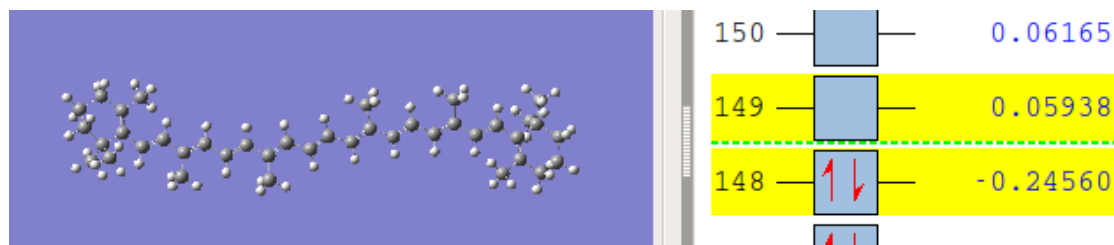


# Assignments to ComputChem

## Q1

### 1. Estimate its HOMO-LUMO energy gap using the particle-in-a-box model.



Command: b3lyp/6-31g(d) pop=(nbo,savenbos) geom=connectivity

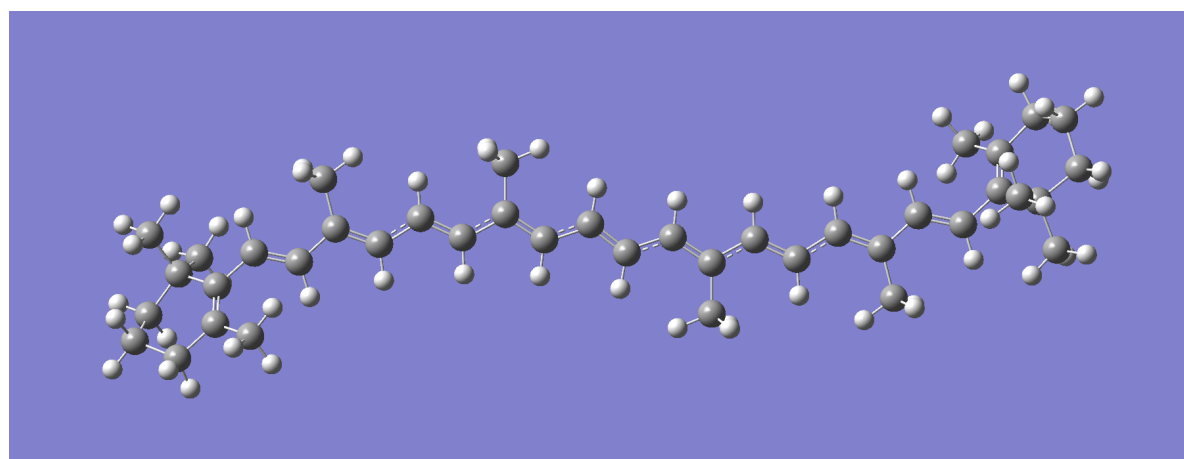
After the implementation of particle in a box model, I get the molecule orbit as follows.

NBO index	Molecular units	Energy(Hartree)	Class
148	CR (1) C 40	-0.024560	HOMO
149	RY*(1) C 1	0.05938	LUMO

Consequently, the HOMO-LUMO energy gap is 0.08394 Hartree

### 2. Obtain its stable structure using a proper quantum mechanical method and briefly

describe the structure.



Command: opt=calcfc b3lyp/6-31g(d)

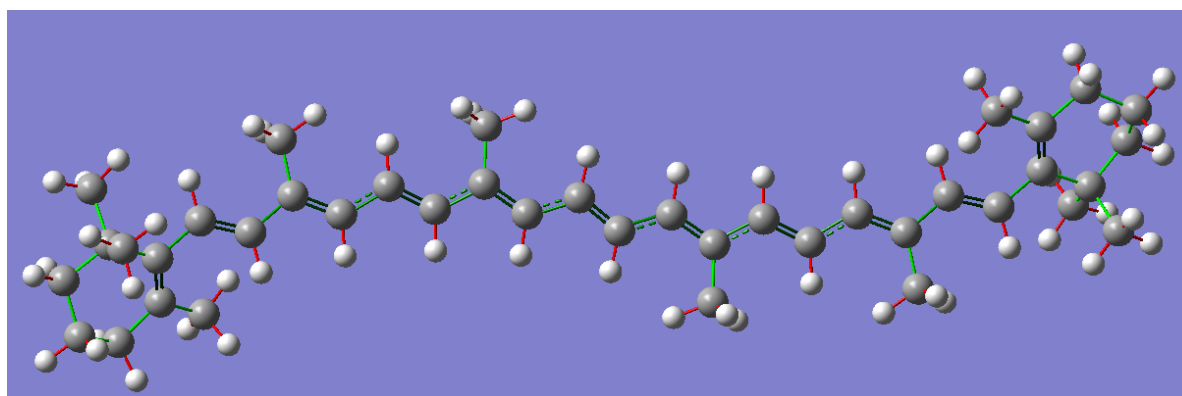
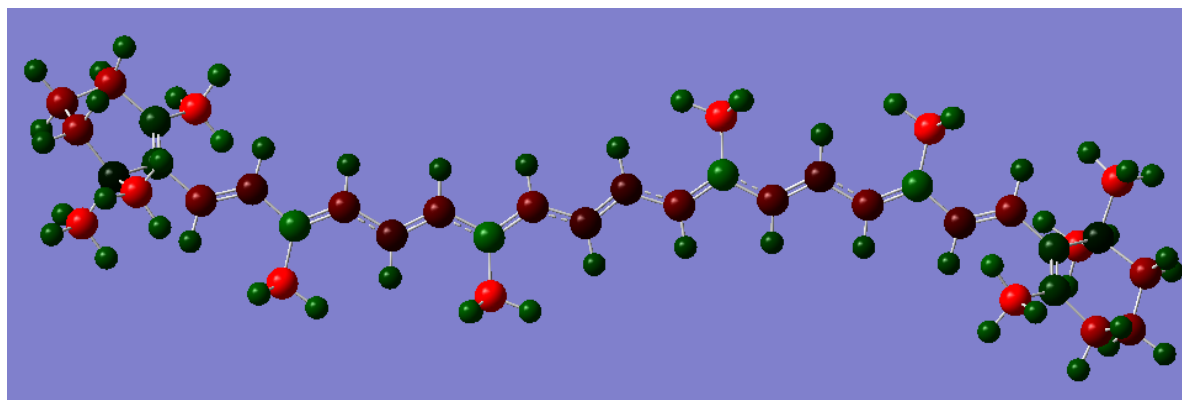
In this case, I choose B3LYP and 6-31G(d) as the calculation parameters. And after 13 steps, the total energy converge at around -1557.9 Hartree. Indicating the normal termination of optimization process. The description of the optimized molecule

Beta-carotene, with the molecular formula  $C_{40}H_{56}$ , owns a long chain of conjugated double bonds together with two retinyl groups. The huge conjugated structure equip this molecule of highly-delocalized electron groups.

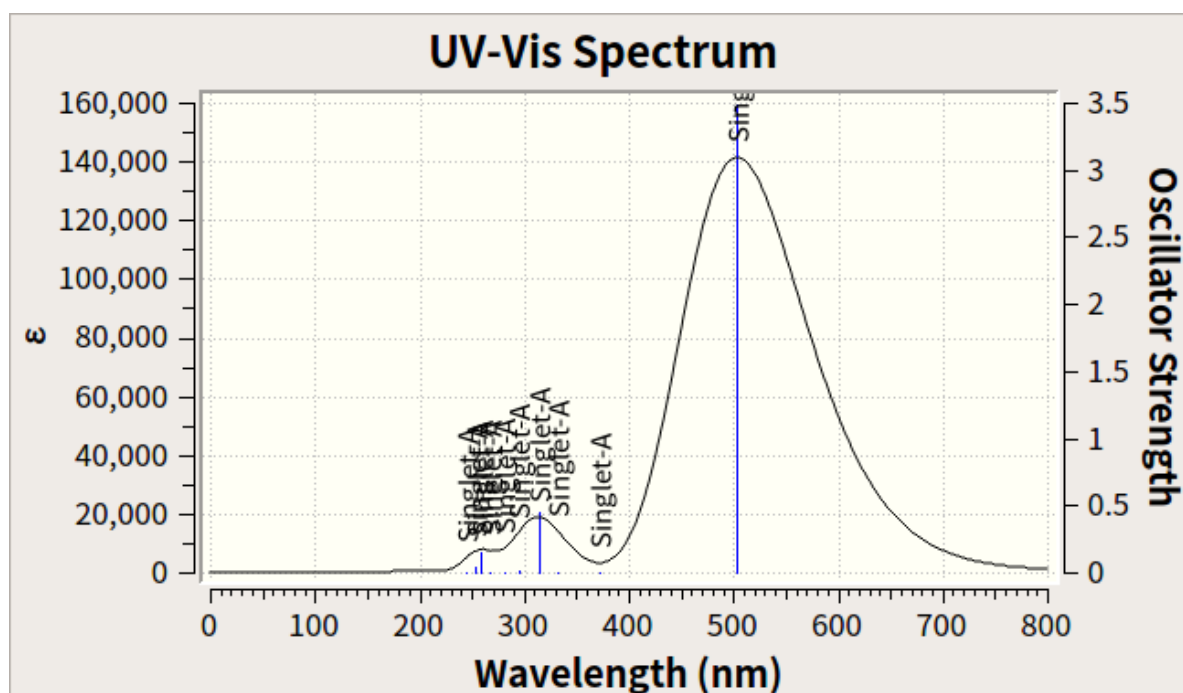
As the picture describes, there are up to 40 electron pairs located in a same energy level, illustrating the delocalization of the electrons.

The distribution of charge and bonds' length also prove the delocalization of electrons. As is shown in the figure, the charge of the central chain goes through a sort of equalization, which also happens in the bond length.

Class	Typical Bond Length(pm)	Typical Bond Order
<i>Ethylene</i>	(C=C) 133.9	2
<i>Ethene</i>	(C-C) 152.8	1
$\beta$ - Carotene	(C=C)137.4 (C-C) 144.3	(C=C)2 (C-C)1.5

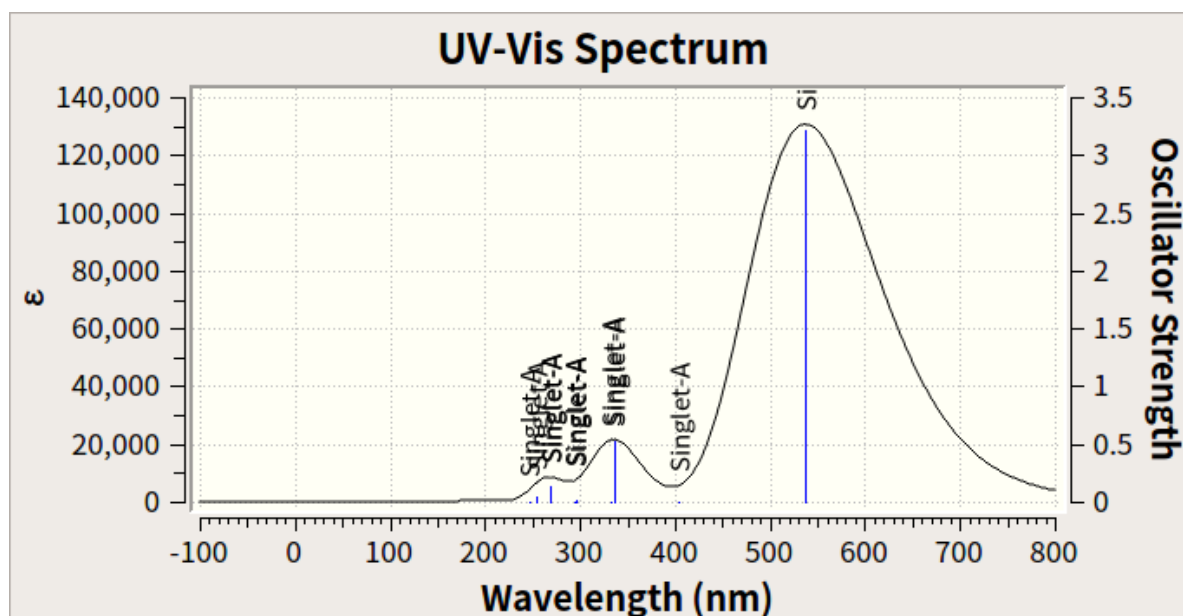


**3. Based on the structure obtained in step 2, compute its UV-Vis spectra in the gas phase, using the ZINDO method (nstates=10).**



Command: zindo=(astates=10)

**4. Re-compute its UV-Vis spectra in ethanol using the same method with the IEFPCM solvation model**



Command: zindo=(nstates=10) scrf=(iefpcm,solvent=ethanol)

**5. The experimentally measured maximum UV-vis absorption peak in ethanol is 450 nm. Discuss all the computed and the experimental excitation energy values and comment on**

The calculated excitation by ZINDO model get an excitation energy of c.a. 540 nm. Frankly speaking, the gap between the experimental and computed data is not even far.

Consequently, i would like to have some discussion about the significant gap. As long as solvation model, compute model and molecular itself are considered, I hold the opinion that the *IEFPCM solvation model* and  $\beta$  – *Carotene's* own properties contribute to the bias. I will elaborate my stand from two aspects ---- the model and the solvent molecular.

First, the IEFPCM solvation model itself plays an important role in generating the bias. An implicit solvent model as it is, it fails to deal with non-electrostatic components in the given situation, which means the hydrogen bond existing in the system can not be take into consideration. Nevertheless, hydrogen bonds contribute significantly to the molecular conformation in polarize environment, in this case, the ethanol. The conformation will then have impacts on the conjugate structure, which mainly provides  $\pi \rightarrow \pi^*$  transition, and the UV-Vis spectrum as well. Second, the  $\beta$  – *Carotene* molecule generate UV-Vis absorption by the  $\pi \rightarrow \pi^*$  transition. But according to the solvent effect upon the UV-Vis spectrum, polar solvent will leads to a phenomena called "Red shift" on the  $\pi \rightarrow \pi^*$  transition which means the absorption peak will shift to a higher position, from 450 nm to 540 nm.

Then i want to have some comments on the ZINDO model.

- As for the efficiency, ZINDO's semi-empirical type shows higher speed in calculation than those *ab initio* methods such as TDDFT. I calculate in both means and make a compare.

TDDFT: Job cpu time: 0 days 19 hours 33 minutes 11.0 seconds.

ZINDO: Job cpu time: 0 days 0 hours 4 minutes 20.8 seconds.

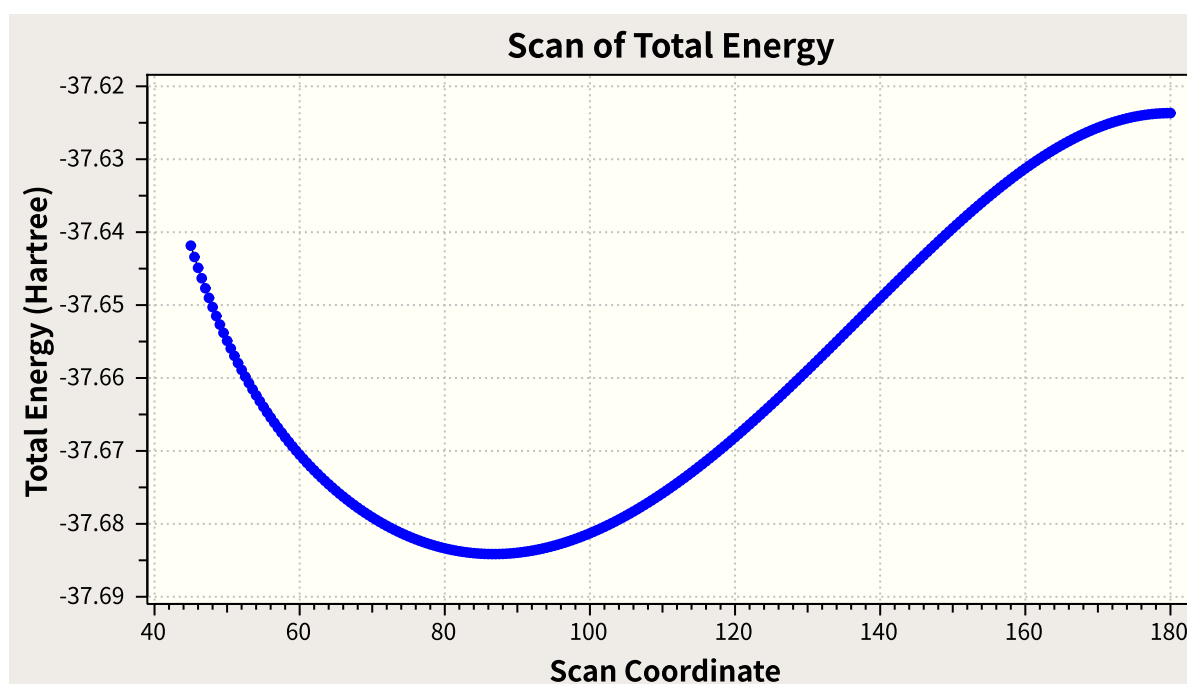
- As for the accuracy, ZINDO's mechanism ----**INDO** method guarantees the accuracy of spectrum calculation.

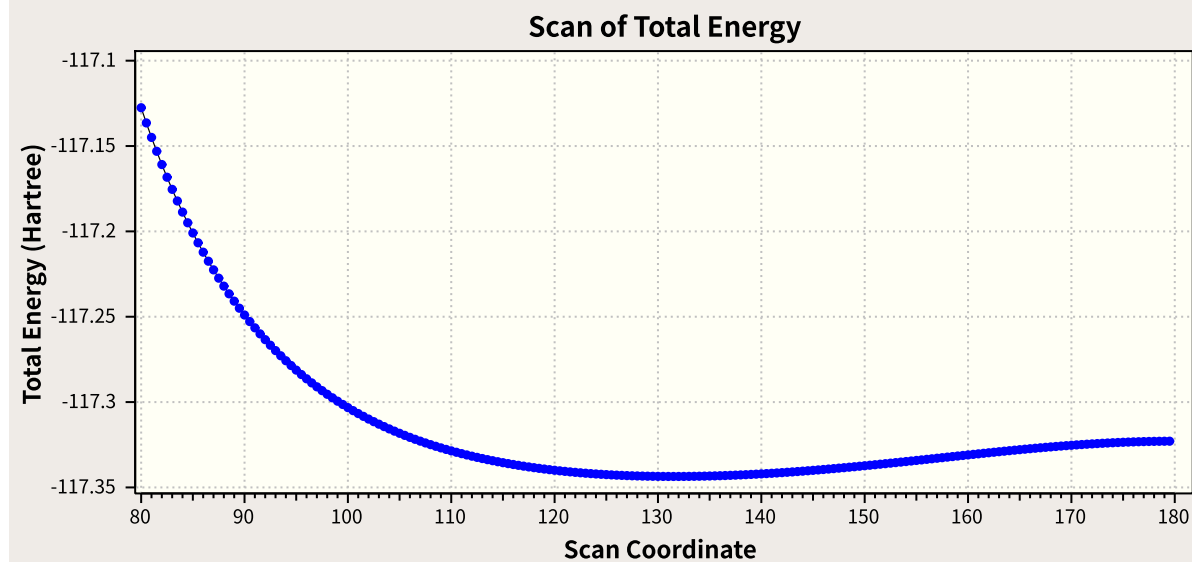
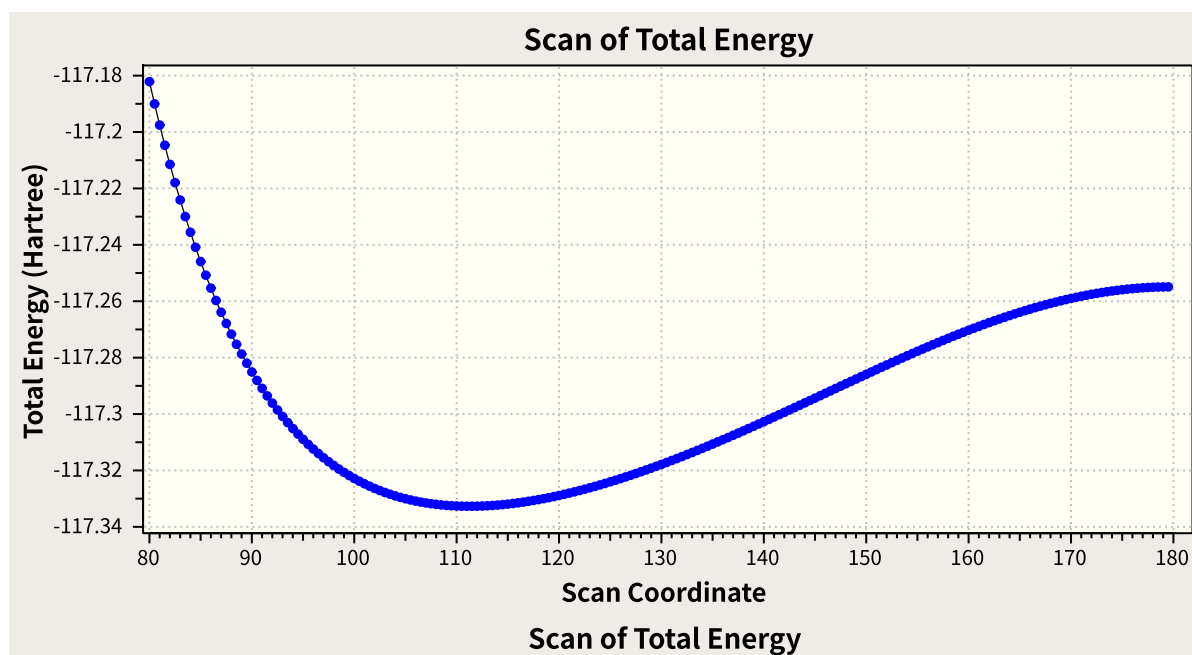
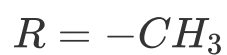
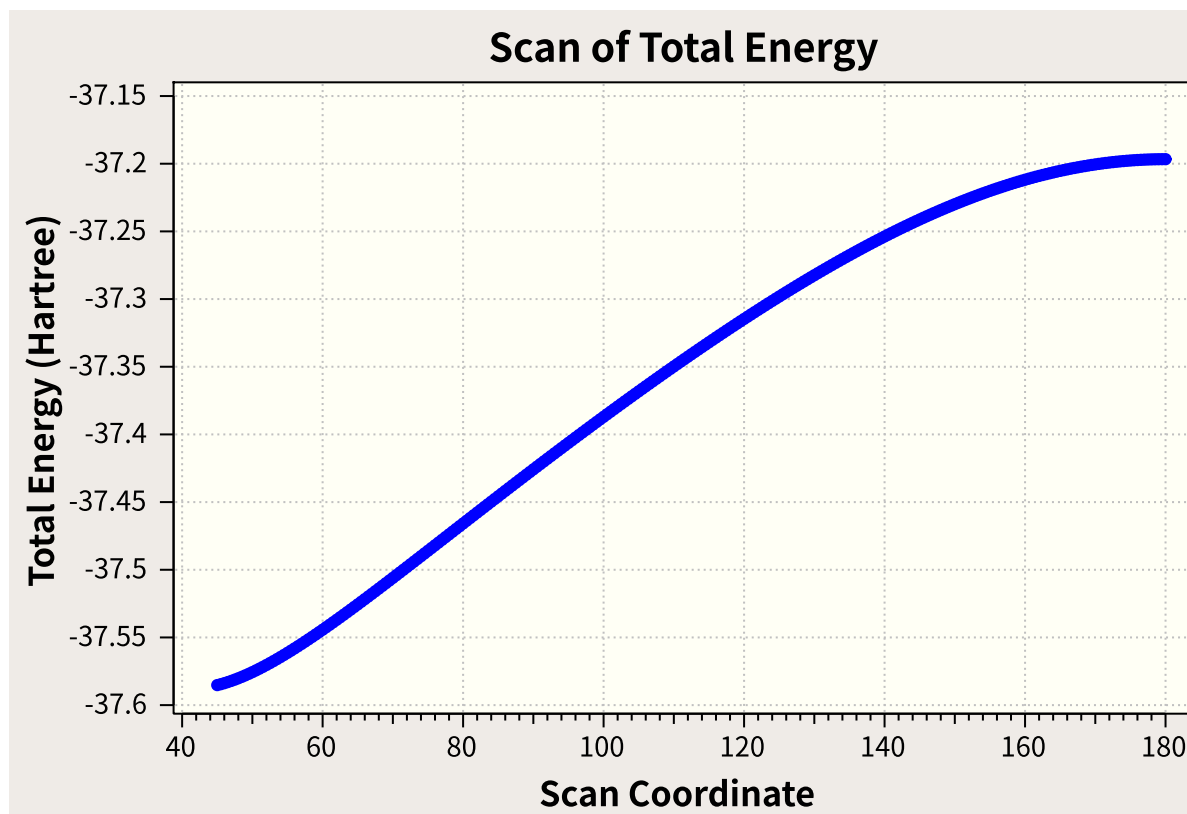
TDDFT : Absorption peak :600 nm

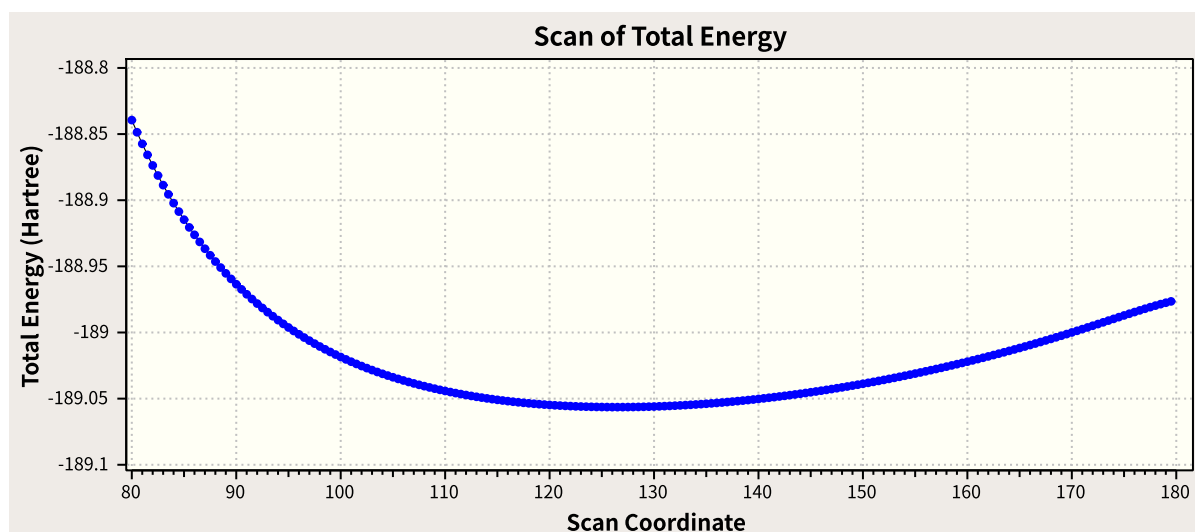
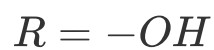
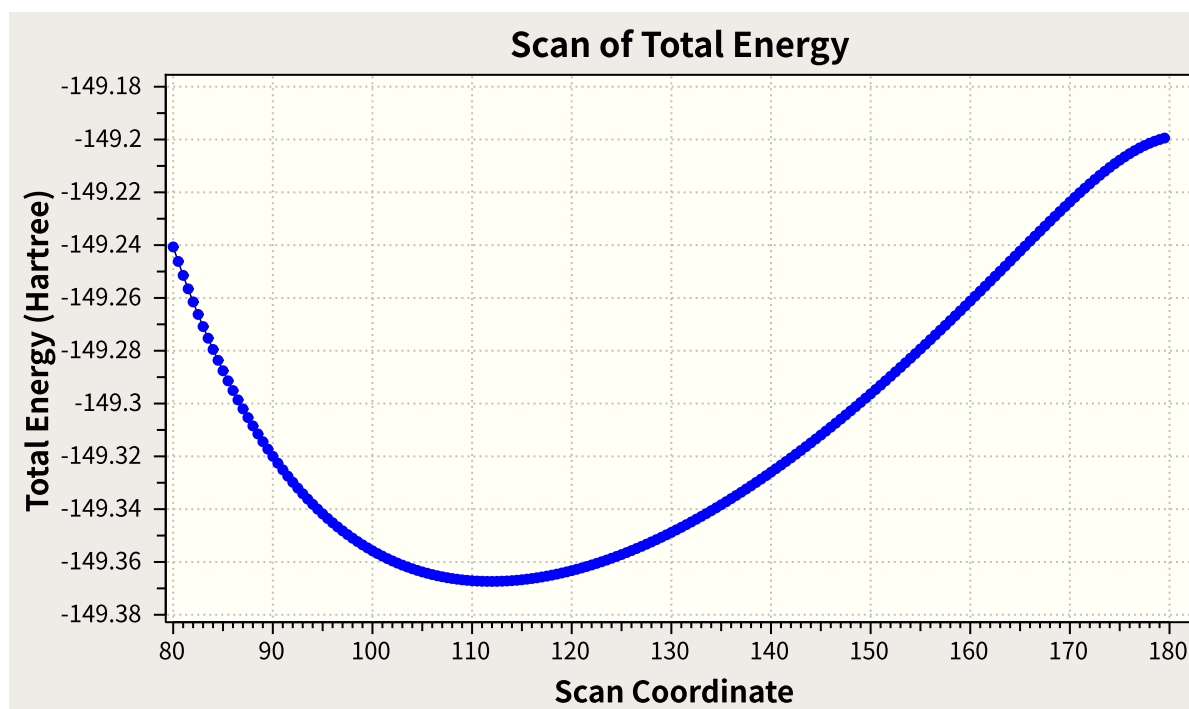
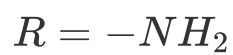
ZINDO: Absorption peak 540 nm

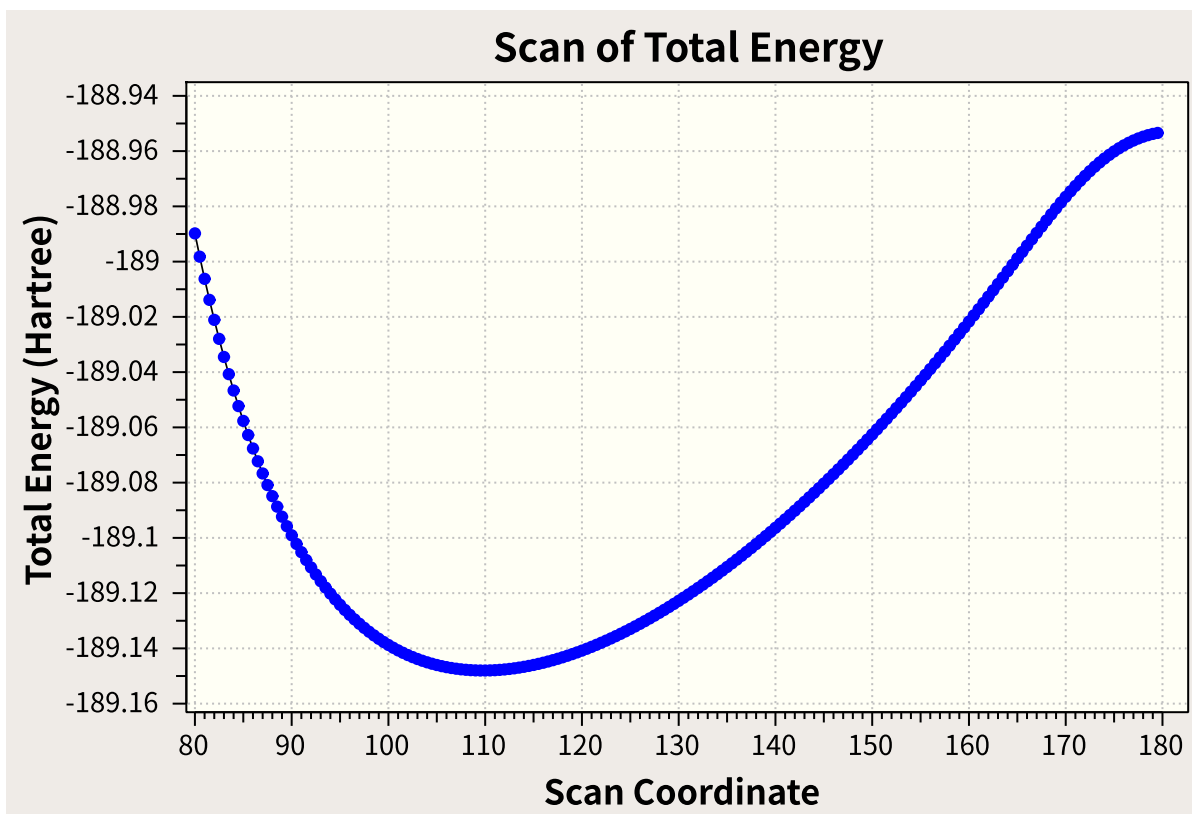
## Q2

$$R = -H$$

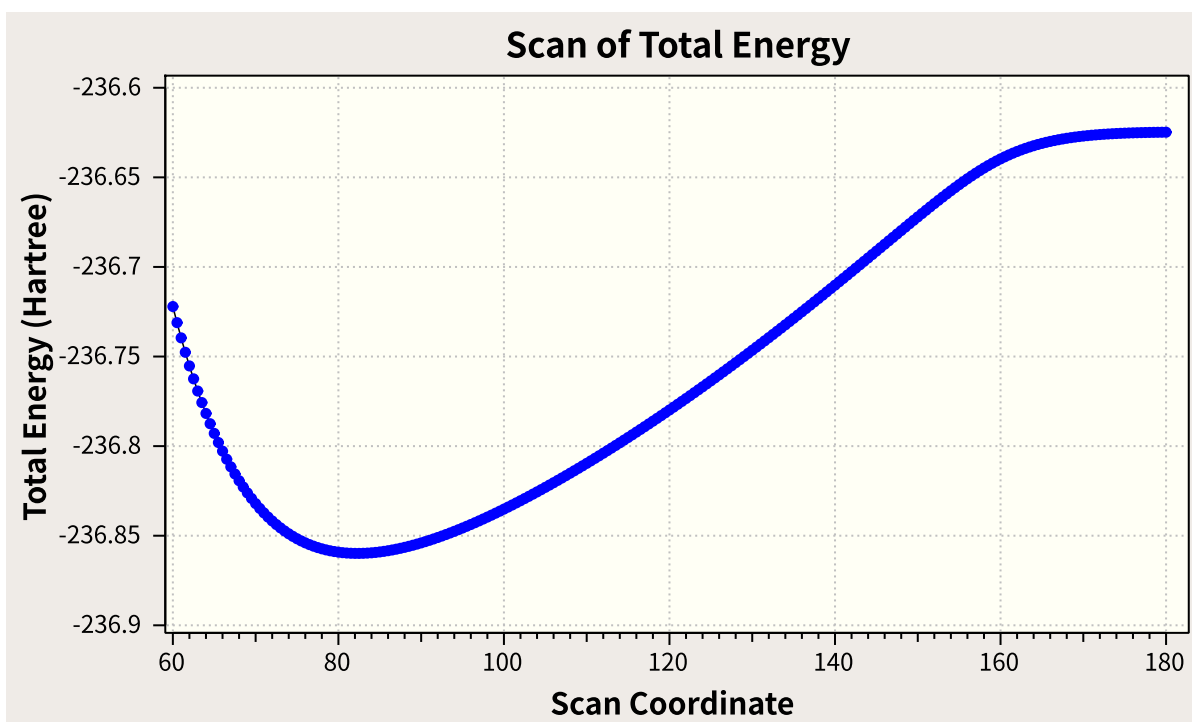


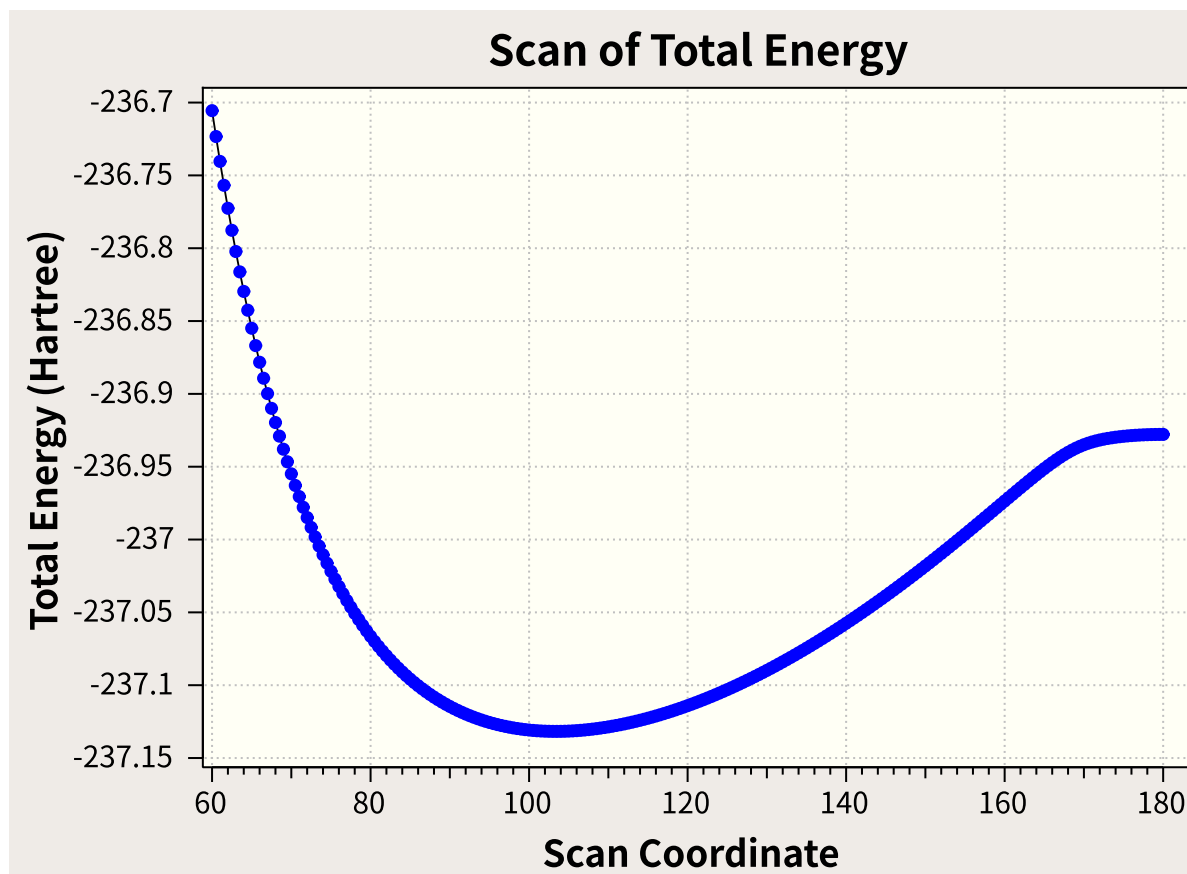






$$R = -F$$





### Q3

**1. Using the 6-31G(d) basis set, determine the transition state for the dehydration of ethanol to ethylene, and record the B3LYP/6-31G(d) and MP2/6-31G(d) values for the barrier height.**

After calculation i have got the possible transition state. Both states have only one imaginary frequency. And the imaginary frequency suits the procedure of the reaction. Hence we can make sure that these transition states are the exception state. According to such a formula:

$$E_{\text{barrier}} = E_{\text{transition}} - E_{\text{reactant}}$$

We can get the barrier energy of this reaction.

**DFT Method:** 293.73kJ/mol

**MP2 Method:** 320.71kJ/mol

### 2. IRC Path

### Q4



## 1. Guess the structures

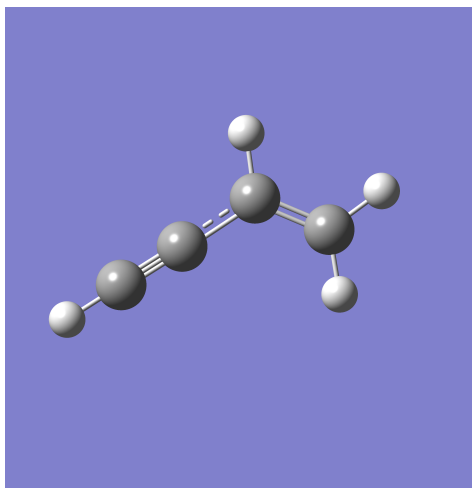
Molecule  $C_4H_4$ , with a degree of unsaturation  $\Omega = 4$ , is likely to contain unsaturation bonds within the molecule. The question mentions several frequencies, and I just started some analysis.

- $215\text{cm}^{-1}$  s Have not found any specific indication, but might refer to conjugate structure
- $852\text{cm}^{-1}$  s This absorption peak indicates  $CH_2$  wagging
- $1608\text{cm}^{-1}$  s This absorption peak indicates  $CC$  stretching)
- 

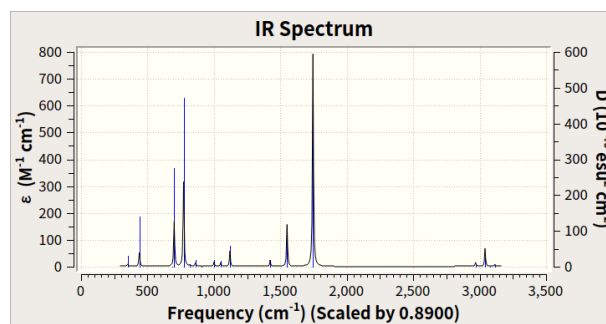
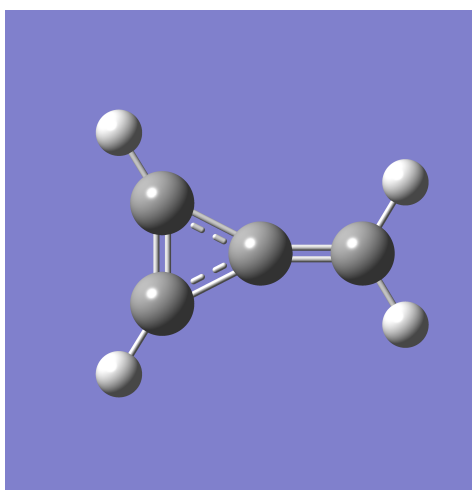
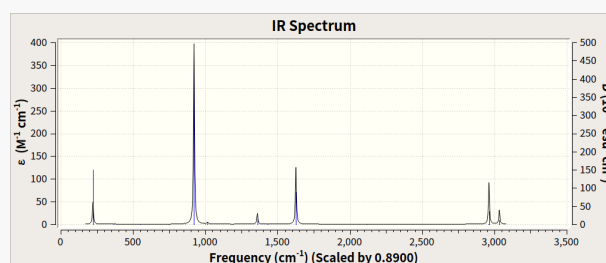
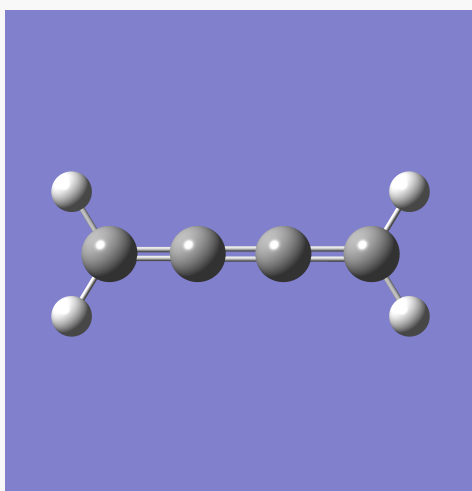
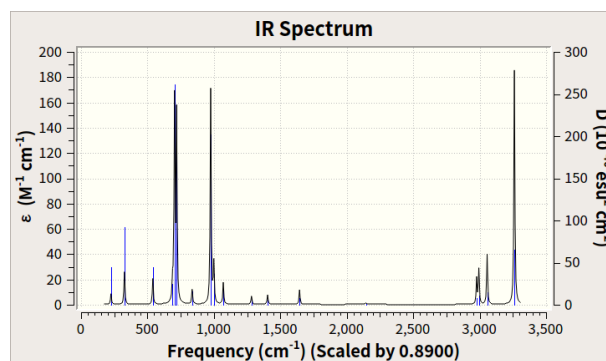
## 2&3. Optimize the lowest singlet states

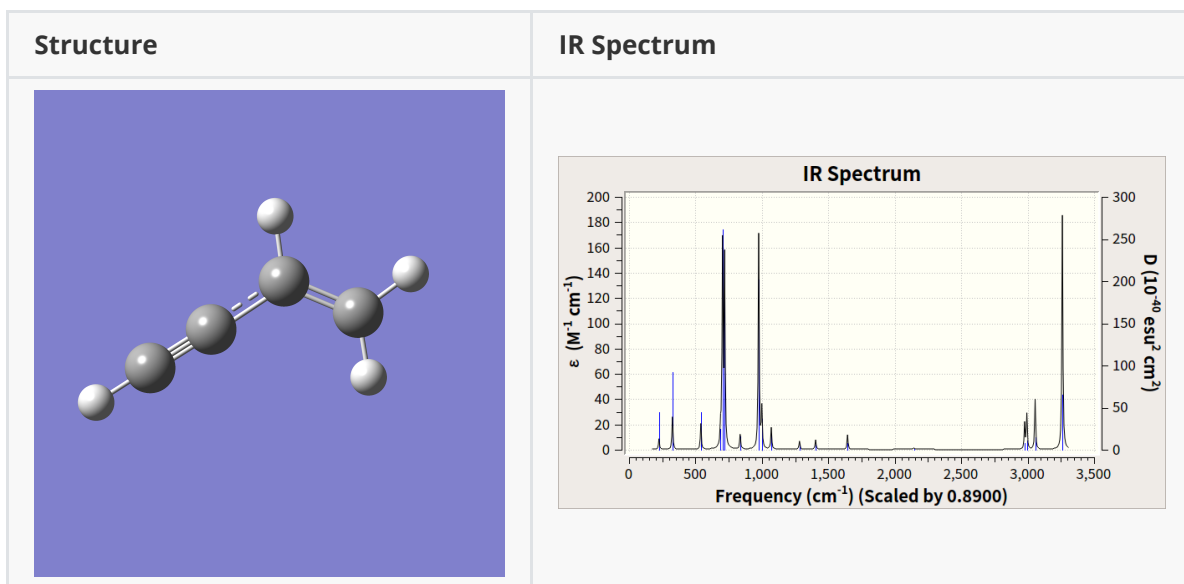
After some calculations, I pick up 4 candidates for this question. They are listed as follows.

## Structure



## IR Spectrum





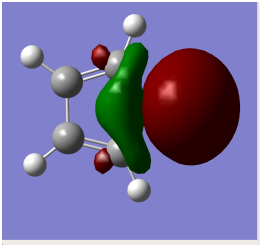
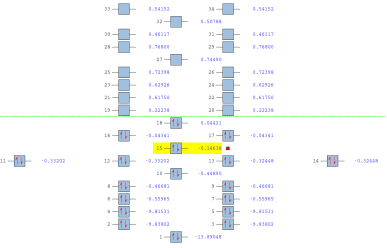
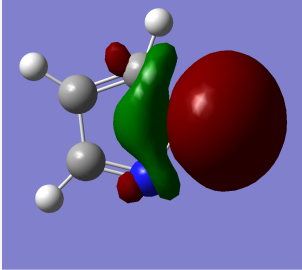
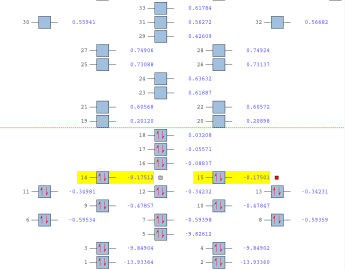
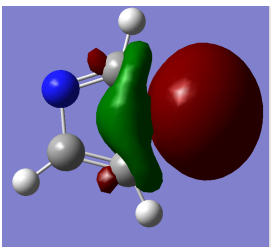
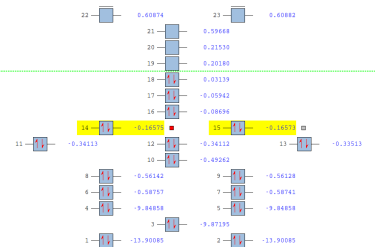
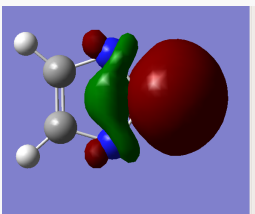
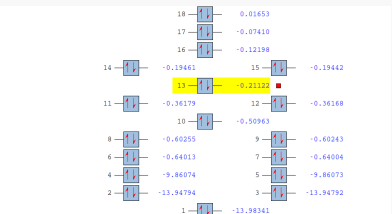
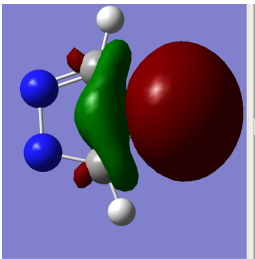
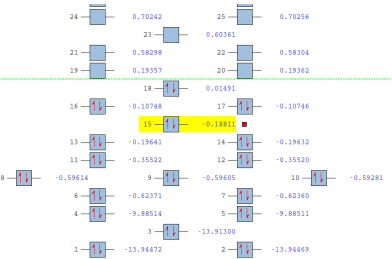
#### 4. Discussion upon the structure

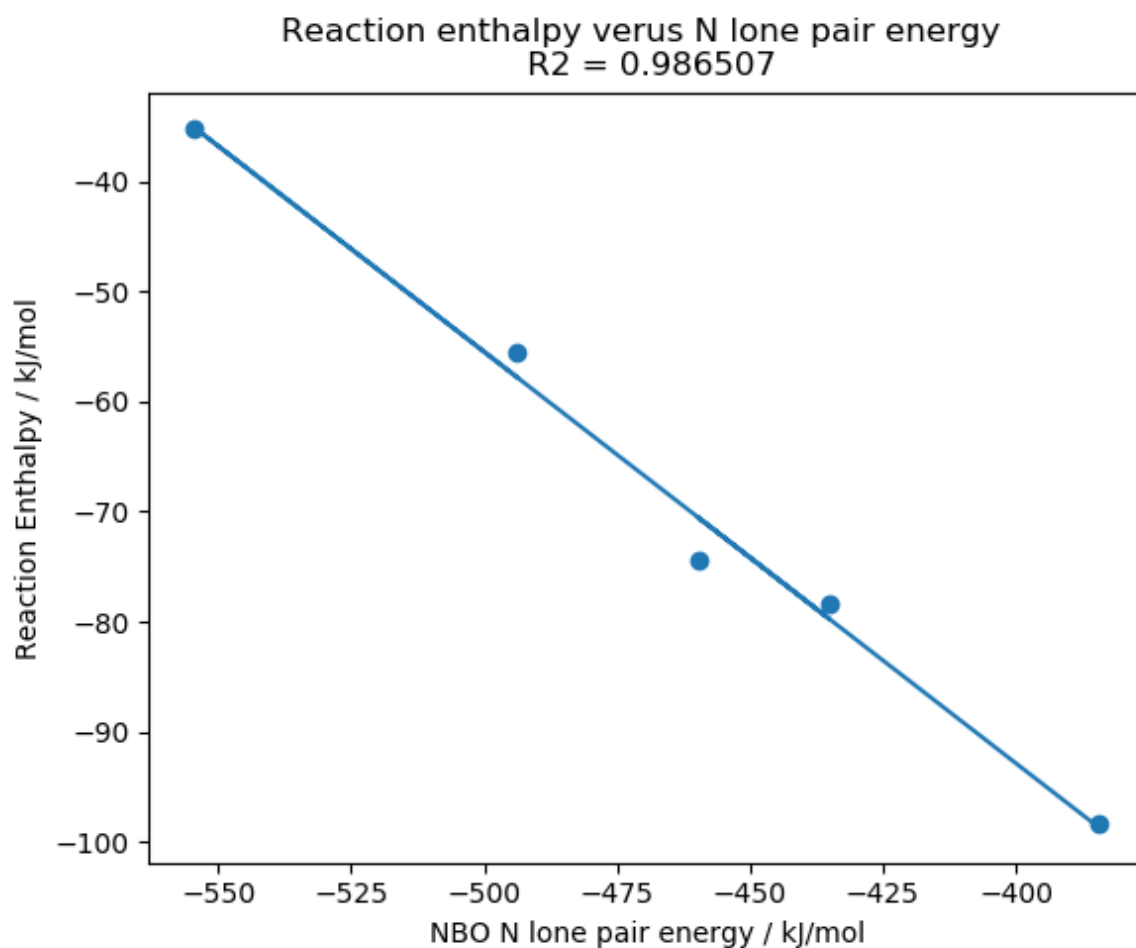
### Q5

#### 1. Compute the reaction enthalpy

Class	Before Hartree	After Hartree	Reaction Enthalpy
Pyrr	-209.573293	-398.242577	-98.3
Pyra	-225.627079	-414.286986	-74.5
Imi	-225.652388	-414.313914	-78.3
Tria123	-241.686778	-430.331907	-35.2
Tria124	-241.710414	-430.363153	-55.5

#### 2. N lone pair energy

Class	Bond Index	Bound Energy (Hartree)	Electron distribution and Energy level	
Pyrr	15	-384.32069		
Pyra	14,15	-459.77756		
Imi	14,15	-435.124		
Tria123	13	-554.55811		
Tria124	15	-493.882805		



**Discuss the geometry change of CO<sub>2</sub> and its reactivity with azole anions**