

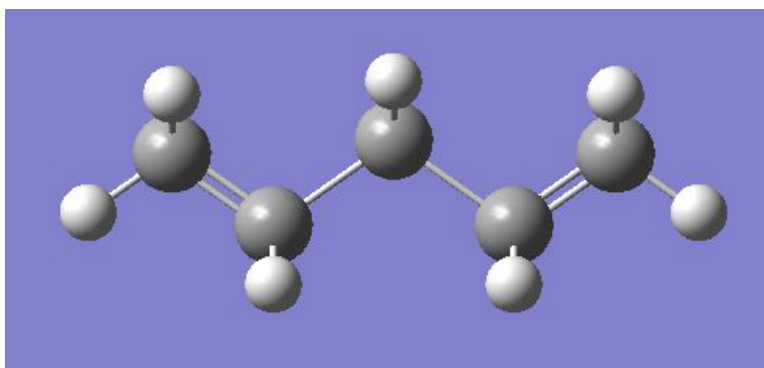
ASSIGNMENT 4 CNS

KUSHAGRA AGARWAL 2018113012

Q1) Stabilisation Through Pi-Conjugation

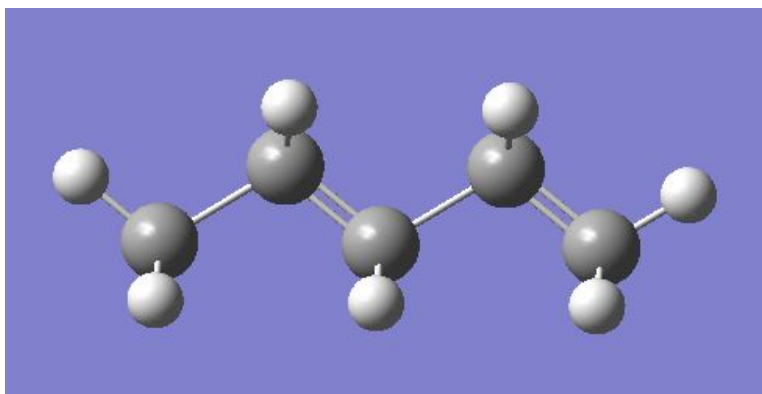
To prove that Pi-Conjugation stabilises a molecule, we shall use the example of Pentadiene. 1-4-Pentadiene does not have Pi conjugation, whereas, 1-3-Pentadiene has Pi Conjugation as the two Pi bonds are alternate, which is the required condition for Pi Conjugation to exist.

1-4-Pentadiene



Energy= -195.147044132 hartrees or -122456.5265164 kJ/mol

1-3-Pentadiene

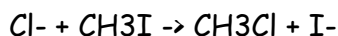


Energy= -195.147816564 hartrees or -122456.5265165 kJ/mol

As can be seen from the results, the energy of 1-3-Pentadiene is more negative, implying that it is more stable than 1-4-Pentadiene. The Pi Conjugation reduces energy of the compound as the canonical structures have the pi bond moving over 3 Carbons, whereas in Non Pi Conjugating compounds, this does not happen, hence the stability is reduced or conversely the energy increases. Therefore, the proposition that Pi Conjugation stabilises organic molecules stands correct.

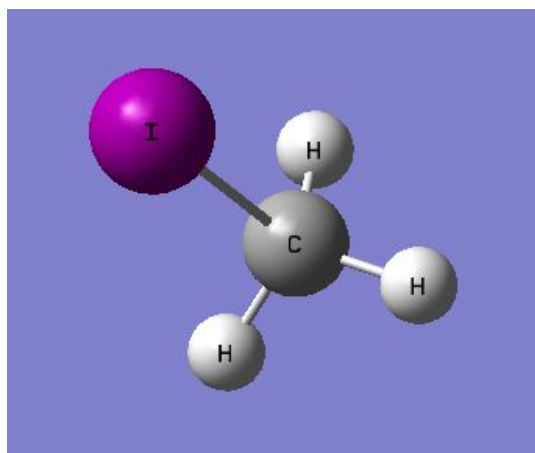
Q2) Energy Comparisons in SN2 Reactions

The SN2 reaction that we are going to analyse is:

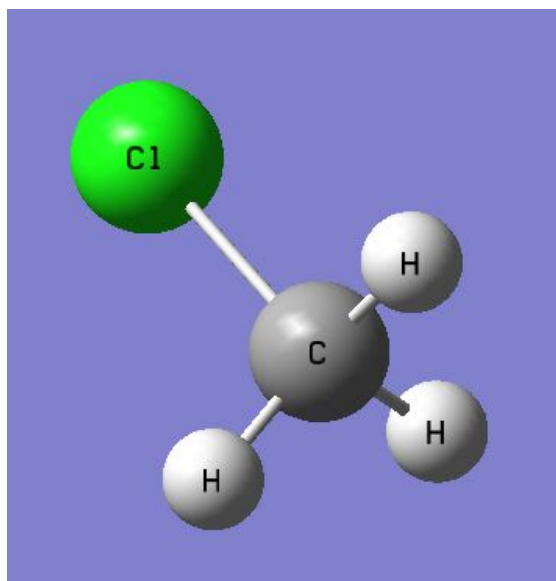


Here the reactants are Cl^- and CH_3I , and the products are I^- and CH_3Cl .

Reactant



Product



Energy of Reactants-

- 1) Cl^- = -454.353585381 hartrees
- 2) CH_3I = -6888.23411281 hartrees

Sum of Energy of Reactants= -7344.58769819 hartrees

Energy of Products-

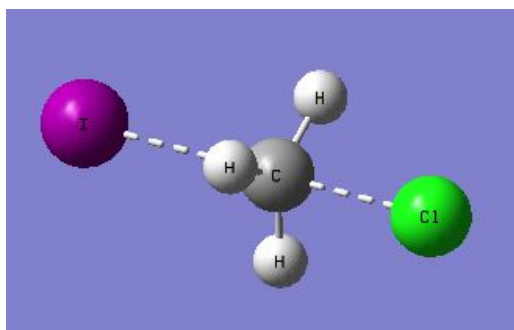
1) I- = -6850.913012591 hartrees

2) CH₃Cl= -493.683411281 hartrees

Sum of Energy of Products= -7344.59645026 hartrees

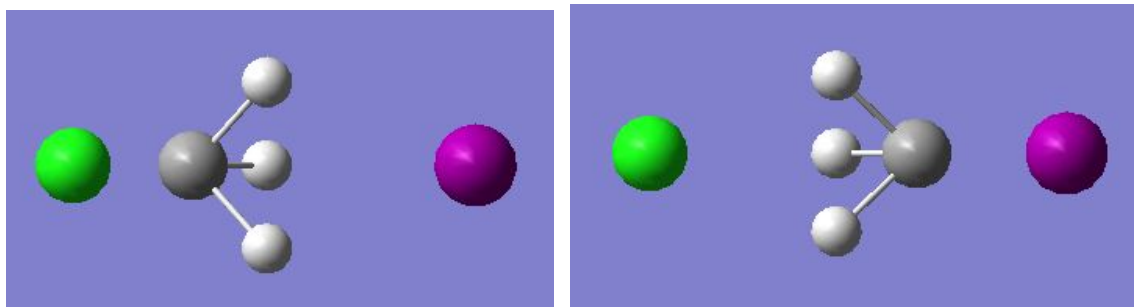
Observe, that Energy of Products is less, clearly showing that they are more stable, hence reaction moves in the forward direction.

Transition State



Energy of TS= -7344.30395324 hartrees

Transition State in Animation



Energy of TS is greater than both the sum of energy of reactants and products. This is an expected result as the Transition State corresponds to the state of the reaction when the energy is highest and stability the least. Therefore, the given statement that the TS must

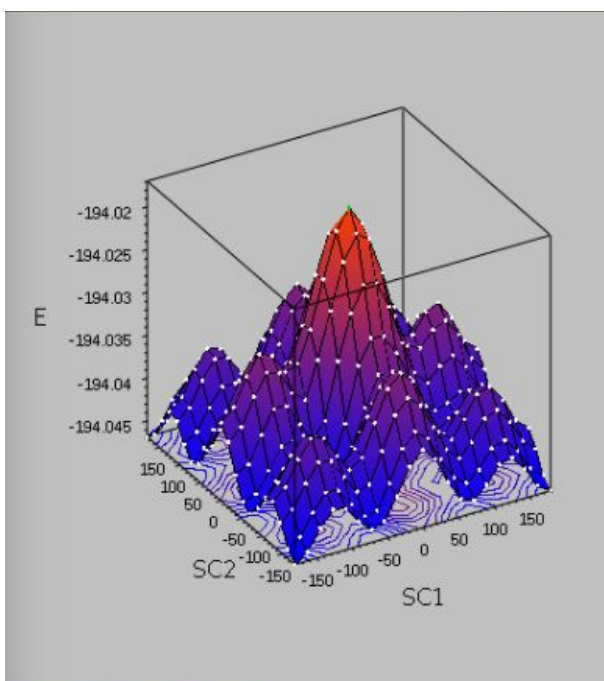
have more stability than sum of energies of reactants and products is false and does not stand.

In fact, we can also calculate the activation energy for the forward reaction :

$$\begin{aligned} E_a &= (\text{Energy of reactants}) - (\text{Energy of TS}) \\ &= (-7344.587619819) - (-7344.30395324) \text{ hartrees} \\ &= -0.283666579 \text{ hartrees} \end{aligned}$$

Q3) 3D Potential Energy Graph

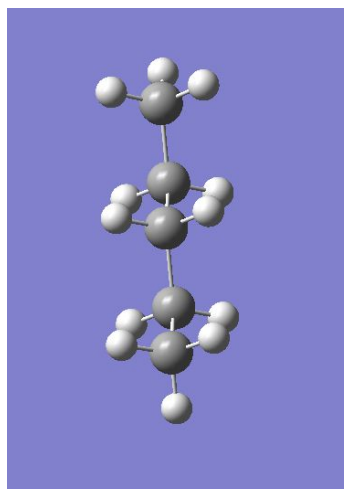
The 3D Potential Energy Graph



The graph was made using 20 modredundants along one C-C bond pair in pentane, and I used two of such pairs. Therefore, we get 400 conformers and their energies were plotted.

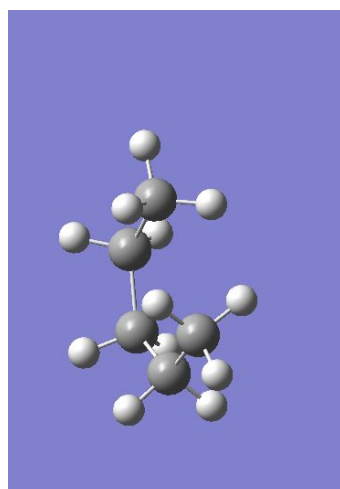
Now, we shall be specifying the most and least stable conformers.

Most Stable Conformer



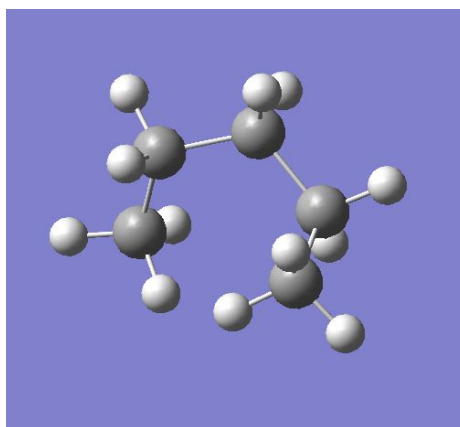
Energy= -194.0463 hartrees

Least Stable Conformer

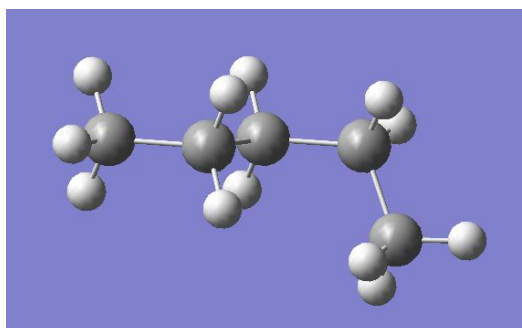


Energy= -194.0168 hartrees

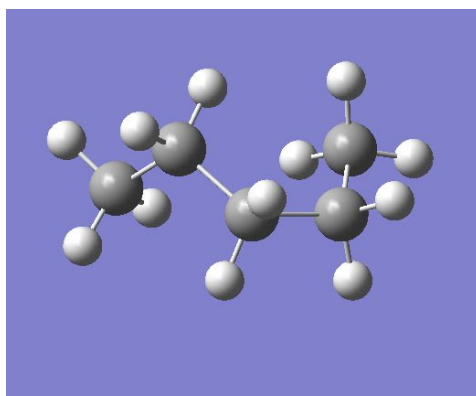
Other Least energy Conformers:



Energy: -194.04 hartrees



Energy: -194.045 hartrees



Energy : -194.034 hatrees

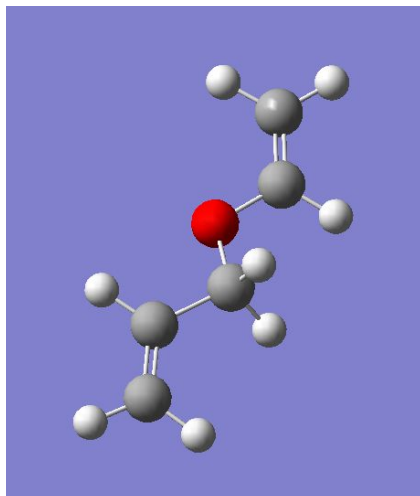
As is evident from the results, the most stable conformer has the least energy and the least stable conformer has the highest energy.

Q4) Modelling the given Reaction

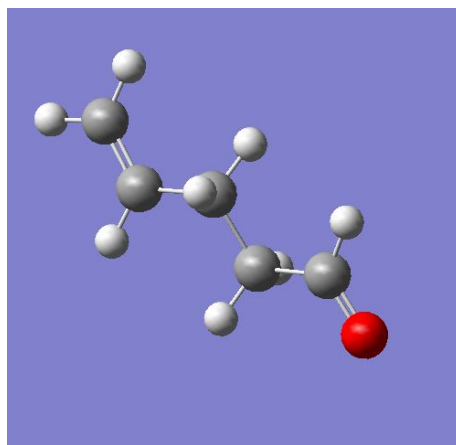
Given reaction is :



Reactant

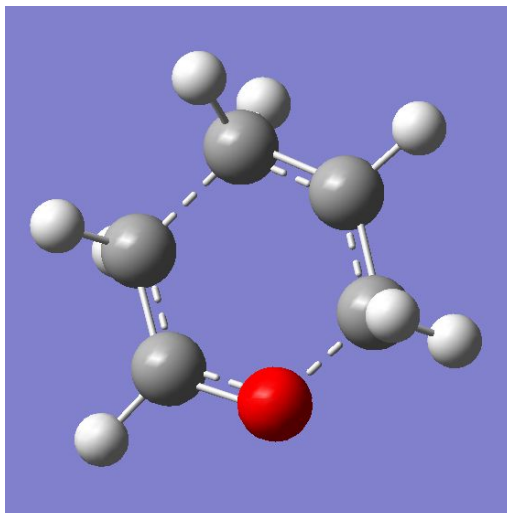


Energy= -265.392 hartrees
Product



Energy= -265.401 hartrees

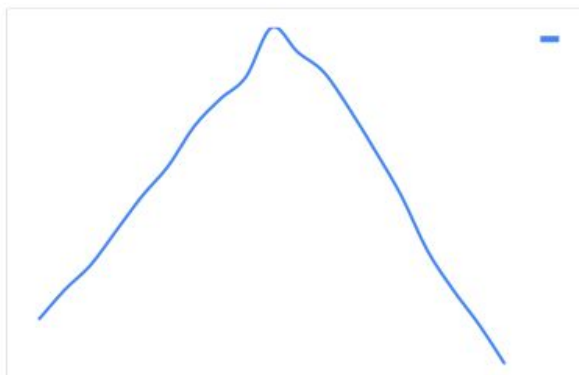
Transition State



Energy= -265.333 hartrees

IRC Graph

-265.392
-265.386
-265.381
-265.374
-265.367
-265.361
-265.353
-265.3475
-265.343
-265.333
-265.338
-265.342
-265.3495
-265.358
-265.367
-265.378
-265.386
-265.393
-265.401



The transition state is a 6 membered ring, which is extremely stable and hence favours the reaction to completion. The Activation energy calculation follows:

$$\begin{aligned}
 E_a &= (\text{Energy of Reactant}) - (\text{Energy of TS}) \\
 &= (-265.392) - (-265.333) \text{ hartrees} \\
 &= -0.059 \text{ hartrees}
 \end{aligned}$$

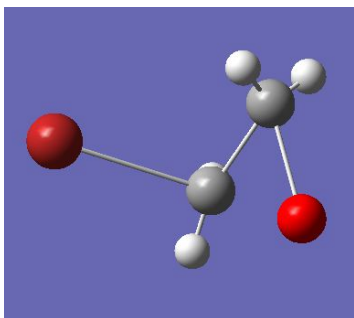
$$\begin{aligned}
 \Delta H &= (\text{Energy of Product}) - (\text{Energy of Reactant}) \\
 &= (-265.401) - (-265.392) \text{ hartrees} \\
 &= -0.009 \text{ hartrees}
 \end{aligned}$$

As ΔH is negative, hence the reaction is favourable in the forward direction.

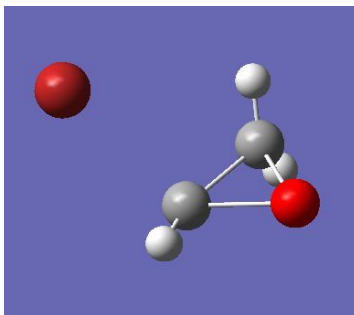
Q5) Qualitative Comparison on Rates of Reactions

1) N=1

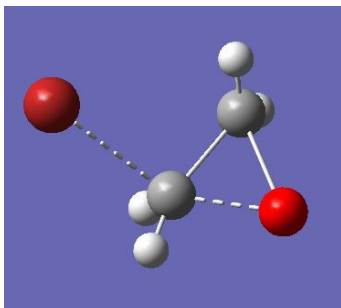
Reactant



Product



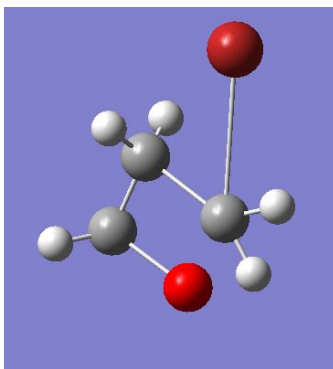
Transition State



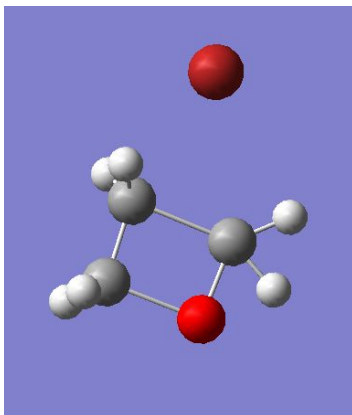
Activation energy = -0.422548 hartrees

2) N=2

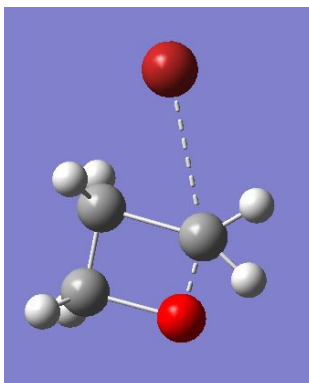
Reactant



Product



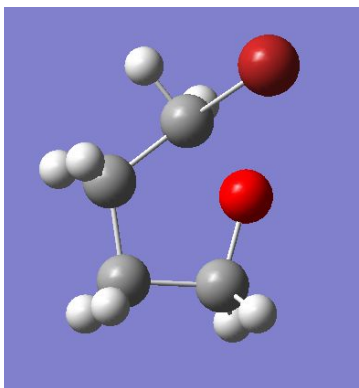
Transition State



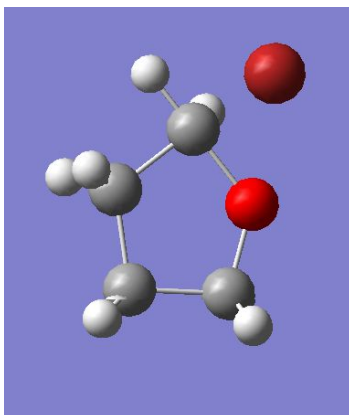
Activation Energy= -0.308973 hartrees

3) N=3

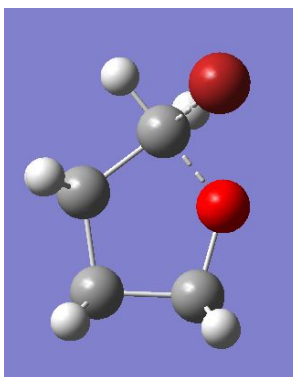
Reactant



Product



Transition State



Activation Energy = -0.016538 hartrees

To Qualitatively compare rates of reactions, we use Arrhenius Equation

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = -\frac{E_a}{RT} + \ln A$$

Where:

k = Chemical Reaction Rate
 A = Pre-exponential Factor
 E_a = Activation Energy
 R = Gas Constant
 T = Temperature in Kelvin

k is directly proportional to $(1/E_a)$

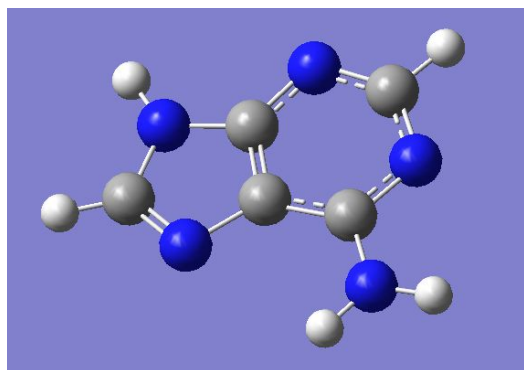
Or k is inversely proportional to E_a

So greater the value of activation energy, lesser is the rate of the reaction at some constant temperature. Comparing activation energies for $n=1, 2, 3$, we find out that activation energies are in the order $1>2>3$, therefore the rates are in the order $3>2>1$.

The trend can be explained on the basis of stability of transition states. $N=1$ has a three membered ring as TS which has high torsional strain and ring strains as the bond angle 60° is far from expected sp^3 bond angle of 109.5° . $N=2$ has a four membered ring as TS which has relatively lower torsional strain as the bond angle 90° is closer to sp^3 109.5° . For $N=3$, we have a five membered ring which has a bond angle of 108° which almost easily accommodates for the expected bond angle of 109.5° . Therefore $N=3$ has the most stable transition state hence qualitatively can be confirmed as the fastest among the three reactions and $N=1$ to be the slowest reaction.

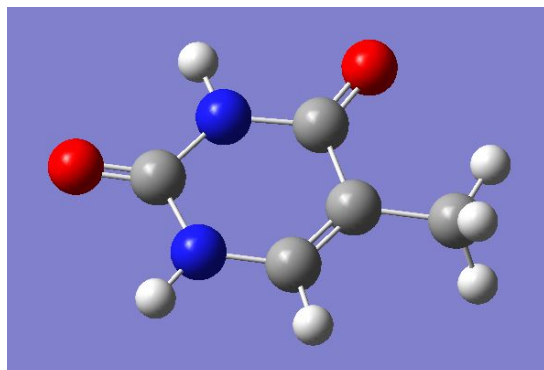
Q6) Comparing Base Pair Interactions in DNA Molecules

Adenine



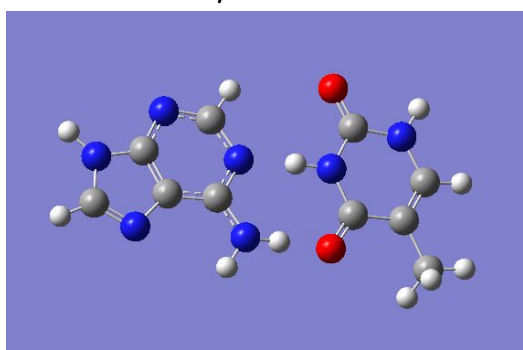
Energy: -458.62155627 hartrees

Thymine



Energy: -445.67005825 hartrees

Adenine-Thymine Interaction

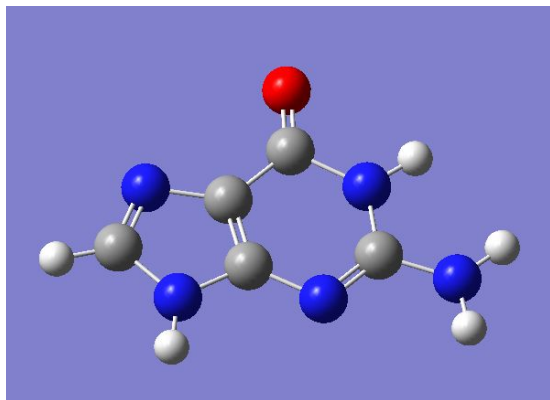


Energy :-904.31875656 hartrees

The Sum of Energies of Adenine and Thymine is -904.29161452 hartrees. It is greater than the energy of A-T pair as the pair forms hydrogen bonds which provide stability and in the process

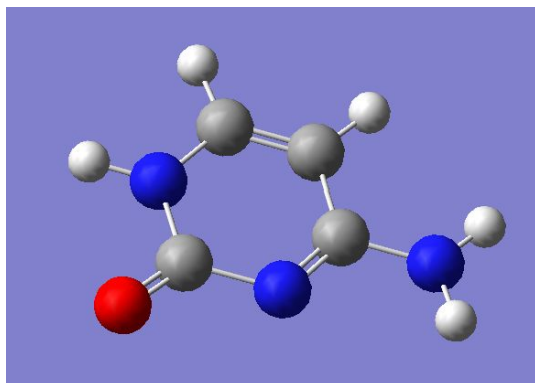
decrease the energy of the molecule. The decrease takes place with a factor of 0.02714204 hartrees.

Guanine



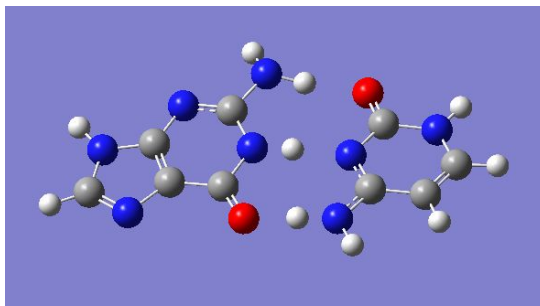
Energy:-532.461929405 hartrees

Cytosine



Energy: -387.54530810 hartrees

Guanine-Cytosine Interaction



Energy:-920.058392974 hartrees

The Sum of Energies of Guanine and Cytosine is -920.007237505 hartrees. It is greater than the energy of G-C pair as the pair forms hydrogen bonds which provide stability and in the process decrease the energy of the molecule. The decrease takes place with a factor of 0.051155469 hartrees.

