

# CNS ASSIGNMENT 4

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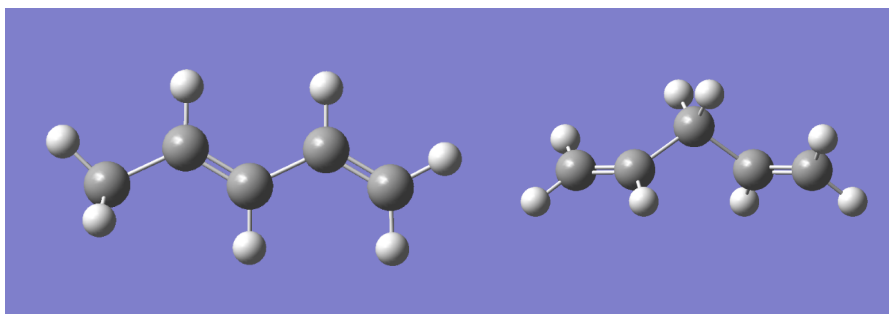
October 6, 2018

## 1 Stabilization due to $\pi$ Conjugation

Considering different isomers of Pentadiene:

- 1,3-Pentadiene
- 1,4-Pentadiene

We observe the energies of the two molecules as:



(a) 1,3-Pentadiene

Energy = -191.60451075 Hartrees

(b) 1,4-Pentadiene

Energy = -191.59406667 Hartrees

In case of fig(b) the double bonds are isolated whereas in fig(a) the double bonds are connected to each other by a single bond and are conjugated.

$$\Delta Energy = 0.0144408 \text{ Hartrees} = 9.0617407476 \text{ kcal/mol} \quad (1)$$

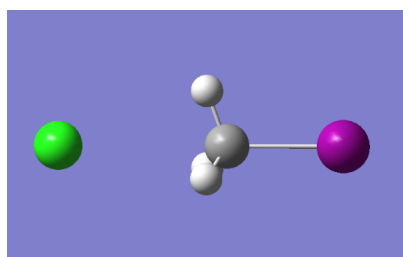
Conjugated dienes are more stable than non-conjugated dienes as the delocalization of electrons in p-orbitals around  $\sigma$  bond takes place due to resonance. The electronic cloud gets dispersed in a conjugated double bonded molecule on the otherhand, the non conjugated double bond systems, the electron density around the double bond is not in dispersed state rather is in localised state and hence makes the  $\pi$  bond weak.

## 2 Energy of Transition State in an $S_N2$ Reaction

The problem statement claims that the energy of the transition state involved in an  $S_N2$  reaction is more stable than the sum of the energies of the reactants or that of the products.

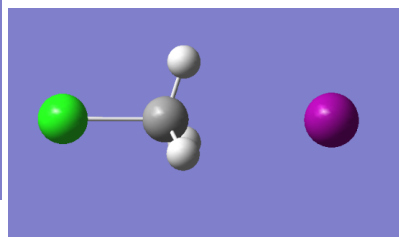
Let us consider the following reaction and analyze the claim made in the problem set :





(a) Initial State

Energy( $\text{CH}_3\text{I}$ )=-6850.60529503  
Hartrees  
Energy( $\text{Cl}^-$ )=-493.72622864  
Hartrees



(b) Final State

Energy( $\text{CH}_3\text{Cl}$ )=-454.4947513  
Hartrees  
Energy( $\text{I}^-$ )=-6889.8397568 Hartrees

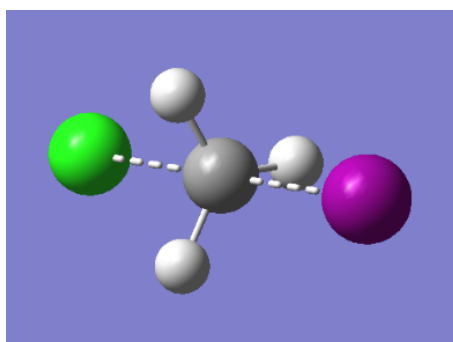


Figure 3: Transition State

Energy=-7344.30800698 Hartrees

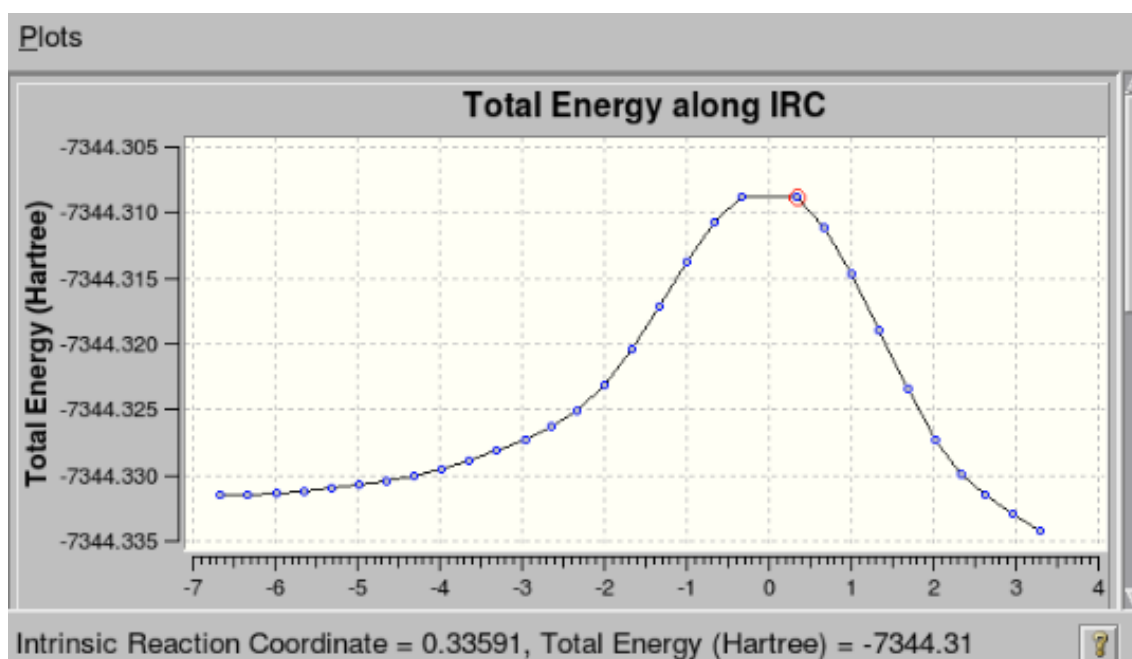


Figure 4: IRC Graph

$$Energy_{\text{Reactants}} = -493.72622864 + -6850.60529503 = -7344.33152367 \text{Hartrees} \quad (3)$$

$$Energy_{\text{Products}} = -454.4947513 + -6889.8397568 = -7344.3345081 \text{Hartrees} \quad (4)$$

$$Energy_{\text{Transition State}} = -7344.30800698 \text{Hartrees} \quad (5)$$

We can clearly infer from the above data that the Energy<sub>Transition State</sub> is less negative than the sum of the products and sum of the reactants both due to intermolecular forces, therefore it is less stable. This can also be verified from the graph. Thus, the question statement is false.

### 3 Potential Energy Surface and Conformations of Pentane

We obtain the different conformers of Pentane using the 'opt=modredundant' keyword and specifying two extra lines at the end of the .com file:

```
X Y Z W (S) [STEPS] [ANGLE]
```

```
Y Z W T (S) [STEPS] [ANGLE]
```

```
1 2 3 6 S 20 18.0
```

```
2 3 6 9 S 20 18.0 .
```

The dihedral angle of plane X-Y-Z and Y-Z-W changes about the central Y-Z bond and same for central Z-W bond, where X, Y, Z, W, T are atoms.

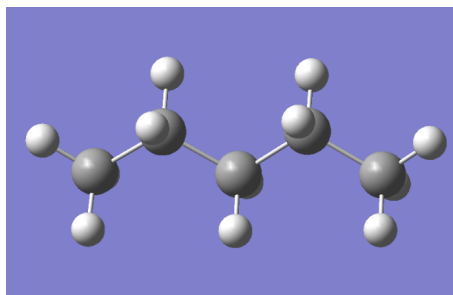


Figure 5: Pentane

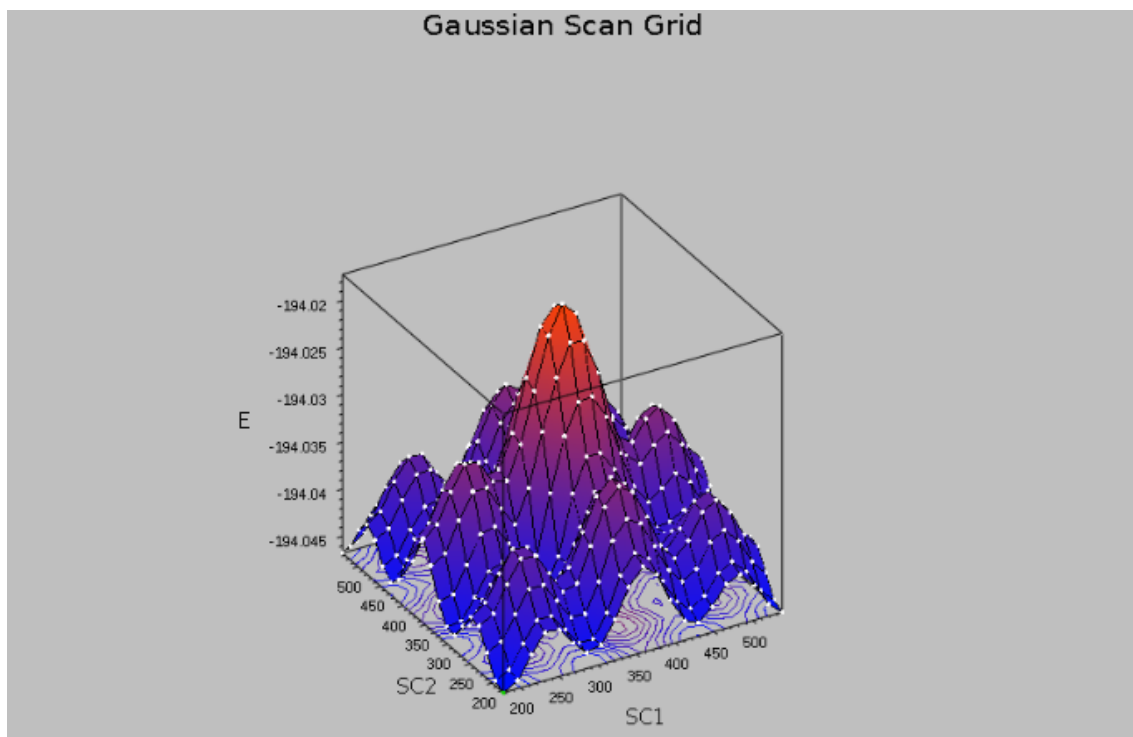
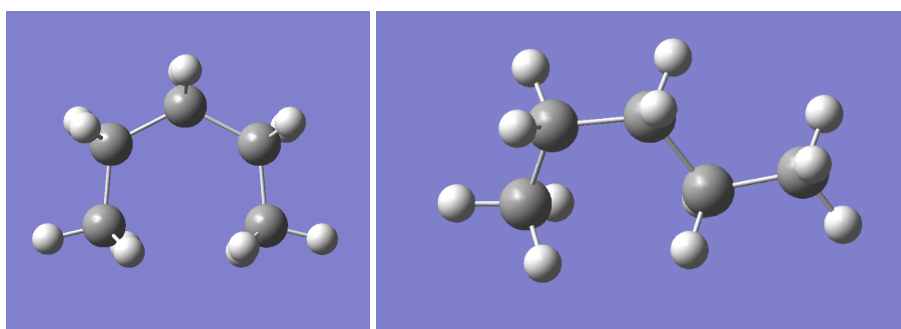
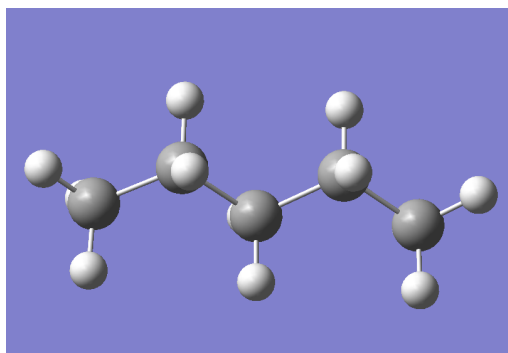


Figure 6: Potential Energy Surface

Several conformers of the Pentane molecule are acquired by rotating the molecule along C2-C3 and C3-C4.



(a) Gauche-Gauche (Maxima - Highest peak ) (b) Anti-Gauche (Intermediate maxima- smaller peaks)



(c) Anti-Anti (Minima - corners)

The energy values of the conformers are as follows:

$$Energy_{\text{Gauche-Gauche}} = -194.017 \text{ Hartrees} \quad (6)$$

$$Energy_{\text{Anti-Gauche}} = -193.031 \text{ Hartrees} \quad (7)$$

$$Energy_{\text{Anti-Anti}} = -194.047 \text{ Hartrees} \quad (8)$$

The order of stability among the conformers is:

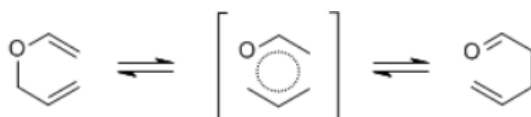
$$Energy_{\text{Gauche-Gauche}} < Energy_{\text{Anti-Gauche}} < Energy_{\text{Anti-Anti}}$$

The conformer with the least energy (most stable) is present at all corners of the scan plot is the Anti-anti conformer, this is because the distance between all of the bonds is as far away from each other as possible and the electron repulsions are the least.

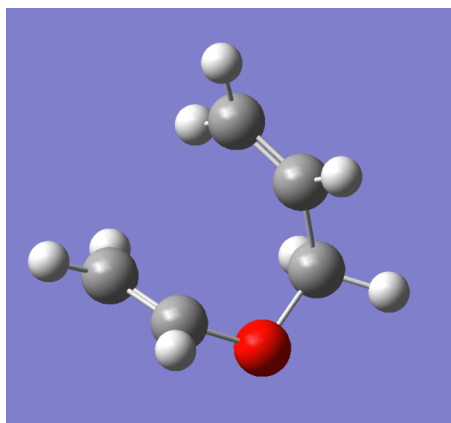
The saddle points contain energy values for Anti-Completely Eclipsed, Gauche-Completely Eclipsed, Anti-Partially Eclipsed and Gauche-Partially Eclipsed conformers.

## 4 Model of a reaction that demonstrates Claisen Rearrangement

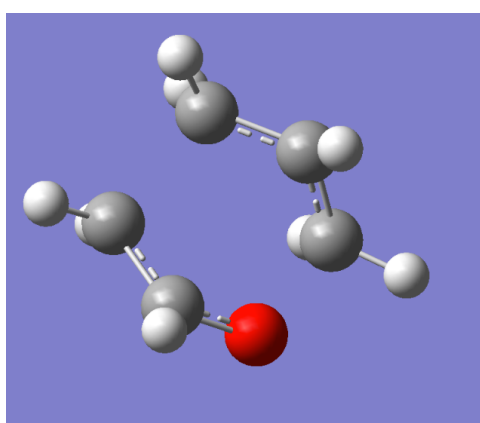
We illustrate and simulate the following reaction using Gaussian and IRC computed values.



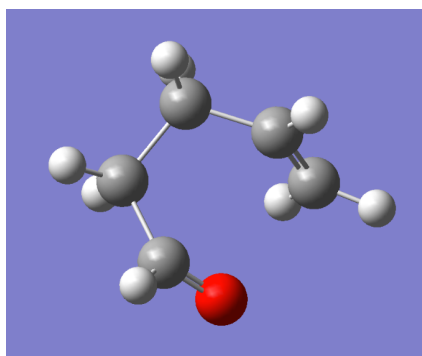
The different stages of the reaction are as follows:



(a) Ether



(b) Pericyclic Transition State



(c) Aldehyde

The graph below corresponds to the reaction as it proceeds from

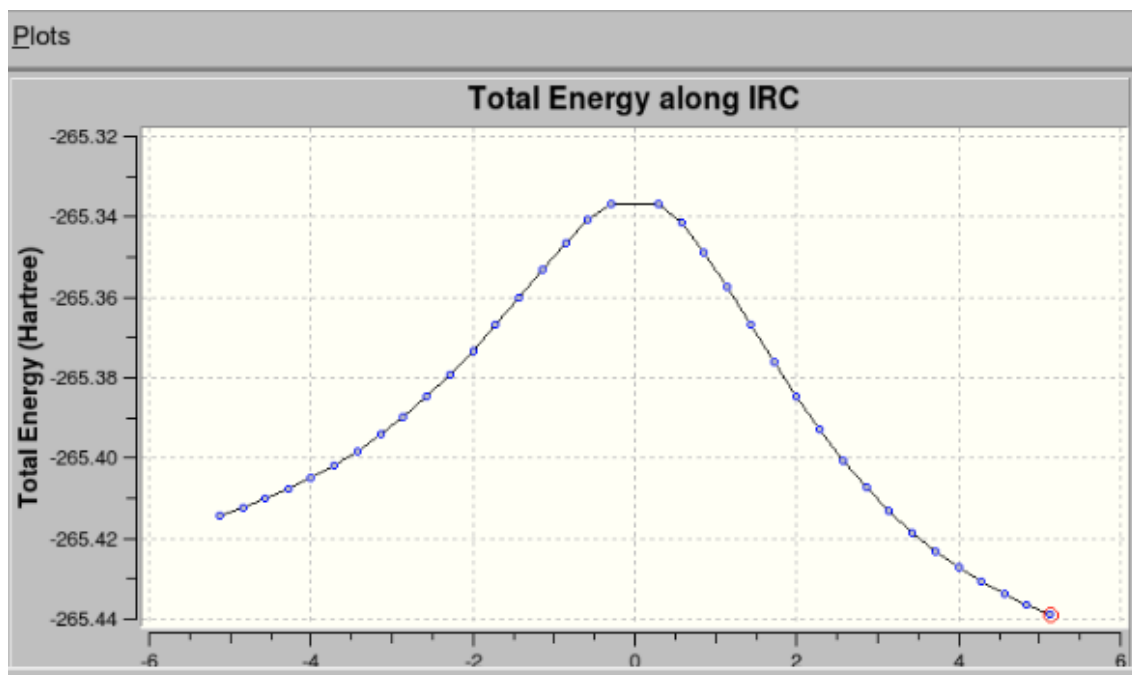
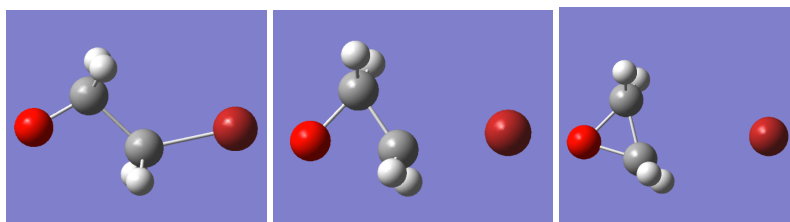


Figure 9: IRC Graph

The Ether changes into a more stable Aldehyde when it is exposed to heat while changing into a pericyclic transition state in the process.

## 5 Cyclic Ether Reactions

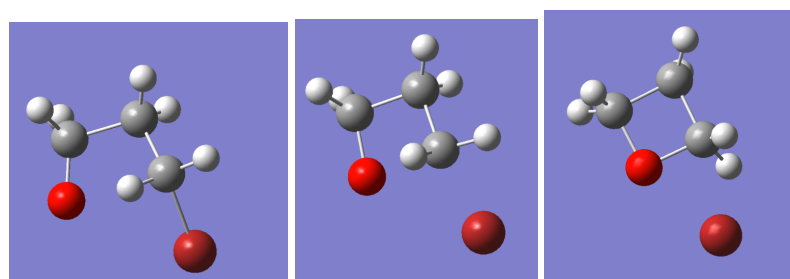
### 5.1 Case1: n=1



(a) Initial State      (b) Transition State      (c) Final State

$$Energy_{\text{Activation}} = 0.01785 \text{ Hartrees} = 11.201047 \text{ kcal/mol} \quad (10)$$

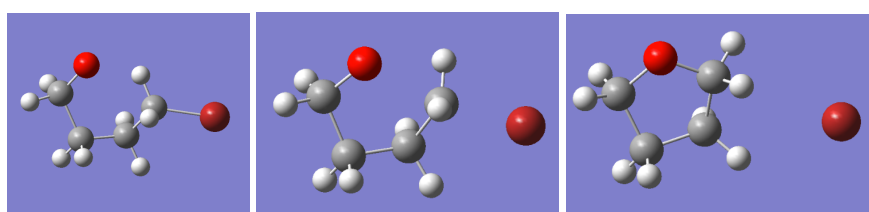
### 5.2 Case2: n=2



(a) Initial State      (b) Transition State      (c) Final State

$$Energy_{\text{Activation}} = 0.01520 \text{ Hartrees} = 9.538146 \text{ kcal/mol} \quad (11)$$

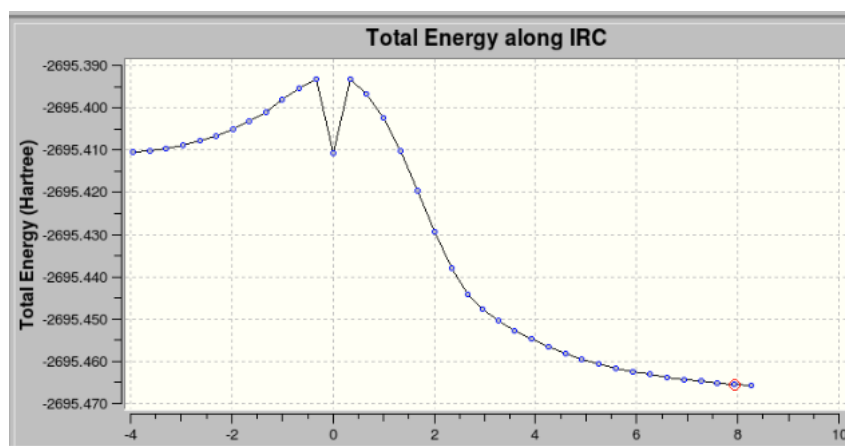
### 5.3 Case3: n=3



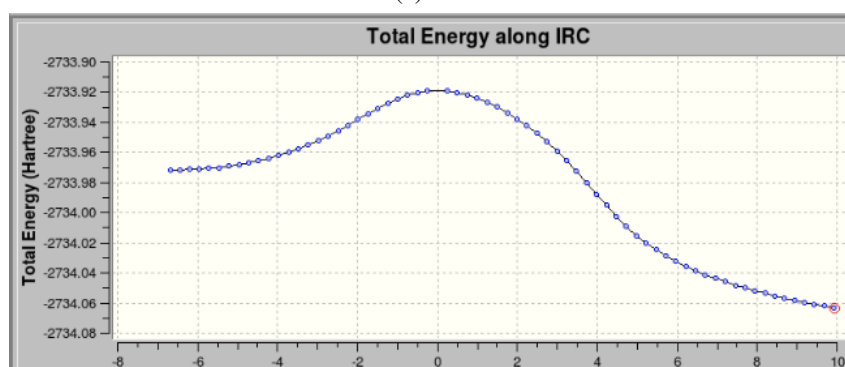
(a) Initial State      (b) Transition State      (c) Final State

$$Energy_{\text{Activation}} = 0.00963 \text{ Hartrees} = 6.0429175 \text{ kcal/mol} \quad (12)$$

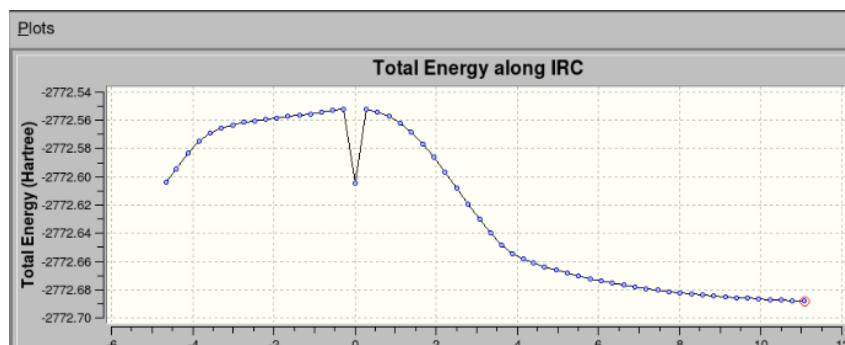
## 5.4 Comparing IRC Graphs of the three cases



(a)  $n=1$



(b)  $n=2$



(c)  $n=3$

**\*\*The drops in the above graphs are attributed to the anomalies in Gaussian\*\***

Case3, where  $n=3$ , is the most favourable as the ring strain in the thus formed product is minimum as compared to when  $n=2$  and  $n=1$ . The instability that occurs due to too close rings or rings where angles are too small is called ring strain, eg. the strain is most common for small rings such as cyclopropanes and cyclobutanes.

## 5.5 Analysing Rates of Reaction

As the ring strain is minimum in case of  $n=3$  which implies that the reaction in Case3 proceeds the fastest. The Rate of each reaction can be acquired from the Arrhenius equation:



$$k = Ae^{-\frac{E_a}{RT}}$$

Figure 14: IRC Graph

Assuming that,

A - Pre-exponential Factor

R - Gas Constant

T - Temperature (Kelvin) is constant .

The ratio of the rates at STP (RT = 0.593 kcal/mol) is:

$$k_1 : k_2 : k_3 \quad (13)$$

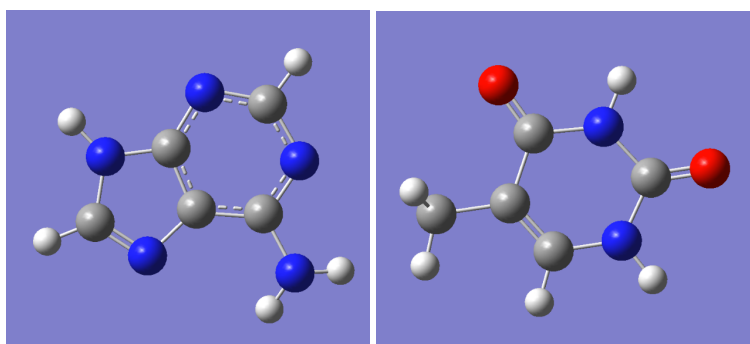
$$= e^{-11.201047/0.593} : e^{-9.538146/0.593} : e^{-6.0429175/0.593} \quad (14)$$

$$= e^{-18.8887} : e^{-16.0845} : e^{-10.1904} \quad (15)$$

⇒ The rate of reaction for n=3 i.e. 5 membered ring is much greater in comparison to the other two cases.

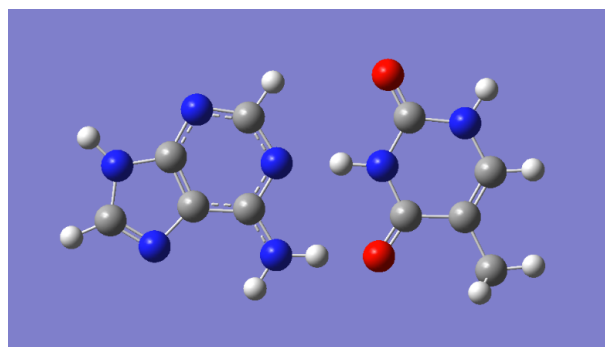
## 6 Analysis of Interactions in G:C and A:T base pairs

### 6.1 Adenine-Thymine base pair



(a) Adenine

(b) Thymine



(c) A:T

The interactions in Adenine-Thymine base pair are:

- Hydrogen bonding between H (Thymine) and N (Adenine)
- Hydrogen bonding between O (Thymine) and H (Adenine)

The energy values of the Adenine-Thymine base pairs are as follows:

$$Energy_{\text{Adenine}} = -458.62425917 \text{ Hartrees} \quad (16)$$

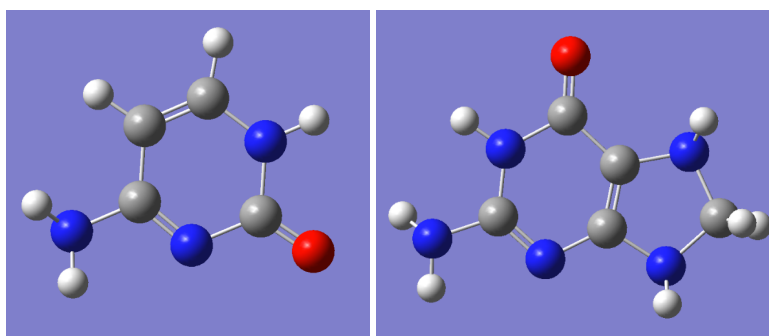
$$Energy_{\text{Thymine}} = -445.67127686 \text{ Hartrees} \quad (17)$$

$$Energy_{\text{A:T}} = -904.31848679 \text{ Hartrees} \quad (18)$$

The lowered energy attributed to the interactions in this base pair is:

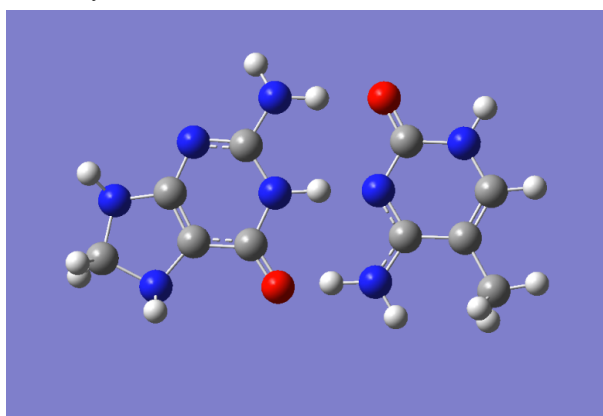
$$\Delta Energy = -0.02295076 \text{ Hartrees} \quad (19)$$

## 6.2 Cytosine-Guanine base pair



(a) Cytosine

(b) Guanine



(c) C:G

The interactions in Cytosine-Guanine base pair are:

- Hydrogen bonding between H (Guanine) and O (Cytosine)
- Hydrogen bonding between H (Guanine) and N (Cytosine)
- Hydrogen bonding between O (Guanine) and H (Cytosine)

The energy values of the Cytosine:Guanine base pairs are as follows:

$$Energy_{\text{Cytosine}} = -387.549253370 \text{ Hartrees} \quad (20)$$

$$Energy_{\text{Guanine}} = -532.02200601 \text{ Hartrees} \quad (21)$$

$$Energy_{\text{C:G}} = -920.058389919 \text{ Hartrees} \quad (22)$$

The lowered energy attributed to the interactions in this base pair is:

$$\Delta Energy = -0.487130539 \text{ Hartrees} \quad (23)$$

As inferred, there are three Hydrogen bonds present in the C:G base pair and two of them are strongly polarised due to the presence of oxygen as compared to A:T base pair which contains only two Hydrogen bonds and only one of which contains an oxygen.

Thus we can conclude that C:G base pair is more stable than A:T base pair as the energy reduces much more in C:G base pair than A:T due to much stronger interactions within each of these base pairs.