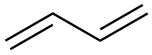
Conjugated Systems

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

Compounds containing conjugated systems:

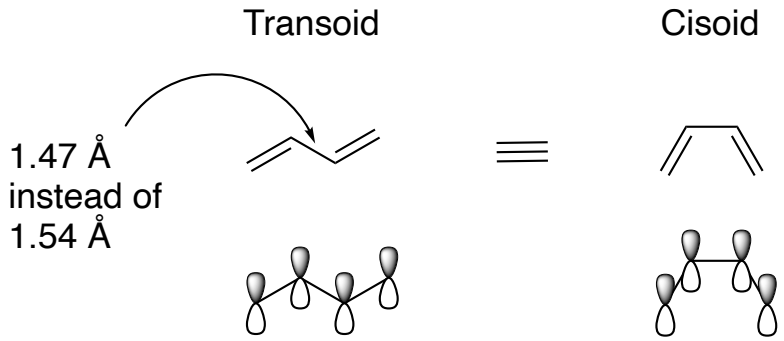
Polyenes:

Example 1: 1,3-butadiene

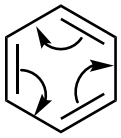


Double bonds are separated by one single bond

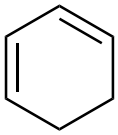
Tends to be planar; p orbitals want to be aligned, even though rotation along the sigma bond is not restricted. Transoid conformation is in equilibrium with cisoid conformation.



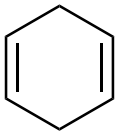
Example 2: Benzene



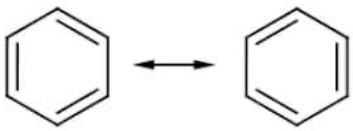
Examples: Conjugated or Not?



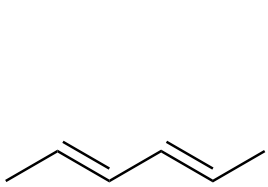
1,3-cyclohexadiene
conjugated



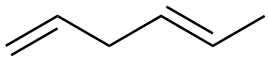
not conjugated



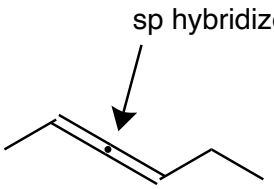
Conjugated (relatively unreactive)



conjugated

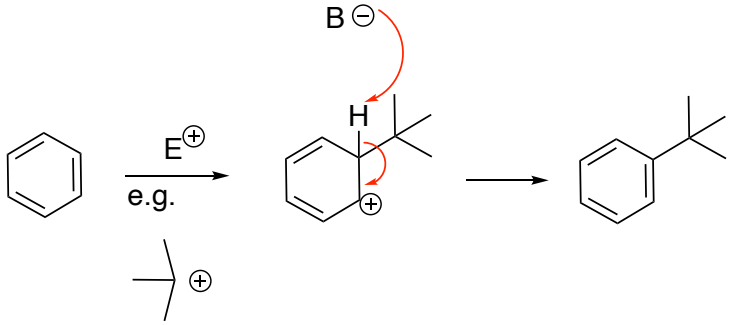


not conjugated



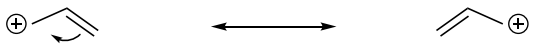
not conjugated

Example of reaction of Benzene:



Conjugated Intermediates:

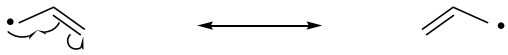
1) Cation:



Allyl Cation

Conjugation stabilizes the positive charge

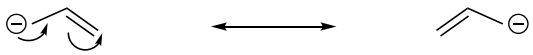
2) Radical:



Allyl Radical

Conjugation stabilizes the radical

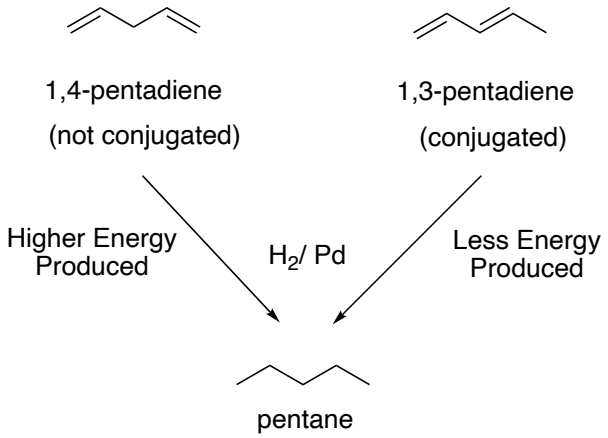
3) Anion:



Allyl Anion

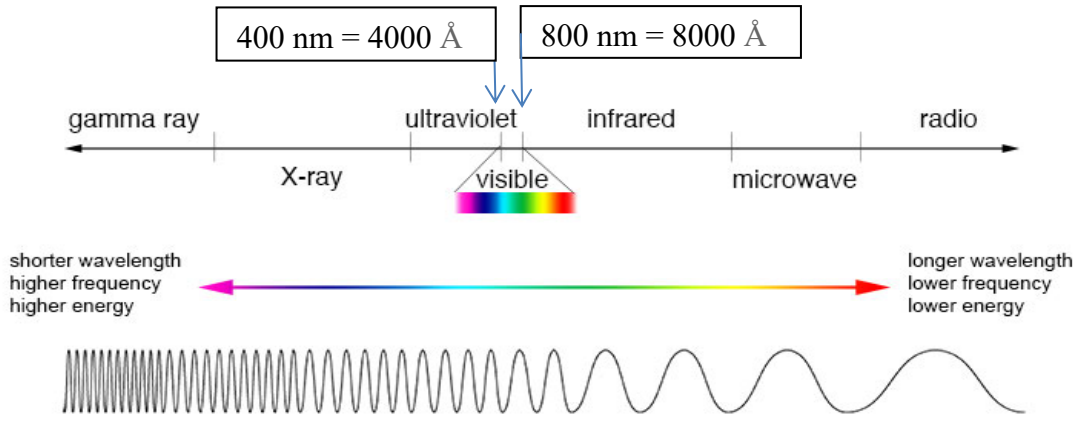
Conjugation stabilizes the negative charge

Example of conjugated and not conjugated system:



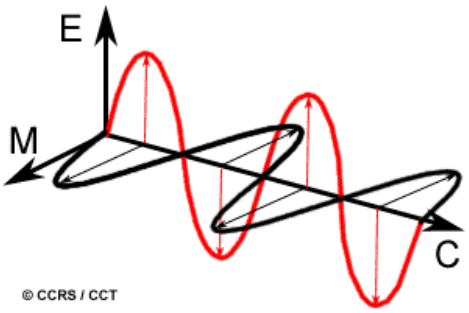
Electromagnetic Spectrum:

1nm = 10 angstrom



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

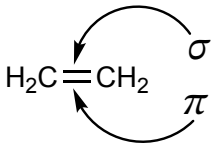
$$E = h\nu = \frac{hc}{\lambda}$$



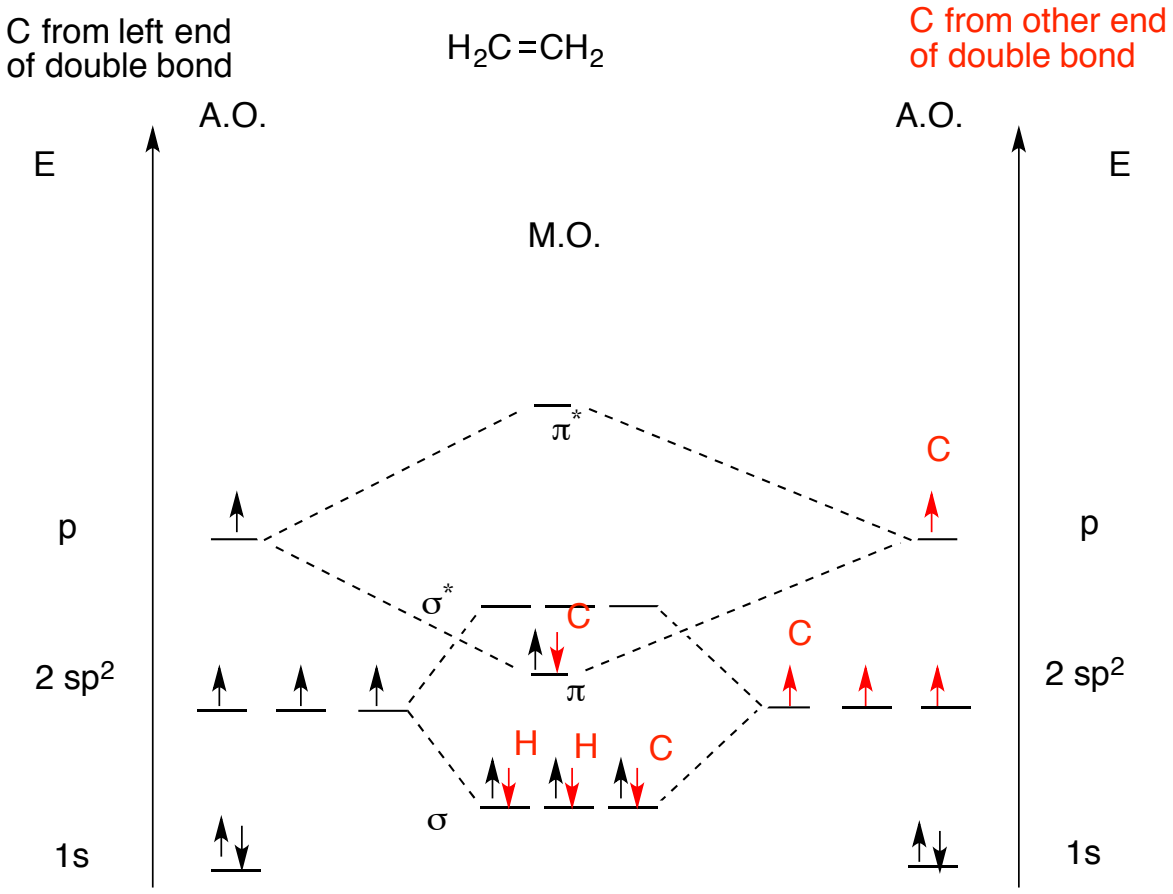
E = energy
H = Planck's Constant (6.6 x 10^{-34} Joules•sec
ν = frequency
λ = wavelength
c = speed of light (3.0 x 10^{10} cm/sec)

Molecular Orbitals:

Example 1: Ethylene

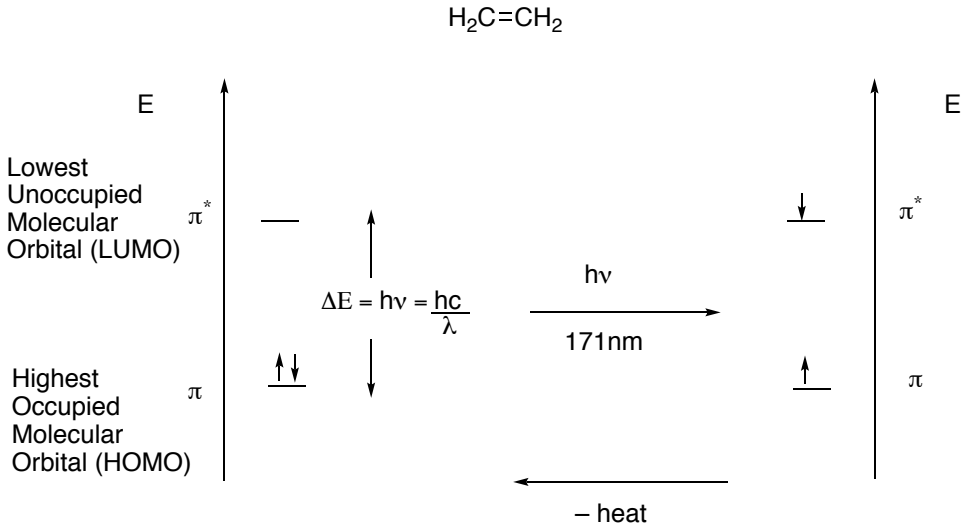


Looking both at sigma and pi orbitals:



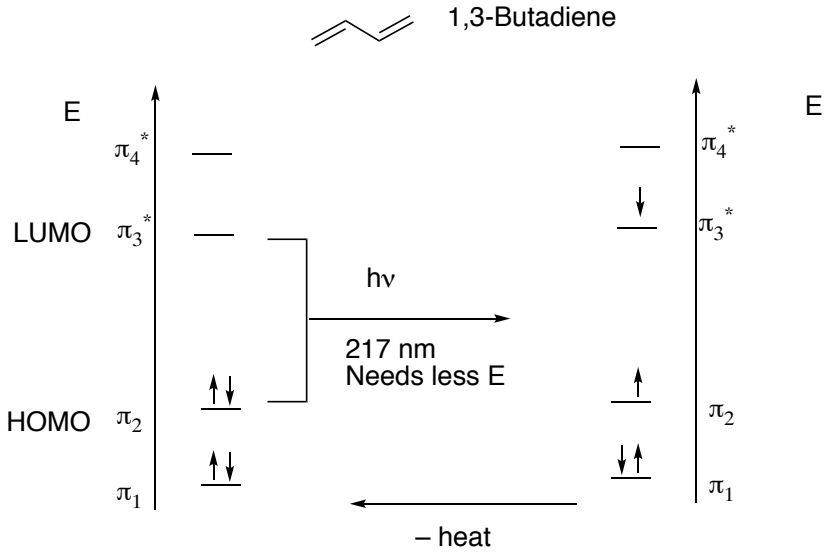
A.O. means atomic orbitals (s, sp^2, p)
M.O. means molecular orbitals (σ , π)

Looking only at the π orbitals:

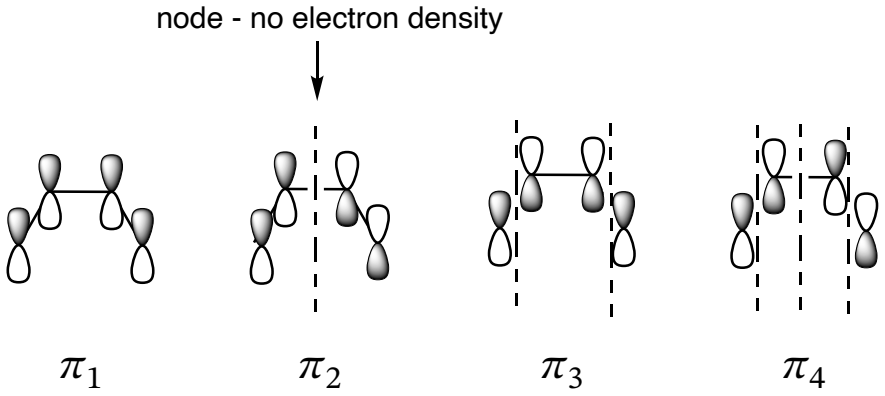


An electron can be excited from the HOMO to the LUMO using light of a precise wavelength dependent on the energy difference between the two orbitals (since the orbitals are quantized). The electron can go back to its original orbital and heat (or light) is produced in the process. When the electron is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

Example 2: 1,3-Butadiene



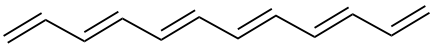
Node: a point or plane of zero electron density in an orbital
HOMO: Highest Occupied Molecular Orbital
LUMO: Lowest Unoccupied Molecular Orbital

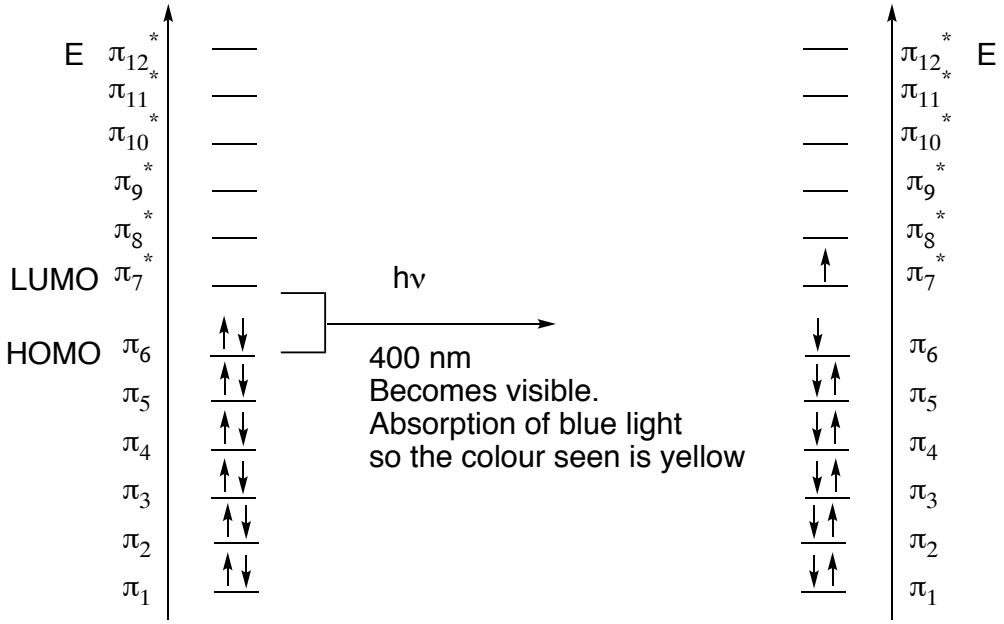


As the number of double bonds in the compound increases, decreasing the HUMO-LUMO gap, the energy of the light needed to excite the compound to its excited state is lower.

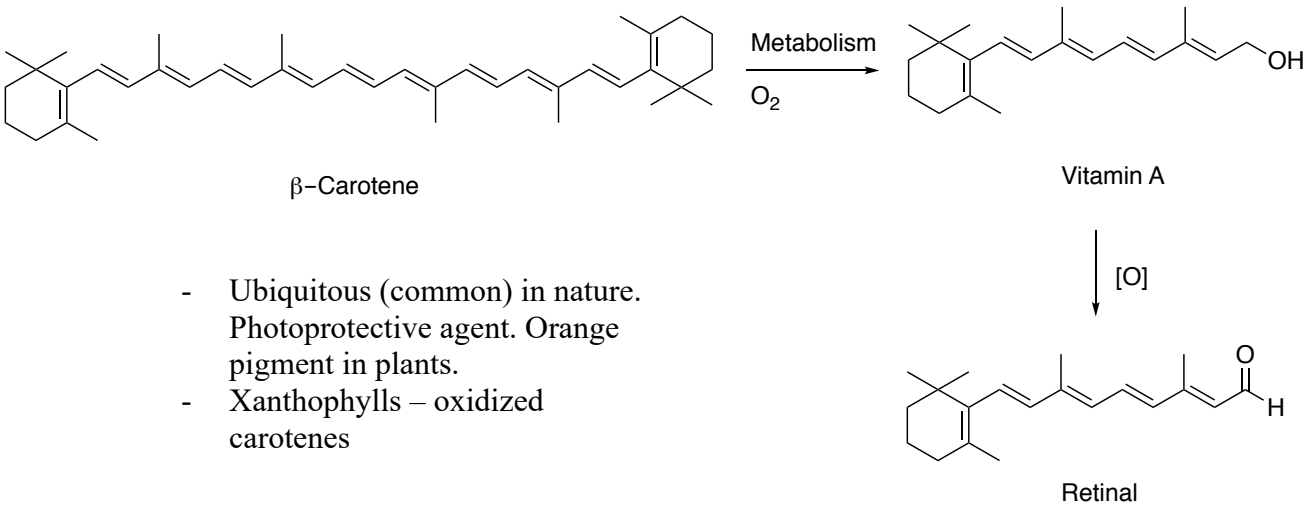
Once the absorption of light leaves the UV range and into the visible range, the transition becomes visible and the color of the compound can be seen.

Example 3: 1,3,5,7,9,11-dodecahexaene





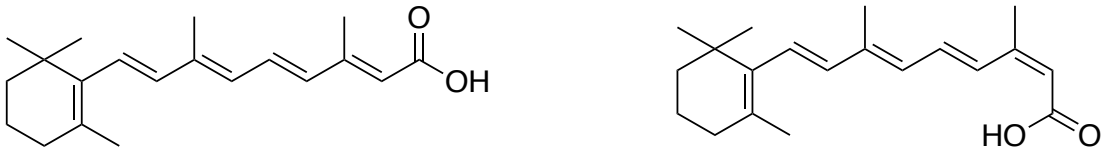
Conjugated molecules in vision:



- Ubiquitous (common) in nature. Photoprotective agent. Orange pigment in plants.
- Xanthophylls – oxidized carotenes

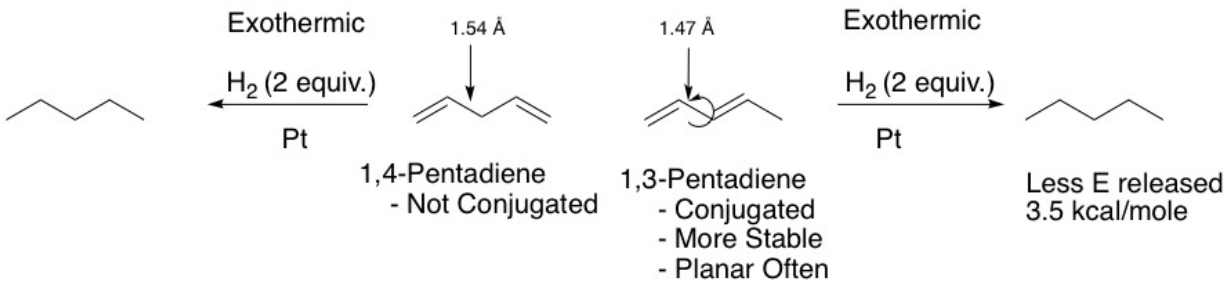
Retinal is combined with the protein opsin in the eye to make rhodopsin, which is a key protein in the mechanism of sight.

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)

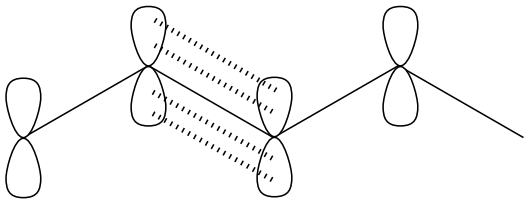


Retinoic acid Accutane

Polyenes:



1,3-Pentadiene is planar often so that p-orbitals can overlap as seen below. The partial interaction of orbitals in the middle bond shortens the bond length due to partial double bond character. There is still rapid rotation about the single bond between the two double bonds, but the preferred conformation all pi bonds aligned. (Transoid preferred over ciosoid)



1,3-Pentadiene prefers to be planar so that p-orbitals can overlap