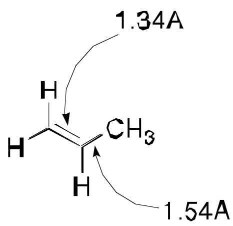
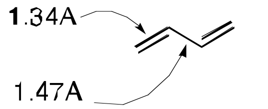
CHEM 261 Notes **Nov 22, 2017**

REVIEW:



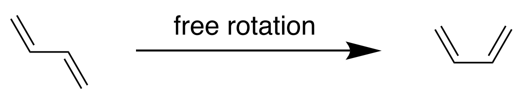
1-propene



1,3-buladiene

Recall how we can show the energy levels of the atomic orbitals of C. If the C is sp^2 hybridized, two of the 2p orbitals "combine" with the 2s orbital to form two sp^2 hybrid orbitals.

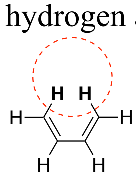
1,3-butadiene



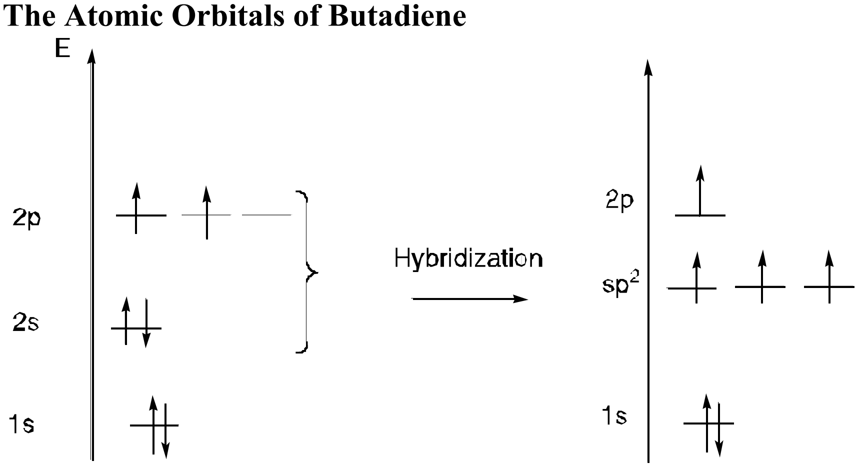
Transoid

Cisoid

- 1,3-butadiene will likely be a choose a planar conformation (conjugated)
- the transoid form is more stable since the the atoms will be less crowded
- the cisoid form is less stable, likely due to steric interactions between the hydrogen atoms shown below (red dotted circle):



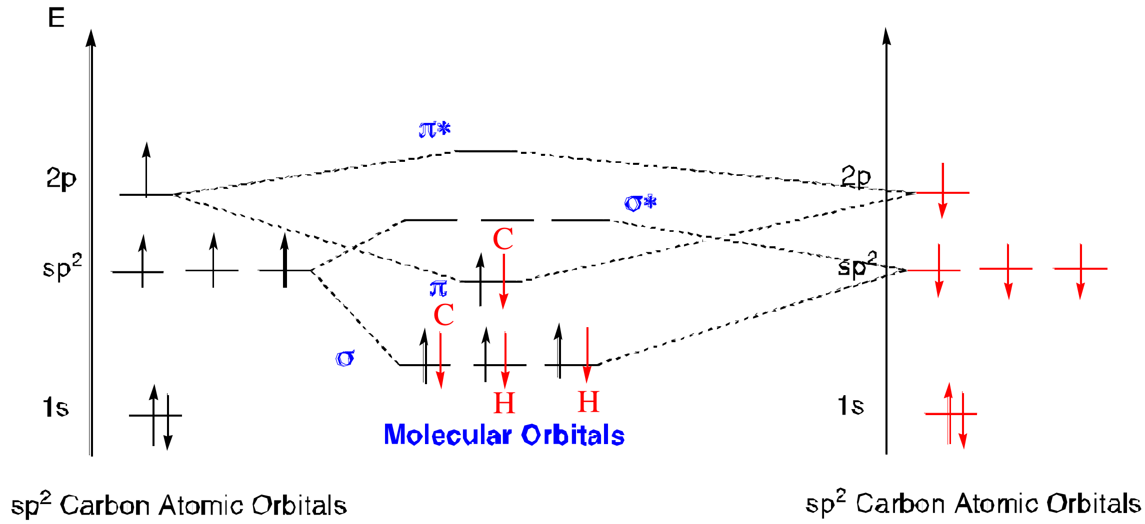
The Atomic Orbitals of Butadiene



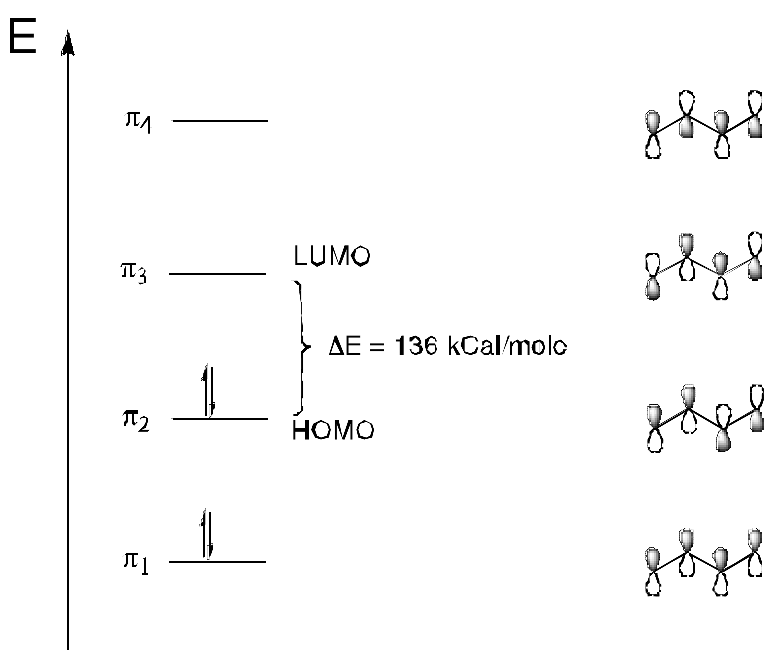
Carbon Atomic Orbitals

sp^2 Carbon Atomic Orbitals

The following molecular orbital (MO) diagram shows the construction of molecular orbitals from the hybrid orbitals of two sp^2 hybridized carbons doubly bonded together (i.e., ethane). One electron pair in the σ MO represents the single bond between the two carbons (and the other two represent C-H bonds), while the electron pair in the π MO represents the double bond (i.e., the π bond) between the two carbons.

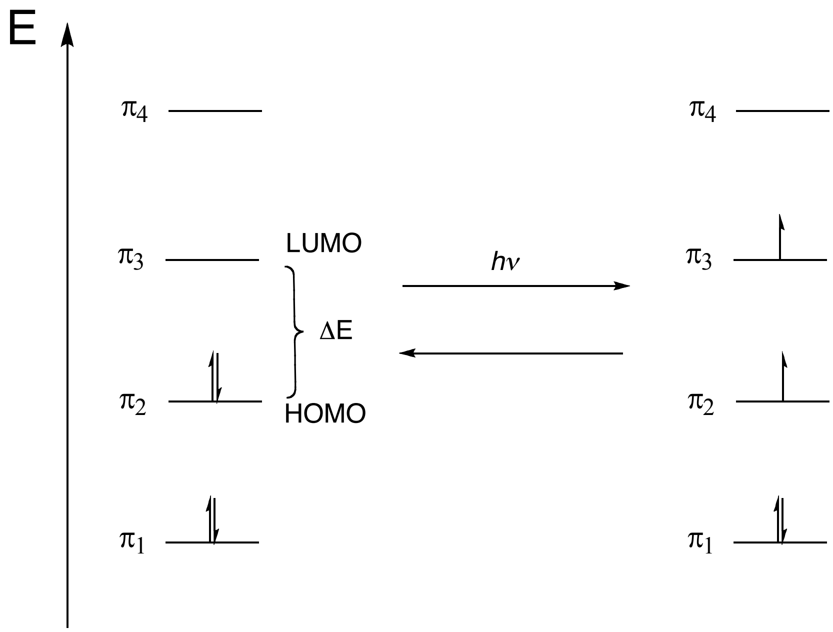


In butadiene, all four-carbon atoms have a *2p* orbital. These four **atomic** *2p* orbitals will combine to produce four π **molecular** orbitals (the number of atomic orbitals combined equals the number of molecular orbitals formed). Since there are two double bonds, there are two bonding (π) and two antibonding (π^*) molecular orbitals (recall each π bond system is made by combining two *2p* atomic orbitals).



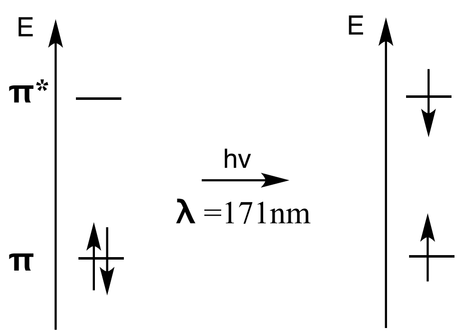
HOMO = Highest Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecular Orbital

Two double bonds means that there are 4 π electrons in the conjugated system (1 double bond has 2 π electrons). We can fill the 4 **molecular** orbitals with these electrons starting from the lowest energy level.



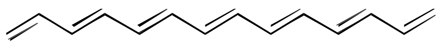
Where $h\nu$ above is also $E = hc/\lambda$

Molecules absorb energy at the specific wavelength corresponding to the ΔE between the HOMO and LUMO. This is the basis for colour (absorption of light with a wavelength corresponding to visible light) and photosynthesis.



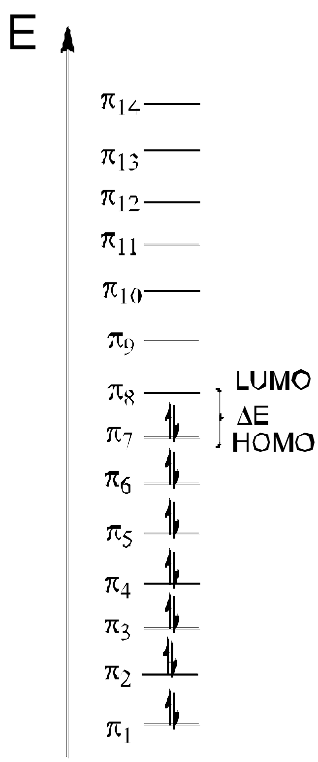
As the molecule becomes more conjugated, the energy gap (ΔE) between the HOMO and LUMO become smaller.

Molecules with ≥ 7 conjugated double bonds absorb light between 4000 – 8000 Å (400-800nm) and are visible to us, such as the compound shown below.

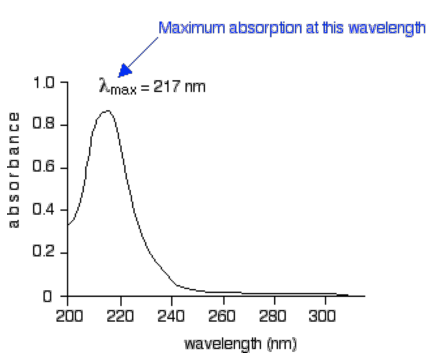


In this molecule, there are 7 bonding and 7 anti-bonding π MO. The energy gap between LUMO and HOMO is very small and is equal to the energy of blue light (~400 nm).

Since E = hc/λ, the wavelength at which this molecule absorbs is long. It absorbs blue light and we see it as yellow.



UV Absorption



Beer's law

A= ε c l

A = absorbance

ε = extinction coefficient

c = molar concentration

l = path length

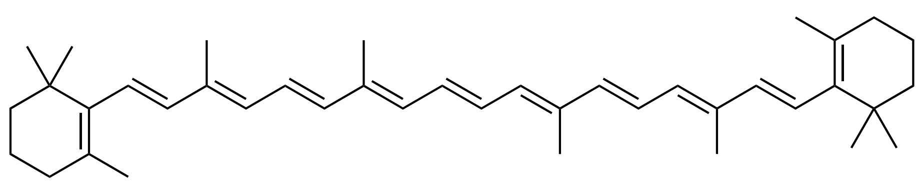
Woodward rules: Predicts wavelength of absorption
The presence of highly conjugated compounds can be measured by using a uv spectrometer

Absorption and Reflection of Visual Light

Absorbed Wavelength (Å)	Colour Absorbed	Visual Colour
4000-4350	violet – blue	yellow – green
4900-5000	blue – green	red
5800-5950	yellow	blue
5950-6050	orange – red	green
6050-7500	red	blue – green

Conjugated Dienes and Colour

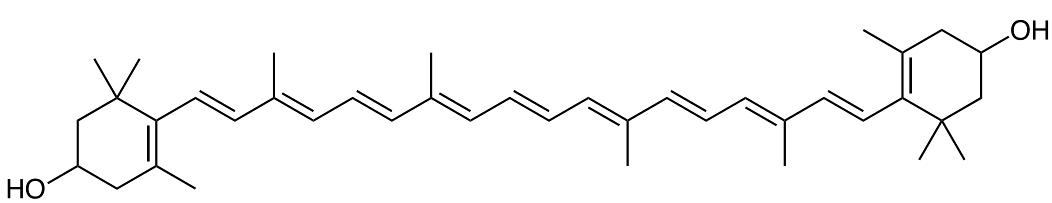
Beta-carotene (depicted below) is responsible for the orange-red colour in carrots. Plants produce 10^9 metric tons of beta-carotene per year. Carotenoids protect plants against photodamage.



β-carotene

Xanthophylls

Xanthophylls are oxygenated or oxidized carotene molecules. Zeaxanthin, shown below is yellow orange (not purple as incorrectly stated in class).



Zeaxanthin (yellow-orange)

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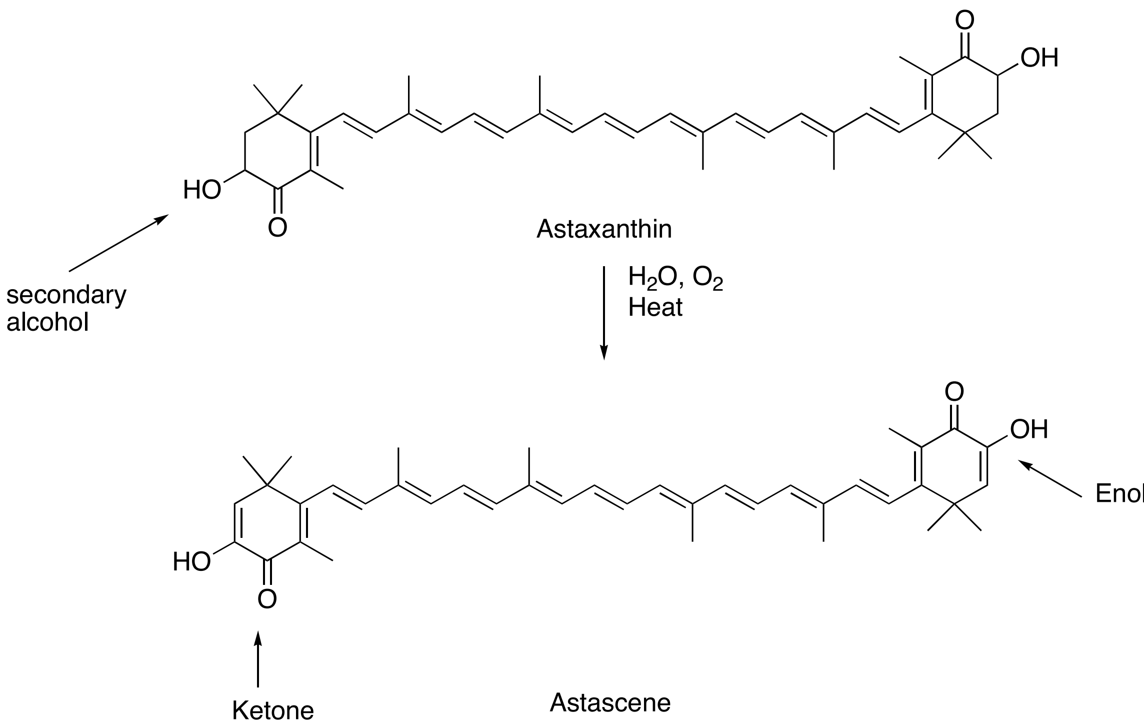
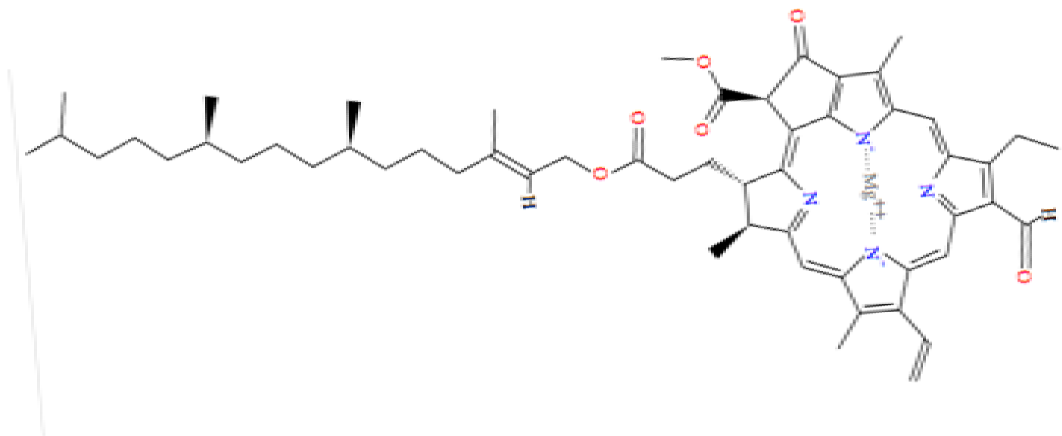
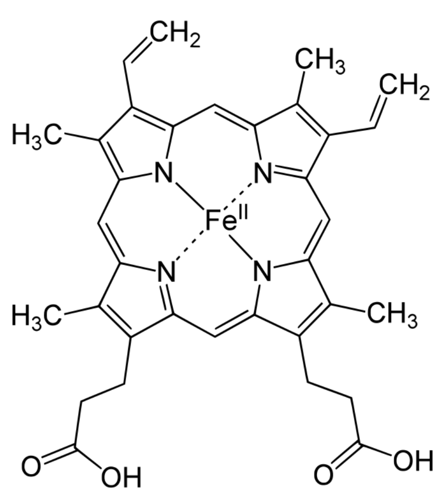
Correction: In the example below, astaxanthin, a red pigment in algae, can bioaccumulate in crustaceans, salmons, flamingo, etc. In crustaceans (e.g. lobsters), when they eat algae and accumulate astaxantin, the pigment gets deposited together with a protein called crustacyanin. Crustacyanin masks the red astaxantin as a blue-green complex, but once heated (when lobster is cooked), the protein denatured leaving free-red astaxanthin. This gives the bright red color of crabs, lobsters and shrimp. Astacene, the oxidation product of astaxanthin is also red and contributes to the colour.



Chlorophyll A (green colour in plants) is another example of a conjugated molecule that absorbs light and is essential for photosynthesis:

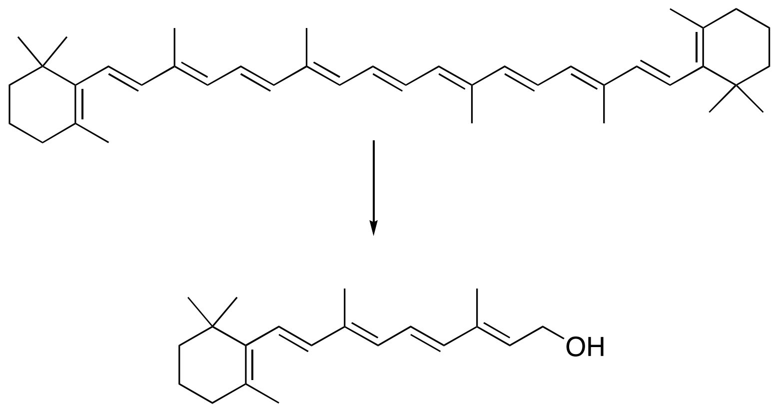


Heme of hemoglobin (red colour in blood) is responsible for the binding and transport of oxygen in the body:



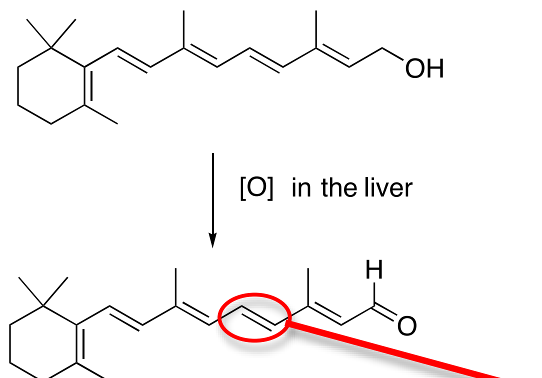
The Chemistry of Vision

Not all conjugated molecules are coloured (need at least 7 conjugated double bonds). They also make up the light sensitive substances responsible for the visual systems of organisms. A key component of our vision arises from the body's ability to synthesize Vitamin A from beta-carotene (shown below) in which the C_{40} beta-carotene is broken down into the C_{20} vitamin A.



Vitamin A

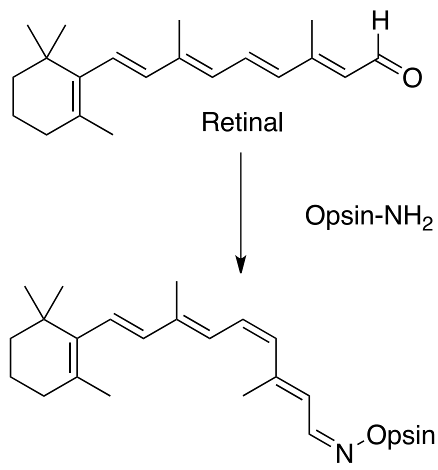
In the liver vitamin A (retinol) is further oxidized to the aldehyde (retinal).



Retinal

This bond changes from **trans to cis**

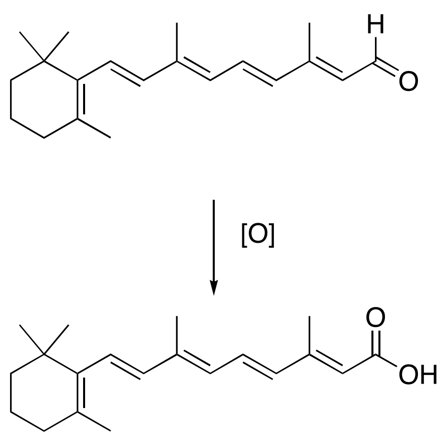
In the eye retinal reacts with a protein called opsin to give rhodopsin, the visual pigment that is the actual light sensitive substance.



Rhodopsin

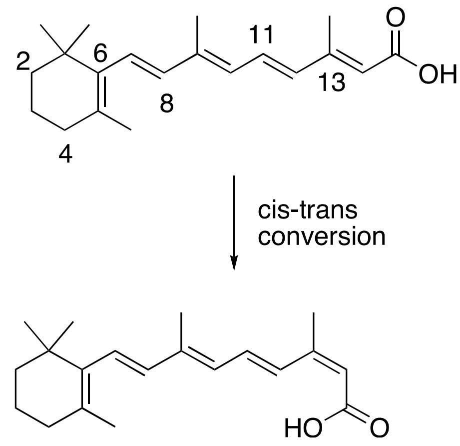
Light causes the C11-C12 bond to isomerize from cis to trans. This causes a change in the 3D conformation of the protein that results in nerve impulses being sent to the brain → vision.

Oxidation of the aldehyde to a carboxylic acid in retinal yields retinoic acid, a chemical messenger in the body that provides signals for fetal development.



Retinoic acid

Conversion of the C13 double bond in retinoic acid to the cis conformation gives the drug Accutane, which is an anti-acne drug. Isomerization is possible due to unpaired electrons in excited state. It has teratogenic properties (i.e. can cause malformations and other birth defects).



Accutane