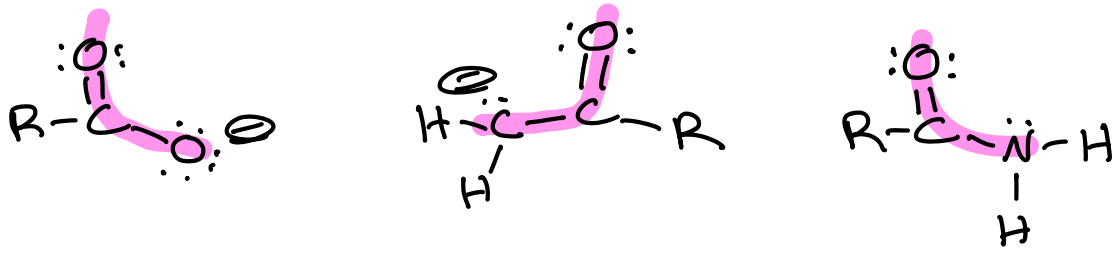
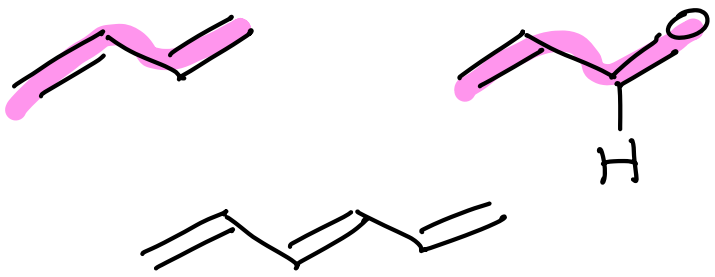
π-Way Recap

3 atom "π-ways" we have seen

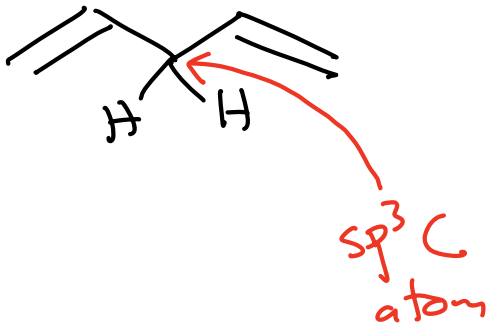


Conjugation → "π way" → 4 atoms or more

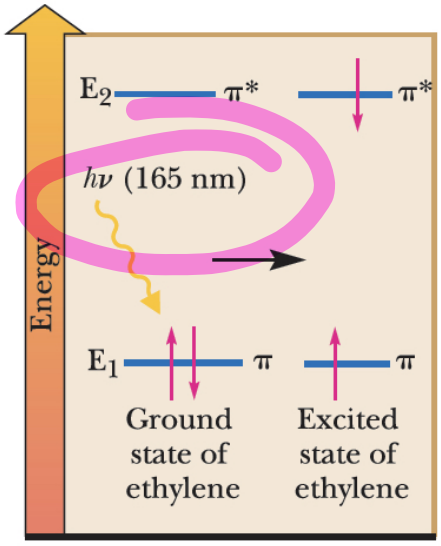
↳ More than one π bond that overlaps



Not conjugated:



As you add 2p orbitals →
the energy gap between
the highest filled
π molecular orbital
and the lowest unfilled
π molecular orbitals
gets smaller ⇒ leads
to longer wavelength
of light photon of
the correct energy
to be absorbed.



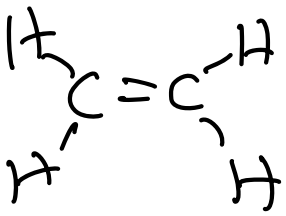
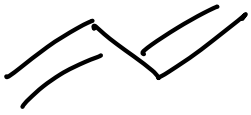


FIGURE 20.6 A $\pi \rightarrow \pi^*$ transition in excitation of ethylene. Absorption of ultraviolet radiation causes a transition of an electron from a π-bonding MO in the ground state to a π-antibonding MO in the excited state. There is no change in electron spin.



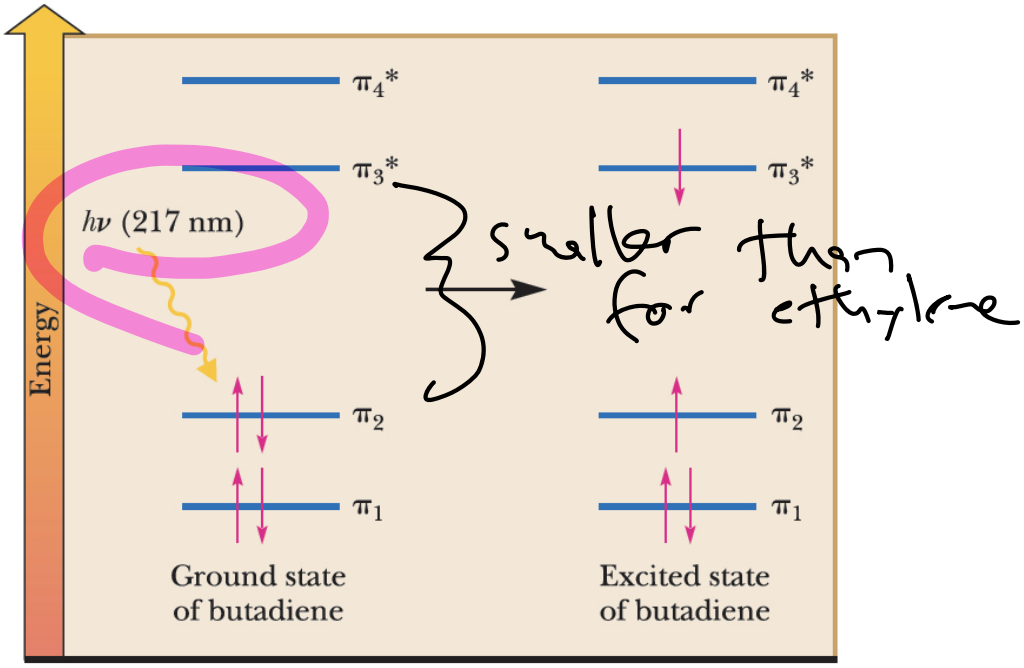
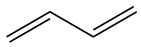
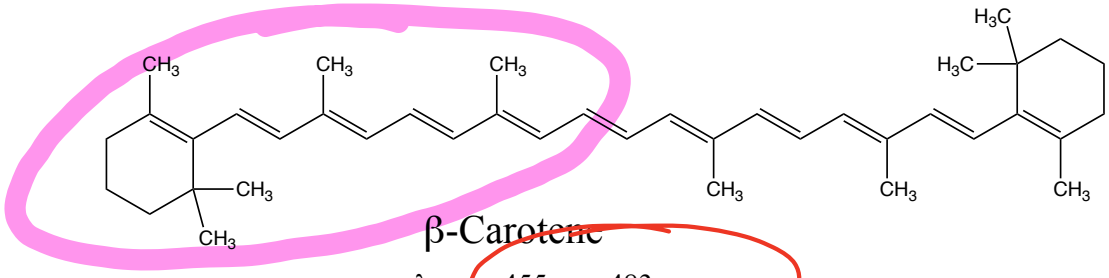


FIGURE 20.7 Electronic excitation of 1,3-butadiene; a $\pi \rightarrow \pi^*$ transition.



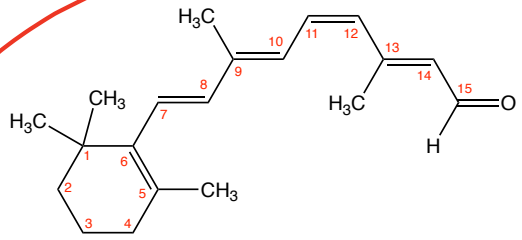
Butadiene

λ_{max} = 217 nm



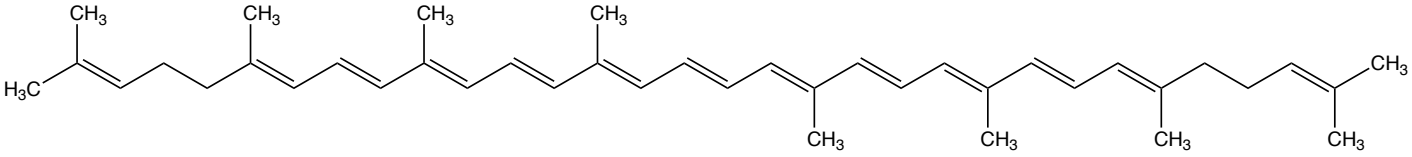
β-Carotene

λ_{max} = 455 nm, 483 nm



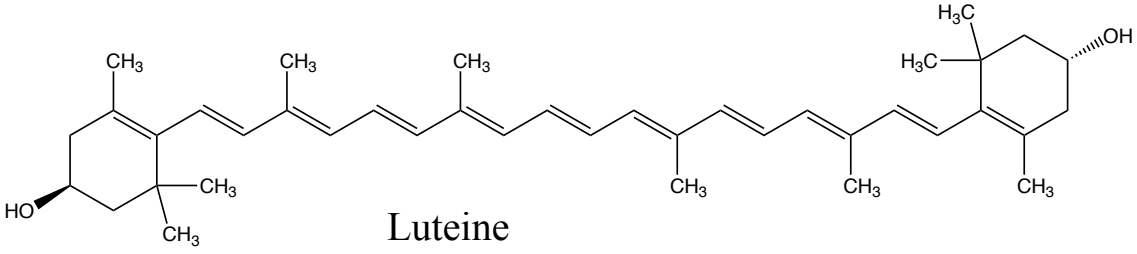
11-*cis*-Retinal

λ_{max} = 380 nm



Lycopene

λ_{max} = 443 nm, 471 nm, 502 nm



Luteine

λ_{max} = 445 nm, 474 nm

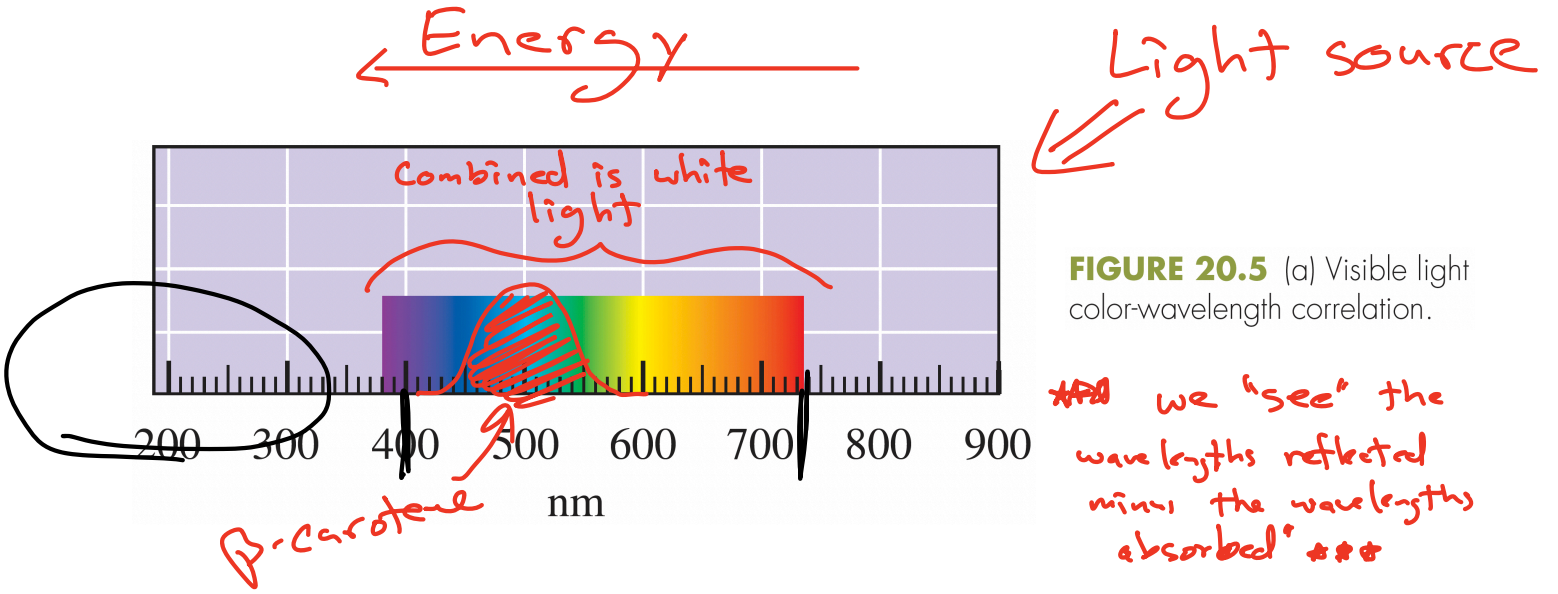
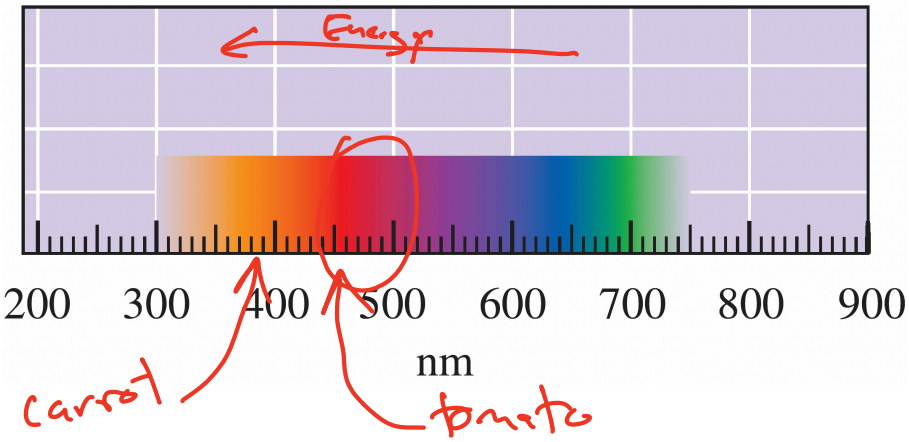
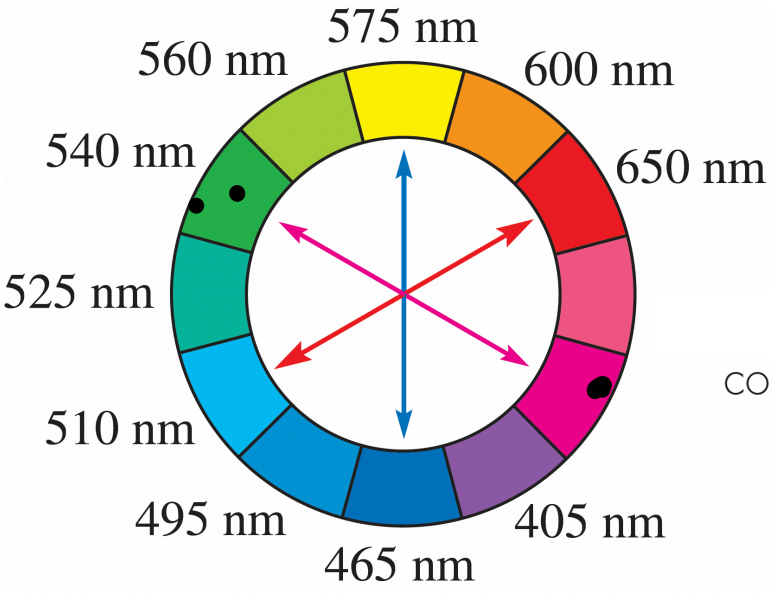


FIGURE 20.5 (a) Visible light color-wavelength correlation.

we "see" the wavelengths reflected minus the wavelengths absorbed



(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the *x*-axis) is absorbed.



(c) Complementary colors on a color wheel.

Colored arrows are complementary

White → reflects all wavelengths of visible light

Black → absorbs all wavelengths of visible light

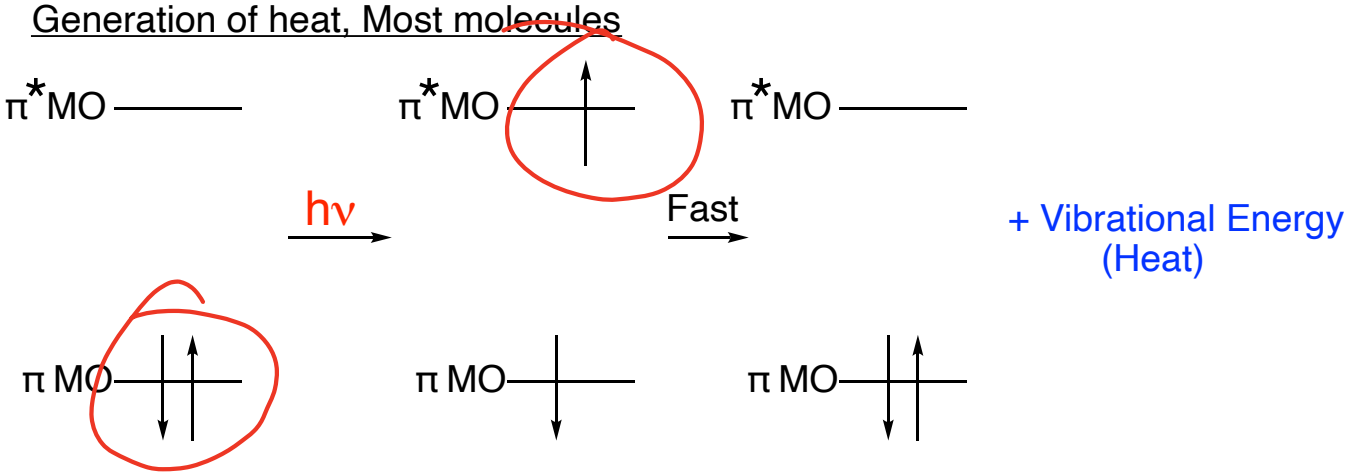
Absorbs all light including orange — it will be black in an orange light.

when illuminated under an orange light — both reflect all of it and look orange

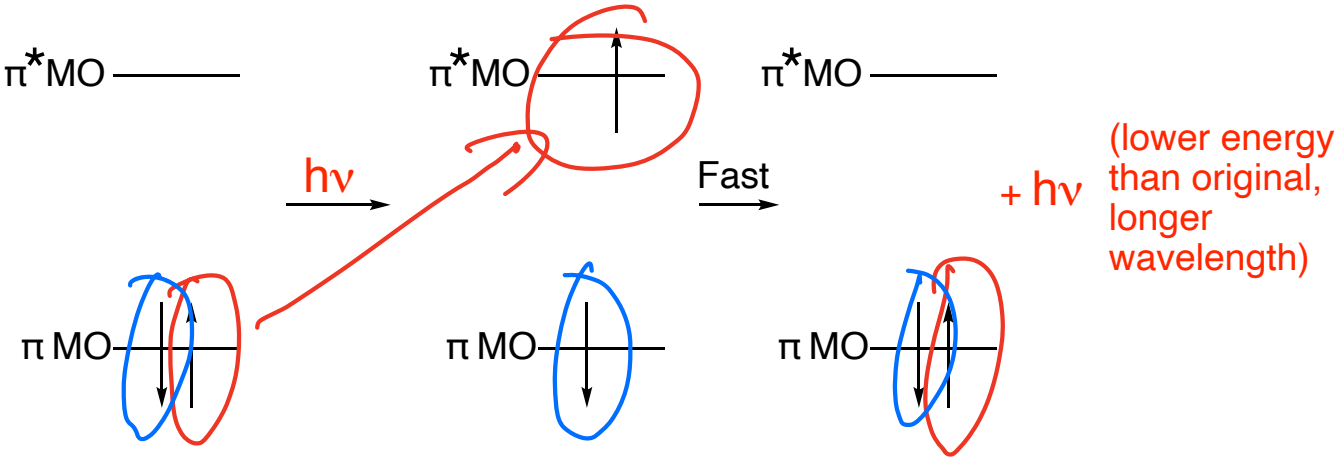
A green laser is entirely absorbed by the red blood (hemoglobin) in your finger because for blood to appear red it must absorb blue and green, while reflecting red.

A red laser is not absorbed by the red blood in your finger — otherwise blood would not be red!!

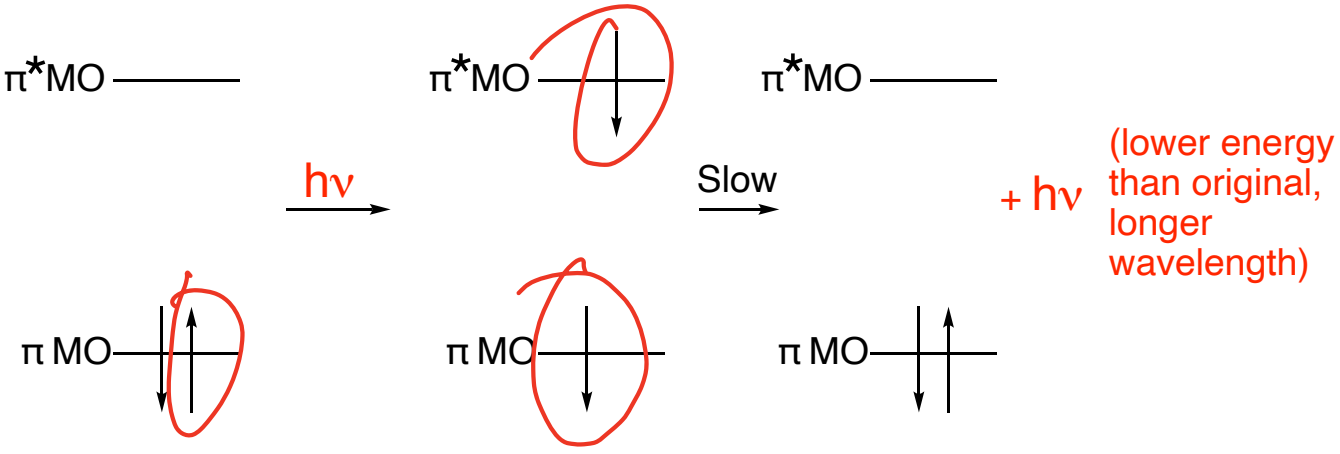
Generation of heat, Most molecules



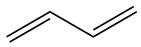
Flourescence - Rigid Molecules, Not uncommon



Phosphorescence - “Glow in the Dark”, Rare

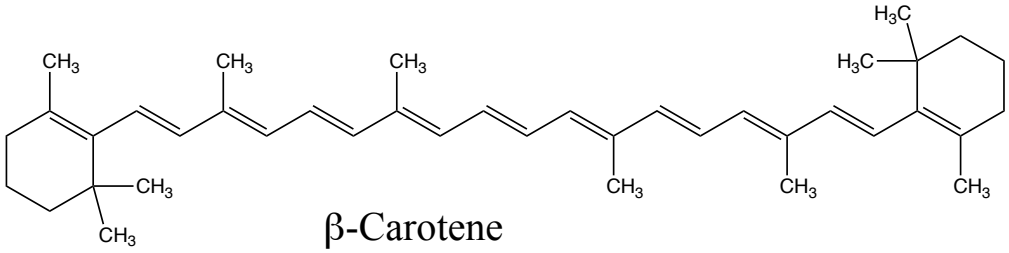


How vision works, the final edition!



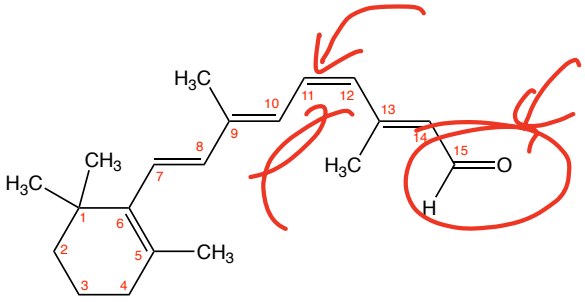
Butadiene

λ_{max} = 217 nm



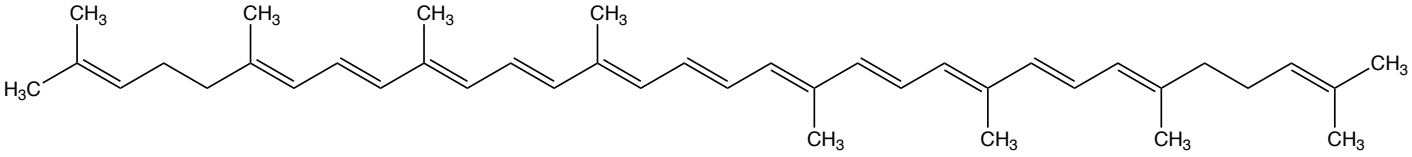
β-Carotene

λ_{max} = 455 nm, 483 nm



11-*cis*-Retinal

λ_{max} = 380 nm



Lycopene

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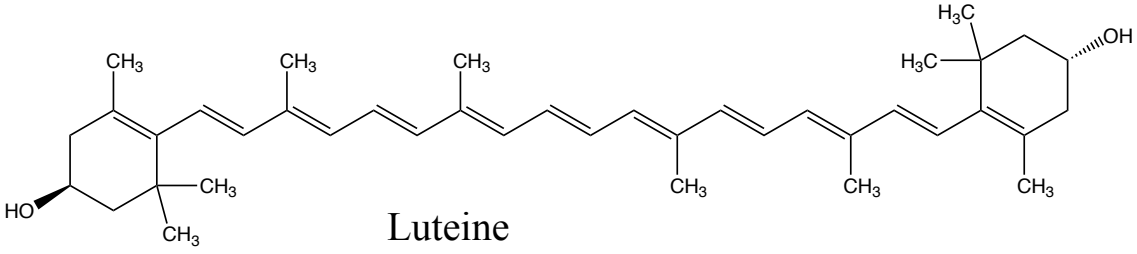
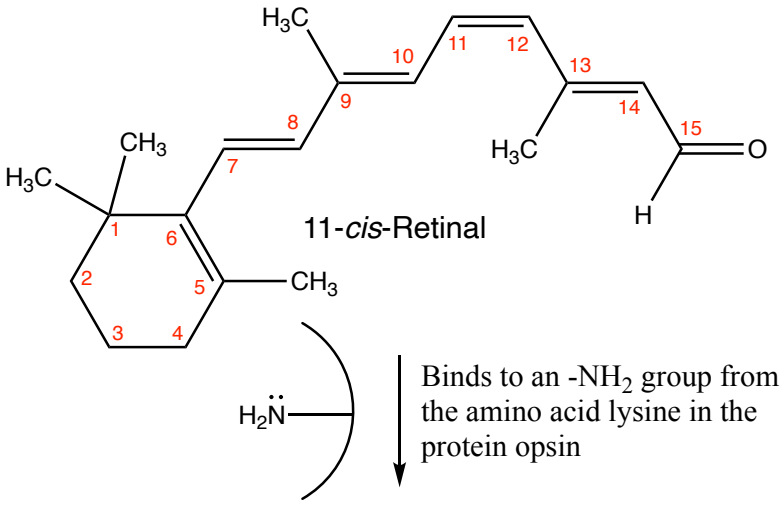


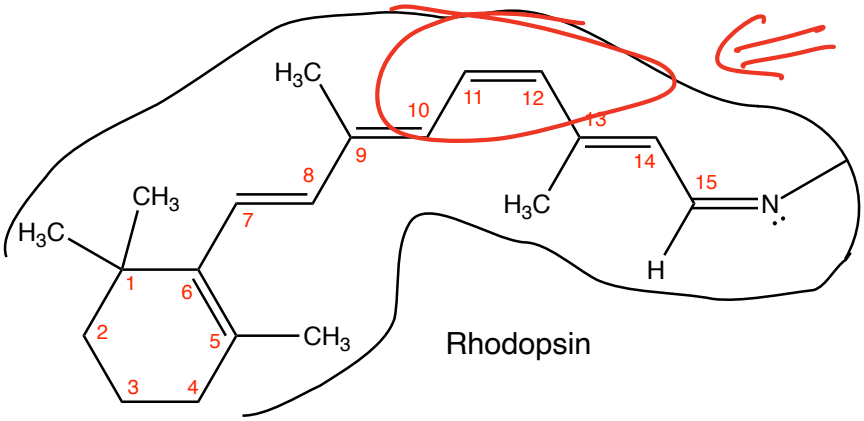
Luteine

λ_{max} = 445 nm, 474 nm

How vision works



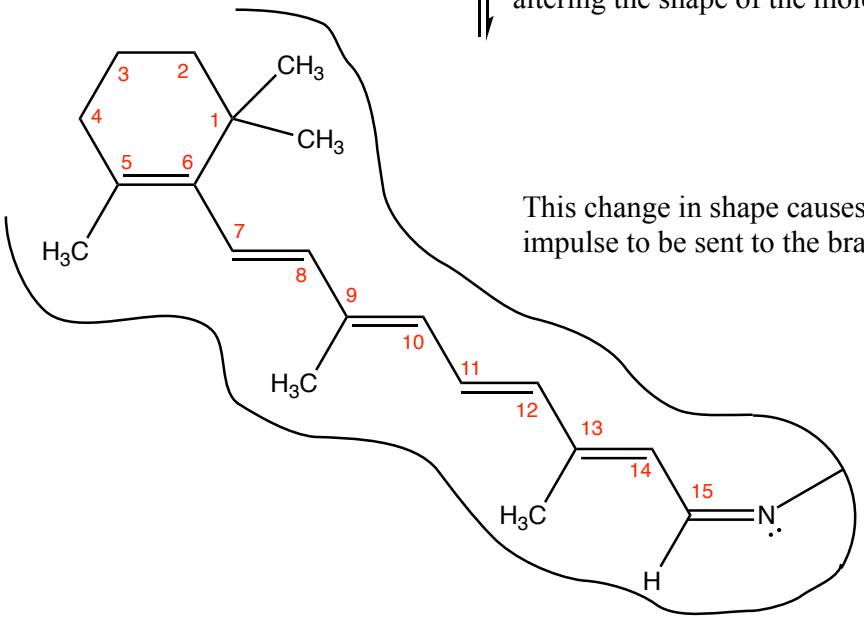
Binds to an -NH_2 group from the amino acid lysine in the protein opsin



Absorbing the photon puts an electron into an antibonding π orbital → weaken π bond, especially around $C_{11}=C_{12}$ so bond can rotate back to more stable trans geometry

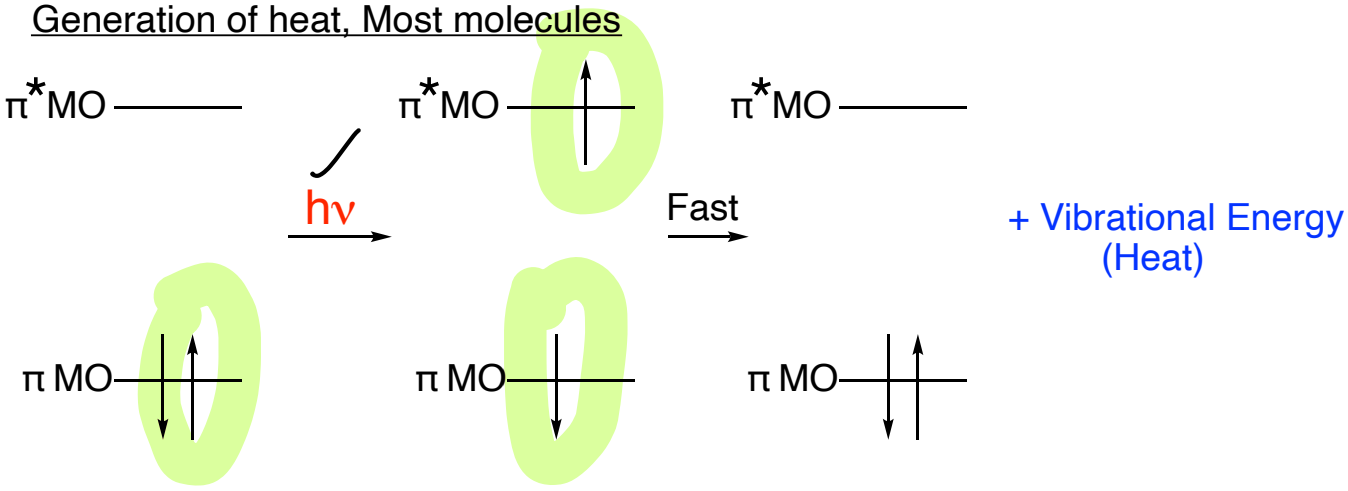
Molecule resets

A photon of visible light is absorbed by the retinal, isomerizing the *cis* bond to *trans*, dramatically altering the shape of the molecule

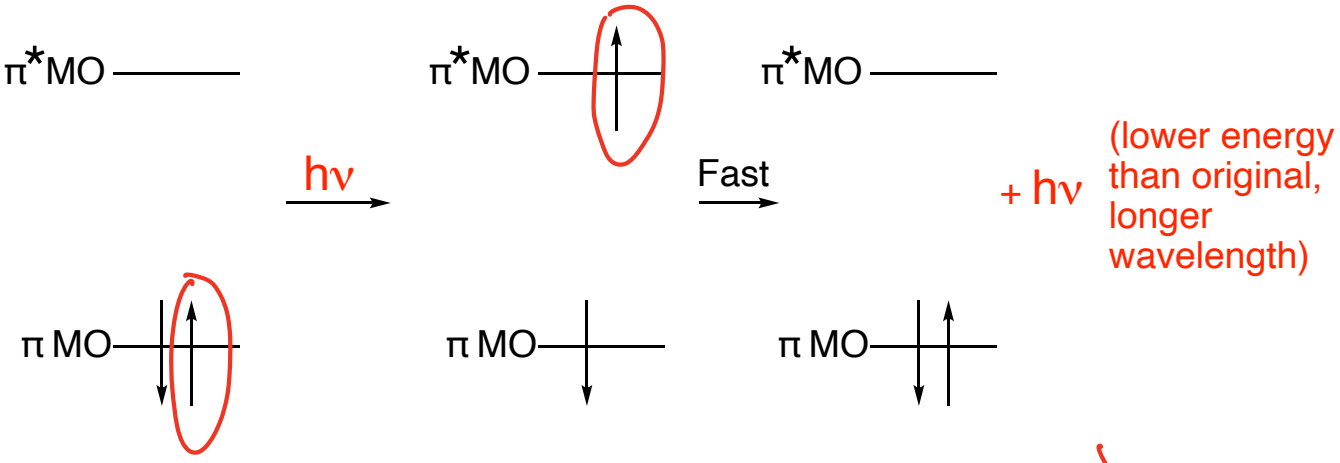


This change in shape causes a nerve impulse to be sent to the brain

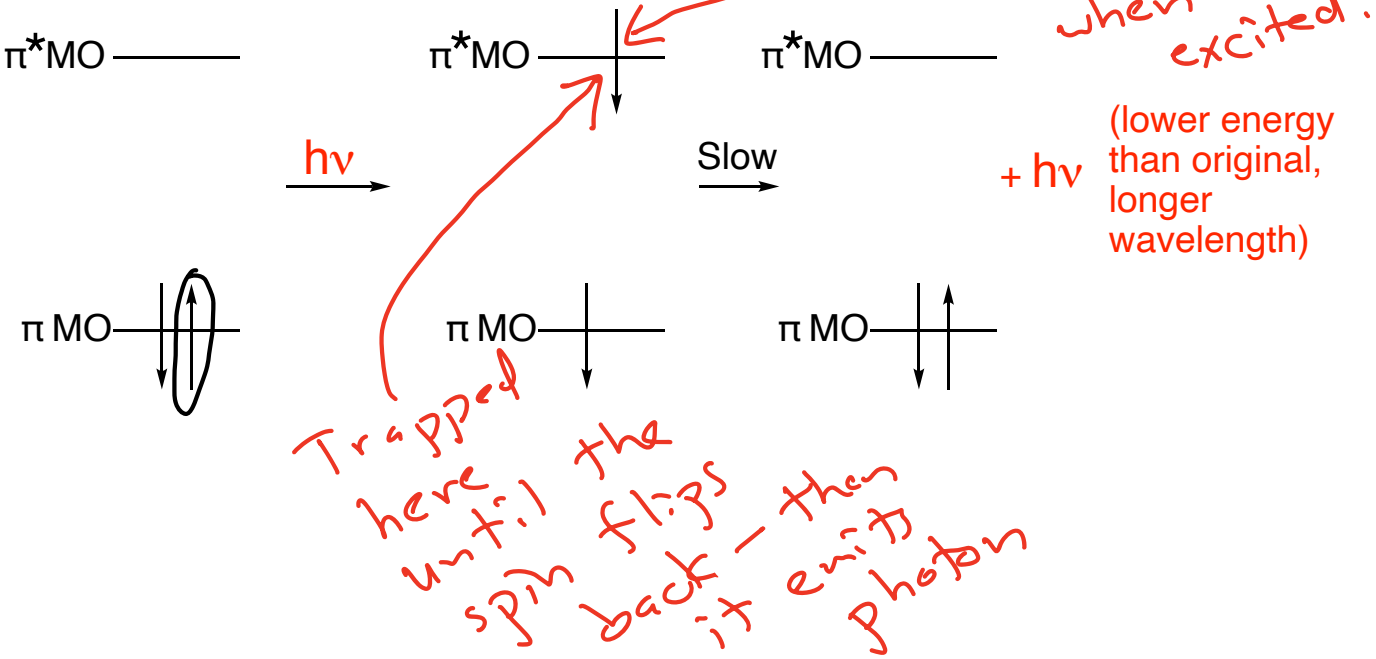
Generation of heat, Most molecules



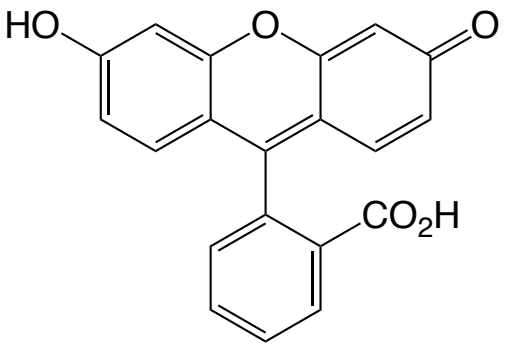
Flourescence - Rigid Molecules, Not uncommon



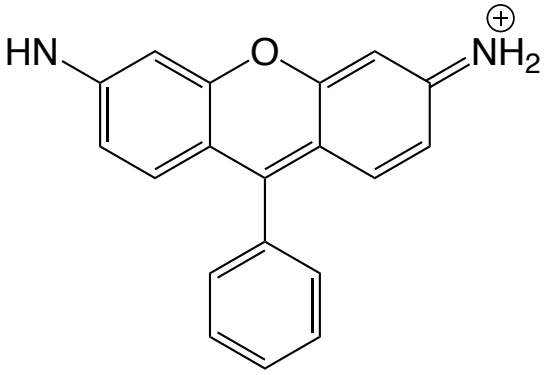
Phosphorescence - "Glow in the Dark", Rare



Flourescence - Rigid Molecules, Not uncommon

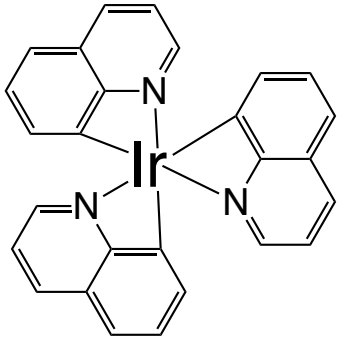


Fluorescein

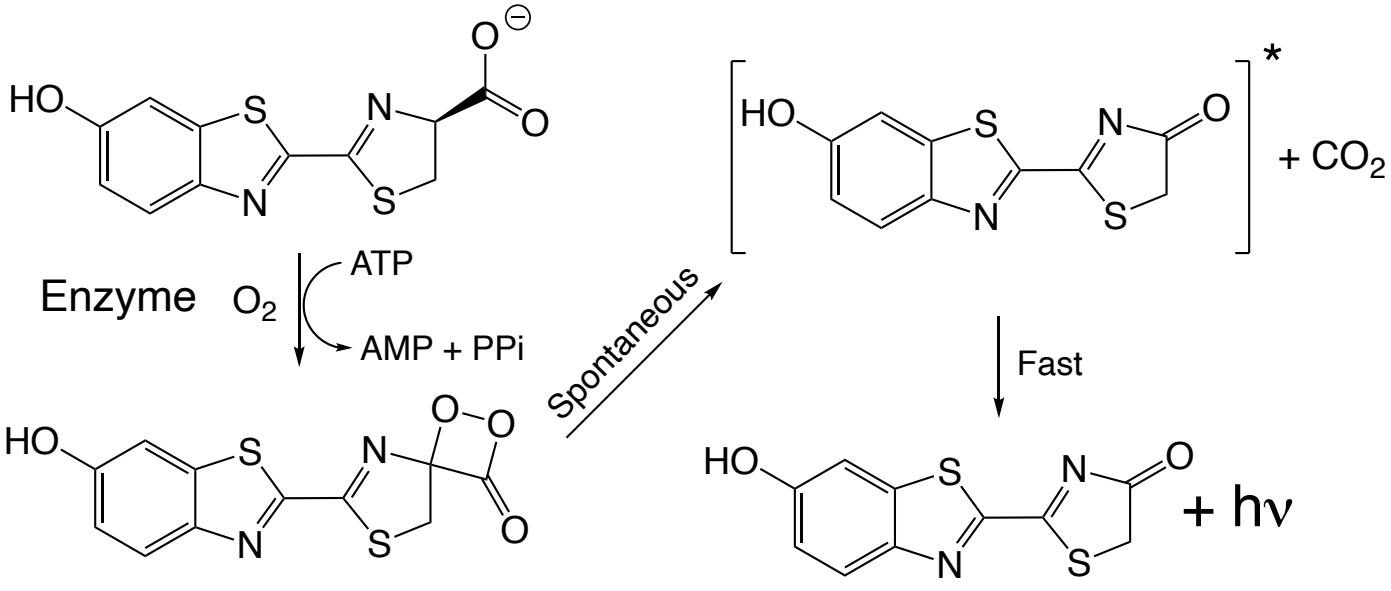


Rhodamine

Phosphorescence - "Glow in the Dark", Rare



Bioluminescence - Fireflies, Deep Sea Creatures - Chemical Reactions



http://photobiology.info/Branchini2.html

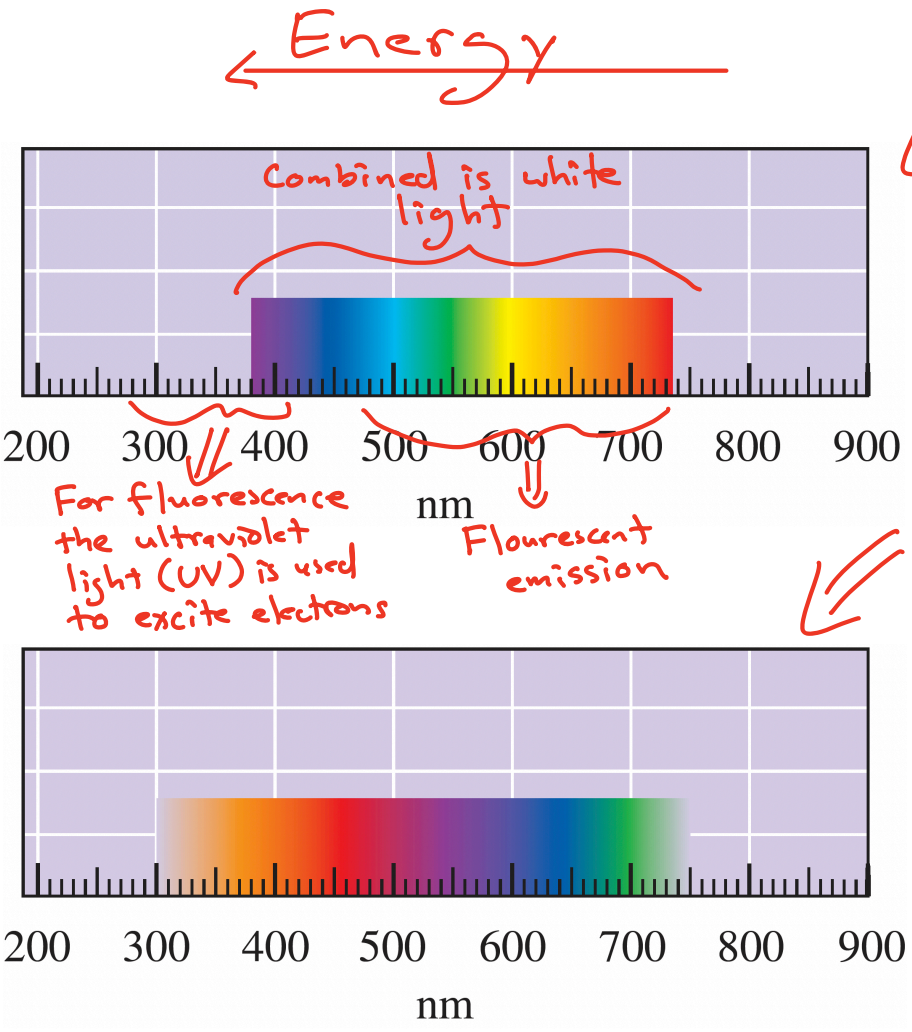
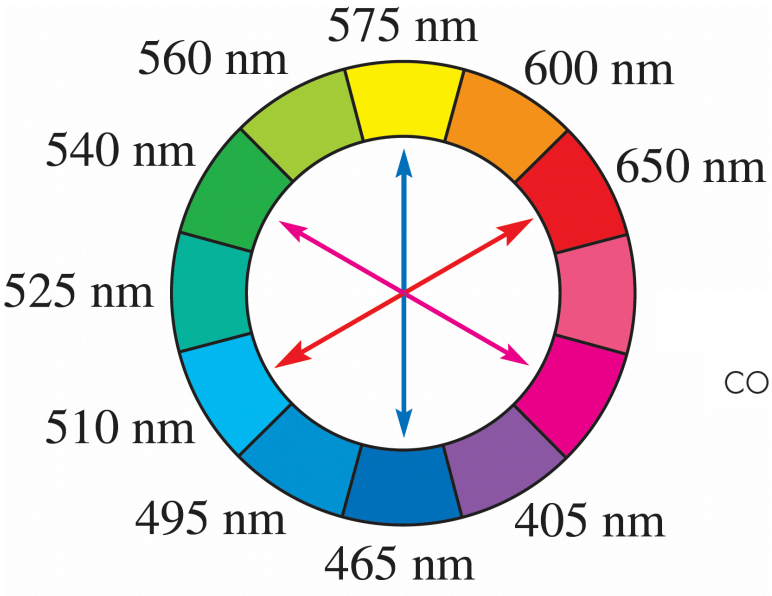


FIGURE 20.5 (a) Visible light color-wavelength correlation.

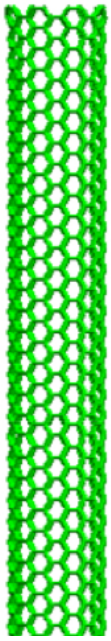
(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the *x*-axis) is absorbed.

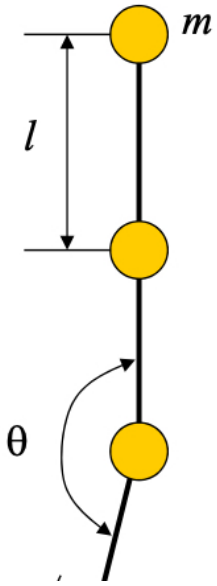


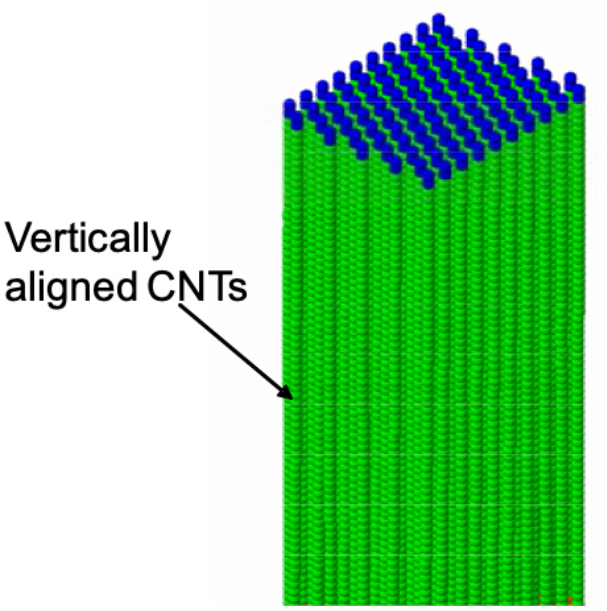
(c) Complementary colors on a color wheel.

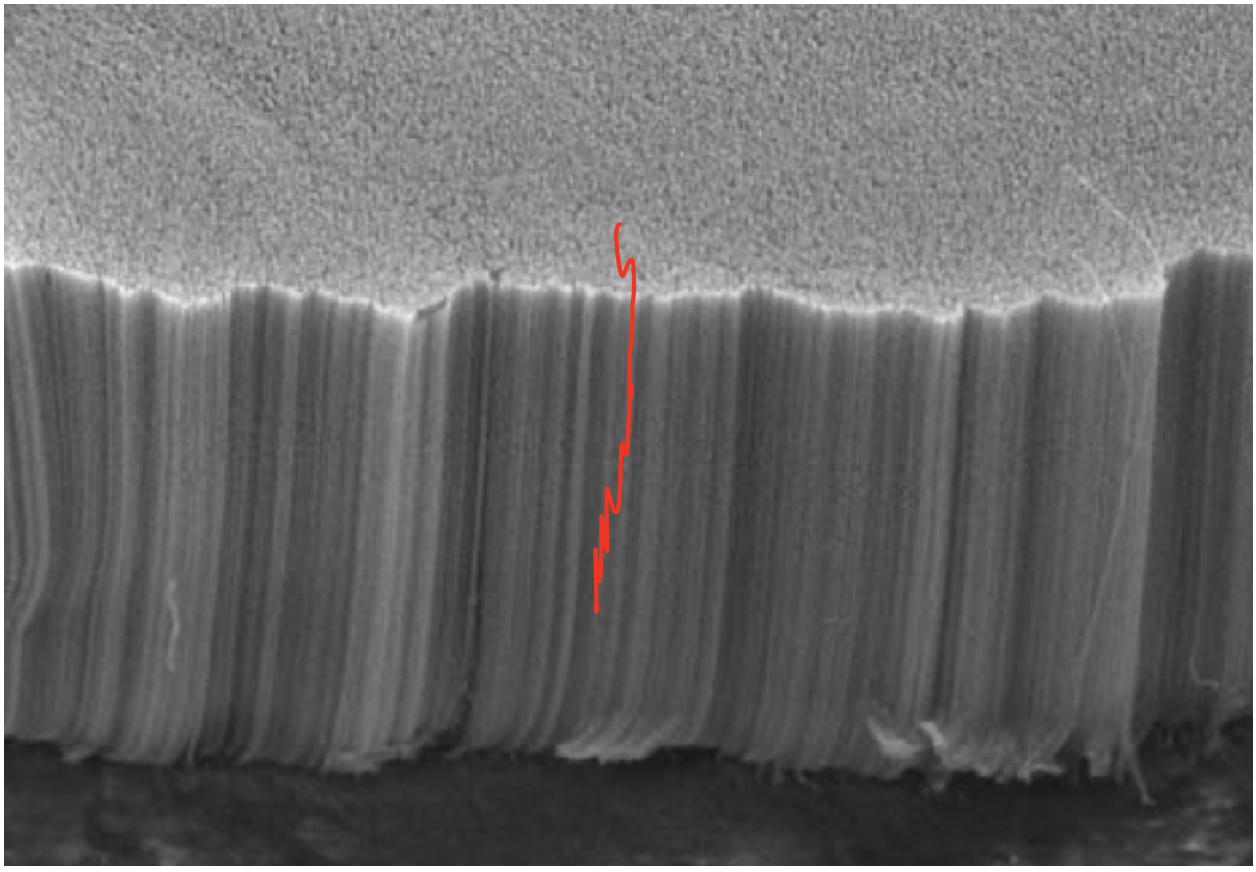
Colored arrows are complementary

Vanta Black → The "blackest" material









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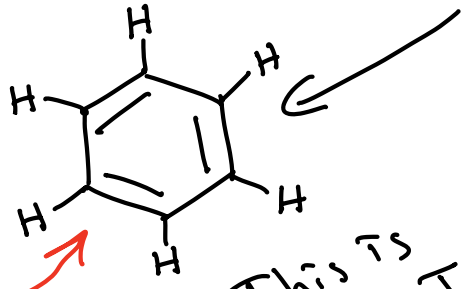
Preview



Extraordinarily Stable!

~36 kcal/mol more stable than expected

This is A LOT

Benzene

Called "aromaticity"

"aromatic" molecule

Pericyclic Reactions → π bonds and σ bonds interchange

→ Happens because the transition state is super stable

"aromatic" character of transition state

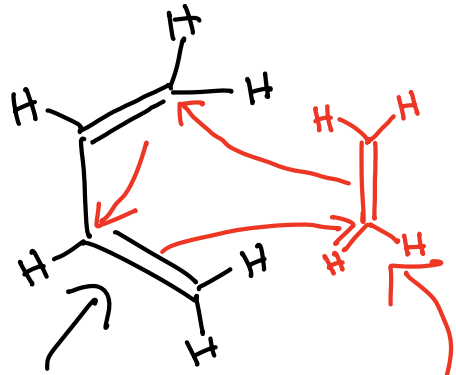
Otto!

↓

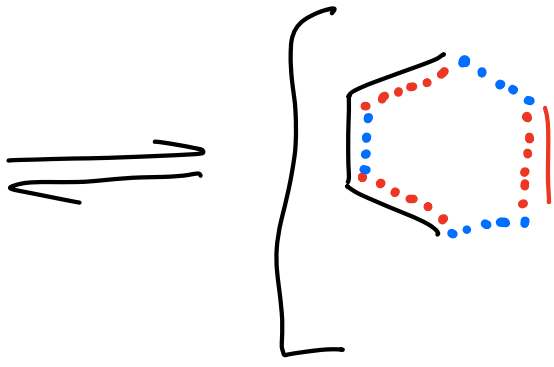
Diels-Alder Reaction

..... bonds being broken

..... bonds forming



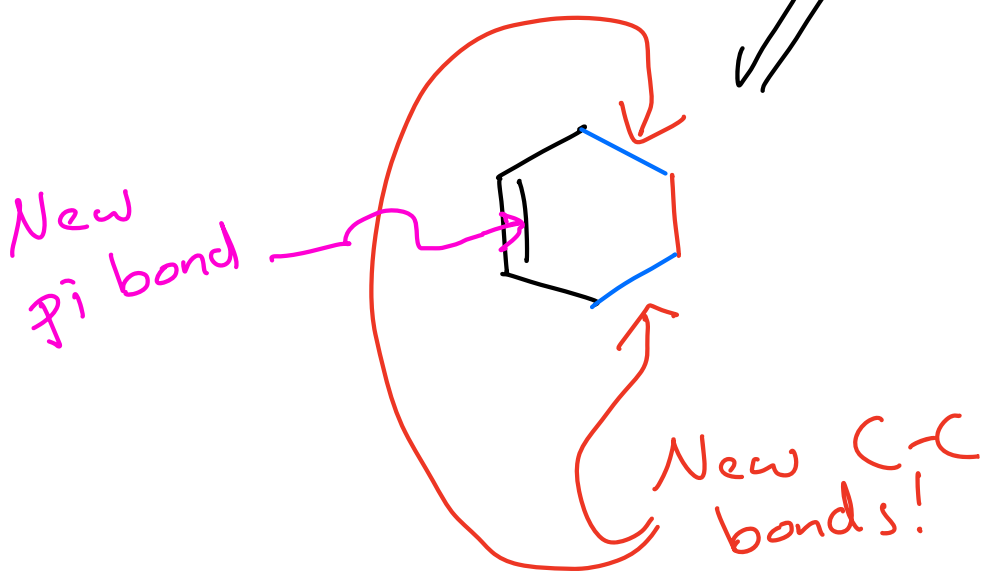
s-cis butadiene



‡

3 π bonds being made or used – all ring atoms are sp^2 hybridized to begin with

"dienophile"



The above reaction gives a poor yield and was used only to illustrate the process → there are many, many known examples of Diels-Alder reactions

The following is the only Diels-Alder reaction you are responsible for in this class