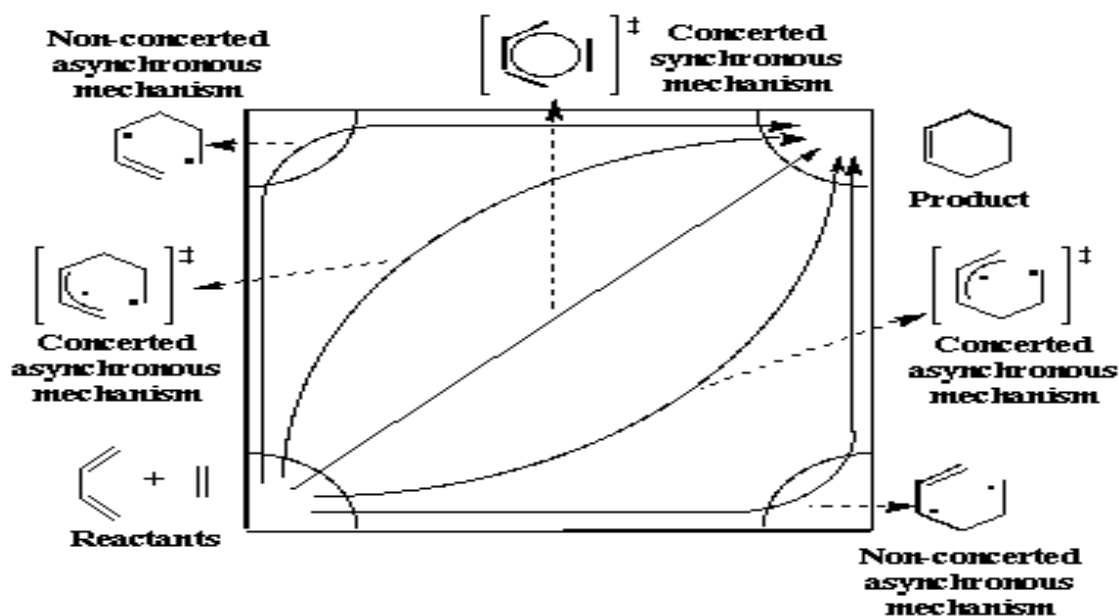
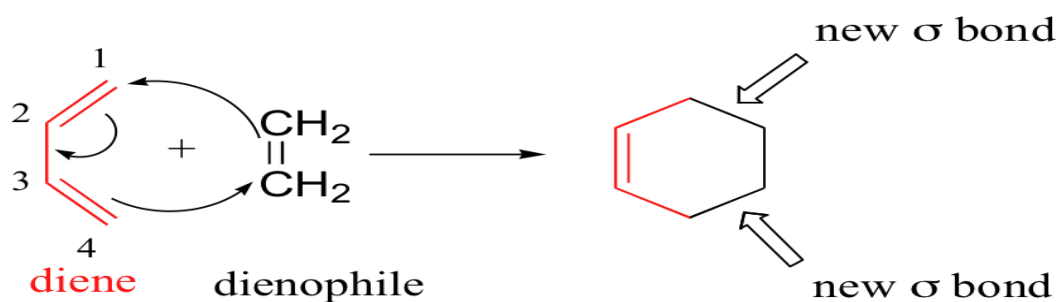
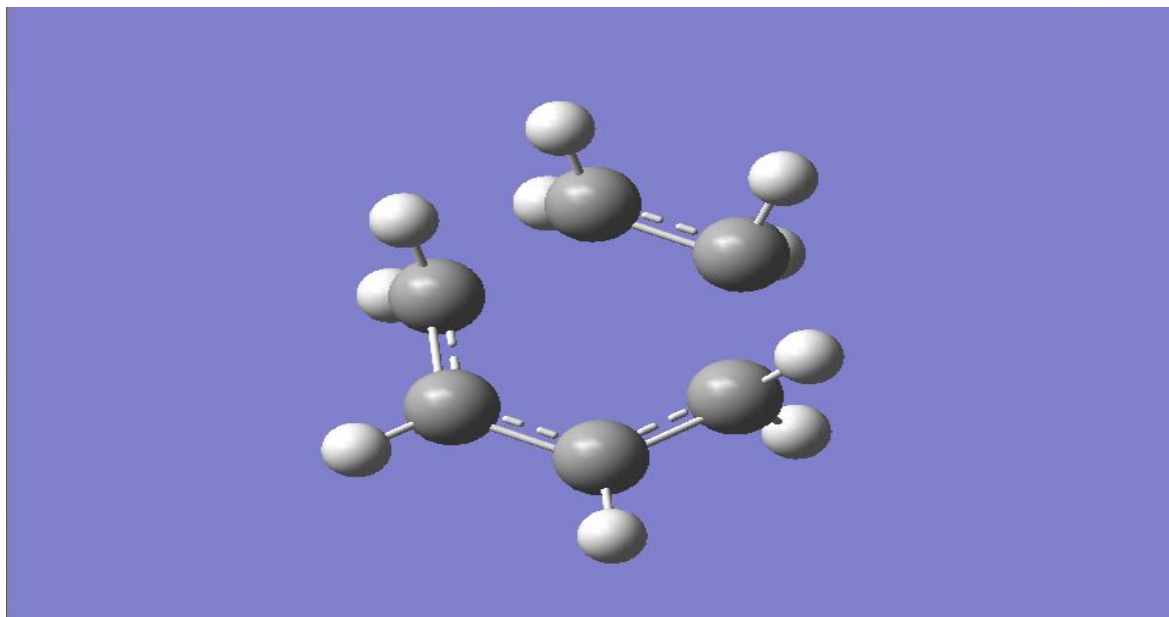


Q1) Diels Alder Reaction

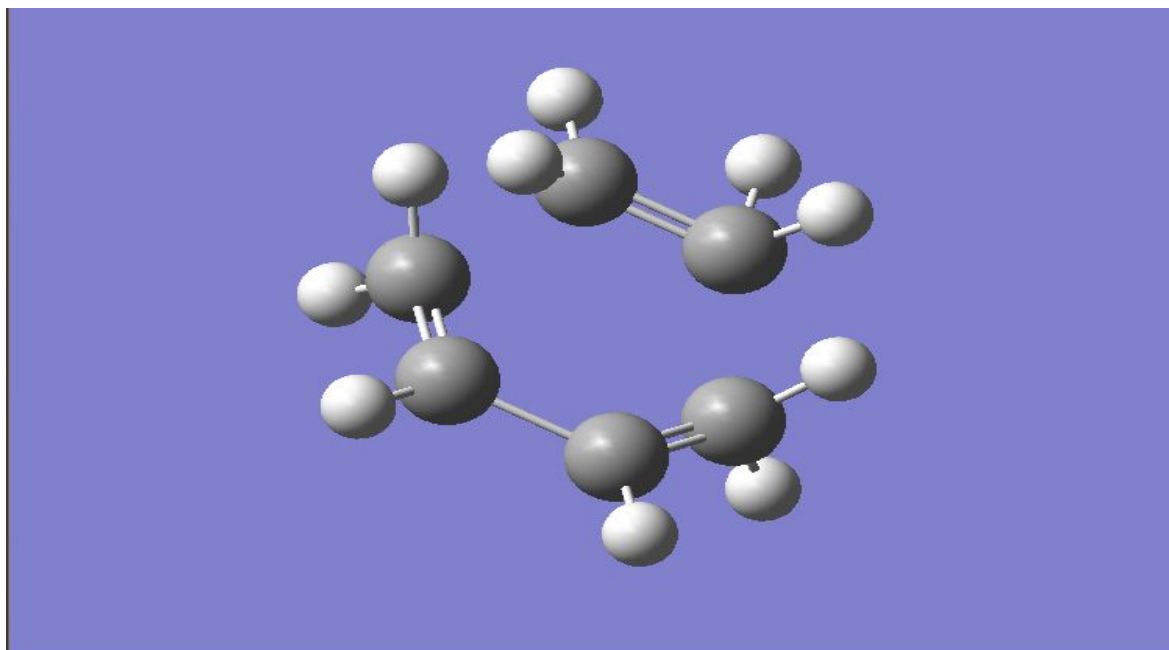
The **Diels-Alder reaction** is an organic chemical reaction between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene derivative. It was first described by Otto Diels and Kurt Alder in 1928, for which work they were awarded the Nobel Prize in Chemistry in 1950. The Diels-Alder reaction is particularly useful in synthetic organic chemistry as a reliable method for forming 6-membered systems with good control over regio- and stereochemical properties. The underlying concept has also been applied to other π -systems, such as carbonyls and imines to furnish the corresponding heterocycles, known as the **hetero-Diels-Alder reaction**. Diels-Alder reactions can be reversible under certain conditions; the reverse reaction is known as the **retro-Diels-Alder** reaction. It is a pericyclic reaction.



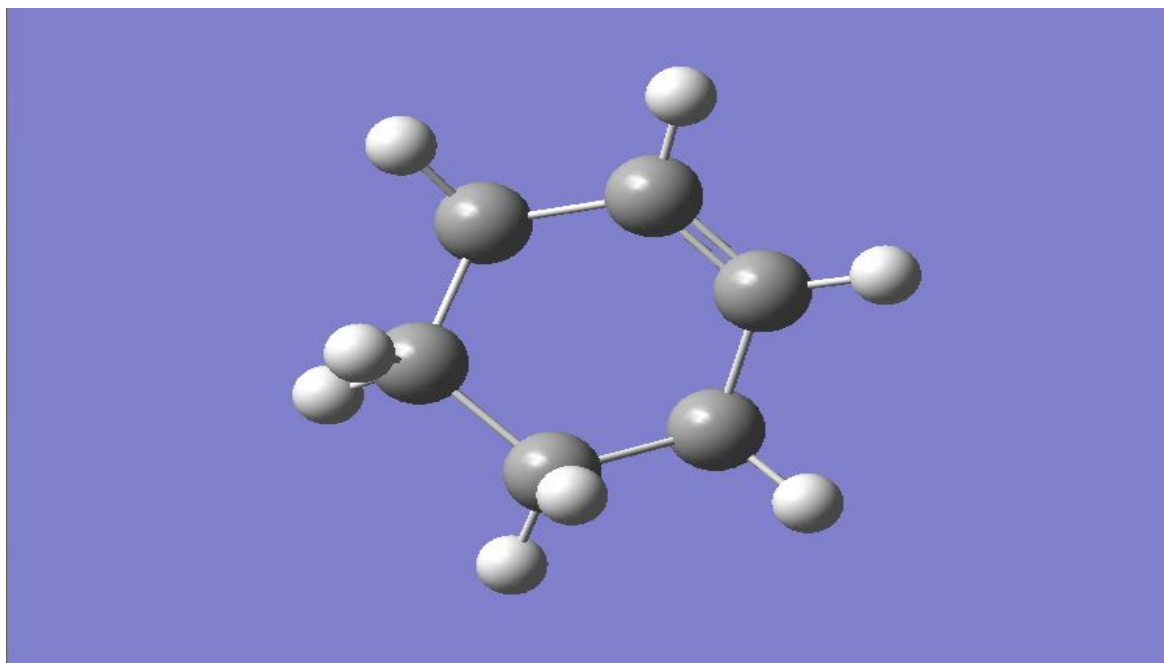
TRANSITION STATE



REACTANTS

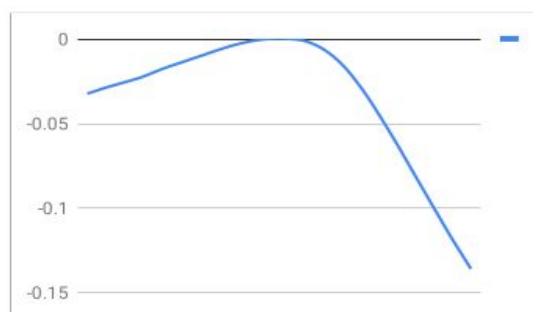


PRODUCT



IRC GRAPH FOR DIELS ALDER

-0.13612
-0.11895
-0.10061
-0.08199
-0.06323
-0.04545
-0.02912
-0.01582
-0.00671
-0.00159
0
0
-0.00134
-0.00381
-0.00721
-0.01089
-0.01451
-0.01824
-0.02261
-0.02582
-0.02891
-0.03244



From the above graph, it is clearly visible that the energy of reactants is more than the energy of products. In principle, a reaction would not like to go forward unless it results in a more stable product, or in clear terms a product with energy less than that of the reactant. Also the Transition State of the reaction, as expected corresponds to the highest value of energy. Thus the Diels Alder Reaction is taking place in the forward direction. Calculations are done using IRC. For this calculation we use #HF STO-3G opt=(ts,calcfc,noeigentest) freq and making a check file to use it for compiling forward and backward log file. Check file can be compiled by using %chk=(name).chk . Forward.com and Reverse.com files can be made using #hf sto-3g irc=(forward or reverse,rcfc) geom=check where geom=check refers to check file. Then we make a backup of check file so that we can run both forward.com and reverse.com file otherwise the file which we ran previously, will change the check file and to run the next file we have to make a check file once again. (ts)=transition state,(calcfc)=calculate force constant,(noeigentest) is a test used to make sure that not more than one frequency becomes imaginary as transition state is found at a saddle point and saddle point has all minimum point except one maximum, and imaginary frequency represents maximum.

$\Delta E = E_{\text{transition state}} - E_{\text{reactants}}$
20.35639196 kcal/mol

$\Delta H = H_{\text{products}} - H_{\text{reactants}}$
-65.060103312 kcal/mol

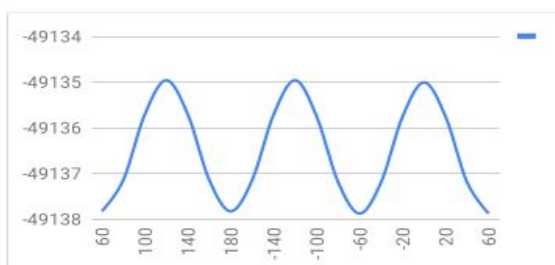
Q2) CONFORMATIONAL ANALYSIS

In 1874, Van't Hoff and Le Bell independently proposed that the four valencies of carbon are directed toward the corners of a tetrahedron with the carbon atom at its center. The model was adopted by other chemists, applied to more complex molecules and further developed culminating with Barton's 1950 paper in which he set foundations of modern conformational analysis.

Configuration of a molecule denotes three-dimensional arrangement of atoms in space. The infinite number of different arrangements of atoms in space that is a result of rotation about a single bond is called conformational isomers, conformers or conformations. Yet another less common term is rotamers. Thus, conformations are not actual isomers as they cannot be separated and isolated. They are different shapes of the same molecule. Conformational analysis is the study of kinetic and thermodynamic properties of molecules that are conformation dependent such as the existence of a preferred conformation, energies and populations of different conformational arrangements, and chemical consequences of it.

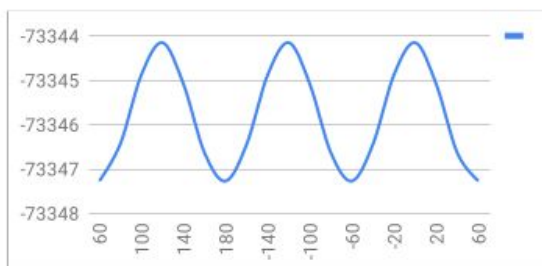
CONFORMATIONAL ANALYSIS OF ETHANE(IN KCAL/MOL)

| | |
|------|--------------|
| 60 | -49137.83271 |
| 80 | -49137.14872 |
| 100 | -49135.71173 |
| 120 | -49134.96499 |
| 140 | -49135.71173 |
| 160 | -49137.14872 |
| 180 | -49137.83271 |
| -160 | -49137.14872 |
| -140 | -49135.71173 |
| -120 | -49134.96499 |
| -100 | -49135.7593 |
| -80 | -49137.19633 |
| -60 | -49137.88032 |
| -40 | -49137.19633 |
| -20 | -49135.7593 |
| 0 | -49135.0126 |
| 20 | -49135.7593 |
| 40 | -49137.19633 |
| 60 | -49137.88032 |



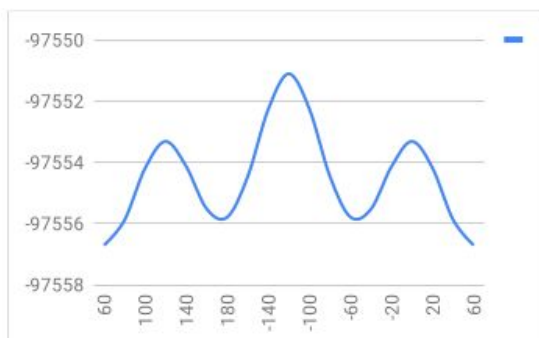
CONFORMATIONAL ANALYSIS OF PROPANE(IN KCAL/MOL)

| | |
|------|--------------|
| 60 | -73347.27425 |
| 80 | -73346.43339 |
| 100 | -73344.87089 |
| 120 | -73344.15553 |
| 140 | -73345.0968 |
| 160 | -73346.64674 |
| 180 | -73347.27425 |
| -160 | -73346.43967 |
| -140 | -73344.87089 |
| -120 | -73344.15553 |
| -100 | -73345.0968 |
| -80 | -73346.64674 |
| -60 | -73347.27425 |
| -40 | -73346.43339 |
| -20 | -73344.86462 |
| 0 | -73344.15553 |
| 20 | -73345.0968 |
| 40 | -73346.64674 |
| 60 | -73347.27425 |



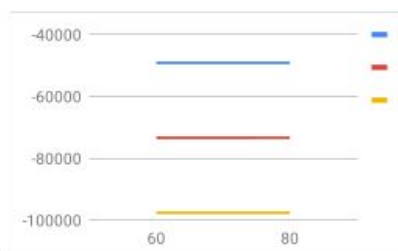
CONFORMATIONAL ANALYSIS OF BUTANE(IN KCAL/MOL)

| | |
|------|--------------|
| 60 | -97556.72207 |
| 80 | -97555.90631 |
| 100 | -97554.21204 |
| 120 | -97553.32725 |
| 140 | -97554.13674 |
| 160 | -97555.52981 |
| 180 | -97555.80591 |
| -160 | -97554.48187 |
| -140 | -97552.27931 |
| -120 | -97551.11842 |
| -100 | -97552.26049 |
| -80 | -97554.46304 |
| -60 | -97555.79964 |
| -40 | -97555.54236 |
| -20 | -97554.14929 |
| 0 | -97553.32725 |
| 20 | -97554.19949 |
| 40 | -97555.88749 |
| 60 | -97556.72207 |



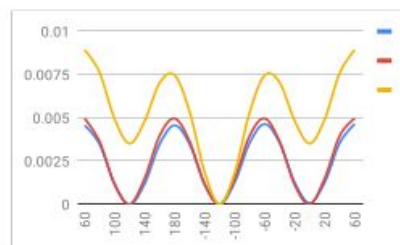
COMPARISON OF ALL THREE WITHOUT TAKING DIFFERENCE(IN KCAL/MOL)

| | | | |
|------|--------------|--------------|--------------|
| 60 | -49137.83271 | -73347.27425 | -97556.72207 |
| 80 | -49137.14872 | -73346.43339 | -97555.90631 |
| 100 | -49135.71173 | -73344.87089 | -97554.21204 |
| 120 | -49134.96499 | -73344.15553 | -97553.32725 |
| 140 | -49135.71173 | -73345.0968 | -97554.13674 |
| 160 | -49137.14872 | -73346.64674 | -97555.52981 |
| 180 | -49137.83271 | -73347.27425 | -97555.80591 |
| -160 | -49137.14872 | -73346.43967 | -97554.48187 |
| -140 | -49135.71173 | -73344.87089 | -97552.27931 |
| -120 | -49134.96499 | -73344.15553 | -97551.11842 |
| -100 | -49135.7593 | -73345.0968 | -97552.26049 |
| -80 | -49137.19633 | -73346.64674 | -97554.46304 |
| -60 | -49137.88032 | -73347.27425 | -97555.79964 |
| -40 | -49137.19633 | -73346.43339 | -97555.54236 |
| -20 | -49135.7593 | -73344.86462 | -97554.14929 |
| 0 | -49135.0126 | -73344.15553 | -97553.32725 |
| 20 | -49135.7593 | -73345.0968 | -97554.19949 |
| 40 | -49137.19633 | -73346.64674 | -97555.88749 |
| 60 | -49137.88032 | -73347.27425 | -97556.72207 |



COMPARISON OF ALL THREE IN HARTREES(TAKING DIFF)

| | | | |
|------|----------------|---------|---------|
| 60 | 0.00457 | 0.00497 | 0.00893 |
| 80 | 0.00348 | 0.00363 | 0.00763 |
| 100 | 0.00119 | 0.00114 | 0.00493 |
| 120 | 0 | 0 | 0.00352 |
| 140 | 0.00119 | 0.0015 | 0.00481 |
| 160 | 0.00348 | 0.00397 | 0.00703 |
| 180 | 0.00457 | 0.00497 | 0.00747 |
| -160 | 0.00348 | 0.00364 | 0.00536 |
| -140 | 0.00119 | 0.00114 | 0.00185 |
| -120 | 0 | 0 | 0 |
| -100 | 0.001265815327 | 0.0015 | 0.00182 |
| -80 | 0.003555870131 | 0.00397 | 0.00533 |
| -60 | 0.004645878402 | 0.00497 | 0.00746 |
| -40 | 0.003555870131 | 0.00363 | 0.00705 |
| -20 | 0.001265337246 | 0.00113 | 0.00483 |
| 0 | 0.000075872234 | 0 | 0.00352 |
| 20 | 0.001265815327 | 0.0015 | 0.00491 |
| 40 | 0.003555870131 | 0.00397 | 0.0076 |
| 60 | 0.00464584653 | 0.00497 | 0.00893 |



Conformational analysis is done by writing #HF STO -3G opt=modredundant and writing (X Y W Z S N A). (X Y W Z) are the numbers of atoms in the Z-Matrix, we wish to rotate the molecule about. N is the number of such rotations and A is the angle of rotation. After compiling the log file we search for the keyword "Potential" and will come across a table representing different energy values. Then we plot the graph by taking Energy on Y-axis and Angle on X-axis. So the above graph represents energy of different conformations of ethane, propane and butane. Here the molecule is rotated 19 times and each time the angle changes by 20 degrees.

Minimum Energy of:

Ethane at 180 degrees: -49137.83271 kcal/mol

Propane at 180 degrees: -73347.27425 kcal/mol

Butane at 60 degrees: -97556.72207 kcal/mol

Maximum Energy of:

Ethane at 0 degrees: -49135.0126 kcal/mol

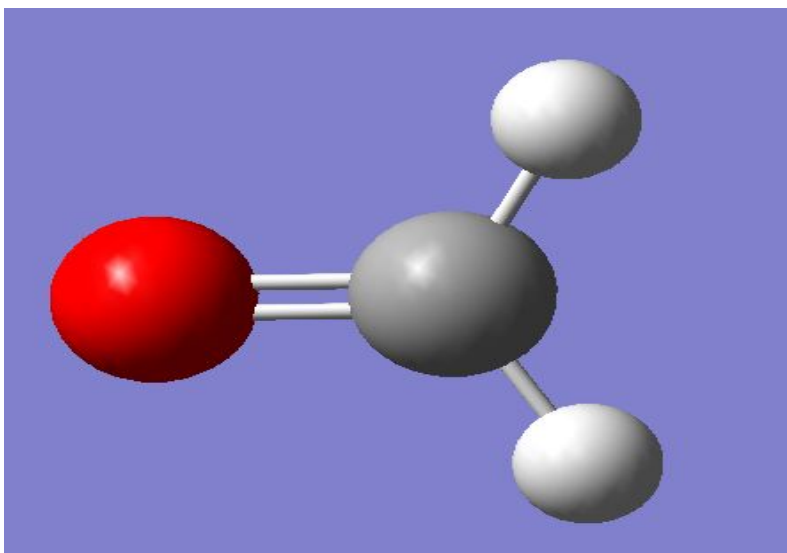
Propane at 0 degrees: -73344.15553 kcal/mol

Butane at -120 degrees: -97551.11842 kcal/mol

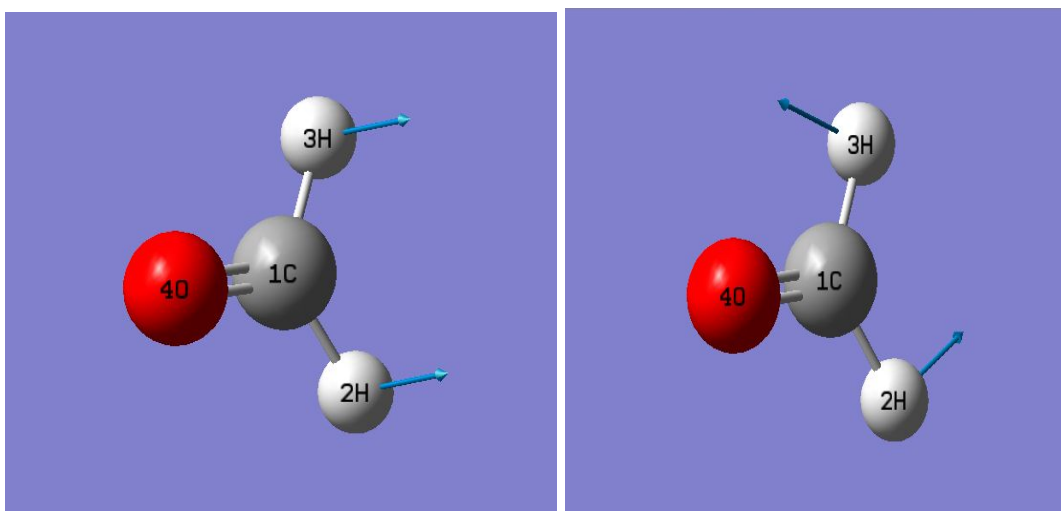
Note: Butane's Atoms to rotate the molecule have been so selected that they are in the anti-staggered form at angle 60 degrees. Therefore the conformation of max energy would be at (60 + 180 = 240 or -120) degrees.

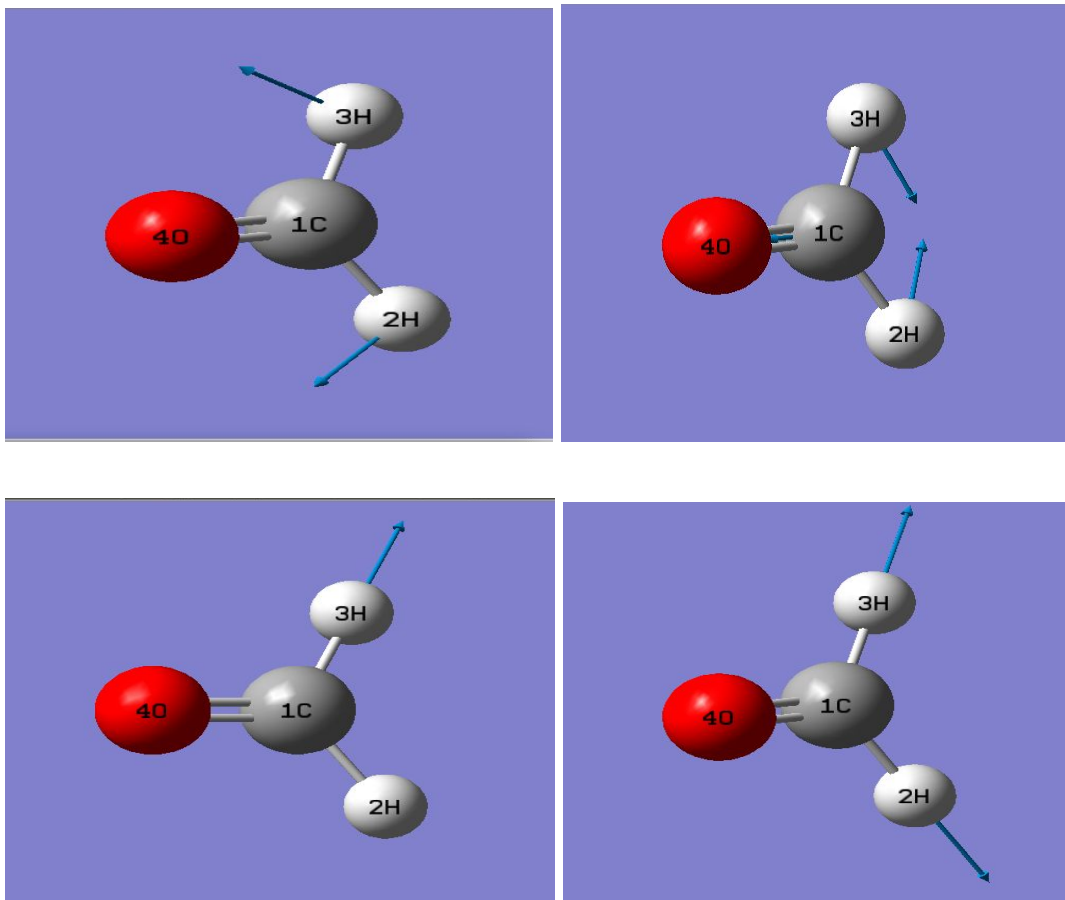
Q3) FORMALDEHYDE

STRUCTURE OF FORMALDEHYDE



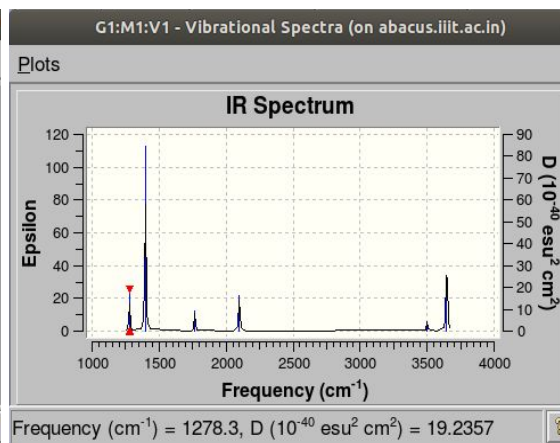
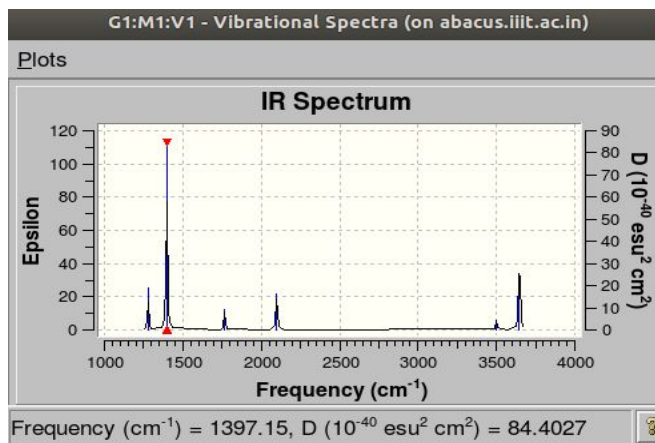
DIFFERENT VIBRATIONAL MODES OF FORMALDEHYDE

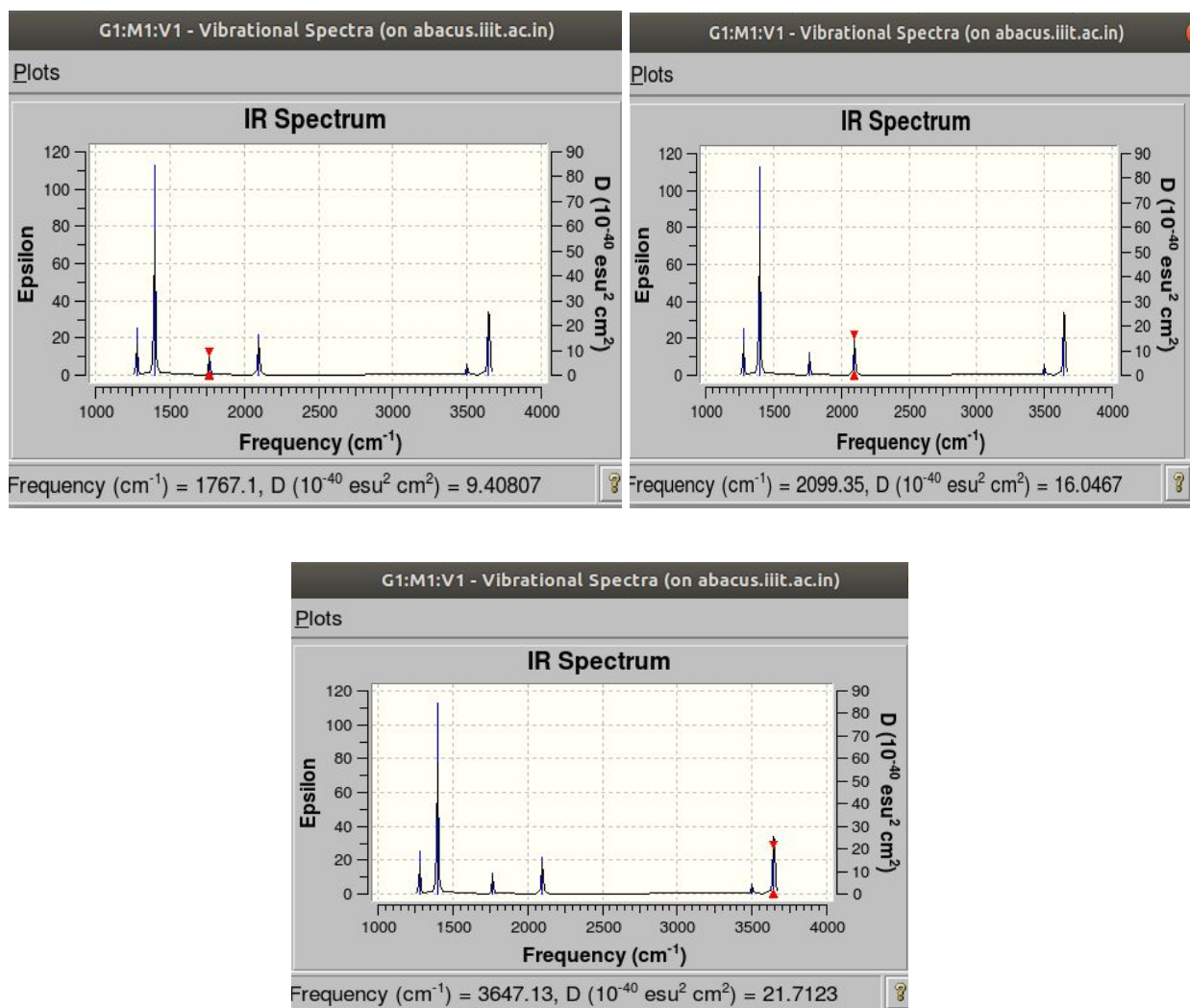




INFRARED SPECTRUM OF FORMALDEHYDE

(VIBRATIONAL) (FORMED USING HF STO=3G METHOD)





The blue vectors indicate the line of motion of the particular atom. In total there are 6 such vector representations corresponding to atoms moving in a certain direction for Formaldehyde.

The Frequencies in increasing order of different peaks (in cm^{-1}) is as follows:

1278.3 1397.15 1767.1 2099.35 3647.13

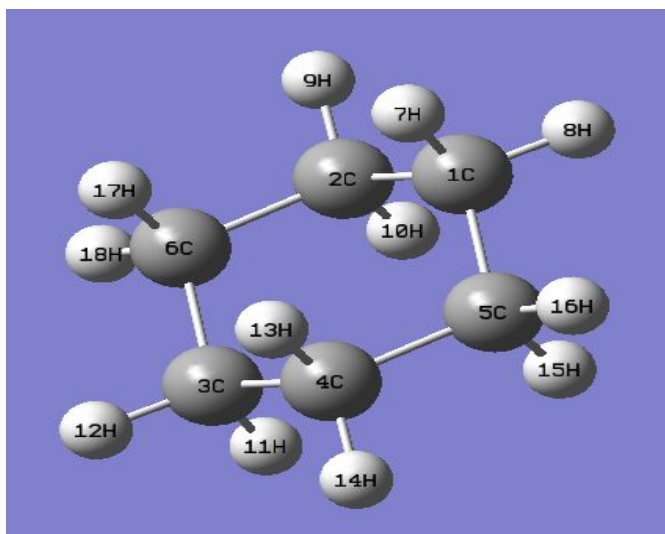
Epsilon vs frequency graph can be found out by first compiling log file of formaldehyde molecule.

If we open log file of formaldehyde in Gview and go to results and open IR spectrum we will get the IR spectrum graph.

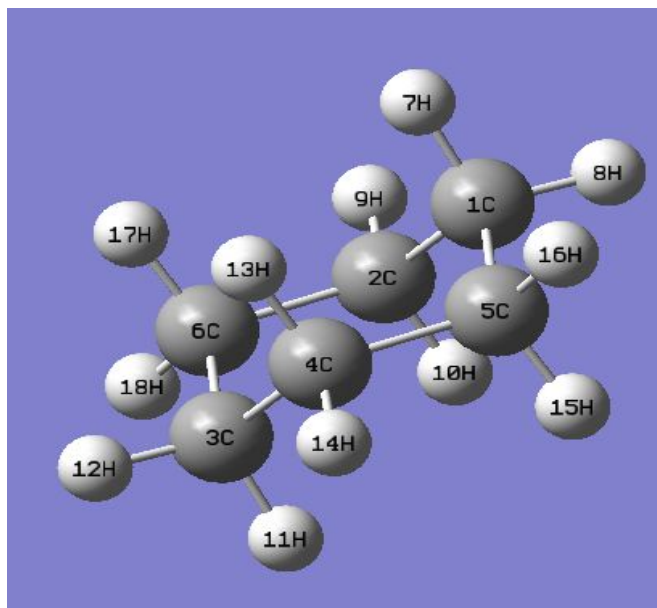
The given IR Spectrum Graph does not exactly match the values indicated in the assignment question (obtained using experiments) but confirms the general pattern of IR graphs.

Q4) COMPARING ENERGIES

(Between Substituents added on Cyclohexane ring in Chair form)

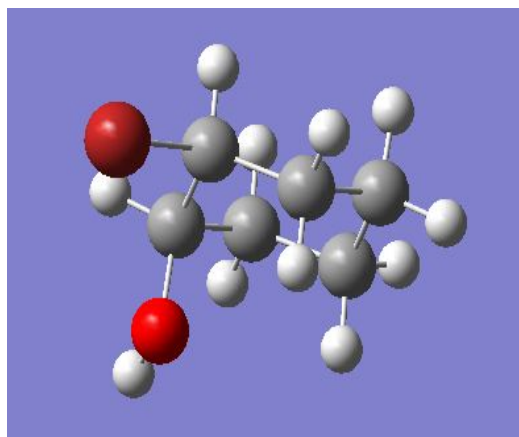


CYCLOHEXANE IN CHAIR FORM



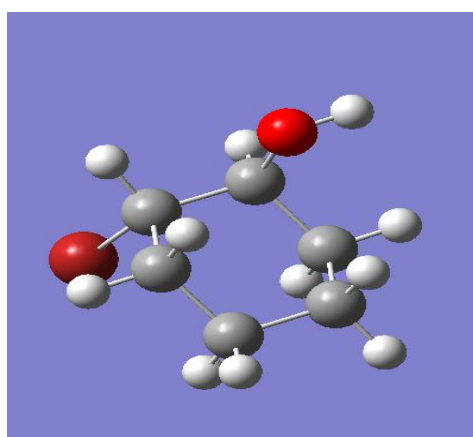
A **cyclohexane conformation** is any of several three-dimensional shapes that a cyclohexane molecule can assume while maintaining the integrity of its chemical bonds.

The internal angles of a flat regular hexagon are 120° , while the preferred angle between carbons in a carbon chain is about 109.5° , the tetrahedral angle. Therefore, the cyclohexane ring tends to assume certain non-planar (warped) conformations, which have all angles closer to 109.5° and therefore a lower strain energy than the flat hexagonal shape. The most important shapes are called ***chair***, ***half-chair***, ***boat***, and ***twist-boat***. The molecule can easily switch between these conformations, and only two of them—*chair* and *twist-boat*—can be isolated in pure form.



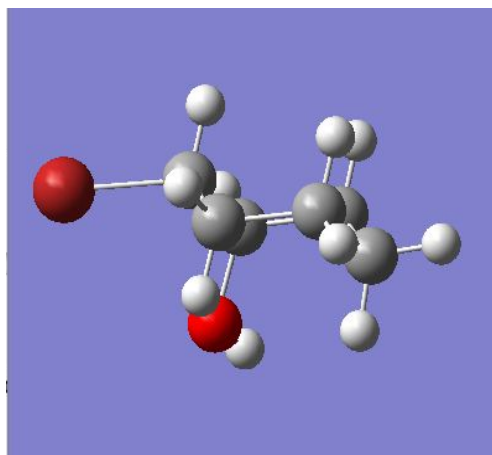
1A

Energy= -2849.40186678



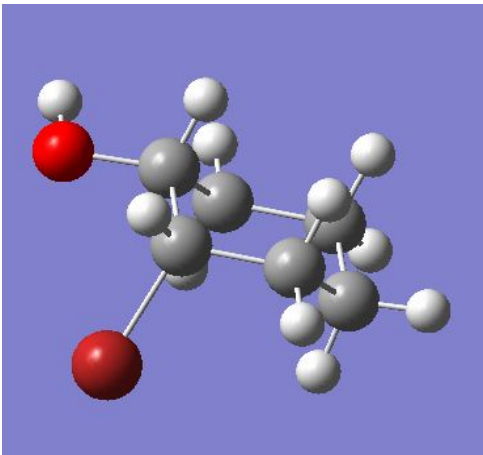
1B

Energy= -2849.40139132



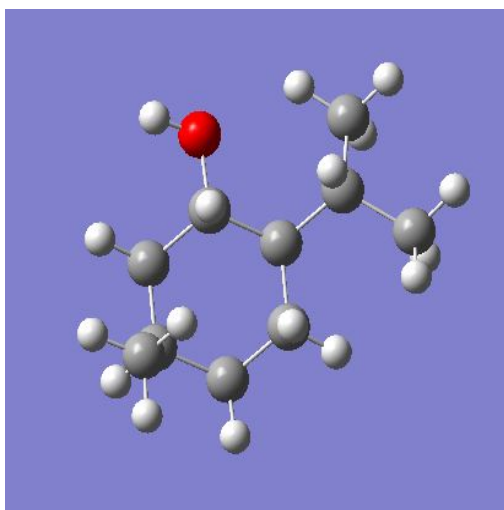
2A

Energy= -2849.4014278



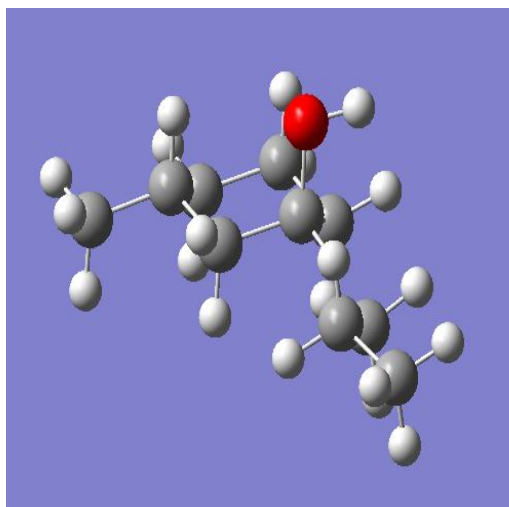
2B

Energy= -2849.40062789



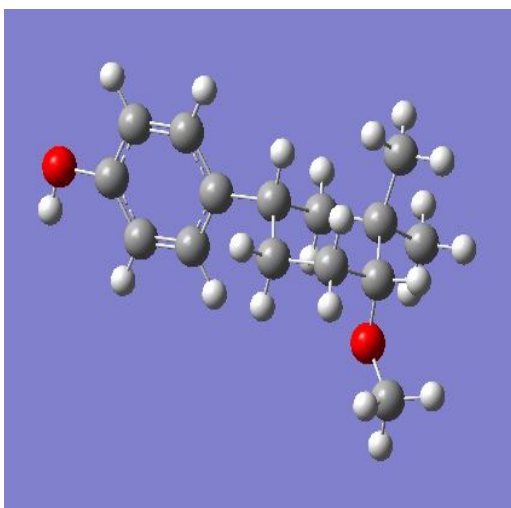
3A

Energy= -459.62556218



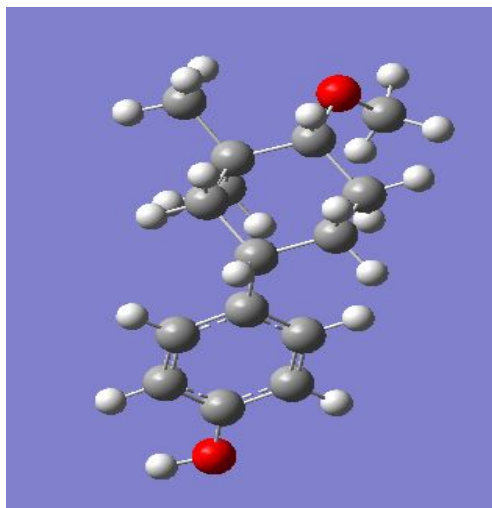
3B

Energy= -459.62390210



4A

Energy= -721.64082710



4B

Energy= -721.62486723

ENERGY OF PAIRS(in kcal/mol)

In all of the cases above, the energy of the left molecule is less than that of the right one, so in all the cases the left molecule is more stable than the right one.

Here 8 molecules were made and their SCF (Self Consistent Field method) values were compared which is an old way to refer to HF (Hartree-Fock method) energies to check which molecule is more stable in each pair.

Hartree Fock method is a method of approximation for the determination of Schrodinger Equation. STO (Slater Type Orbitals) as it mimics Slater functions to reduce computational complexity. (3G= 1) basis set is used per orbital to calculate in which 3 Gaussian functions are used per orbital to mimic Slater functions. Though 3G technique is not the most accurate yet we use it to reduce computational time, which increases in the process of increasing accuracy. Example of such a technique is -6-31G which is computationally more expensive but uses better approximations.
