Chemical Bonding Theory

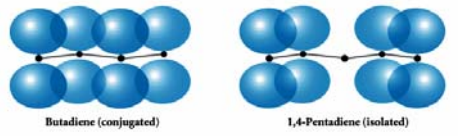
An explanation for observed chemical and spectroscopic behavior

Items to explain

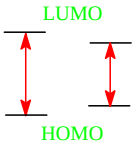
1. Polarity of bonds
   - IR spectroscopy
   - NMR chemical shifts
2. Electrochemistry
   - Oxidation and reduction potentials lower with conjugation
3. UV spectroscopy
   - Alkanes don't absorb well
   - Conjugation increases λ_{max}
   - Benzene (178 nm) vs. 2,4-hexadiene (240 nm)

Conjugation

- Conjugated bonds: p atomic orbitals form a continuous system
- Isolated bonds: p atomic orbitals do not form a continuous system



Conjugation and UV/VIS Spectroscopy

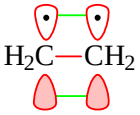


butadiene hexatriene

- UV/VIS measures "HOMO-LUMO gap"
- Conjugation lowers energy gap between HOMO and LUMO
- **Conjugation → longer λ_{max}**

Conjugation in π-Systems: Ethene

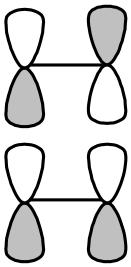
VB picture of ethene



$\equiv$ $H_2C{=}CH_2$

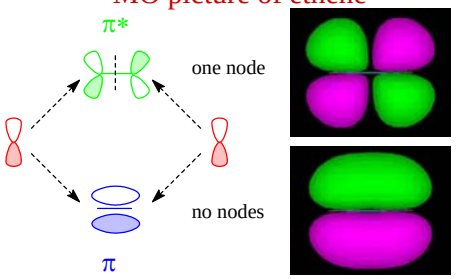
Conjugation in π-Systems: Ethene

MO picture of ethene

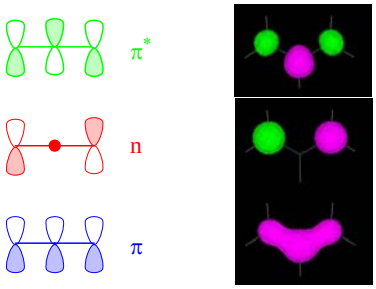


Conjugation in π-Systems: Ethene

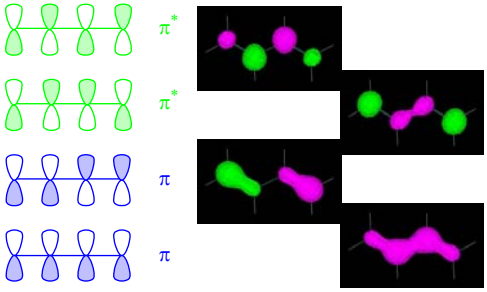
MO picture of ethene



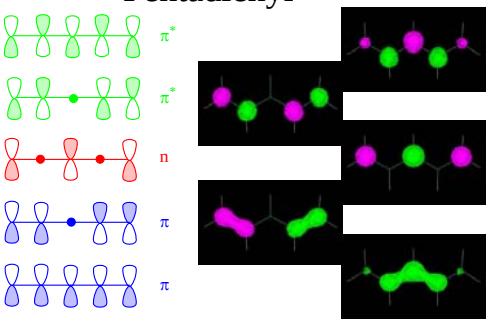
Conjugation in π-Systems: Allyl



Conjugation in π-Systems: Butadiene



Conjugation in π-Systems: Pentadienyl



Conjugation in π-Systems: Hexatriene