A diene is a hydrocarbon chain that has two double bonds that may or may not be adjacent to each other. This section focuses on the delocalization of pi systems by comparing two neighboring double bonds. The arrangements of these double bonds can have varying affects on the compounds reactivity and stability.

### Naming Dienes

First identify the longest chain containing both carbons with double bonds in the compound. Then give the lowest possible number for the location of the carbons with double bonds and any other functional groups present (remember when naming alkenes that some groups take priority such as alcohols). Do not forget stereochemistry or any other orientation of the double bond such as (E/Z,cis or trans).

Examples:

![Examples_naming.bmp](Examples_naming.bmp)

### Conjugated vs. Nonconjugated vs. Cumulated Dienes

Conjugated dienes are two double bonds separated by a single bond

![conjugated_diene2 (1).bmp](conjugated_diene2 (1).bmp)

Nonconjugated (Isolated) Dienes are two double bonds are separated by more than one single bond.

![nonconjugated_diene (1).bmp](nonconjugated_diene (1).bmp)

Cumulated Dienes are two double bond connected to a similar atom.
When using electrostatic potential maps, it is observed that the pi electron density overlap is closer together and delocalized in conjugated dienes, while in non conjugated dienes and cumulated dienes the pi electron density is located differently across the molecule. Since having more electron density delocalized makes the molecule more stable conjugated dienes are more stable than non conjugated and cumulated dienes.

Stability of Conjugated Dienes

Conjugated dienes are more stable than non conjugated dienes (both isolated and cumulated) due to factors such as delocalization of charge through resonance and hybridization energy. This can also explain why allylic radicals are much more stable than secondary or even tertiary carbocations. This is all due to the positioning of the pi orbitals and ability for overlap to occur to strengthen the single bond between the two double bonds.

The resonance structure shown below gives a good understanding of how the charge is delocalized across the four carbons in this conjugated diene. This delocalization of charges stablizes the conjugated diene:

Along with resonance, hybridization energy effect the stability of the compound. For example in 1,3-butadiene the carbons with the single bond are sp2 hybridized unlike in nonconjugated dienes where the carbons with single bonds are sp3 hybridized. This difference in hybridization shows that the conjugated dienes have more 's' character and draw in more of the pi electrons, thus making the single bond stronger and shorter than an ordinary alkane C-C bond (1.54Å).
Another useful resource to consider are the heats of hydrogenation of different arrangements of double bonds. Since the higher the heat of hydrogenation the less stable the compound, it is shown below that conjugated dienes (~54 kcal) have a lower heat of hydrogenation than their isolated (~60 kcal) and cumulated diene (~70 kcal) counterparts.

Here is an energy diagram comparing different types of bonds with their heats of hydrogenation to show relative stability of each molecule:

energychart.bmp

Different conformations of Conjugated Dienes

There are two different conformations of conjugated dienes which are s-cis and s-trans conformations. s-cis is when the
double bonds are cis in reference to the single bond and s-trans is when the two double bonds are trans in reference to the single bond. The cis conformation is less stable due to the steric interaction of hydrogens on carbon. One important use of the cis conformation of a conjugated diene is that it is used in diels-aldar cycloaddition reactions. Even though the trans conformation is more stable the cis conformation is used because of the molecule’s ability to interconvert and rotate about the single bond.

Molecular Orbitals

The four pi electrons from the two double bonds are placed in the bonding orbitals with no nodes (2 electrons) and one node (2 electrons). The orbital with the Highest occupied molecular orbital (HOMO) is used in cycloaddition reactions as dienophiles.

Here is a clear representation of what is going on in the Highest occupied molecular orbital of the conjugated diene:
References


Problems

1) Draw the following: 1,3-cycloheptadiene

2) Name the following:

3) Draw both s-cis and s-trans conformations of 1,3-pentadiene and state which is more stable and why?

4) What do you think is more stable *trans*-1,3-pentadiene or 1,4-pentadiene? and why?

5) Draw the molecular orbital for 1,3-butadiene

Answers

1)
2) (Z)-4-Chloro-1,3-hexadiene

3) s-trans is more stable because there is less steric interaction between the methyl and hydrogens unlike in s-cis.

4) trans-1,3-pentadiene because it is a conjugated diene, which is more stable than an isolated diene such as 1,4-pentadiene. This is due to many reasons such as resonance energy and hybridization.

5) Molecular_orbitals.bmp

Contributors

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