Conjugated Systems

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

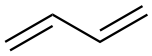
Compounds containing conjugated systems:

Polyenes:

Example:

1,3-Butadiene

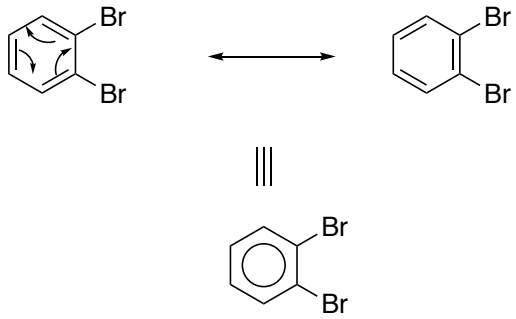
Double bonds are separated by one single bond



Aromatic Compounds:

1) Cyclic
2) Conjugated throughout
3) Planar
4) 4n + 2 electrons, where n is an integer (n=1,2,3,4….)

Example: 1,2-Dibromobenzene



Benzene:

- 36 kcal/mole more stable than is expected

6 π electrons

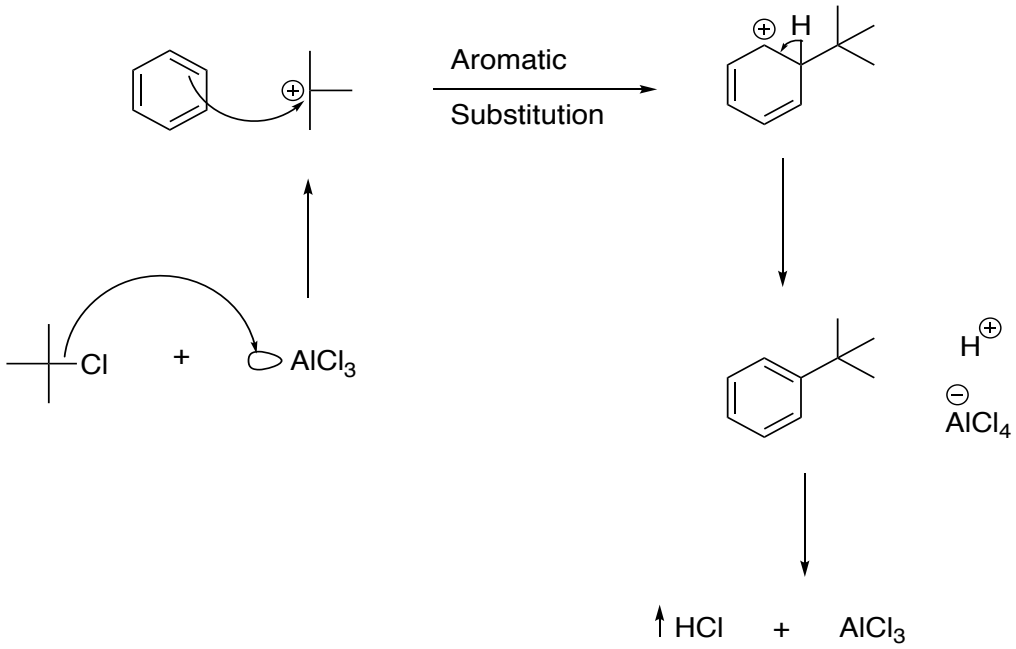
Therefore it satisfies 4n + 2 rule, where n=1

4 π electrons

Therefore it cannot satisfy 4n + 2 rule because n would need to be 1.5 (must be an integer)

Aromatic Compounds Are Not Like Alkenes:

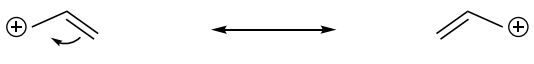
- Much less reactive
- **e.g. of reactivity** Friedel-Crafts Alkylation



Aromatic compounds do not undergo simple addition reactions like alkenes do, but rather they require a catalyst (such as $AlCl_3$ in this case) to produce a highly electrophilic species than can draw out the π electrons. Once the cation (conjugated) forms, elimination is fast to regenerate the aromatic system (does not add the negative species such as chloride)

Conjugated Intermediates:

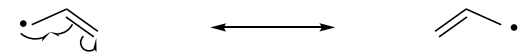
1) Cation:



Allyl Cation

Conjugation stabilizes the positive charge

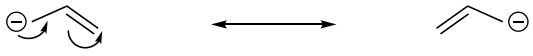
2) Radical:



Allyl Radical

Conjugation stabilizes the radical

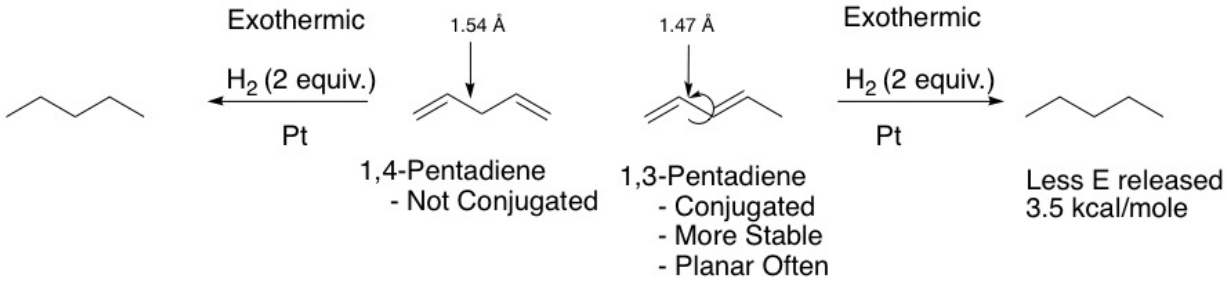
3) Anion:



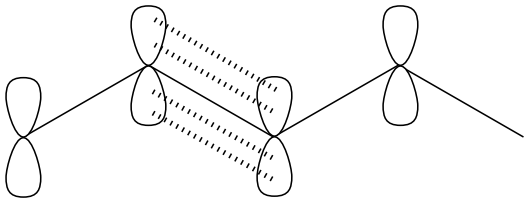
Allyl Anion

Conjugation stabilizes the negative charge

Polyenes:



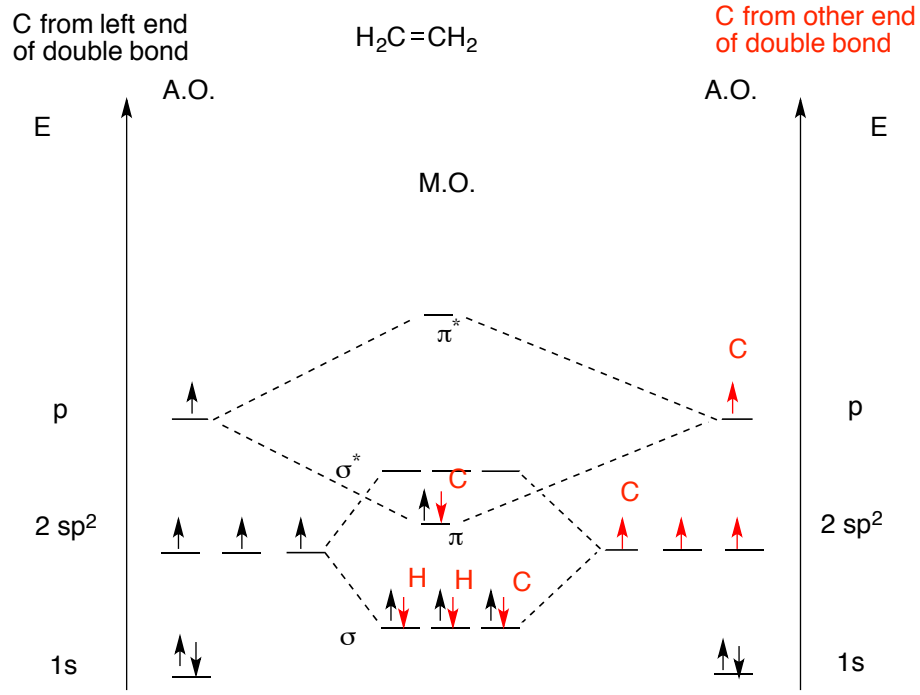
1,3-Pentadiene is planar often so that p-orbitals can overlap as seen below. The partial interaction of orbitals in the middle bond shortens the bond length due to partial double bond character. There is still rapid rotation about the single bond between the two double bonds, but the preferred conformation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



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

Molecular Orbitals:

Example 1: Ethylene

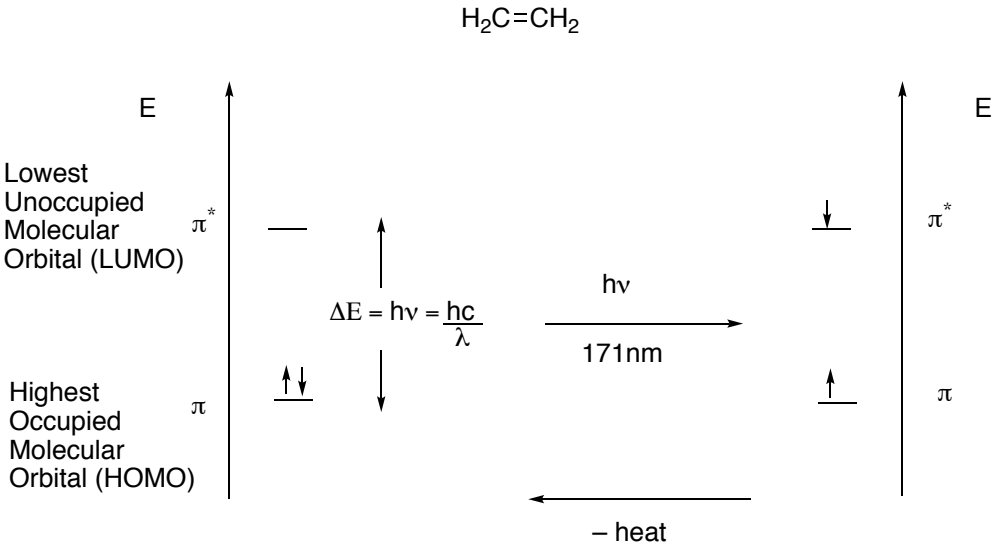


Looking at both sigma and pi bonds

A.O. means atomic orbitals (s, sp^2, p)

M.O. means molecular orbitals (σ , π)

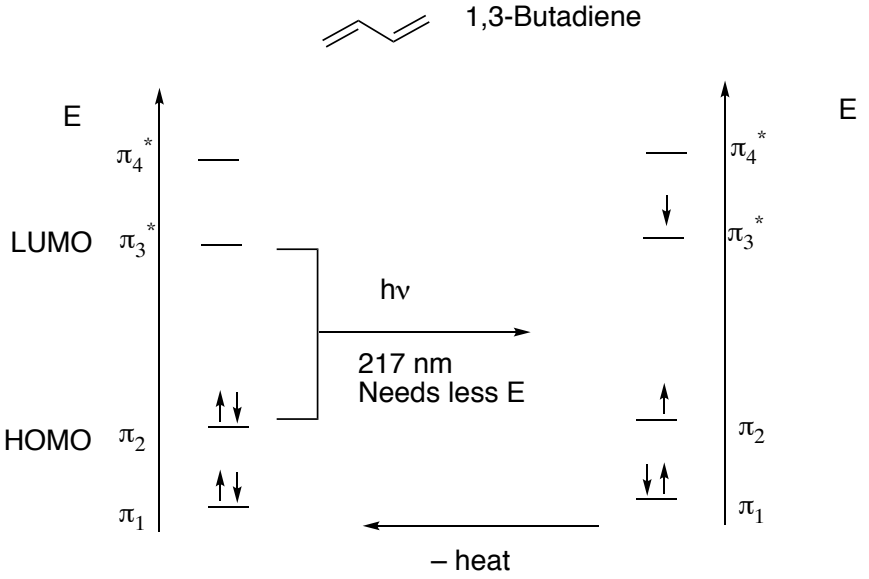
Looking only at the π orbitals:



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 it's original orbital and heat (or light) is produced in the process.

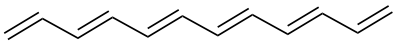
Example 2: 1,3-Butadiene

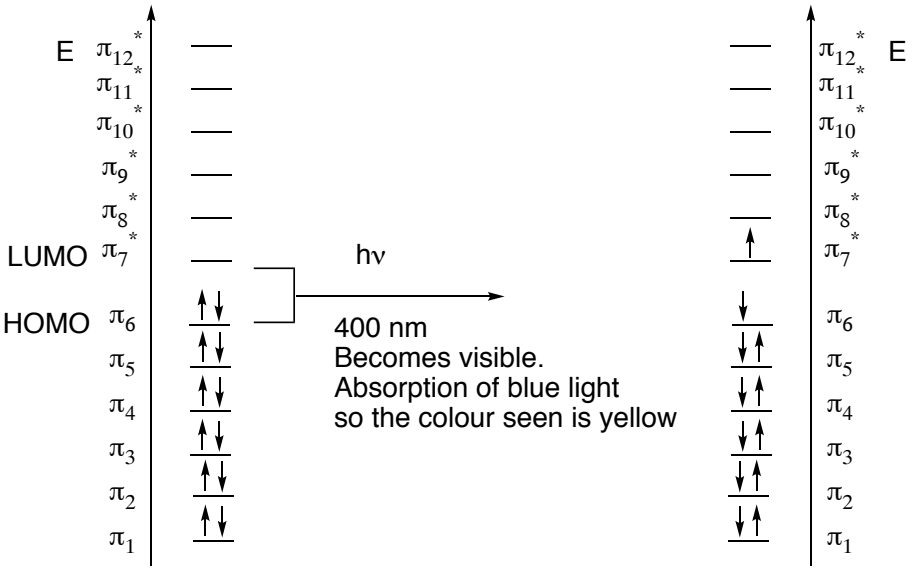


As the # of double bonds in the compound increases, decreasing the HUMO-LUMO gap, the energy of the light needed to excite the compound to its excited state is lower.

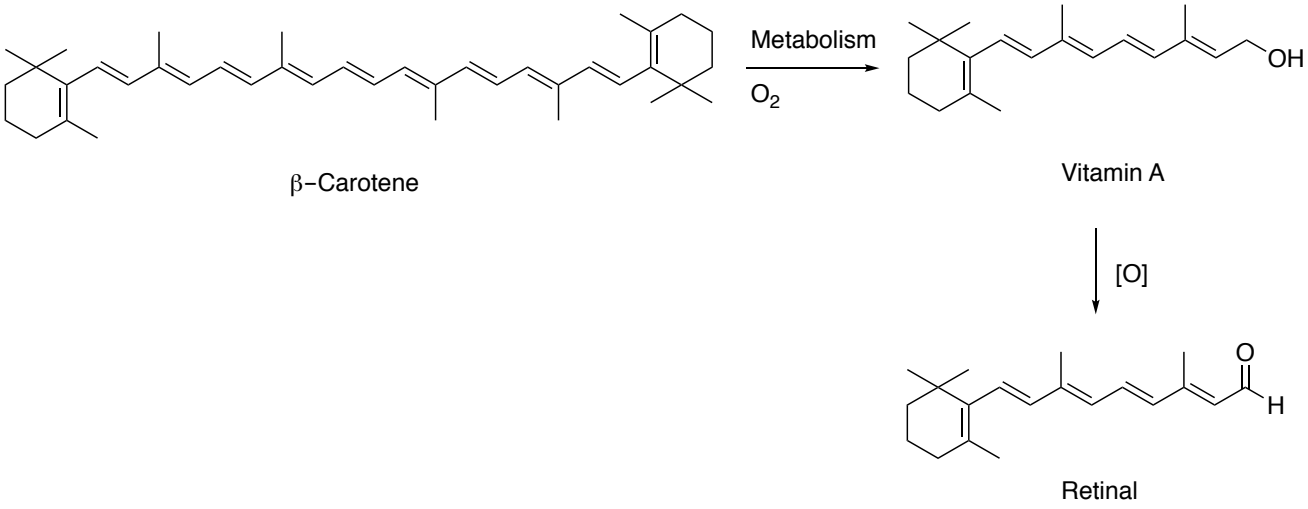
Once the absorption of light leaves the UV range and into the visible range, the transition becomes visible and the colour of the compound can be seen.

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





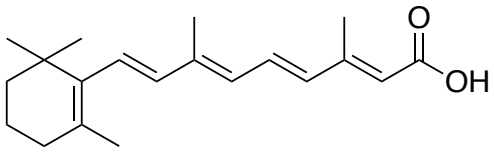
Conjugated molecules in vision:



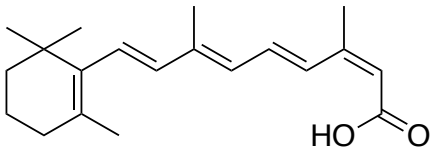
Retinal is combined with the protein opsin in the eye to make rhodopsin, which is a key protein in the mechanism of sight.

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)



Retinoic acid



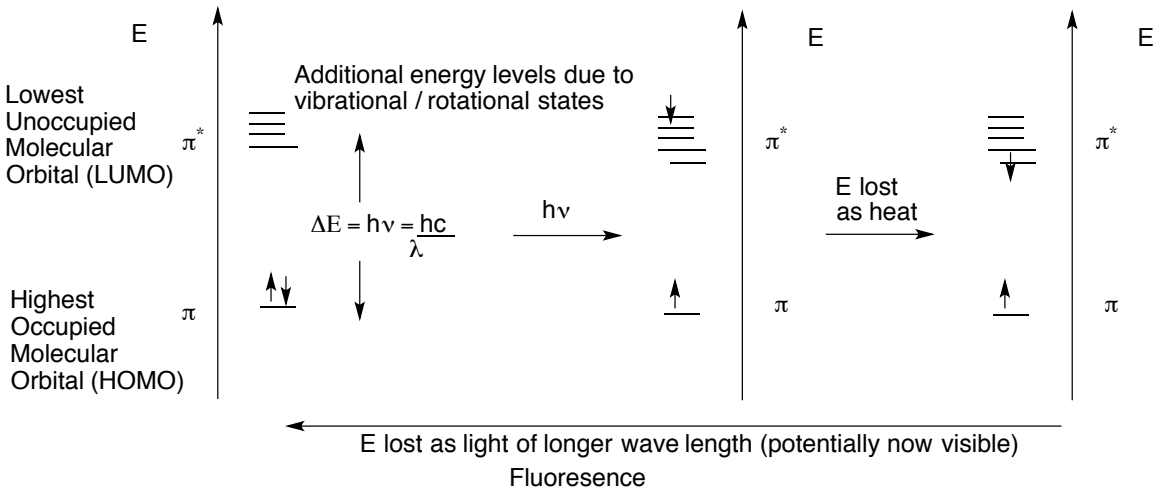
Accutane

<u>Light Emission</u>

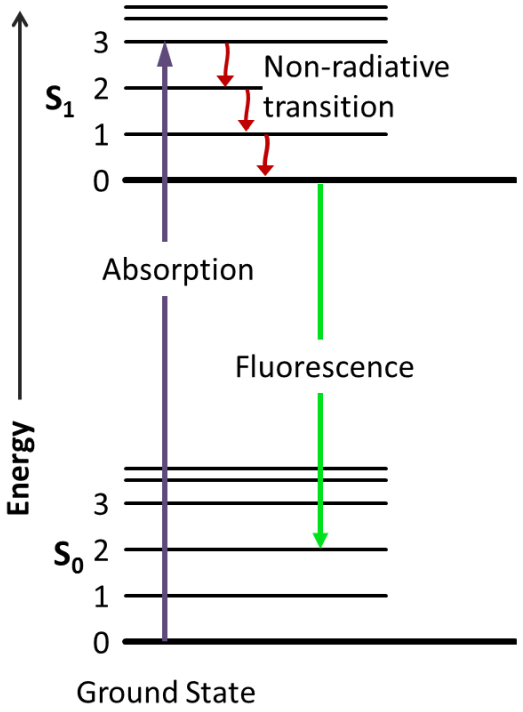
1) Fluorescence
- Absorb UV and emit either UV or Visible
- Short life (singlet state – electrons paired)

2) Phosphorescence
- Absorb UV and emit Visible
- Long life (triplet state – electrons not paired)

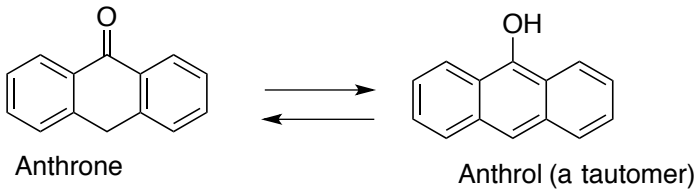
3) Chemiluminescence
- Reactions that produce light



Another diagram (from Wikipedia) depicting the same idea with additional vibrational energy states is shown below



Many commercial clothes detergents contain fluorescent dyes. These absorb in UV and emit in blue, thereby making colours appear brighter and whites appear white. Some are anthrone / anthrol or derivatives. The two compounds are tautomers (rapidly interconverting structural isomers)



Anthrone

Anthrol (a tautomer)