds want to change their positions, to which the answer lies in the oxygen, which being highly electronegative will attract the π bond's electron pair, thus starting the domino effect, which the other π bonds will have to follow.

V. CONCLUSION

From this experiment, the Claisen reaction was modeled, also helping us in gaining a perspective on how to properly run an IRC scan to get the product that we want.

SN_i Reactions

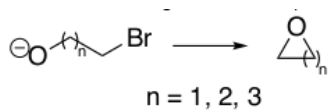


Fig. 1. Reaction to be modelled

Abstract—Modelling similar SN_i reactions and comparing them quantitatively.

I. INTRODUCTION

IN the following project we are going to model similar SN_i reactions and find their relative rates of reactions.

II. CONSTRUCTION

Find the transition state of the reaction and model it using Gaussian. It should look something like this :

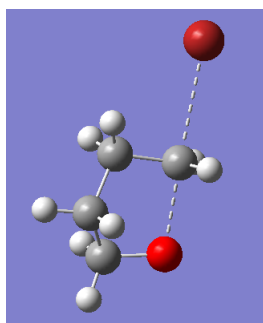


Fig. 2. Reaction to be modelled

Then model the IRC calculation file and run it to find the reactant and the product of the reaction.

III. RESULTS

For each of the reaction the IRC graphs are similar. They are :

- For $n=1$

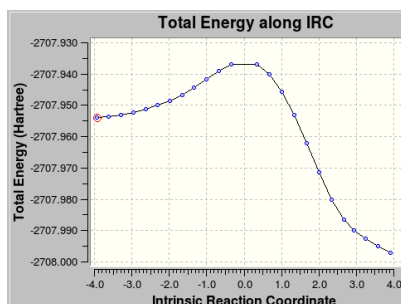


Fig. 3. IRC

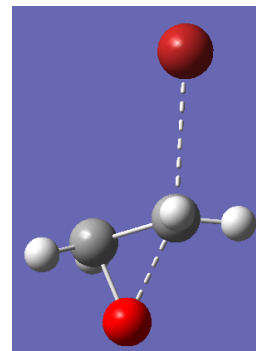


Fig. 4. Transition State

- For $n=2$

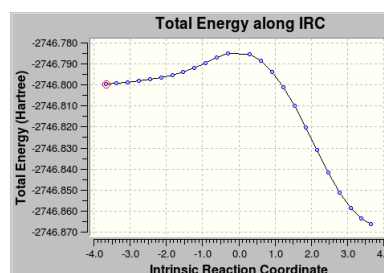


Fig. 5. IRC

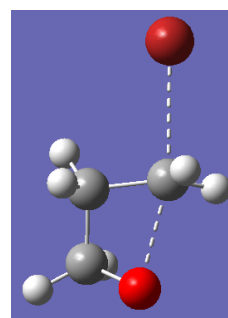


Fig. 6. Transition State

- For $n=3$

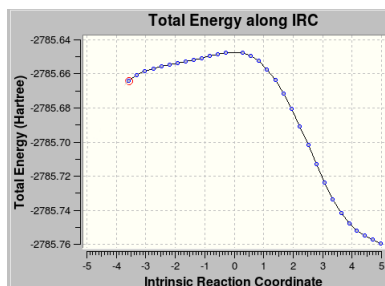


Fig. 7. IRC

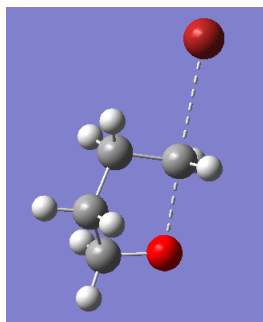


Fig. 8. Transition State

IV. ANALYSIS

It can be seen that the E_a reduces as the number of carbons in the chain increases. The following relation is known :

$$k \propto e^{-E_a/RT}$$

$$k \propto dA/dT$$

This equations tells us that the rate of reaction increases with reduction in activation energy. From the IRC graphs the E_a of the reaction can be calculated. That is :

$$E_{a1} = 0.01784$$

$$E_{a2} = 0.01508$$

$$E_{a3} = 0.00971$$

From this $e^{-E_a/RT}$ can be calculated. It is as follows (taking $T = 300$ K and $RT = 0.593$ kcal/mol) :

$$k_1 \propto 6.33035869 \times 10^{-9}$$

$$k_2 \propto 1.17440316 \times 10^{-7}$$

$$k_3 \propto 3.448742 \times 10^{-5}$$

Thus relatively, the five ring structure will progress the fastest followed by chain of four and finally ended by a carbon chain of three.

The change in the rate of reaction is due to ring strain.

Ring strain occurs because all the sp_3 carbons want to have a bond angle of 109.28° but in a ring can only get a certain angle. This difference creates a strain, which increases the energy, thus making the product more unstable than the reactant. This makes the transition state more unstable, thus decreasing the rate of reaction.

For example, the ring is of three members, each angle will be of about 60° degrees. But the carbons want the angle of 109.8° thus making the molecule highly unstable and subsequently the reactant that much more stable(reactively).

The order of $e^{-E_a/RT}$ also tells us that the reaction with $n = 3$ progresses at a much rapid rate than that of reactions with $n = 2$ & $n = 1$. This fact puts out a point that a five member ring is exceptionally stable thus making the transition state that much more stable and thus allowing the reaction to take place more easily.

V. CONCLUSION

This experiment concludes that the rate of reaction depends on the relative stability of the reactants and the products. One of the factors contributing to the stability of the molecule is the ring strain, whose effect is quite apparent in the experiment conducted.

We also concluded that a ring with a five members is exceptionally stable and thus has a much higher rate of reaction.

Base Pair Interactions in DNA

Abstract—Finding out the energies of the interactions between the base pairs in a DNA molecule.

I. INTRODUCTION

IN the following project we are going to model the base pairs in the DNA molecule, them in the same universe, thus forming an interaction between the base pairs, availing us the values of the molecules.

II. CONSTRUCTION

Model the molecules using Gaussian and place them close enough to enable them to interact with each other and thus form H-bonds. It should look like this :

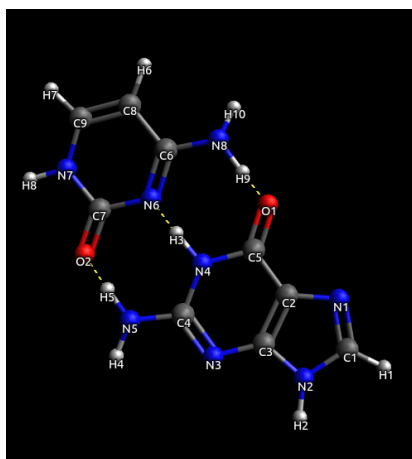


Fig. 1. DNA molecule

III. RESULTS

The energies of the following molecules is :

- Adenine

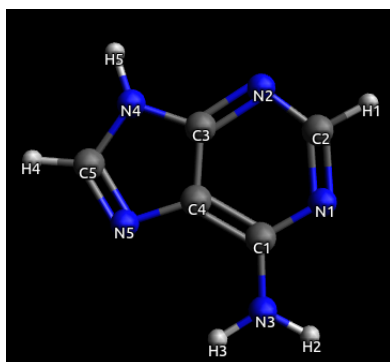


Fig. 2. DNA molecule

$$\Delta E = -458.624259192$$

- Thymine

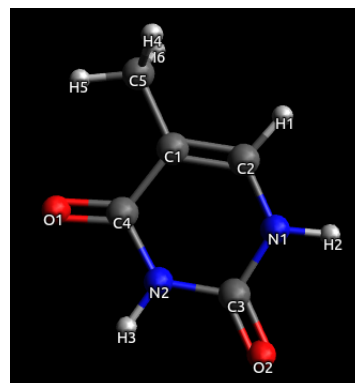


Fig. 3. DNA molecule

$$\Delta E = -445.671276532$$

- Guanine

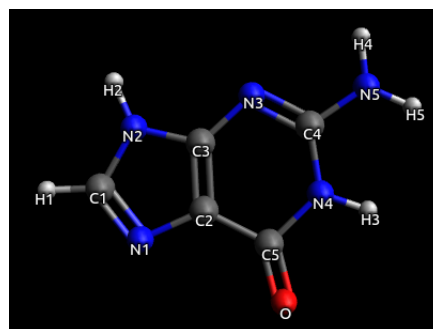


Fig. 4. DNA molecule

$$\Delta E = -532.460423455$$

- Cytosine

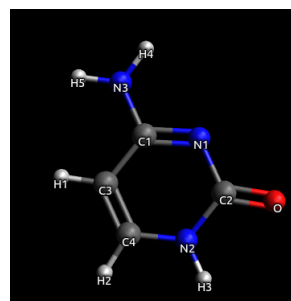


Fig. 5. DNA molecule

$$\Delta E = -387.549253356$$

- Adenine-Thymine

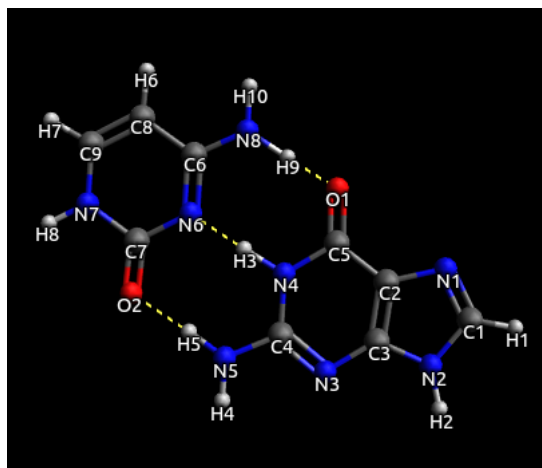


Fig. 6. DNA molecule

$$\Delta E = -904.316526978$$

- Guanine-Cytosine

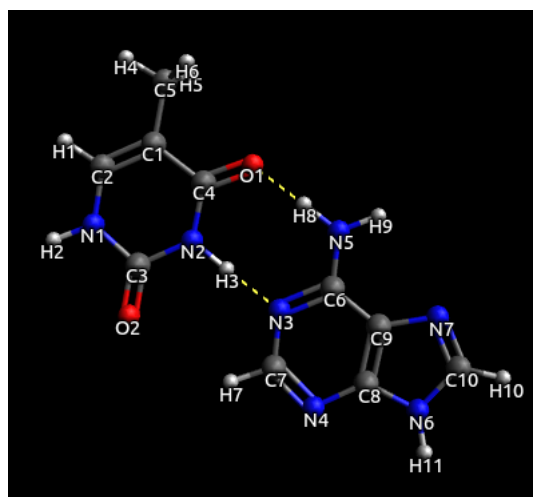


Fig. 7. DNA molecule

$$\Delta E = 920.05838953$$

IV. ANALYSIS

From the following data, the interaction energy can be extracted in the following manner :

$$\Delta E_{Interaction} = \Delta E_{Combined} - \Delta E_{Separate}$$

Hence, the H bonding energy for Adenine Thymine Base :

$$\Delta E_{AT-R} = -0.023425514$$

$$\Delta E_{GC-R} = -0.048713053$$

V. CONCLUSION

From this experiment, it can be shown that the base pair interactions help the DNA base molecules to be much more stable than they would be without it. It also provides us with the fact that the Guanine - Cytosine interaction is much more stable than that of the interaction between Adenine - Thymine.