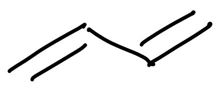
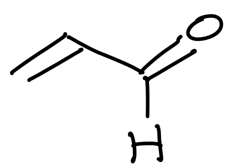
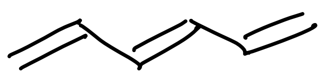
Conjugation → "π way"

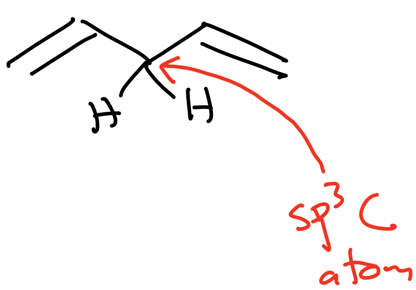
↳ More than one π bond that overlaps



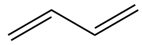




Not conjugated:

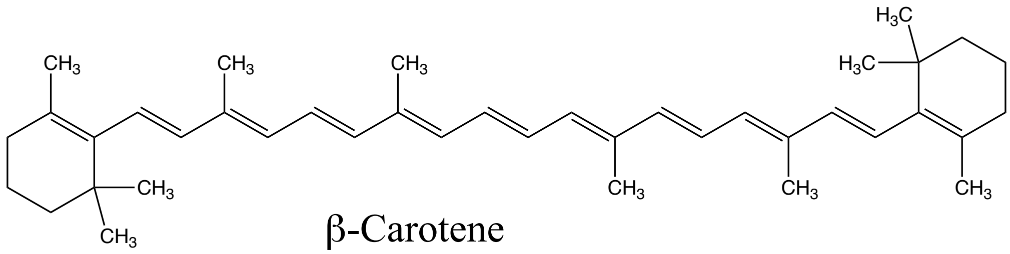


Some conjugated molecules:



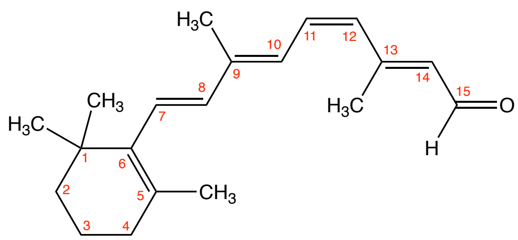
Butadiene

λ_{max} = 217 nm



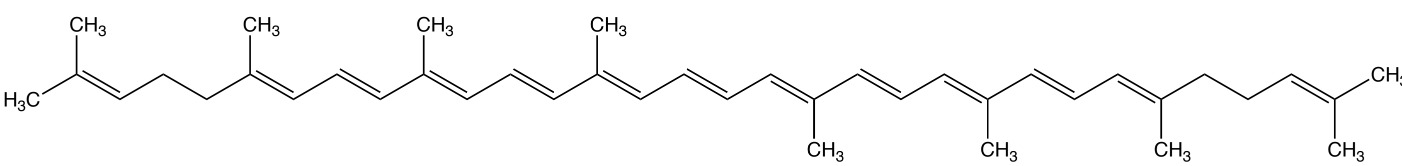
β-Carotene

λ_{max} = 455 nm, 483 nm



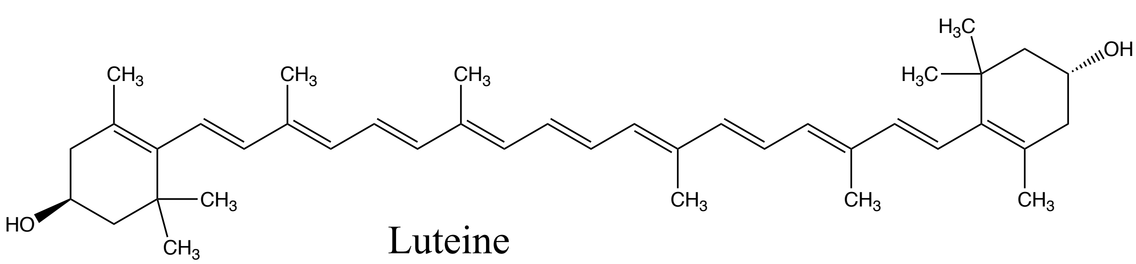
11-*cis*-Retinal

λ_{max} = 380 nm



Lycopene

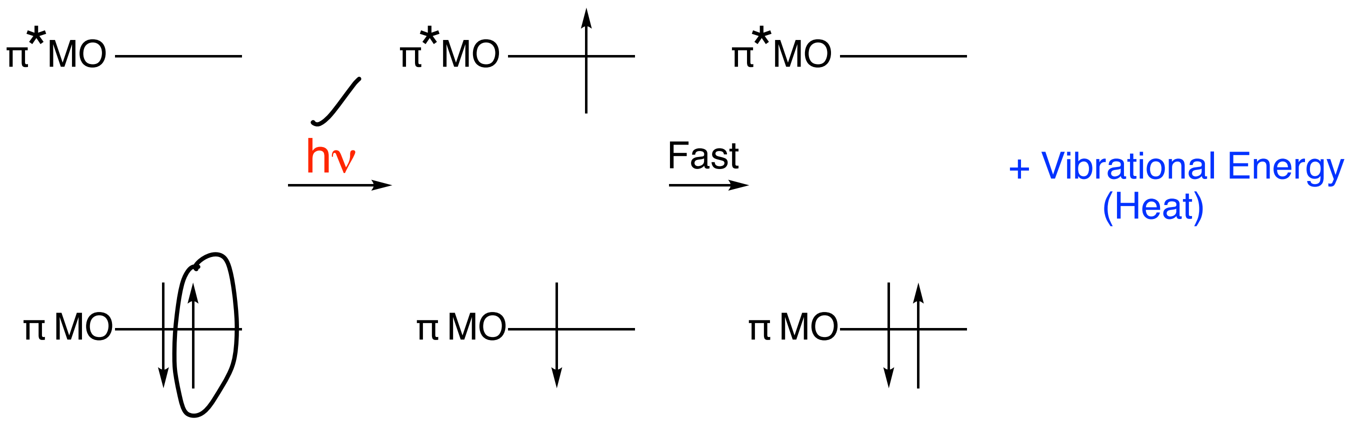
λ_{max} = 443 nm, 471 nm, 502 nm



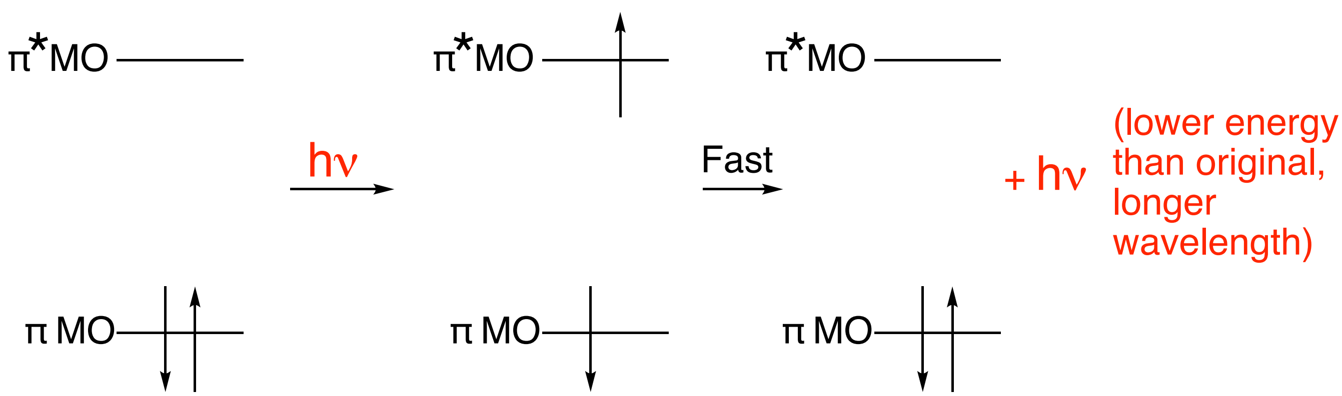
Luteine

λ_{max} = 445 nm, 474 nm

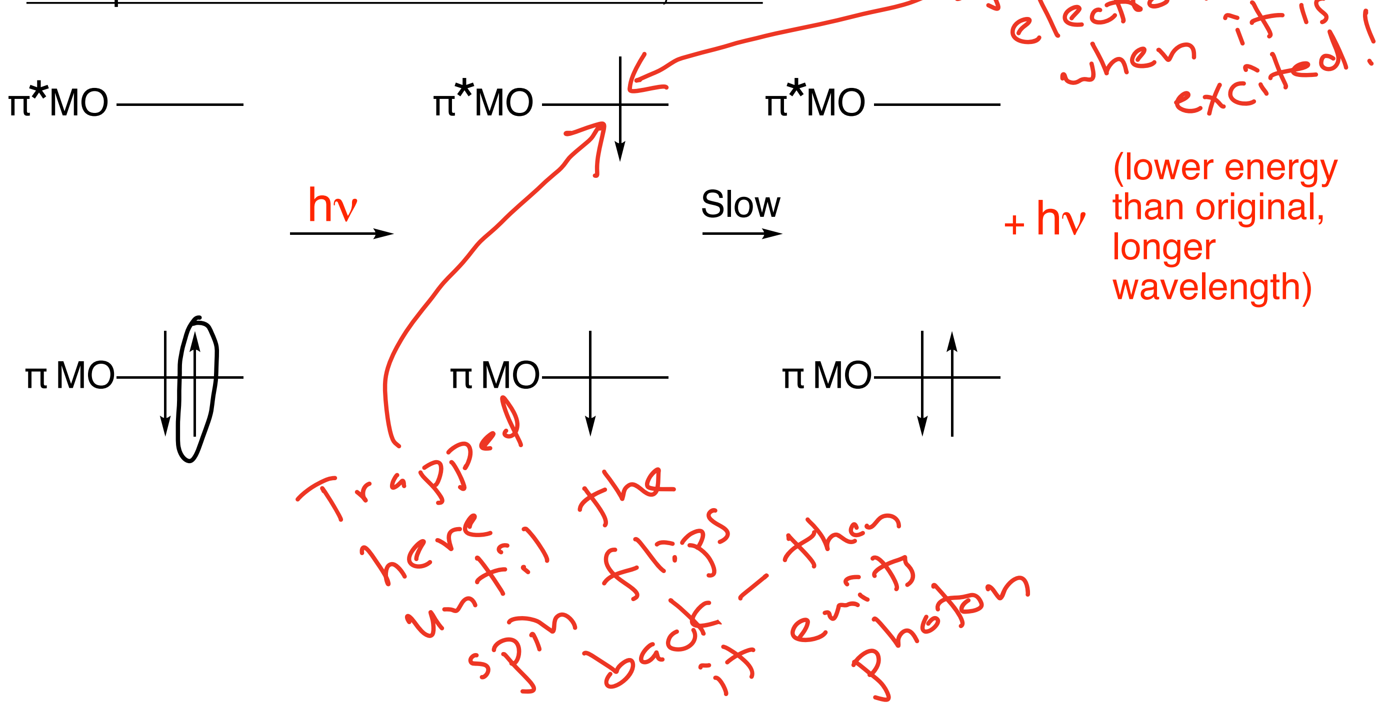
Generation of heat, Most molecules



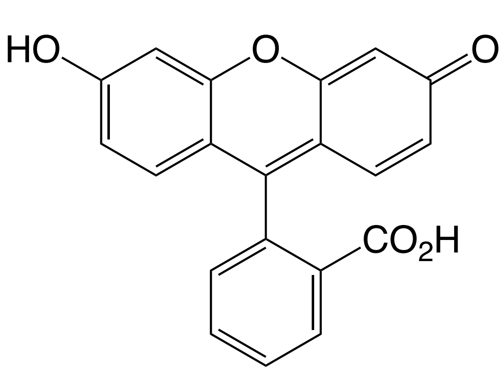
Flourescence - Rigid Molecules, Not uncommon



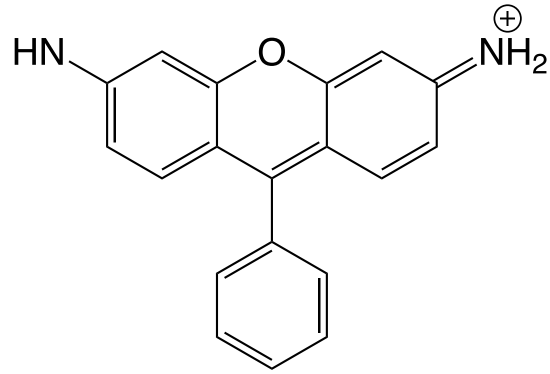
Phosphorescence - “Glow in the Dark”, Rare



Flourescence - Rigid Molecules, Not uncommon

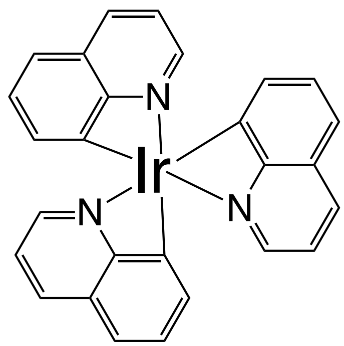


Fluorescein



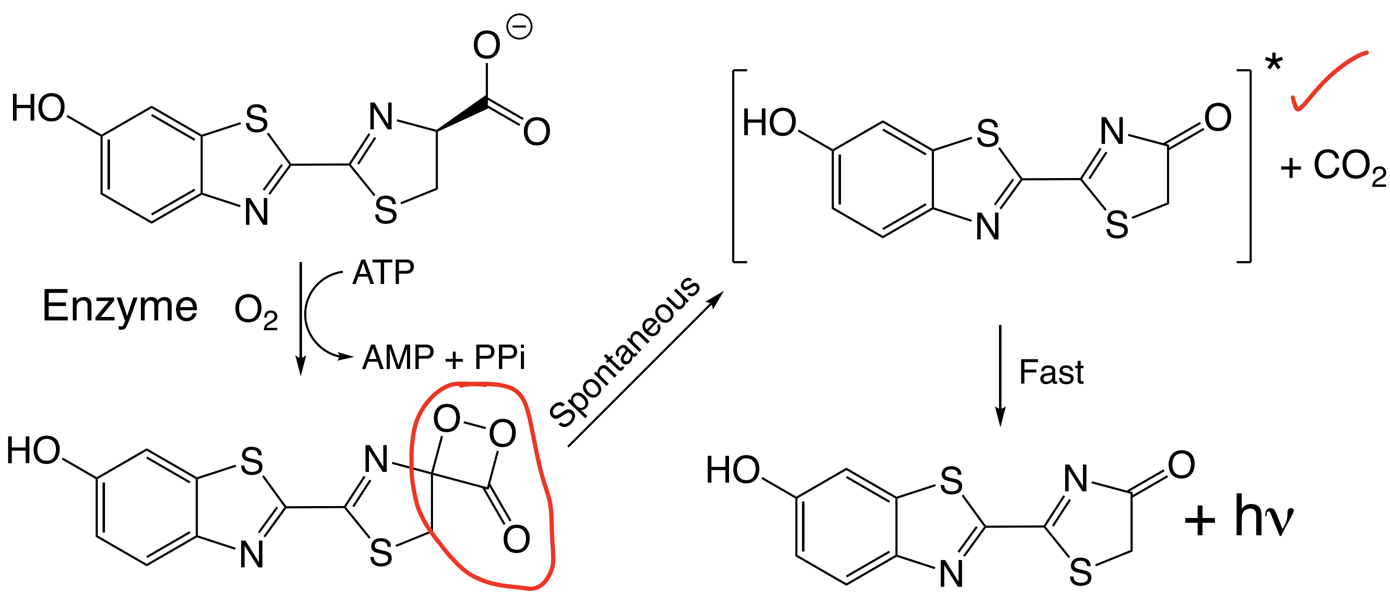
Rhodamine

Phosphorescence - “Glow in the Dark”, Rare



The metal is responsible for the electron spin flipping upon absorbing a photon

Bioluminescence - Fireflies, Deep Sea Creatures - Chemical Reactions



http://photobiology.info/Branchini2.html

Energy ←

Light source

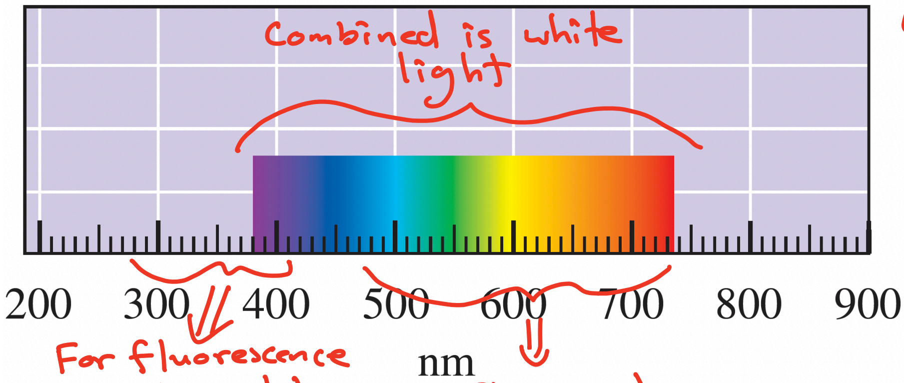
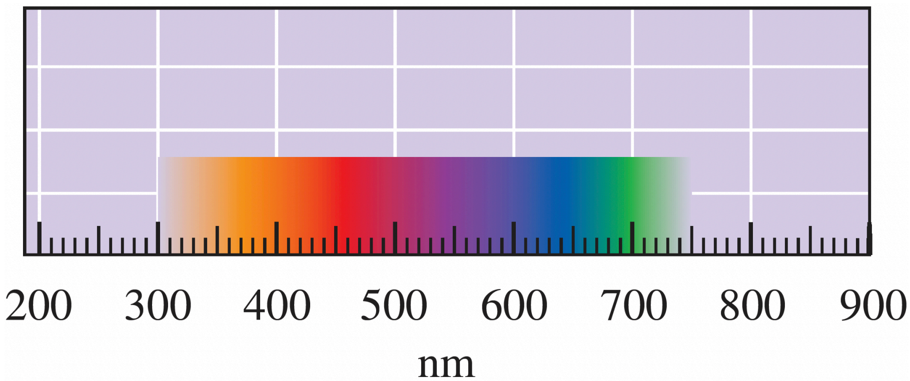


FIGURE 20.5 (a) Visible light color-wavelength correlation.

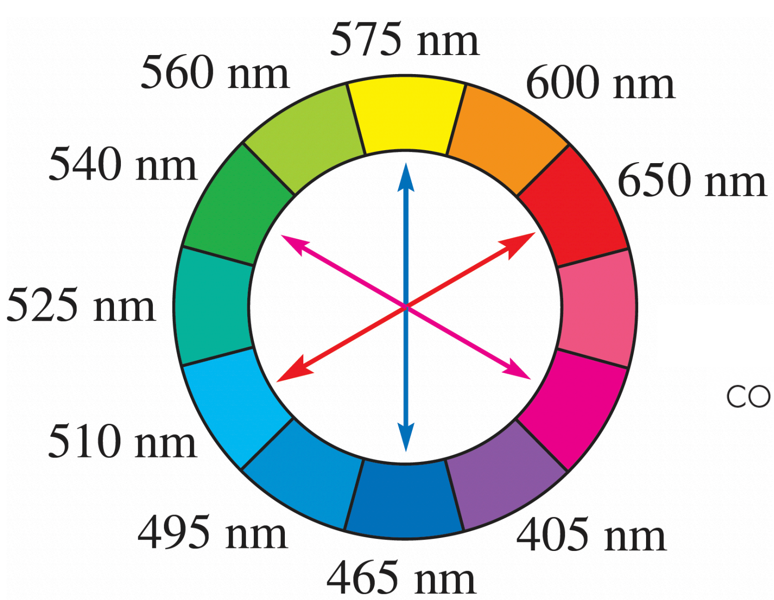
For fluorescence the ultraviolet light (UV) is used to excite electrons

Flourescent emission

*** We "see" the wavelengths reflected minus the wavelengths absorbed ***

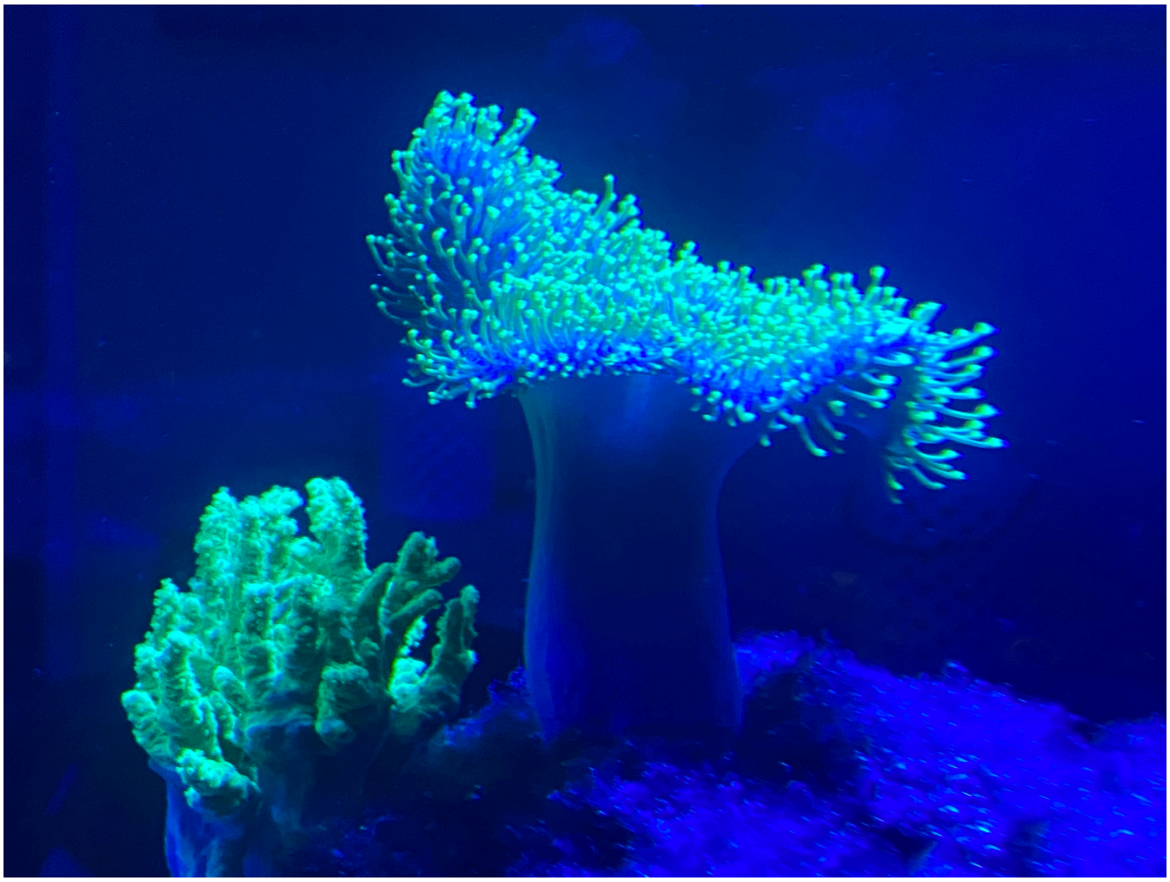


(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the *x*-axis) is absorbed.



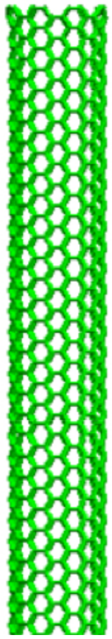
Colored arrows are complementary

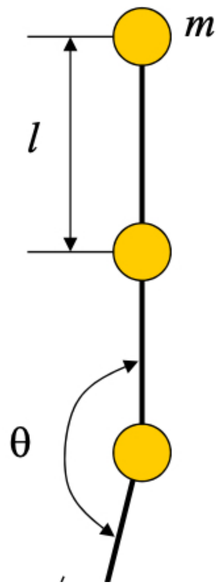
(c) Complementary colors on a color wheel.

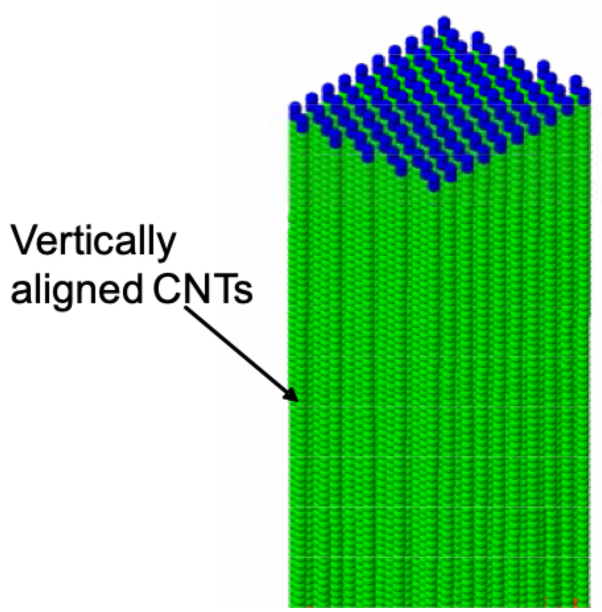


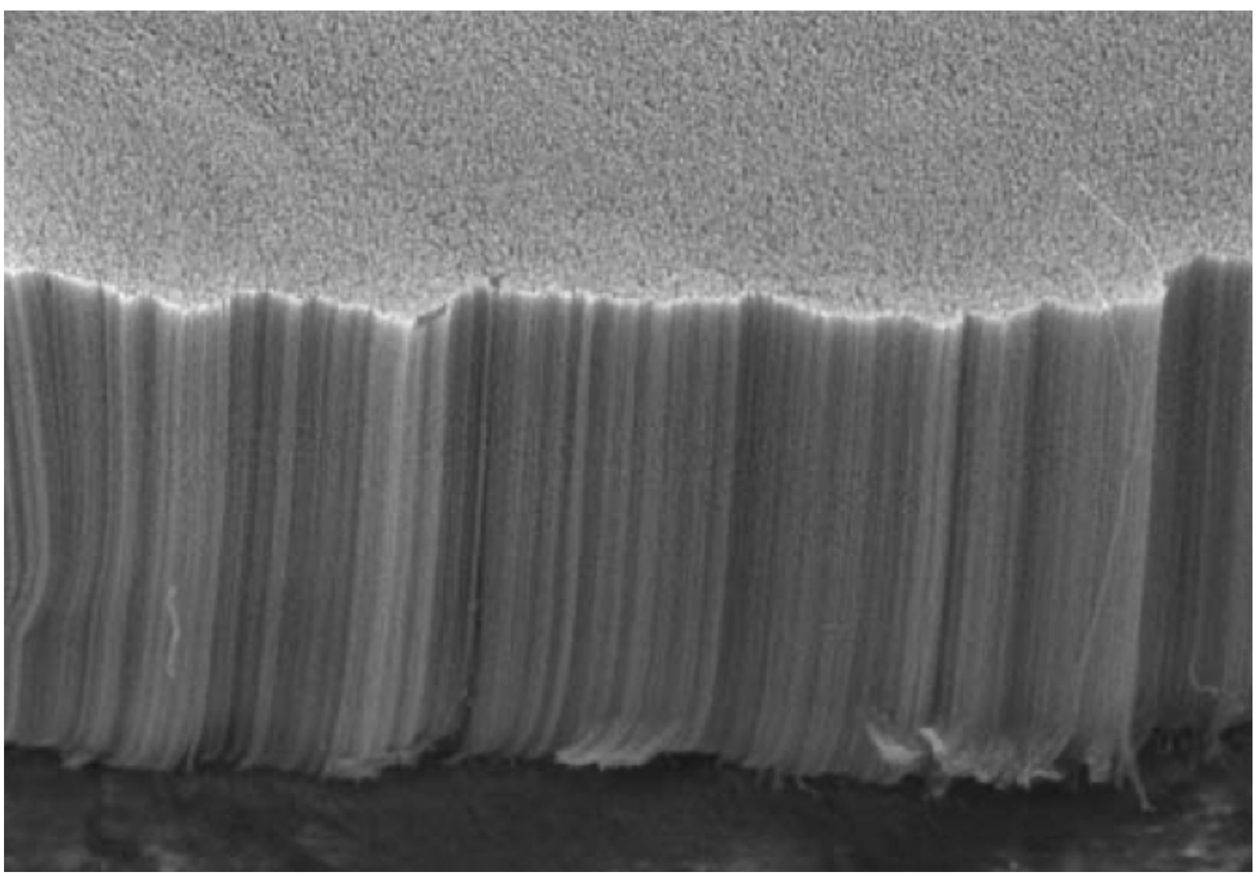
Many natural pigments are highly flourescent, especially in the ocean

Vanta black → all photons are absorbed between the long carbon nanotubes









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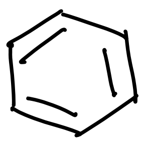
Preview



Extraordinarily Stable!

~36 kcal/mol more stable than expected

This is A LOT

Pericyclic Reactions → π bonds and σ bonds interchange

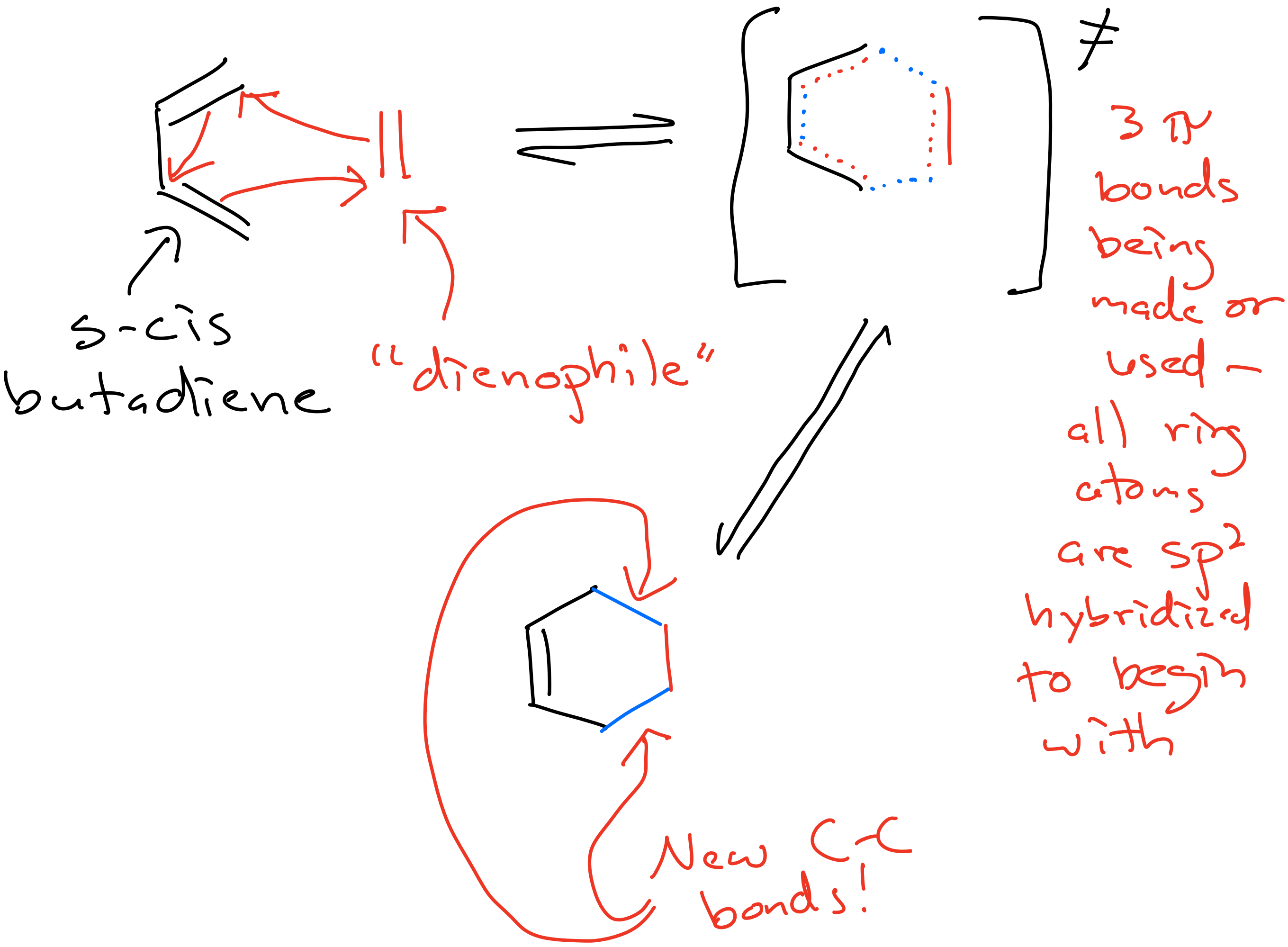
→ Happen because the transition state is super stable

"aromatic" character of transition state

Otto!
↓
Diels-Alder Reaction

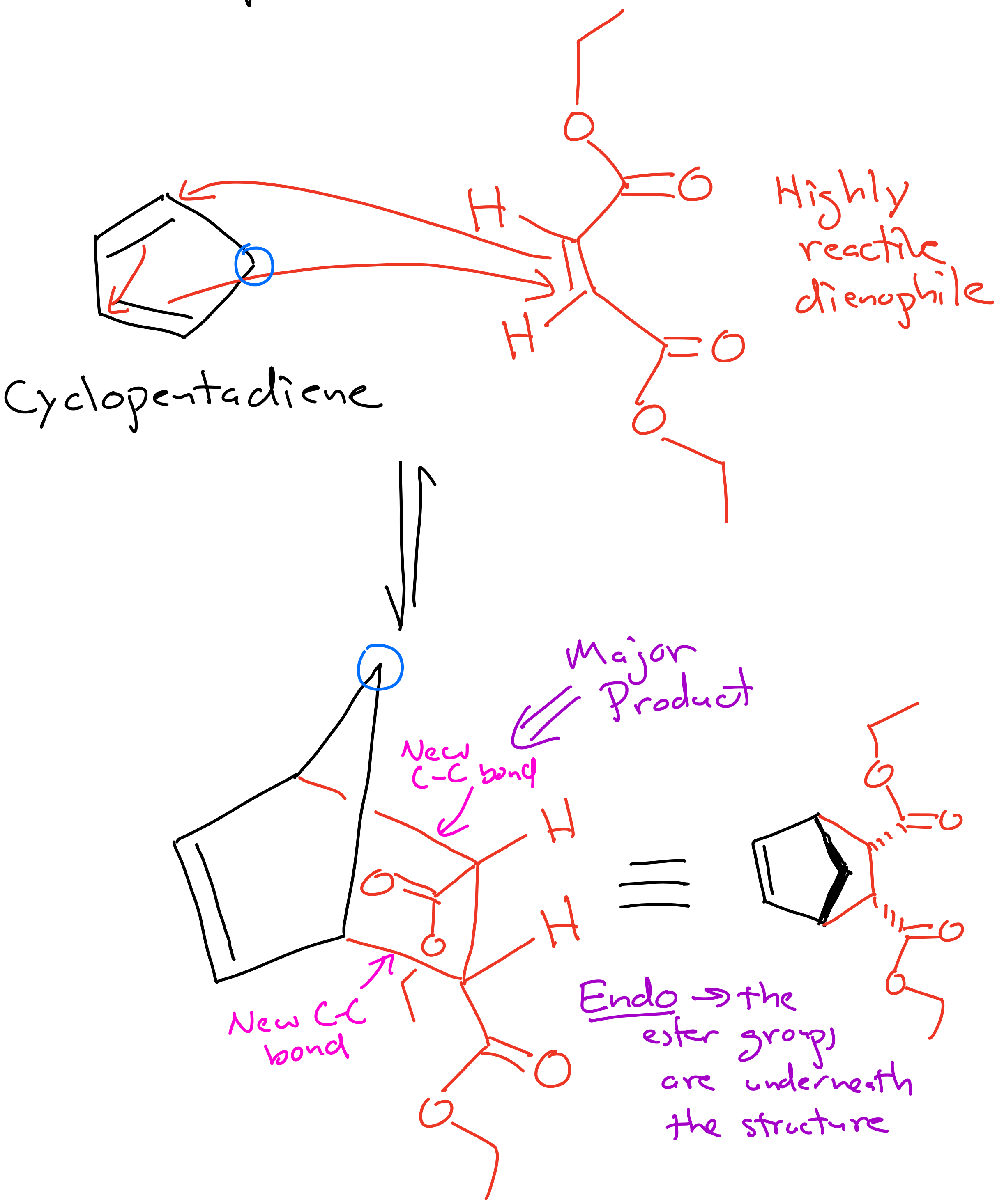
..... bonds being broken

..... bonds forming

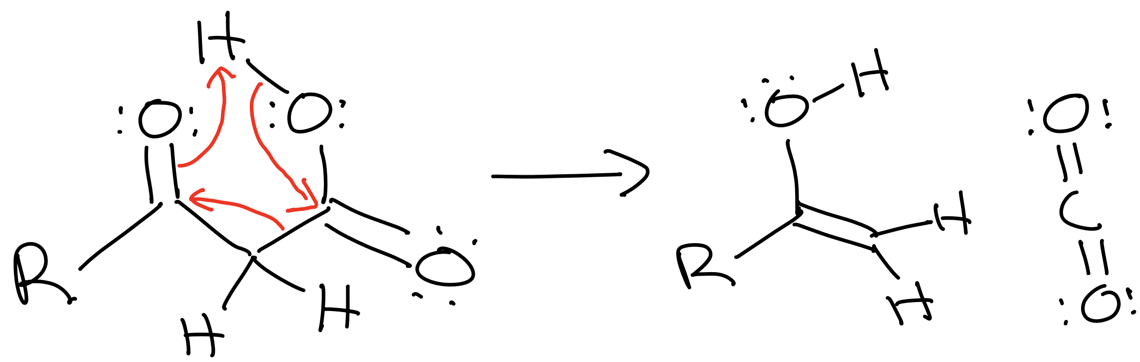


The above reaction gives a poor yield and was used only to illustrate the process → there are many, many known examples of Diels-Alder reactions

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



You have seen one other example of this type of reaction:



3 π bonds being broken or formed in the transition state → very stable transition state!

That is why β-keto acids and β-diacids decarboxylate when you heat them!

All conjugated systems are extra stable, but there is a certain class that is particularly stable:

Aromatic Rings ⇒ Hückels Rules (definition)

1) All ring atoms are sp^2 hybridized (have a 2p orbital)

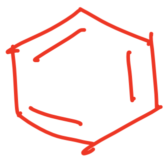
2) Ring is flat

3) Monocyclic

4) 2, 6, 10, 14, 20, 24.... π electrons

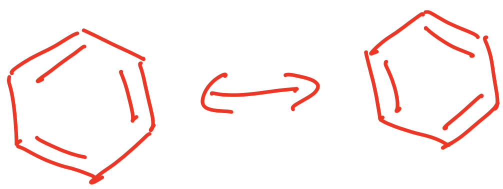
$4n+2$ π electrons

$n = 0, 1, 2, 3, 4, 5.....$



Benzene

The π electrons of benzene are much less reactive than normal alkenes → benzene only reacts under harsh conditions



All bonds are the same length!

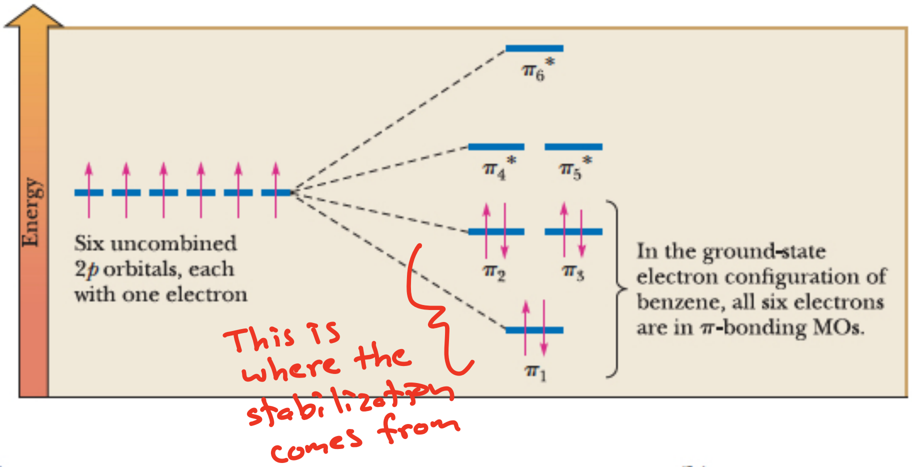


FIGURE 21.2 The molecular orbital representation of the π bonding in benzene.

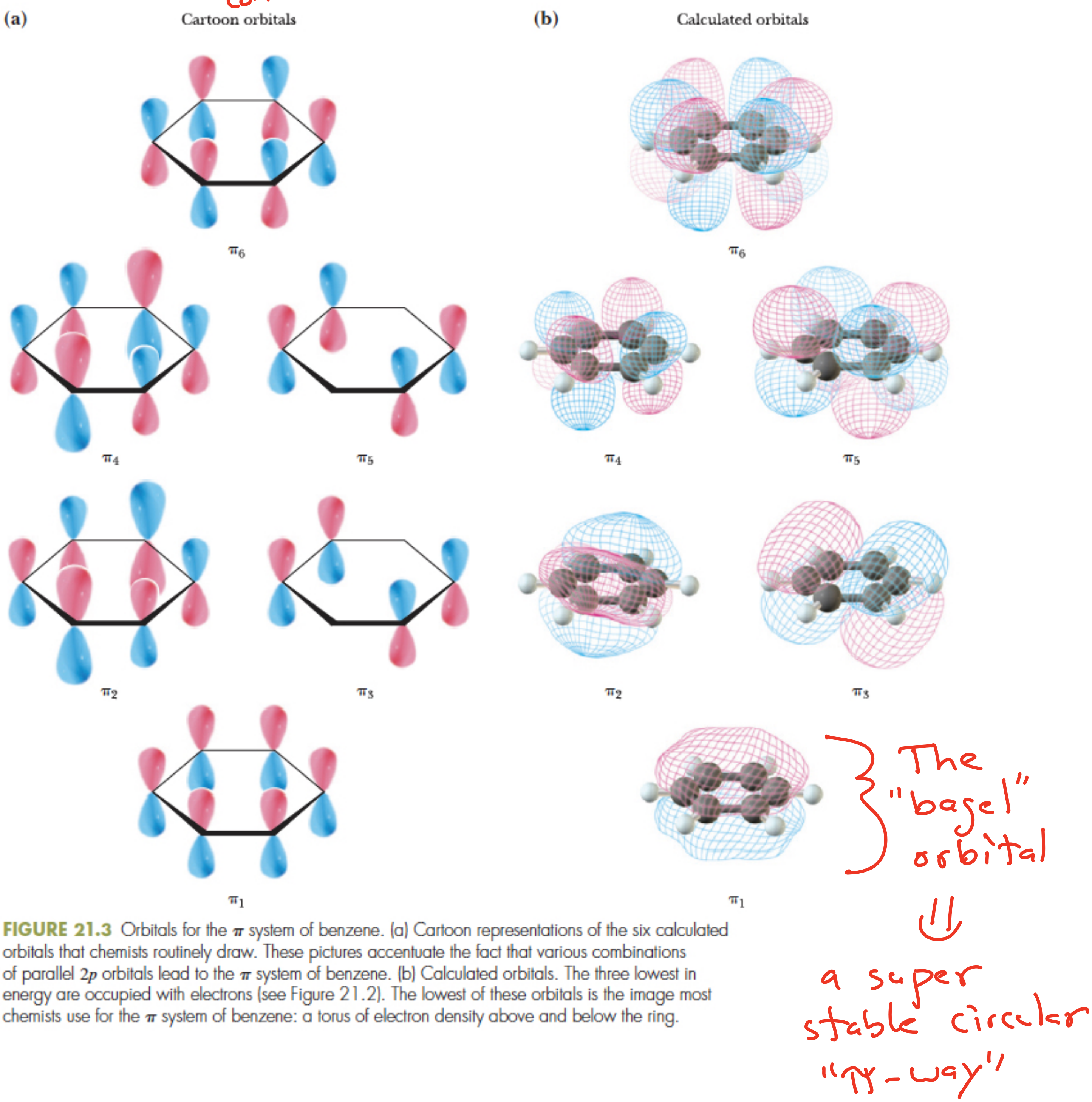


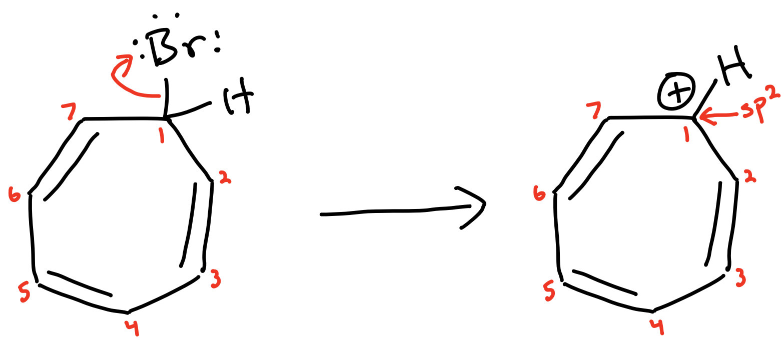
FIGURE 21.3 Orbitals for the π system of benzene. (a) Cartoon representations of the six calculated orbitals that chemists routinely draw. These pictures accentuate the fact that various combinations of parallel 2*p* orbitals lead to the π system of benzene. (b) Calculated orbitals. The three lowest in energy are occupied with electrons (see Figure 21.2). The lowest of these orbitals is the image most chemists use for the π system of benzene: a torus of electron density above and below the ring.

Two Important Consequences of Aromaticity

1) Aromaticity stabilizes ions → anions and cations

2) Atoms in molecules will be sp^2 if that produces aromaticity

Tropylium Ion



all ring atoms sp^2

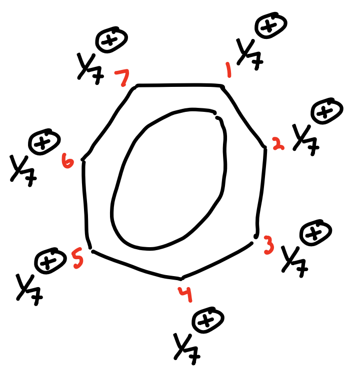
flat

monocyclic

6 π electrons

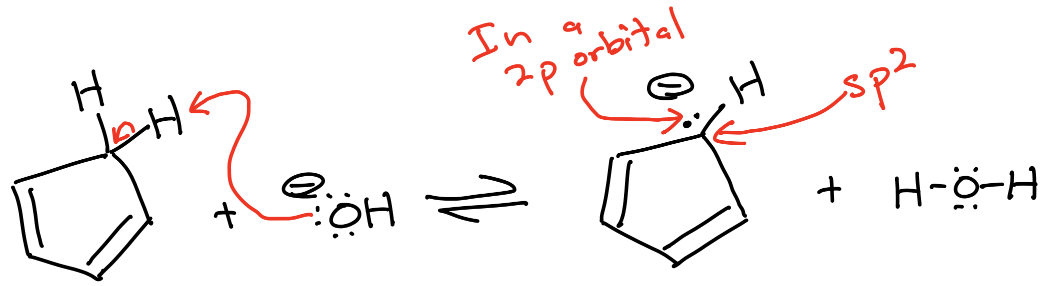
Aromatic!

Super stable cation



All atoms are equivalent → 7 equal contributing structures!

Cyclopentadienyl Anion

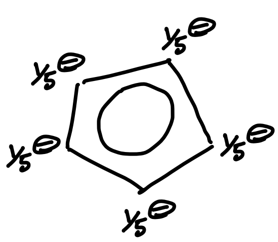


$pK_a = 16$

Aromatic!

Super stable anion

- all ring atoms sp^2
- flat
- monocyclic
- 6 π electrons
  - → 2 electrons of lone pair
  - → 4 electrons in the 2 π bonds



All atoms are equivalent → 5 equal contributing structures!