Conjugated Systems

Definition: Systems that are separated by exactly one single bond from a double bond

Compounds containing conjugated systems:

Polyenes:

Example 1: 1,3-butadiene

Double bonds are separated by one single bond

Tends to be planar; p orbitals want to be aligned, even though rotation along the sigma bond is not restricted. Transoid conformation is in equilibrium with cisoid conformation.

1.47 Å instead of 1.54 Å

Example 2: Benzene



Examples: Conjugated or Not?





1,3-cyclohexadiene conjugated

not conjugated



Conjugated (relatively unreactive)



Electromagnetic Spectrum:

1nm = 10 angstrom



UV and visible light: conjugated double bond systems absorb UV light and some visible light



Molecular Orbitals:

Example 1: Ethylene





A.O. means atomic orbitals (s, sp², p) M.O. means molecular orbitals (σ , π)

Looking only at the π orbitals:



An electron can be excited from the HOMO to the LUMO using light of a precise wavelength dependent on the energy difference between the two orbitals (since the orbitals are quantized). The electron can go back to its original orbital and heat (or light) is produced in the process. When the electron is promoted to a higher energy state (excited to a higher energy molecular orbital), it attains a **singlet state**. The electron can go back to its original orbital and heat (or light) is produced in the process.





Node: a point or plane of zero electron density in an orbital **HOMO**: Highest Occupied Molecular Orbital **LUMO**: Lowest Unoccupied Molecular Orbital



As the number of double bonds in the compound increases, decreasing the HUMO-LUMO gap, the energy of the light needed to excite the compound to its excited state is lower.

Once the absorption of light leaves the UV range and into the visible range, the transition becomes visible and the color of the compound can be seen.





Conjugated molecules in vision:



Retinal is combined with the protein opsin in the eye to make rhodopsin, which is a key protein in the mechanism of sight.

Human vision covers the range of 400 nm (4000 Å) to 800 nm (8000 Å), anything outside of these wavelengths is invisible to the naked eye.

The further oxidized form of retinal is retinoic acid. Changing the double bond bearing the carboxylic acid from trans to cis gives the drug Accutane, used to treat acne. (Can cause birth defects = teratogen)

Ο ЭH

нобо

Retinoic acid

Accutane