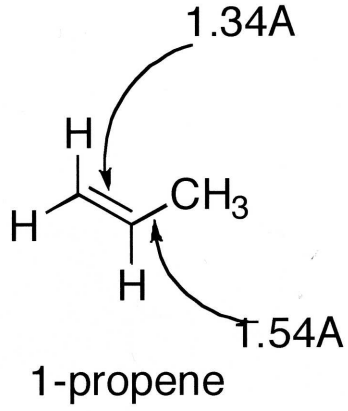
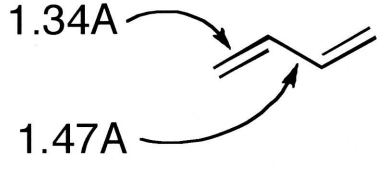
Bond & Energy Characteristics of Conjugated Systems



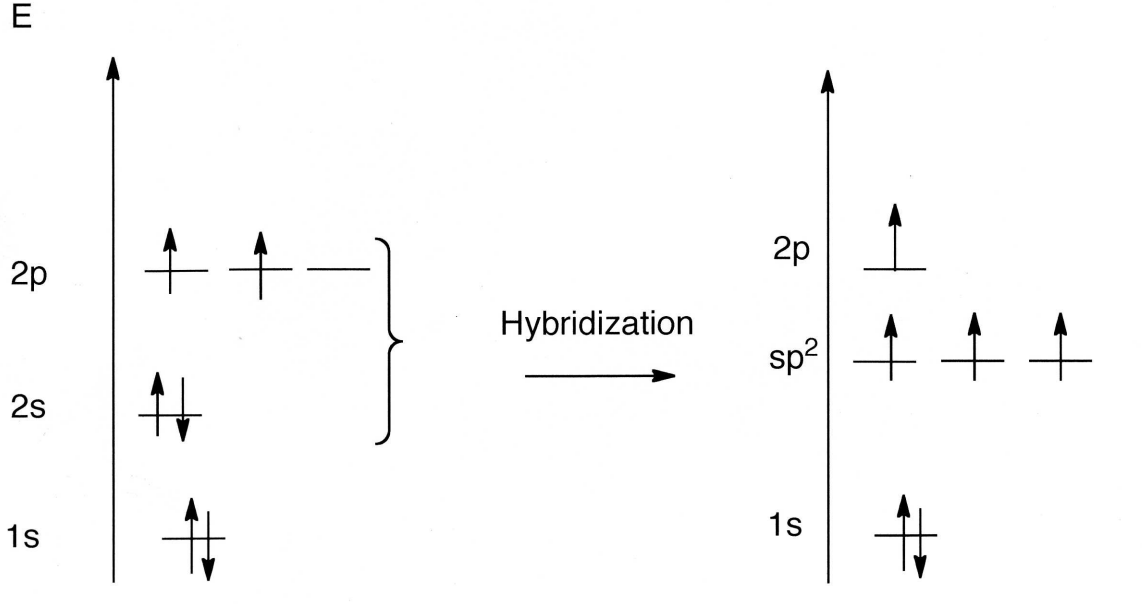
1-propene



1,3-butadiene

1,3-butadiene likes to be planar because of **π molecular orbitals** that align to overlap

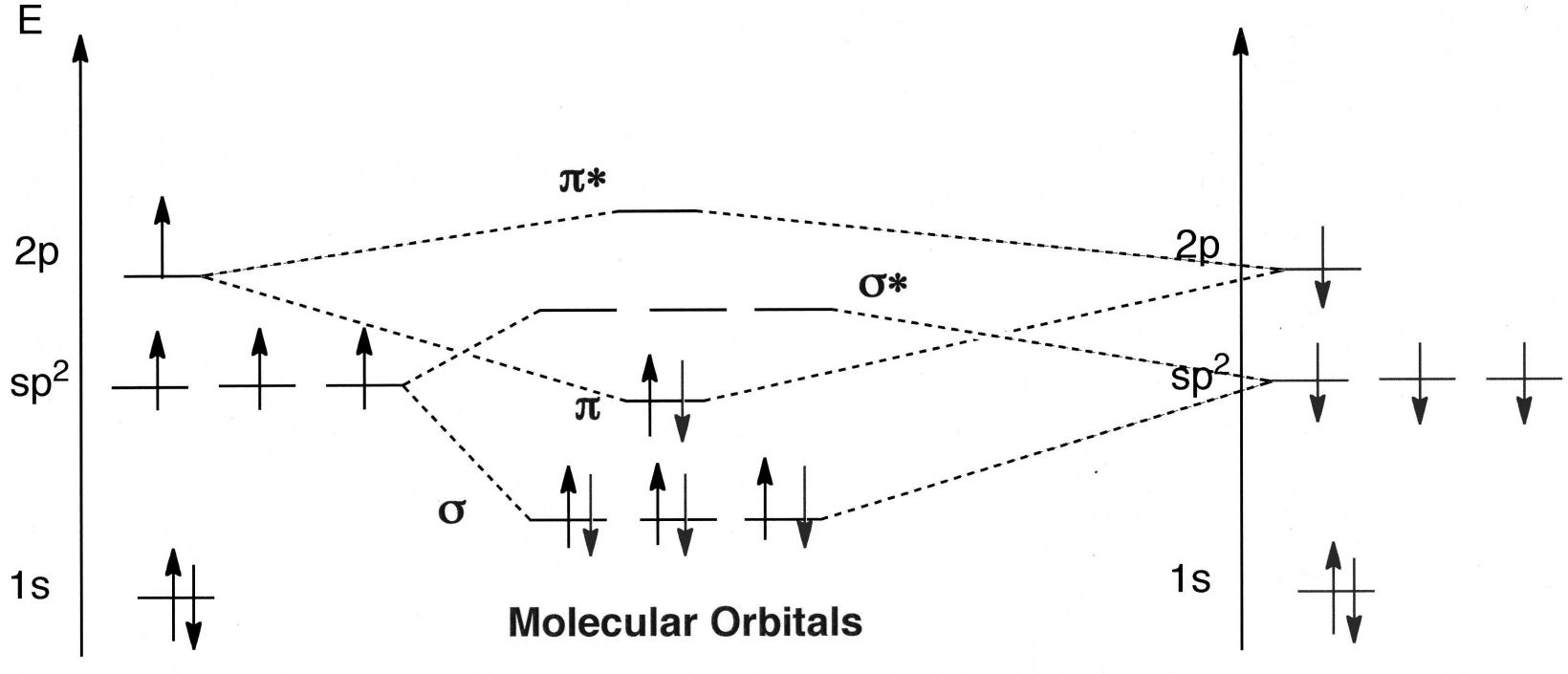
Review formation of pi (π) molecular orbitals from p atomic orbitals



Carbon Atomic Orbitals

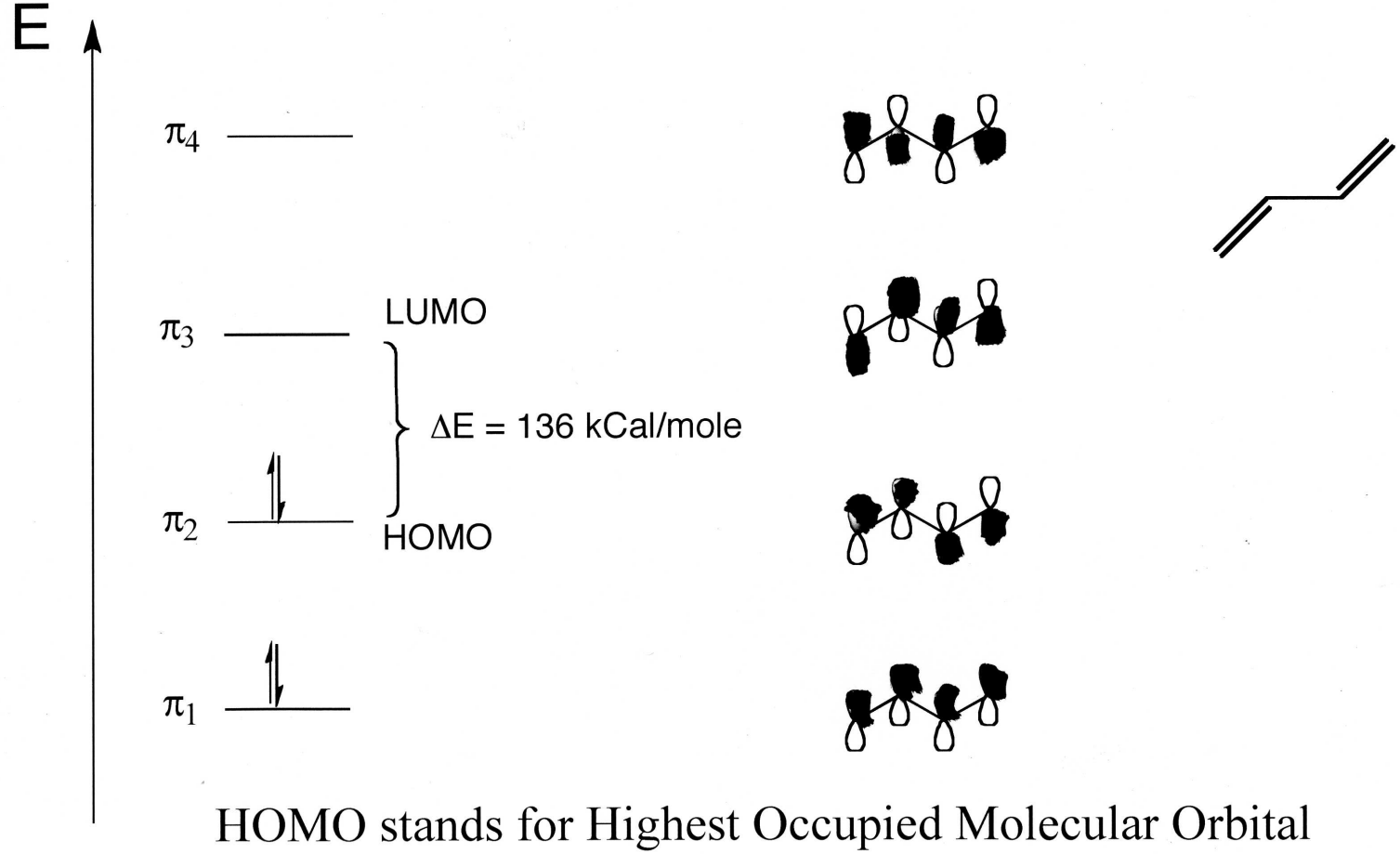
sp^2 Carbon Atomic Orbitals

Review formation of pi (π) molecular orbitals from p atomic orbitals



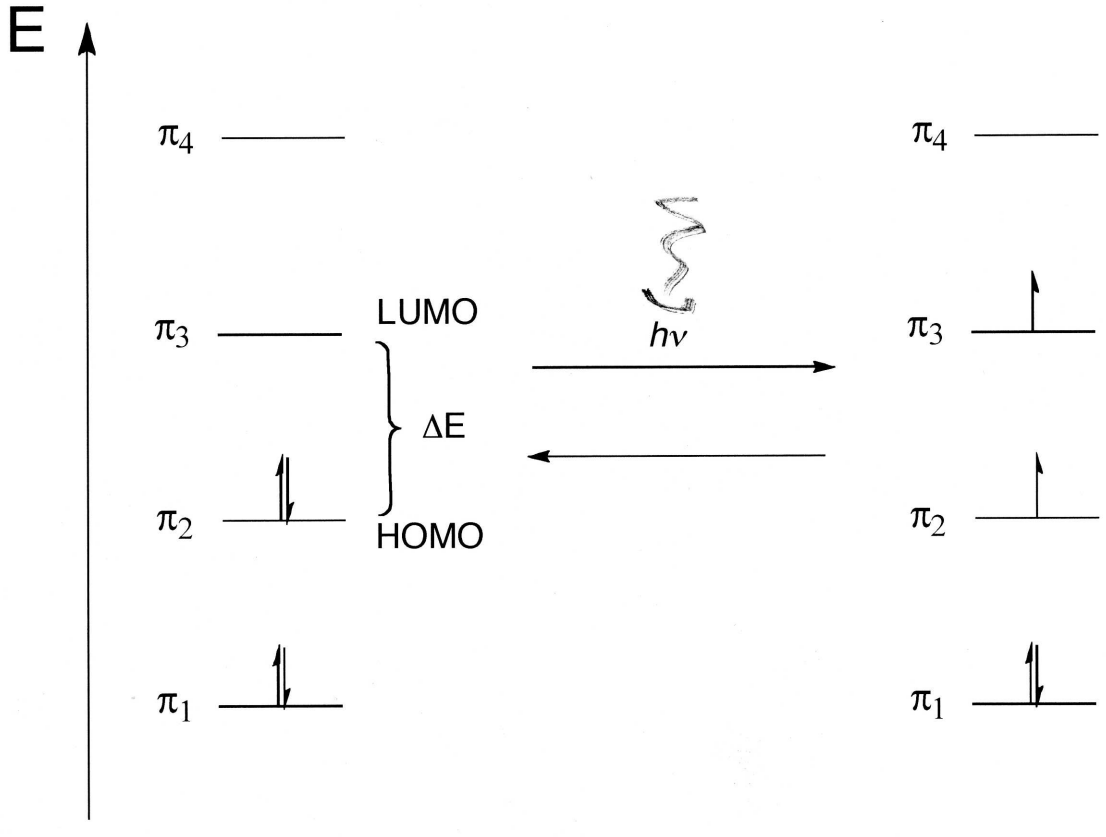
Butadiene: the 4 carbon atoms all have a *2p* orbital

These **atomic** *2p* orbitals will combine to produce 4 π **molecular** orbitals
the number of atomic orbitals combined gives the same number of molecular orbitals



HOMO stands for Highest Occupied Molecular Orbital
LUMO stands for Lowest Unoccupied Molecular Orbital

Molecules absorb energy at specific wavelength corresponding to ΔE



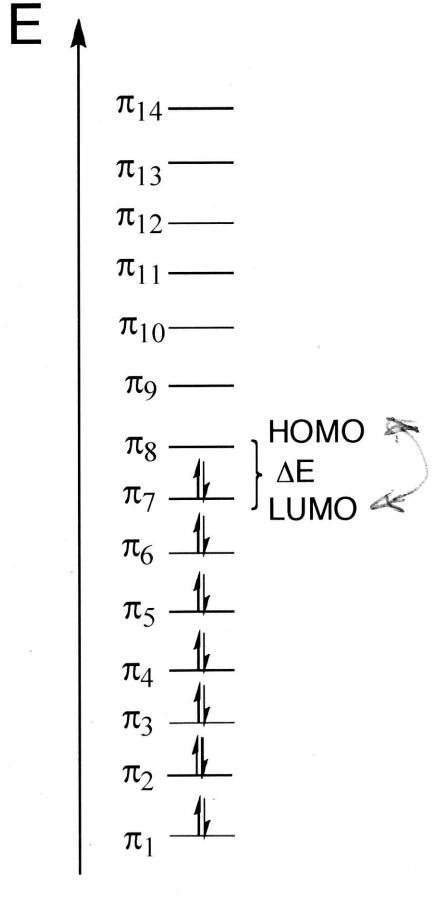
This is the basis for colour and photosynthesis

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

molecule with ≥ 7 conjugated double bonds absorbs light between 4000 – 8000 Å
becomes visible to us

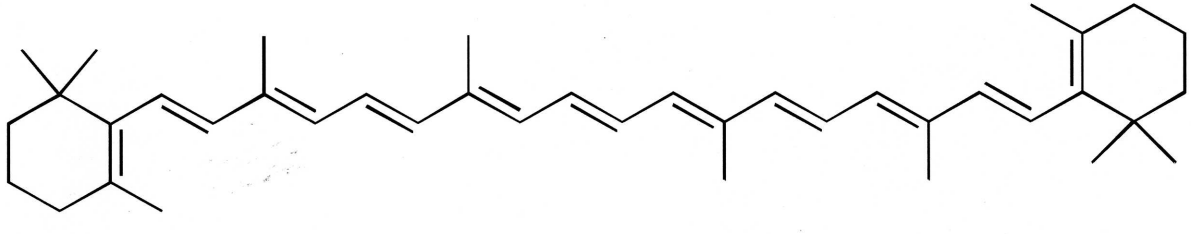
In this molecule, there are 7 bonding and 7 anti-bonding π molecular orbitals
Absorbs blue appears yellow

The energy gap between the LUMO and HOMO is quite small



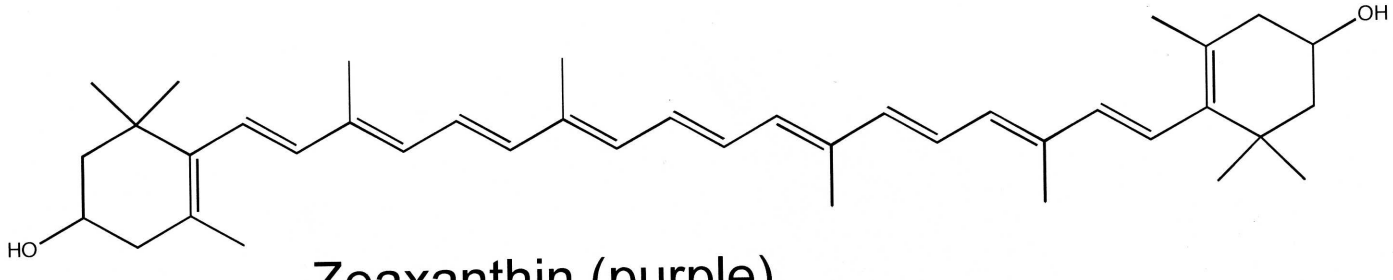
Absorption and Reflection of Visual Light

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

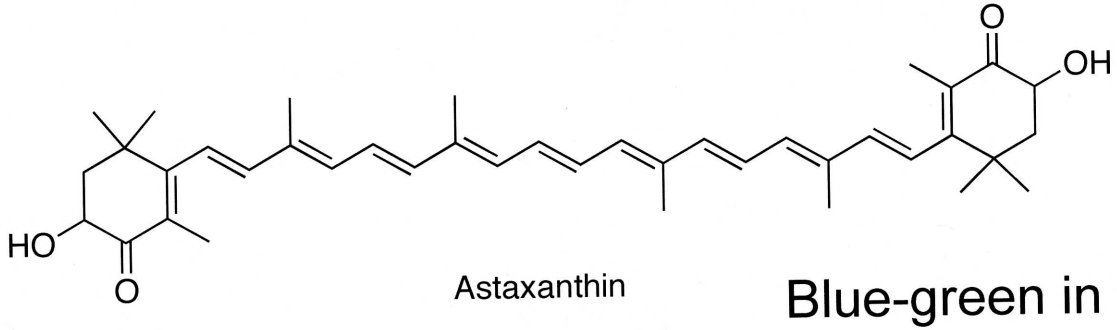


β-carotene

Xanthophylls: oxygenated carotenes



Zeaxanthin (purple)

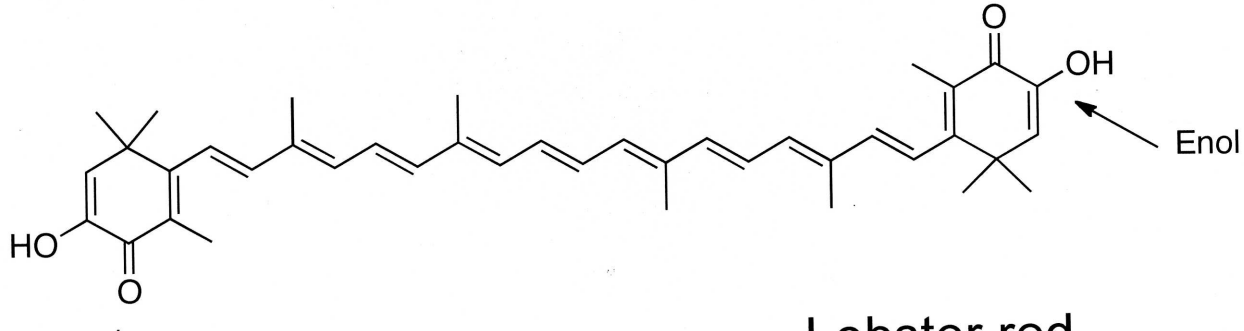


Astaxanthin

Blue-green in crustaceans

secondary alcohol

H_2O, O_2
Heat

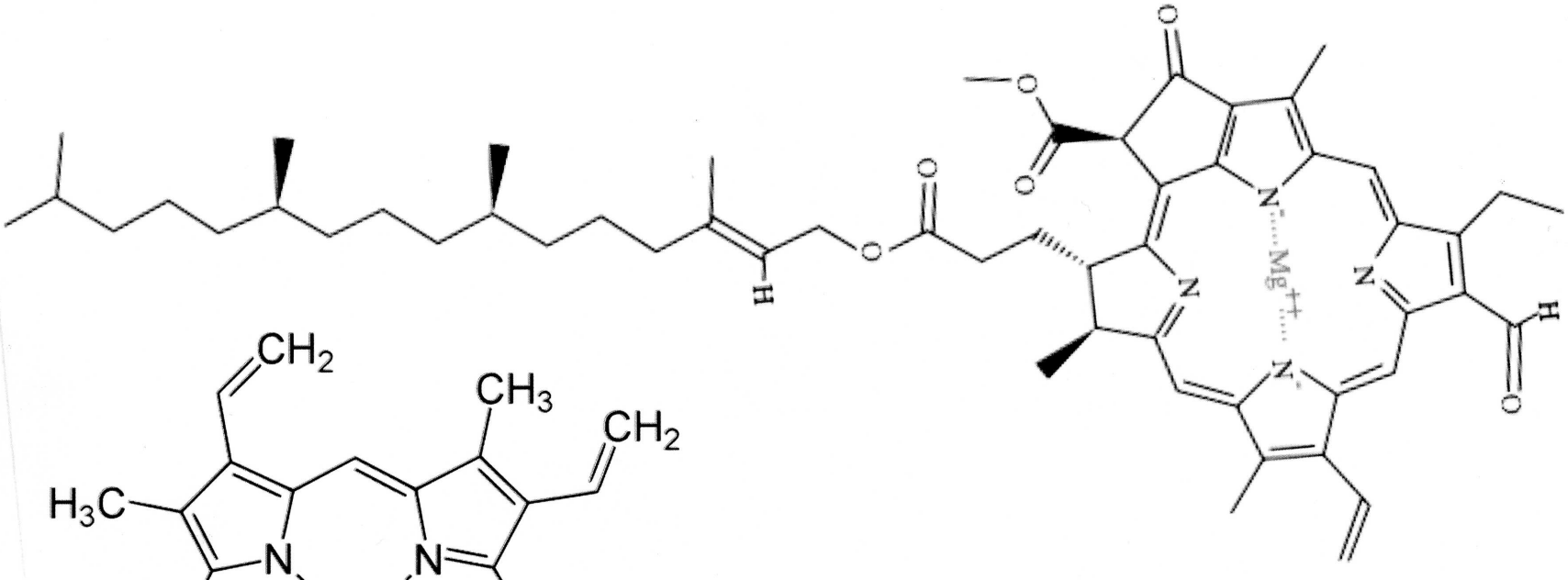


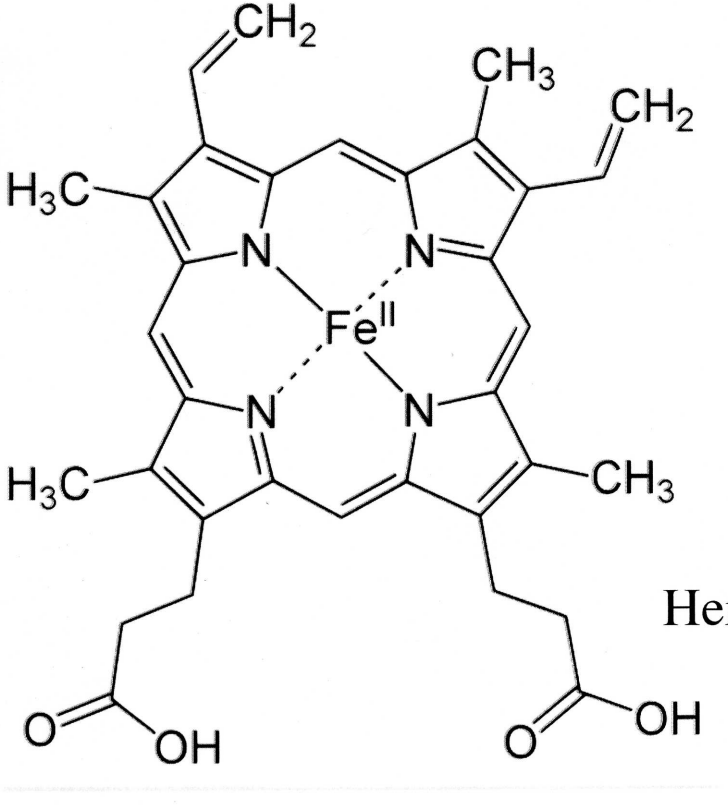
Lobster red

Ketone

Astascene

chlorophyll A (green colour in plants)

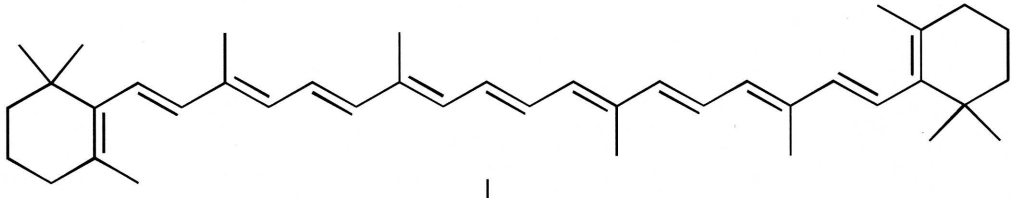




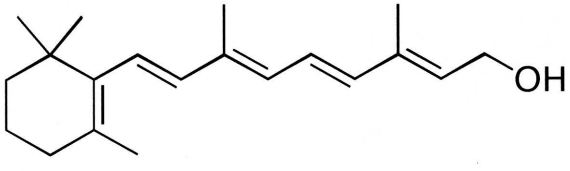
Heme of hemoglobin (red colour in blood) and

The Chemistry of Vision

component of our vision arises from the body's ability to synthesize Vitamin A from beta-carotene

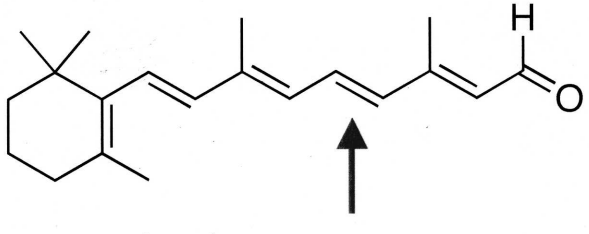


beta-carotene



Vitamin A (retinol)

[O] in liver

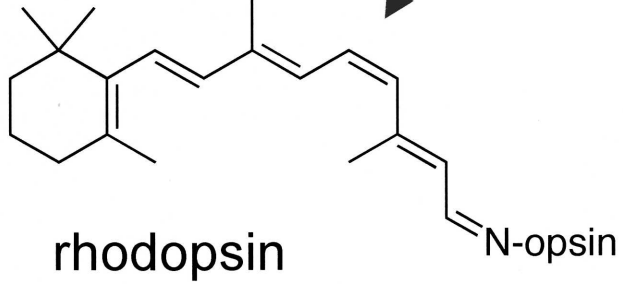


retinal

trans

opsin

cis ⇌ **trans**

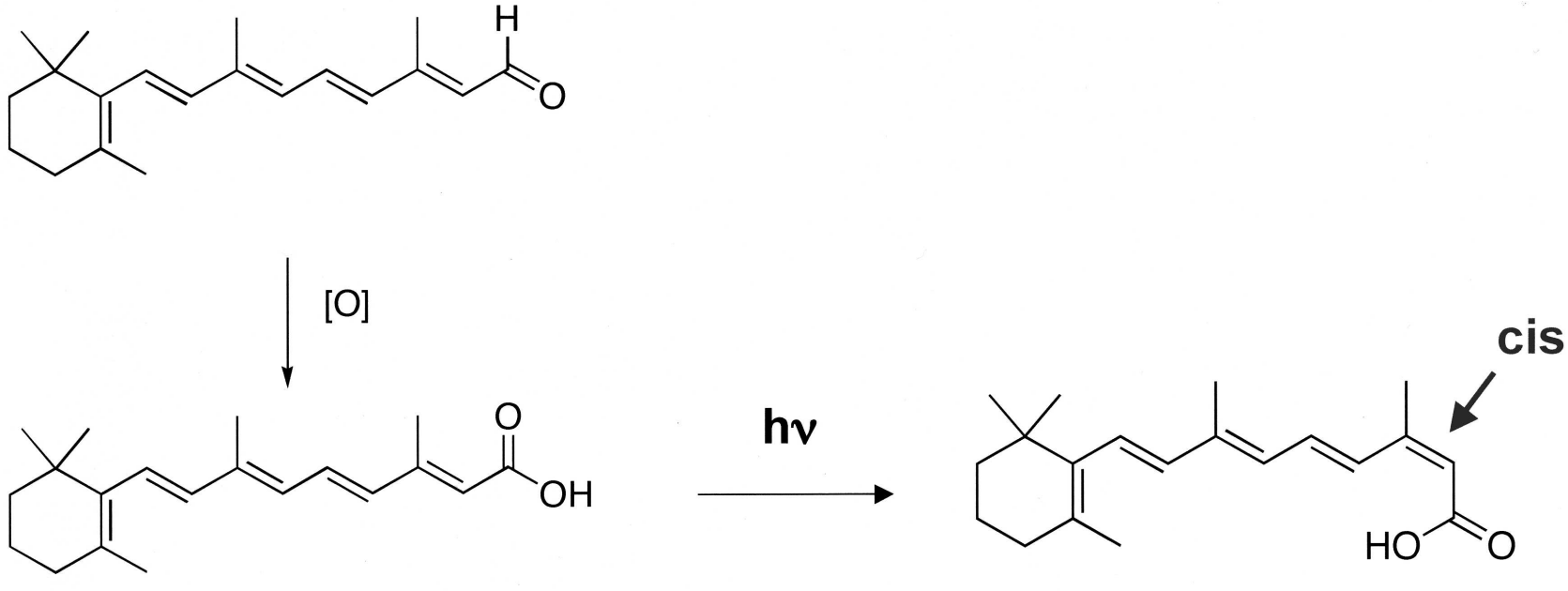


rhodopsin

light causes cis to trans isomerization -> vision

Retinoic acid : developmental signal (e.g. fetal development)

oxidation of the aldehyde to a carboxylic acid in retinal yields retinoic acid



all trans retinoic acid

Accutane

isomerization possible due to unpaired electrons in excited state

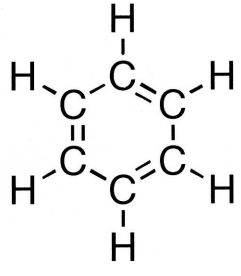
Accutane is an anti-acne drug: causes birth defects / malformations

Slides 57-59 not covered

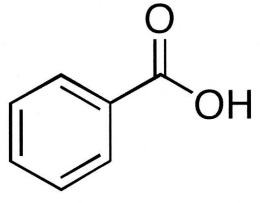
Lecture Outline 2 : Aromatic Compounds

Benzene was first isolated in 1825 by Michael Faraday

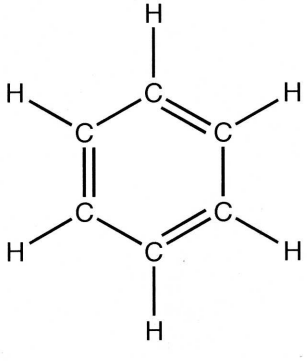
Structure by Josef Loschmidt & August Kekule

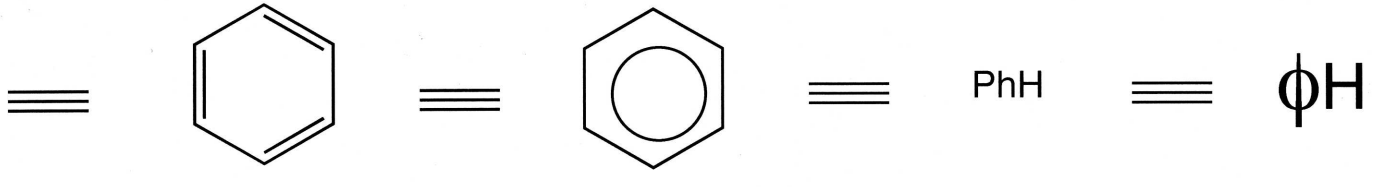


benzene

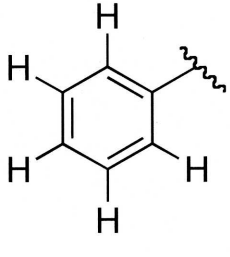


benzoic acid (gum benzoin)





Ph ≡ ϕ ≡

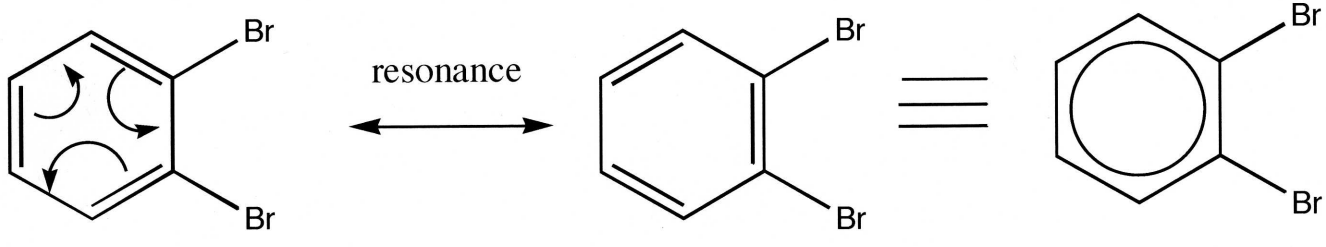


Phenyl group

Aromaticity

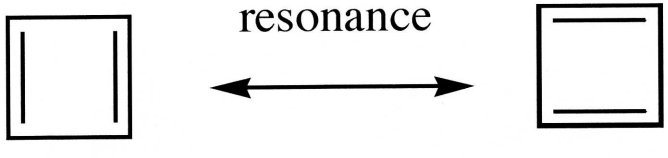
equivalent resonance forms give stability

central circle can be used to represent the resonance within the aromatic



1,2-dibromobenzene

But the number of conjugated pi (π) electrons plays a key role for stability



cyclobutadiene

Cyclobutadiene is very unstable
(anti-aromatic)

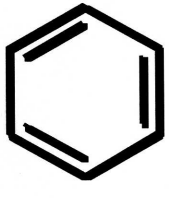
Aromaticity

To be aromatic, compound or ion must:

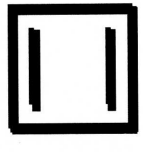
1. be cyclic and conjugated around the ring
2. be planar
3. Have 4n+2 π electrons where n=), 1, 2, ….

Benzene has 6 π electrons, fits rule with n = 1
and is 36 kcal/mol more stable than expected for cyclohexatriene

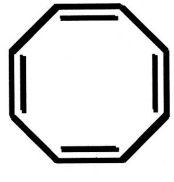
Cyclobutadiene has 4 π electrons, cannot fit 4n+2 rule



aromatic



not aromatic



cyclooctatetraene
not aromatic