C343 Lab Report 3

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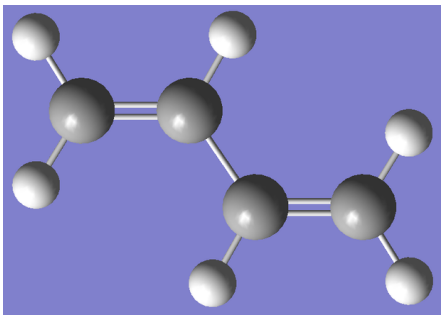
1 Energetics of the different forms

Level of Theory Used for Q 1,2,3: B3LYP/6-31G*

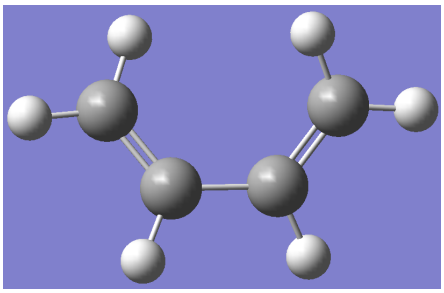
- **Conformers of Butadiene**



(a) trans-Butadiene Energy: -155.9066543 Ha

(b) Frequency: All positive (minima)

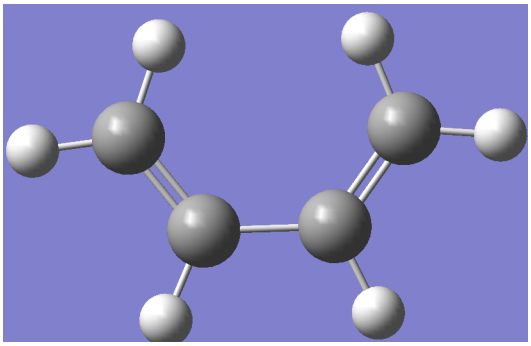
(c) Point Group: C_2h



(d) gauge-Butadiene Energy: -155.90114 Ha

(e) Frequency: All positive (minima)

(f) Point Group: C_2



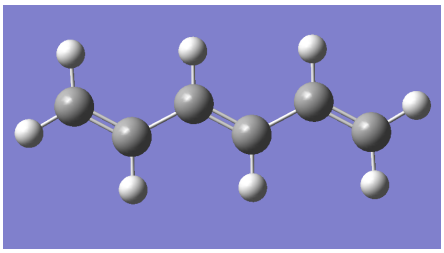
(g) cis-Butadiene Energy: -155.8680045 Ha

(h) Frequency: 1 negative (TS)

(i) Point Group: C_2v

Please Note: The conformers for Hexatriene and Octatetraene are named, based on the configuration about the C-C bonds. If both the C=C lies on the same side of C-C bond it has been termed as cis and trans if they are on opposite side.

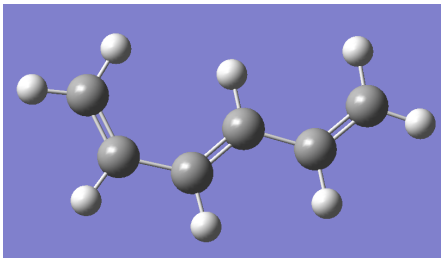
- **Conformers of Hexatriene**
  I use three different conformers of Hexatriene generated by changing the orientation of the C=C about the two C-C bonds for comparing the energetics.



(a) all-trans-Hexatriene Energy: -233.279373 Ha

(b) Frequency: All positive (minima)

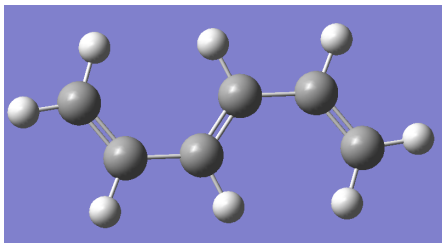
(c) Point Group: C_2h



(d) 1-cis-Hexatriene Energy: -233.2738231 Ha

(e) Frequency: 1 negative (TS)

(f) Point Group: C_s

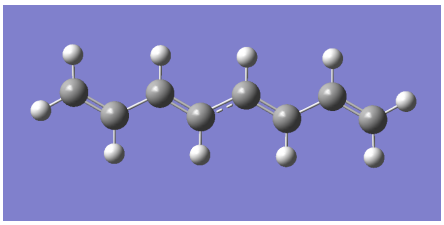


(g) 1,2-cis-Hexatriene Energy: -233.2678607 Ha

(h) Frequency: 2 negative

(i) Point Group: C_2h

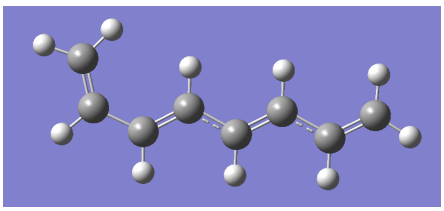
- **Conformers of Octatetraene**
  I use six different conformers of Octatetraene generated by changing the orientation of the C=C about the three C-C bonds for comparing the energetics.



(a) all-trans-Octatetraene

(b) Energy: -310.6528359 Ha, Point Group: C_2h

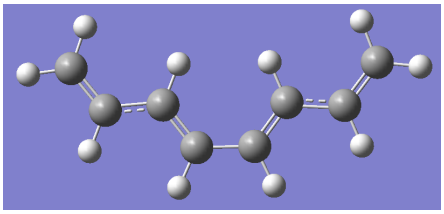
(c) Frequency: All positive (minima)



(d) 1-cis-Octatetraene

(e) Energy: -310.6473412 Ha, Point Group: C_s

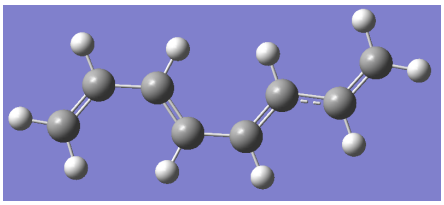
(f) Frequency: 1 negative (TS)



(a) 2-cis-Octatetraene

(b) Energy: -310.647478 Ha, Point Group: C_2v

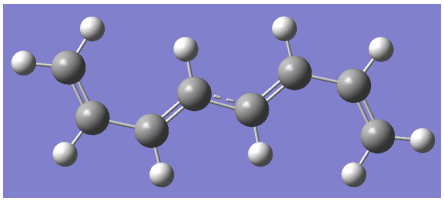
(c) Frequency: All positive (minima)



(d) 1,2-cis-Octatetraene

(e) Energy: -310.6415528 Ha, Point Group: C_s

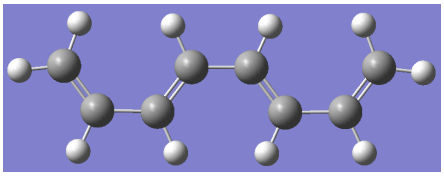
(f) Frequency: 1 negative (TS)



(a) 1,3-cis-Octatetraene

(b) Energy: -310.6419118 Ha, Point Group: C_2h

(c) Frequency: 2 negative



(d) 1,2,3-cis-Octatetraene

(e) Energy: -310.6358052 Ha, Point Group: C_2v

(f) Frequency: 3 negative

2 Most Stable form of the isomers

- Butadiene: all trans configuration (Energy = -155.9066543 Ha)
- Hexatriene: all trans configuration (Energy = -233.279373 Ha)
- Octatetraene: all trans configuration (Energy = -310.6528359 Ha)

3 HOMO-LUMO energy gaps

$$\begin{aligned} \text{HOMO-LUMO energy gap of Butadiene} &= E_{LUMO} - E_{HOMO} \\ &= -0.02251 - (-0.22902) \text{ Hartree} \\ &= 0.20651 \text{ Hartree} \end{aligned} \tag{1}$$

$$\begin{aligned} \text{HOMO-LUMO energy gap of Hexatriene} &= E_{LUMO} - E_{HOMO} \\ &= -0.04436 - (-0.20924) \text{ Hartree} \\ &= 0.16488 \text{ Hartree} \end{aligned} \tag{2}$$

$$\begin{aligned} \text{HOMO-LUMO energy gap of Octatetraene} &= E_{LUMO} - E_{HOMO} \\ &= -0.05768 - (-0.19702) \text{ Hartree} \\ &= 0.13934 \text{ Hartree} \end{aligned} \tag{3}$$

4 Comparison with 1-D particle in a box

Energy **E** of particle in 1-D box(PIB) of length **L** in energy state with quantum number **n**

$$E(n) = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{4}$$

Considering the length of the conjugated polyene system as the length of the box, and then the highest filled energy level as HOMO and the lowest empty energy level as LUMO

$$\begin{aligned} \text{L}(\textbf{Butadiene}) &= 2 * 1.34 + 1.45 \ \mathring{A} \\ &= 4.13 \ \mathring{A} \\ &= 7.807 \text{ bohr} \end{aligned} \tag{5}$$

$$\begin{aligned} \text{L}(\textbf{Hexatriene}) &= 2 * 1.34307 + 2 * 1.45 + 1.35225 \ \mathring{A} \\ &= 6.93839 \ \mathring{A} \\ &= 13.116 \text{ bohr} \end{aligned} \tag{6}$$

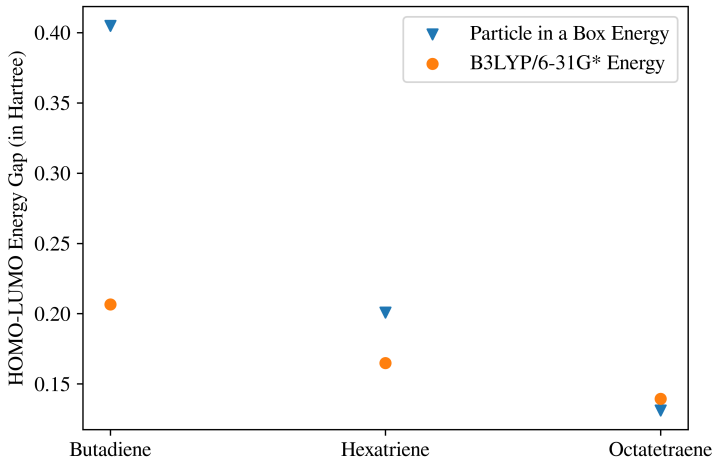
$$\begin{aligned} \text{L}(\textbf{Octatetraene}) &= 2 * 1.34407 + 2 * 1.44775 + 2 * 1.35571 + 1.44098 \ \mathring{A} \\ &= 9.73604 \ \mathring{A} \\ &= 18.405 \text{ bohr} \end{aligned} \tag{7}$$

$$\begin{aligned} \text{PIB HOMO-LUMO energy gap of Butadiene} &= E(3) - E(2) \\ &= \frac{(3^2 - 2^2) * 3.142^2}{2 * 7.807^2} \text{ Hartree} \\ &= 0.40493 \text{ Hartree} \end{aligned} \tag{8}$$

$$\begin{aligned} \text{PIB HOMO-LUMO energy gap of Hexatriene} &= E(4) - E(3) \\ &= \frac{(4^2 - 3^2) * 3.142^2}{2 * 13.116^2} \text{ Hartree} \\ &= 0.20085 \text{ Hartree} \end{aligned} \tag{9}$$

$$\begin{aligned} \text{PIB HOMO-LUMO energy gap of Octatetraene} &= E(5) - E(4) \\ &= \frac{(5^2 - 4^2) * 3.142^2}{2 * 18.405^2} \text{ Hartree} \\ &= 0.13114 \text{ Hartree} \end{aligned} \tag{10}$$

Figure 6 clearly shows, particle in a box model captures the HOMO-LUMO energy gap better with a increase in length of conjugated polyenes (when compared with ab-initio energies calculated at B3LYP-6-31G* level of theory)



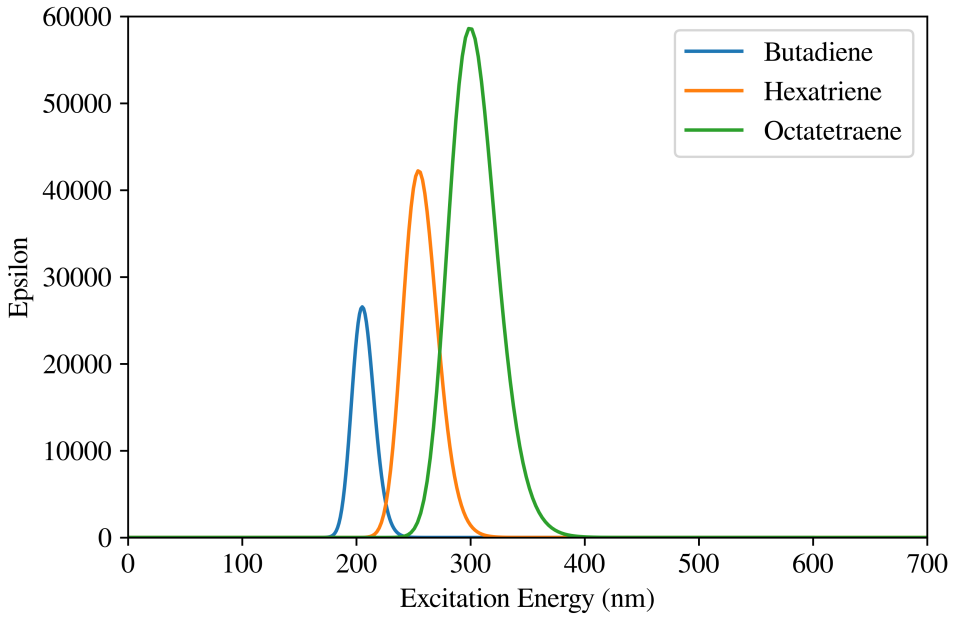
Figuur 6: Comparison of ab-initio energies with 1-D particle in a box energies

5 Vertical transition energy

- **Butadiene**
  Vertical Transition Energy: 6.0426 eV (205.19 nm)
  Type of Transition: $\pi \longrightarrow \pi^*$ transition M.O.(15)[HOMO] $\longrightarrow$ M.O.(16)[LUMO]

- **Hexatriene**
  Vertical Transition Energy: 4.8700 eV (254.59 nm)
  Type of Transition: $\pi \longrightarrow \pi^*$ transition M.O.(22)[HOMO] $\longrightarrow$ M.O.(23)[LUMO]

- **Octatetraene**
  Vertical Transition Energy: 4.1379 eV (299.63 nm)
  Type of Transition: $\pi \longrightarrow \pi^*$ transition M.O.(29)[HOMO] $\longrightarrow$ M.O.(30)[LUMO]



Figuur 7: Simulated UV-VIS Spectrum showing the Vertical Transitions