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

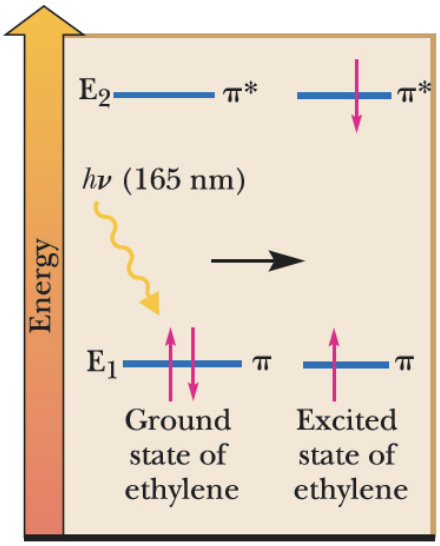


FIGURE 20.6 A $\pi \rightarrow \pi^*$ transition in excitation of ethylene. Absorption of ultraviolet radiation causes a transition of an electron from a π-bonding MO in the ground state to a π-antibonding MO in the excited state. There is no change in electron spin.

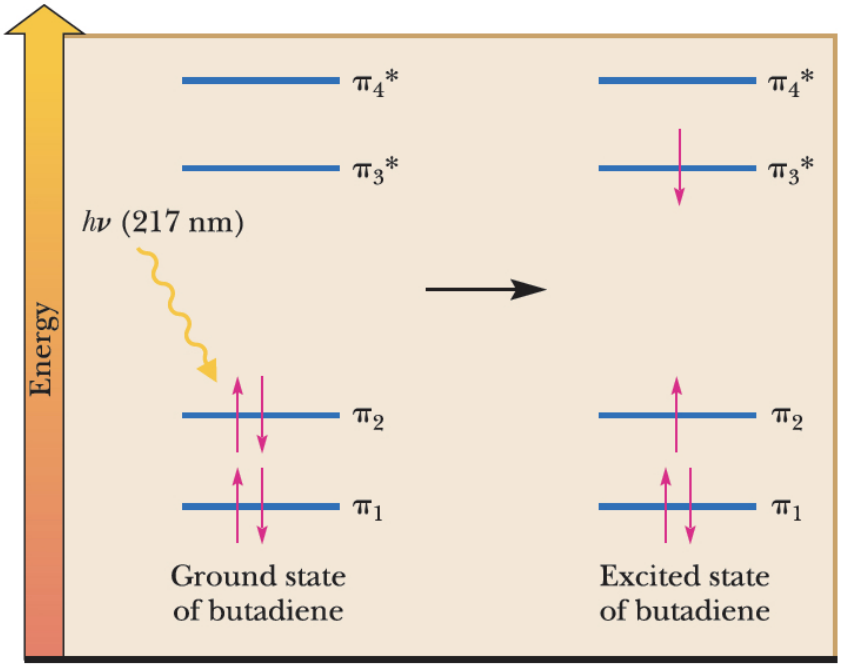
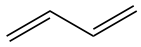
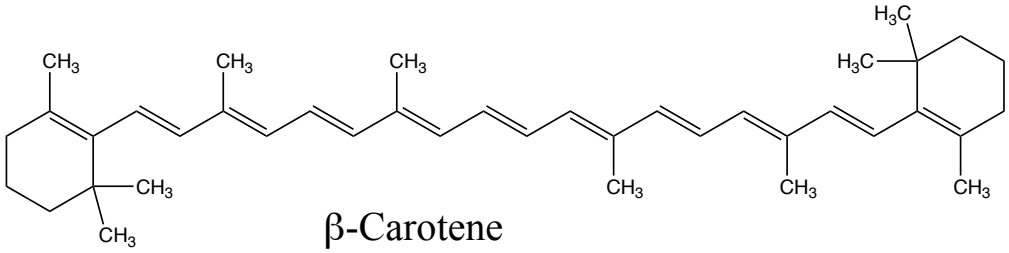


FIGURE 20.7 Electronic excitation of 1,3-butadiene; a $\pi \rightarrow \pi^*$ transition.



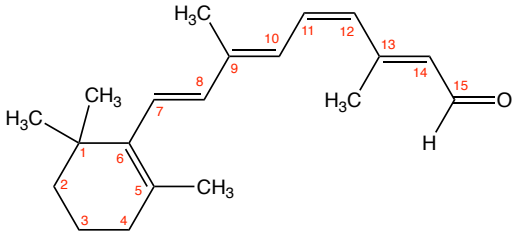
Butadiene

λ_{max} = 217 nm



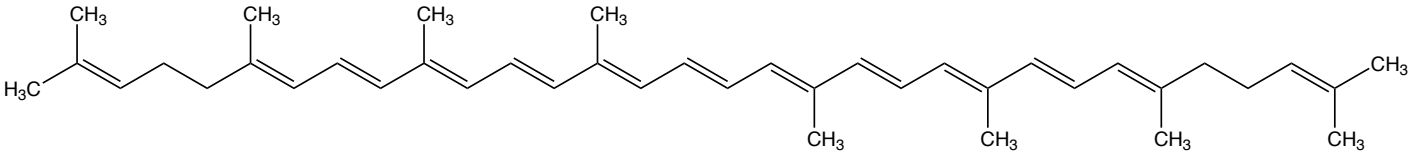
β-Carotene

λ_{max} = 455 nm, 483 nm



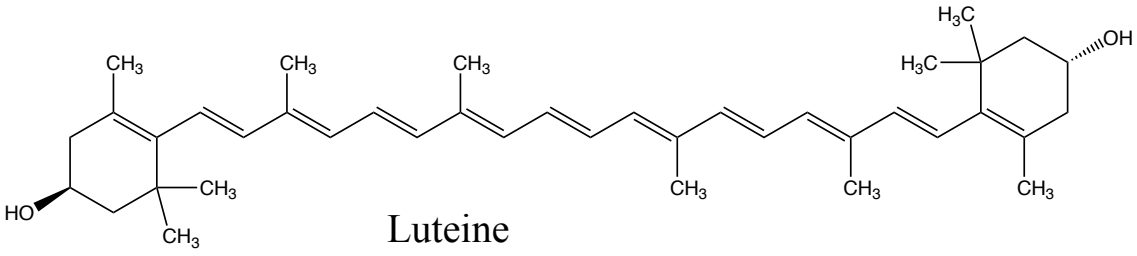
11-*cis*-Retinal

λ_{max} = 380 nm



Lycopene

λ_{max} = 443 nm, 471 nm, 502 nm



Luteine

λ_{max} = 445 nm, 474 nm

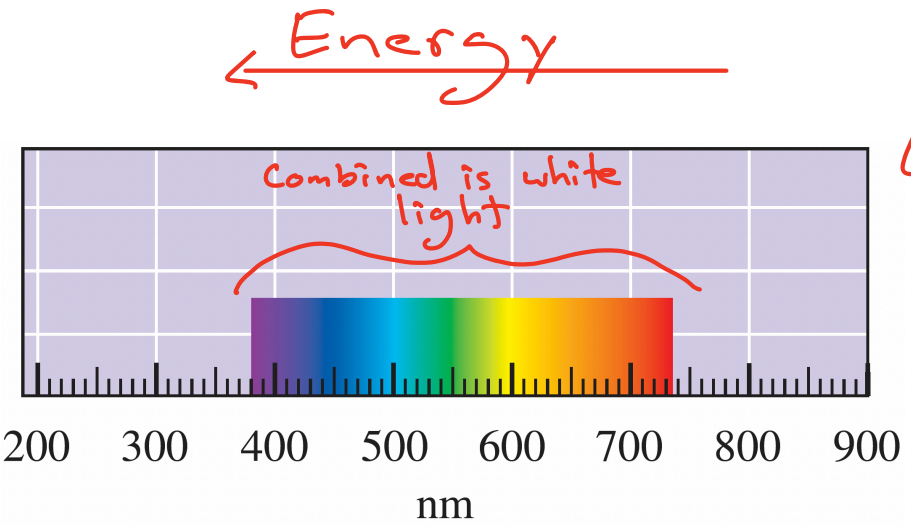
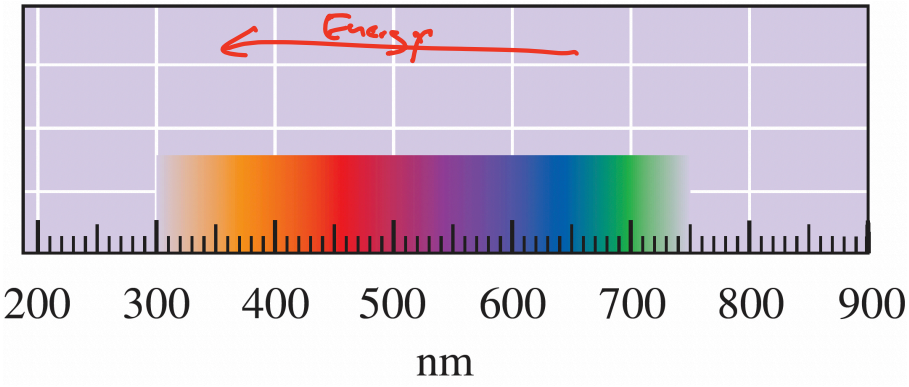
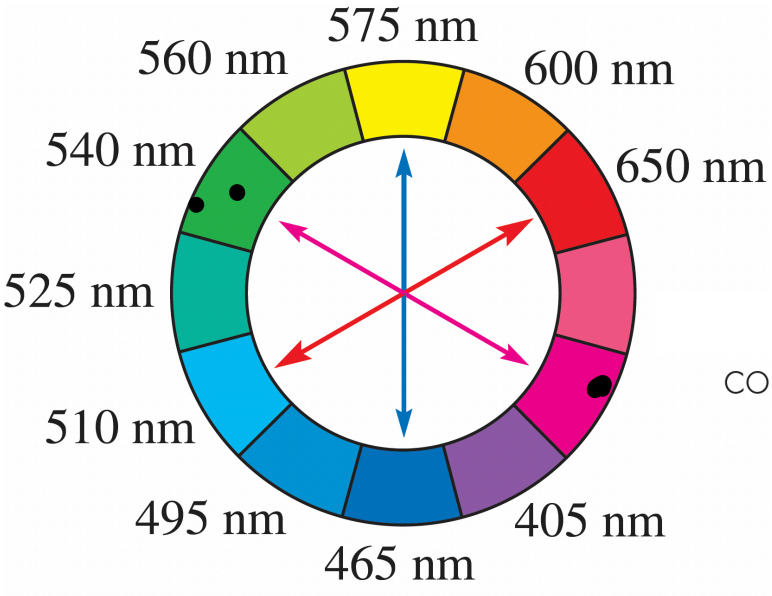


FIGURE 20.5 (a) Visible light color-wavelength correlation.



(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.

White → reflects all wavelengths of visible light

Black → absorbs all wavelengths of visible light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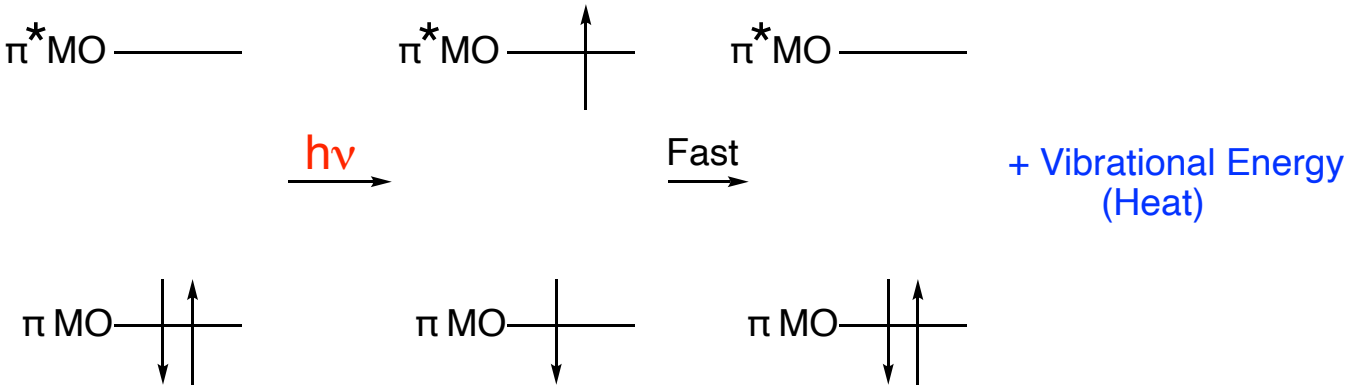
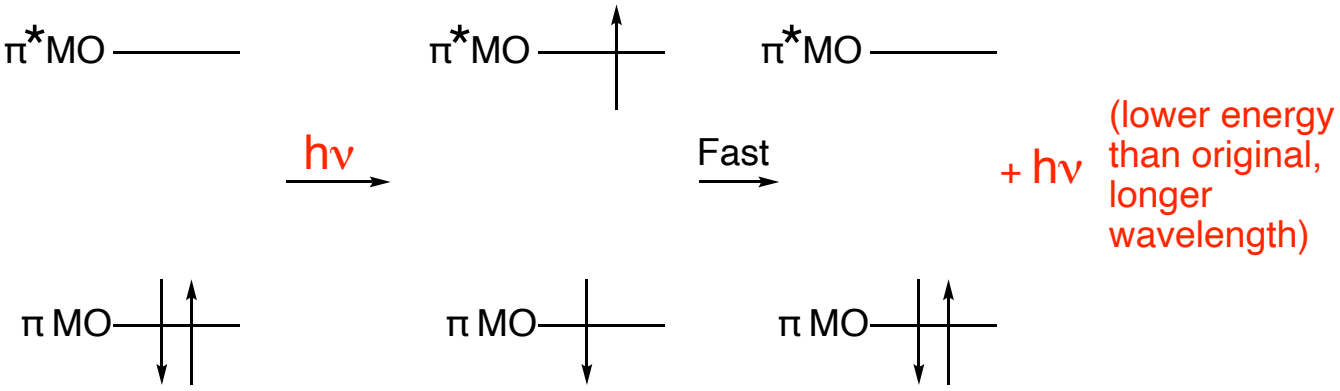
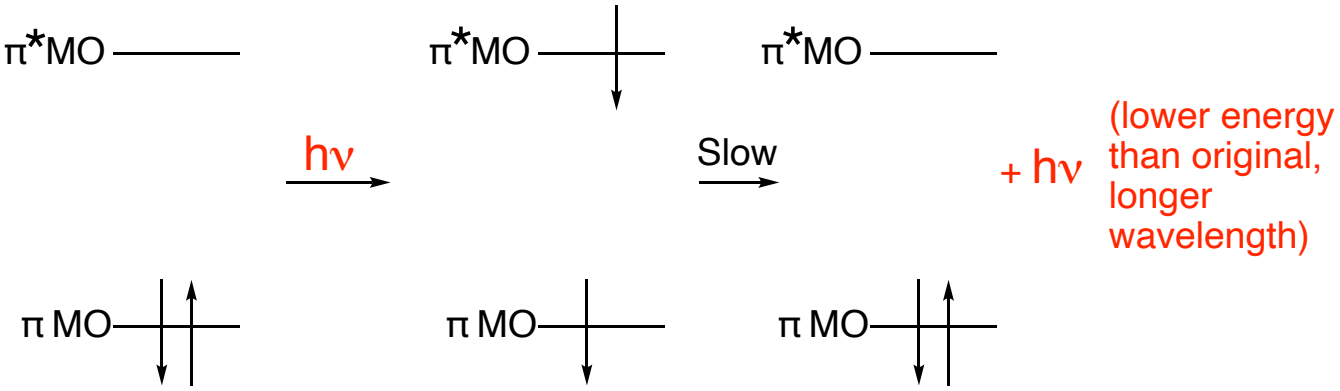
Generation of heat, Most molecules



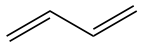
Flourescence - Rigid Molecules, Not uncommon



Phosphorescence - “Glow in the Dark”, Rare



How vision works, the final edition!



Butadiene

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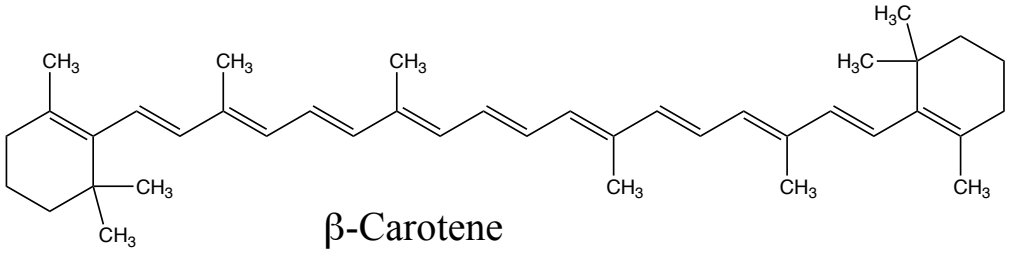

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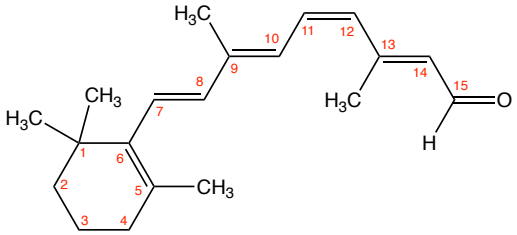

11-*cis*-Retinal

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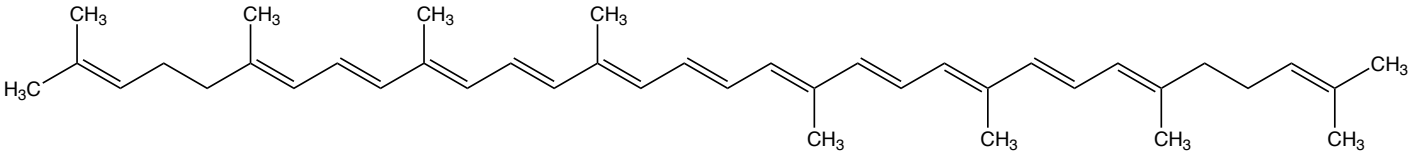

Lycopene

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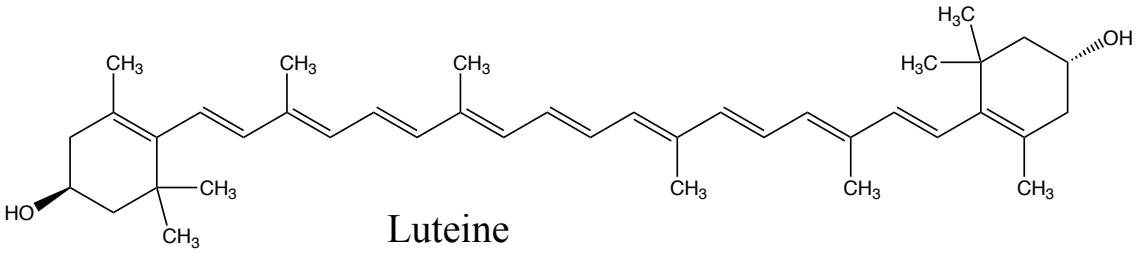
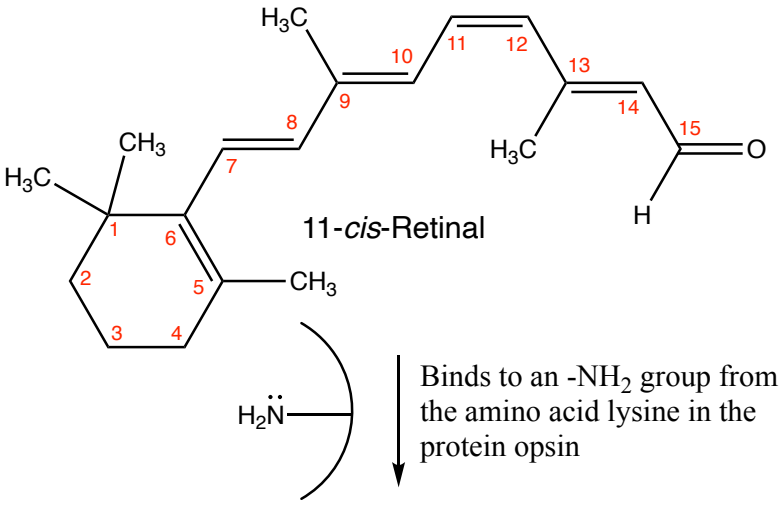


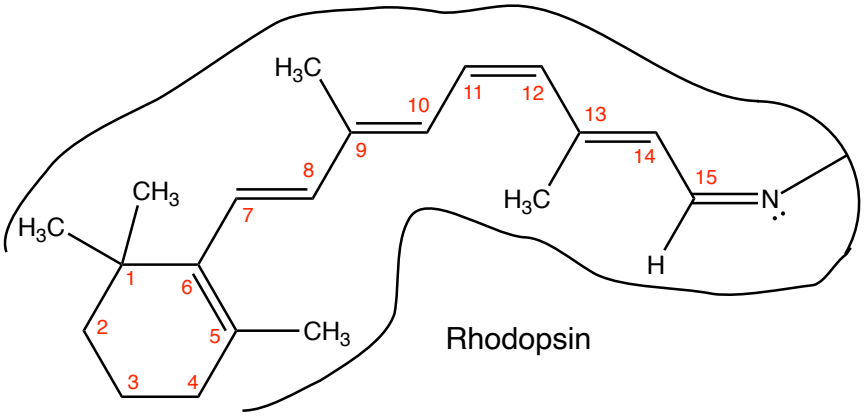
Luteine

λ_{max} = 445 nm, 474 nm

How vision works

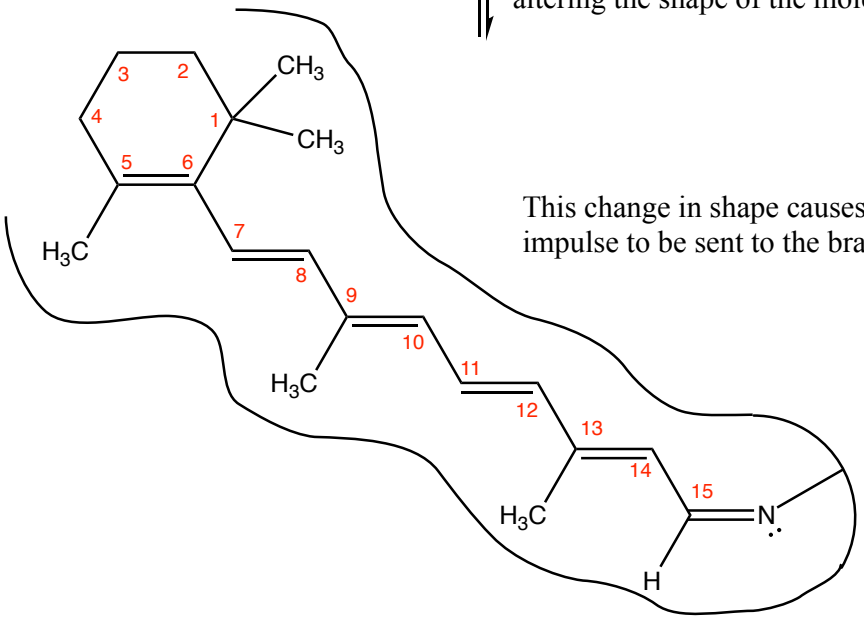


Binds to an -NH_2 group from the amino acid lysine in the protein opsin



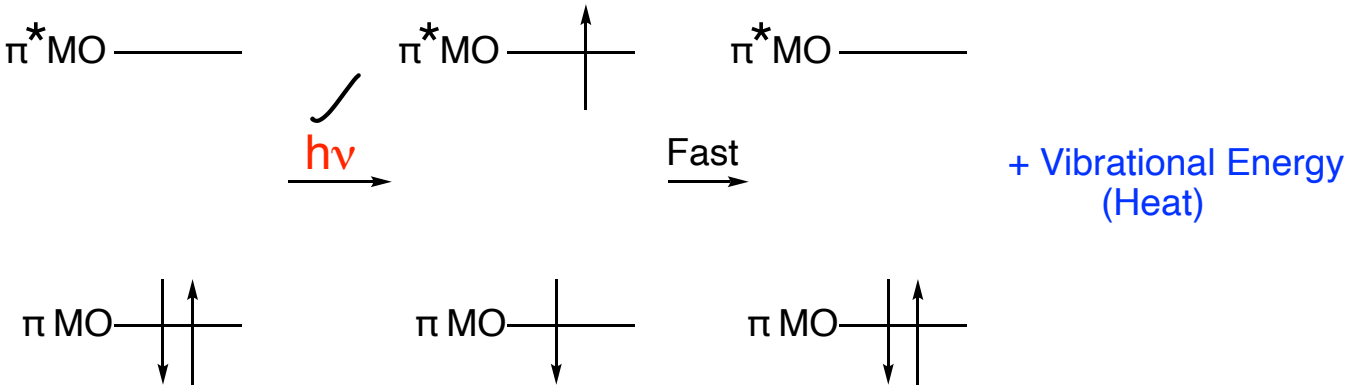
Molecule resets

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

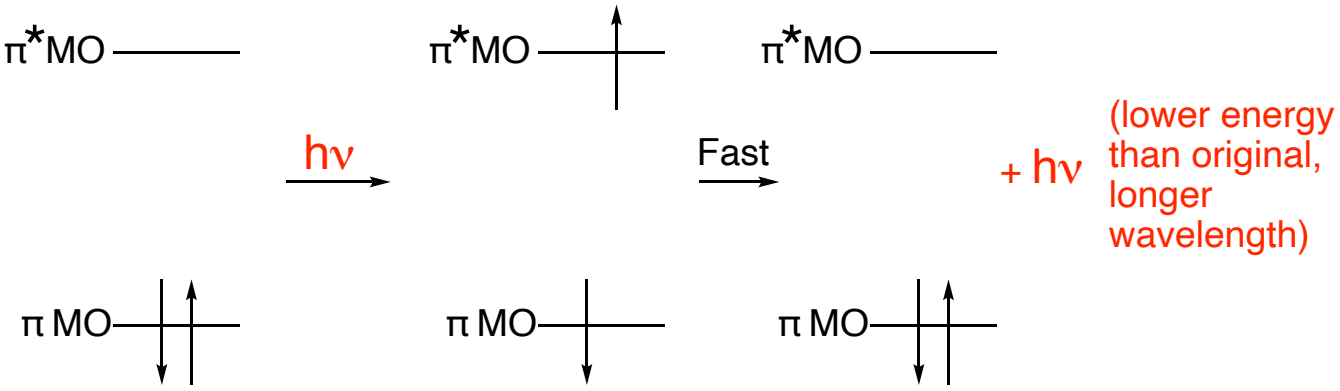


This change in shape causes a nerve impulse to be sent to the brain

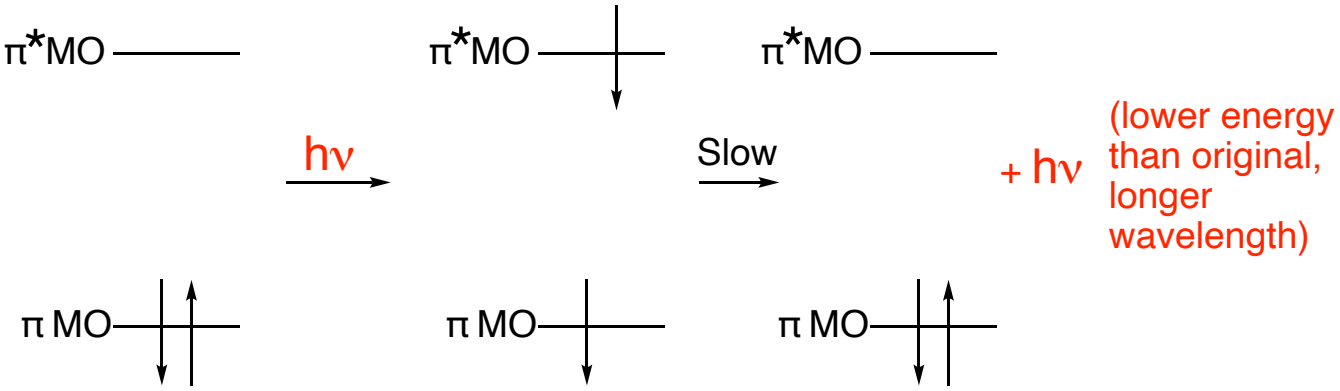
Generation of heat, Most molecules



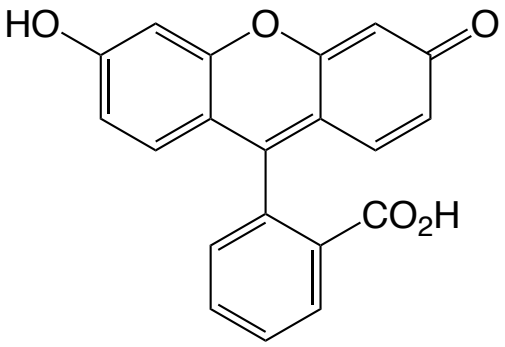
Flourescence - Rigid Molecules, Not uncommon



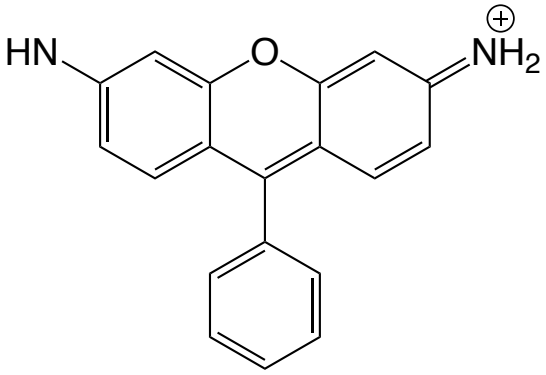
Phosphorescence - “Glow in the Dark”, Rare



Flourescence - Rigid Molecules, Not uncommon

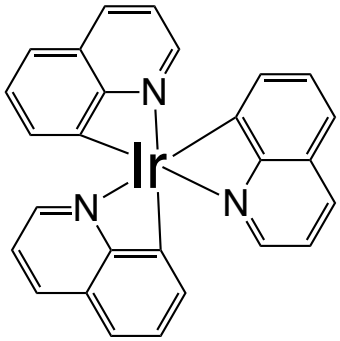


Fluorescein

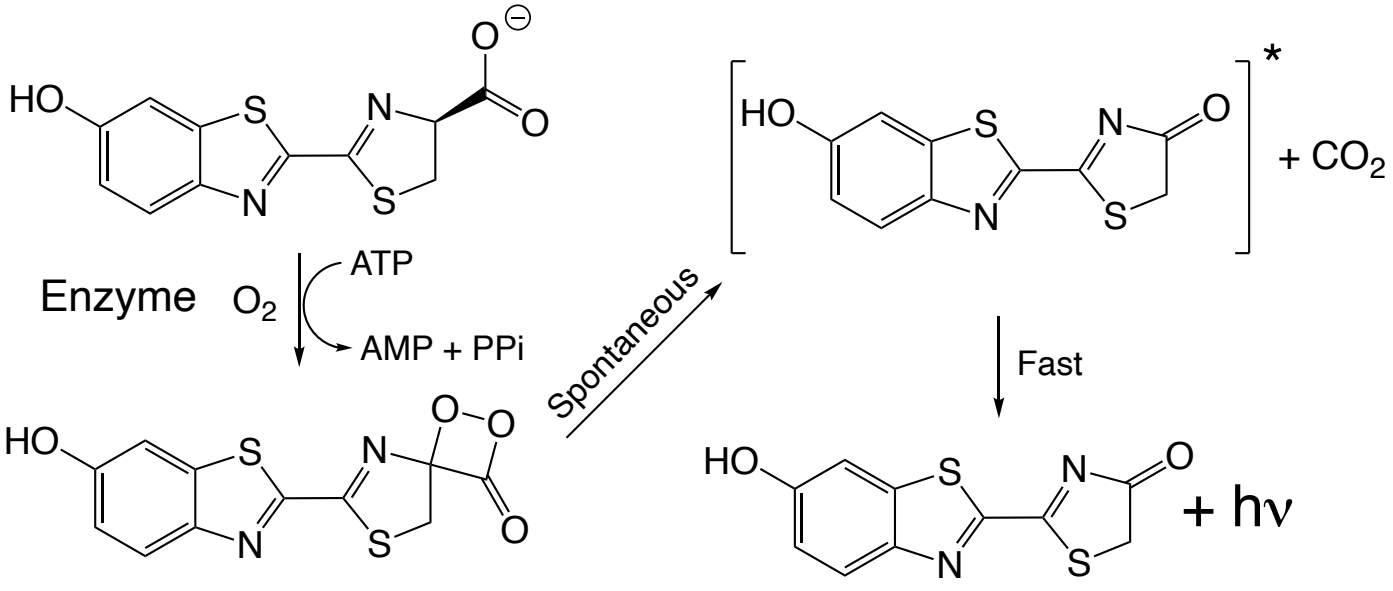


Rhodamine

Phosphorescence - “Glow in the Dark”, Rare



Bioluminescence - Fireflies, Deep Sea Creatures - Chemical Reactions



http://photobiology.info/Branchini2.html

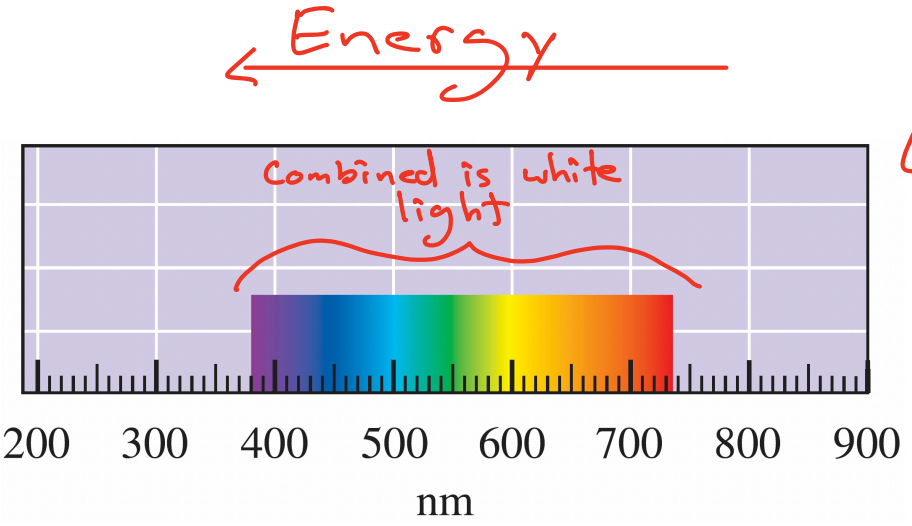
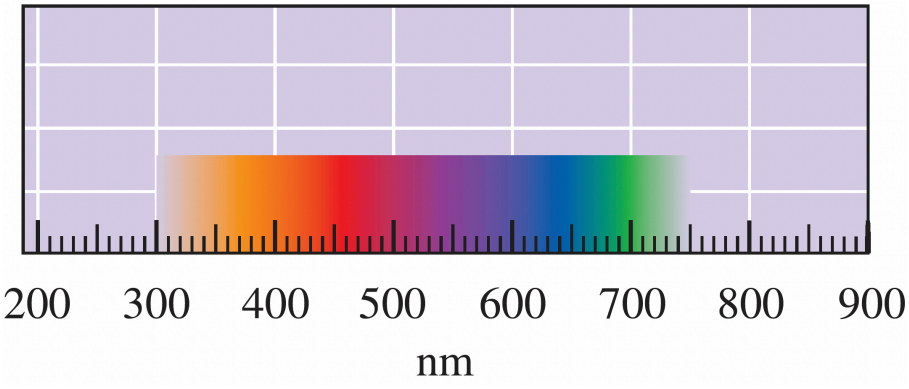
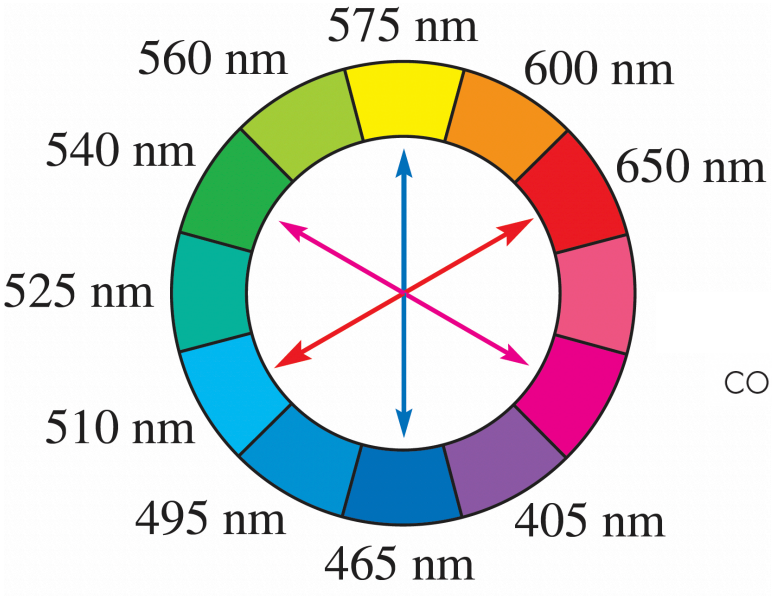


FIGURE 20.5 (a) Visible light color-wavelength correlation.

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



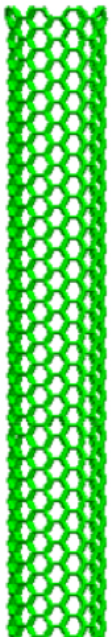
(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the *x*-axis) is absorbed.

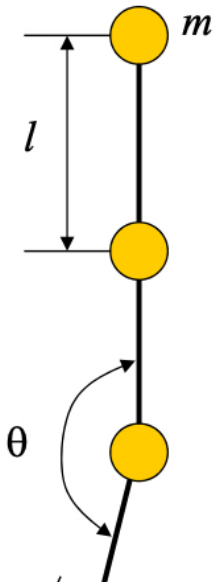


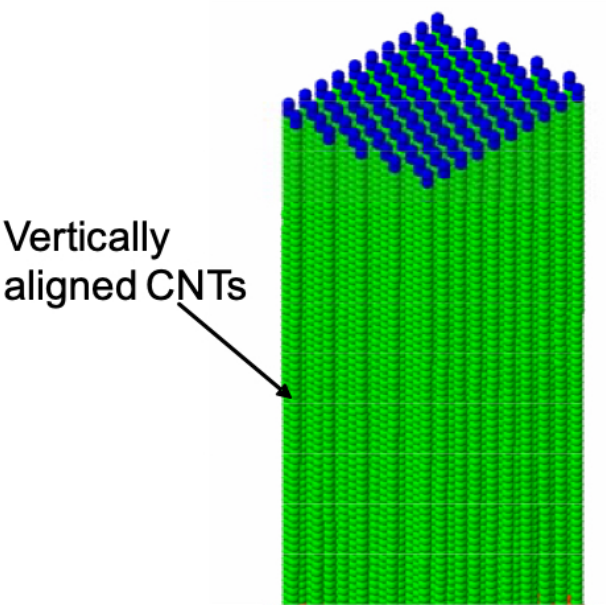
(c) Complementary colors on a color wheel.

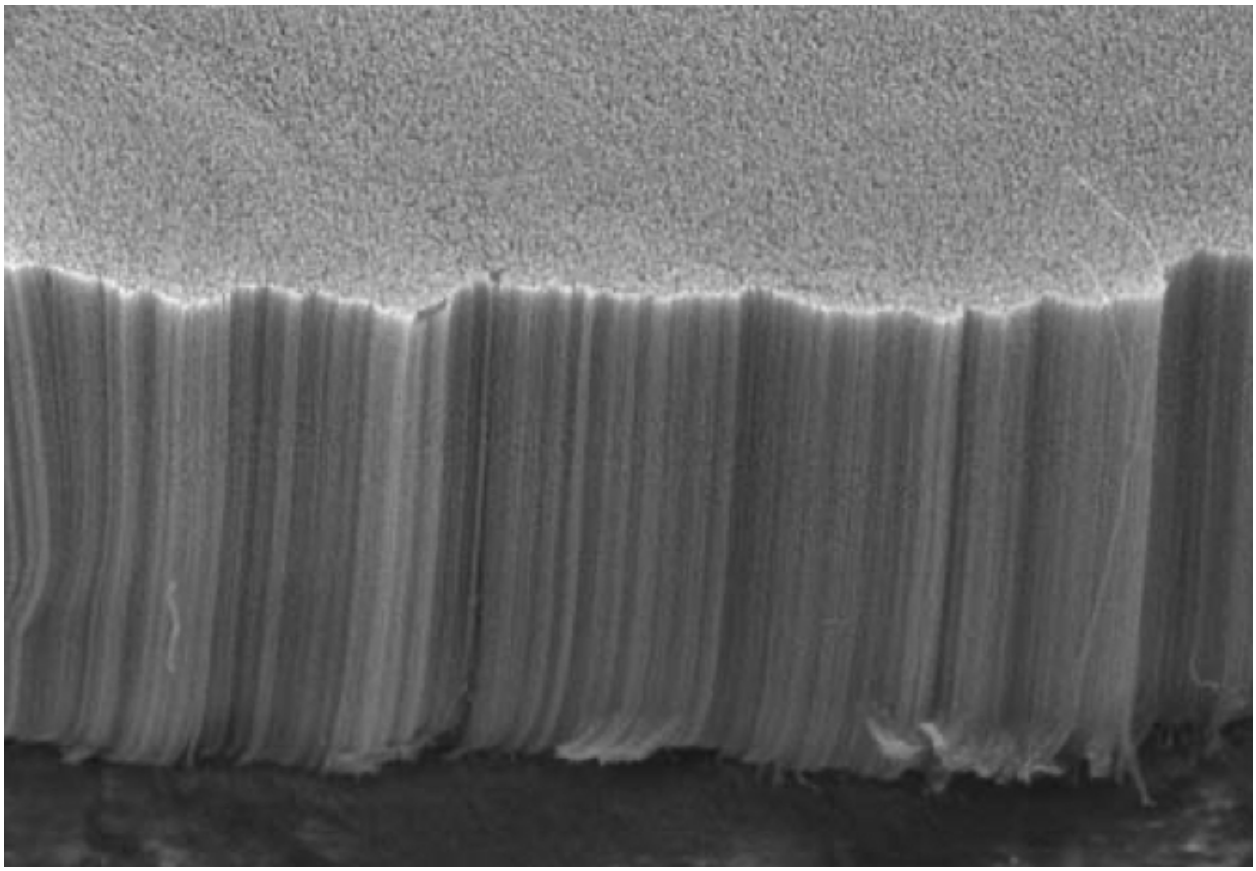
Colored arrows are complementary

Vanta Black → The "blackest" material



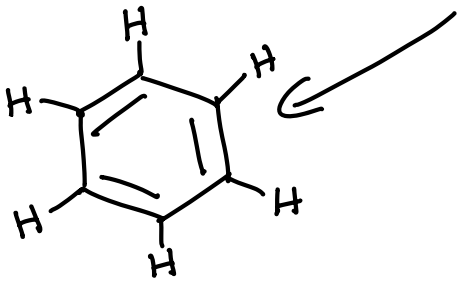






Science **322**, 238 (2008)

Preview



Benzene

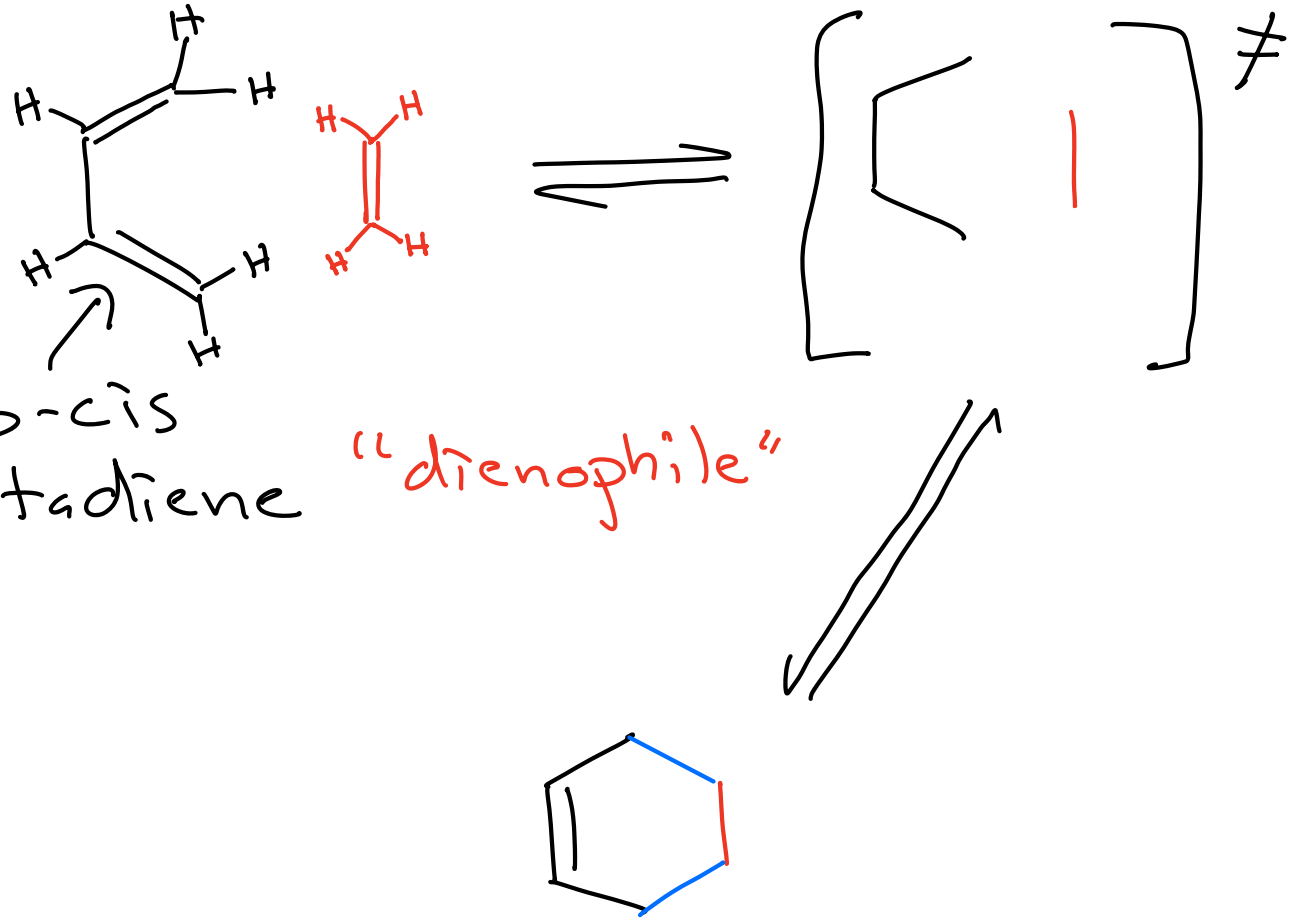
Extraordinarily Stable!

Pericyclic Reactions → π bonds and σ bonds interchange

..... bonds being broken

..... bonds forming

Diels-Alder Reaction

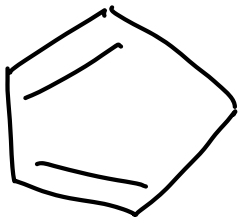


s-cis butadiene

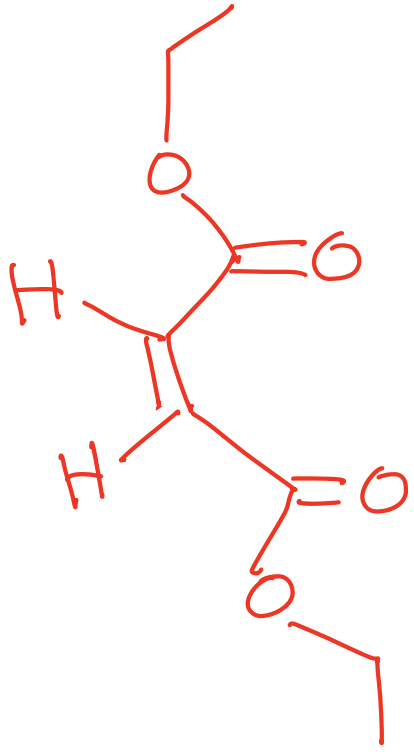
"dienophile"

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

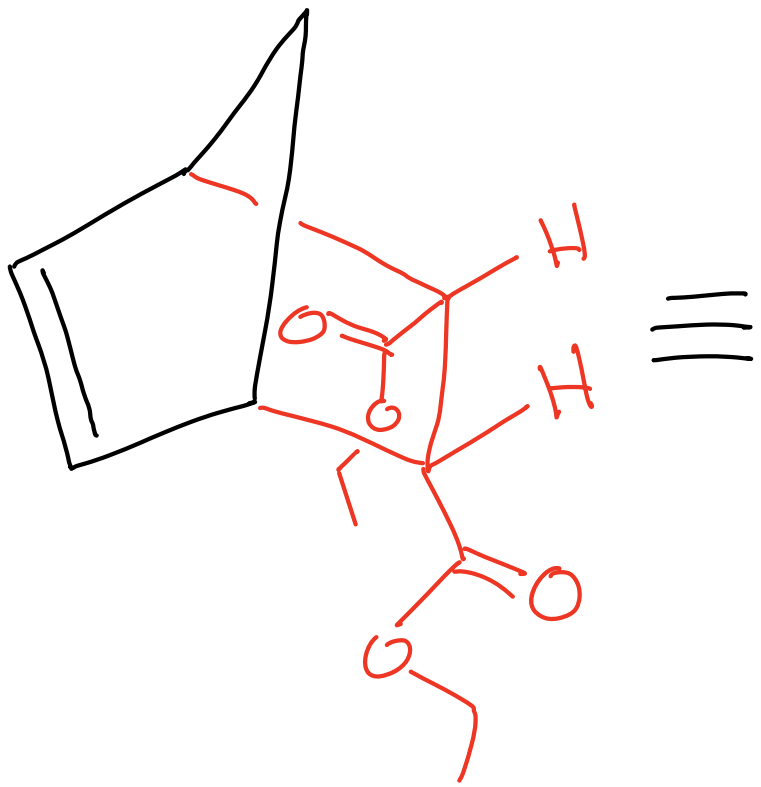
The following is the only Diels-Alder reaction you are responsible for in this class



Cyclopentadiene



Highly reactive dienophile



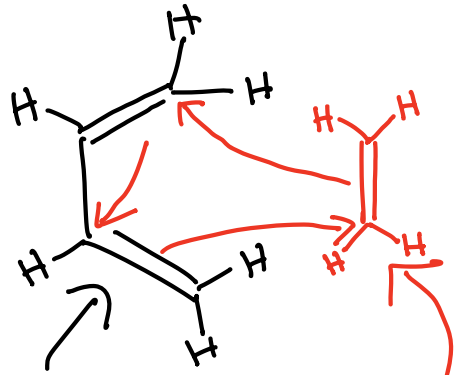
Otto!

↓

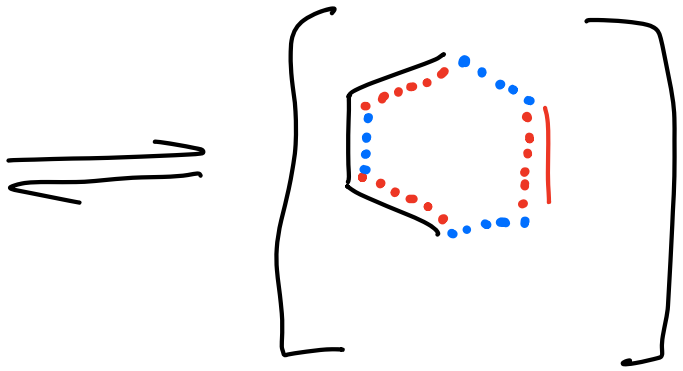
Diels-Alder Reaction

..... bonds being broken

..... bonds forming



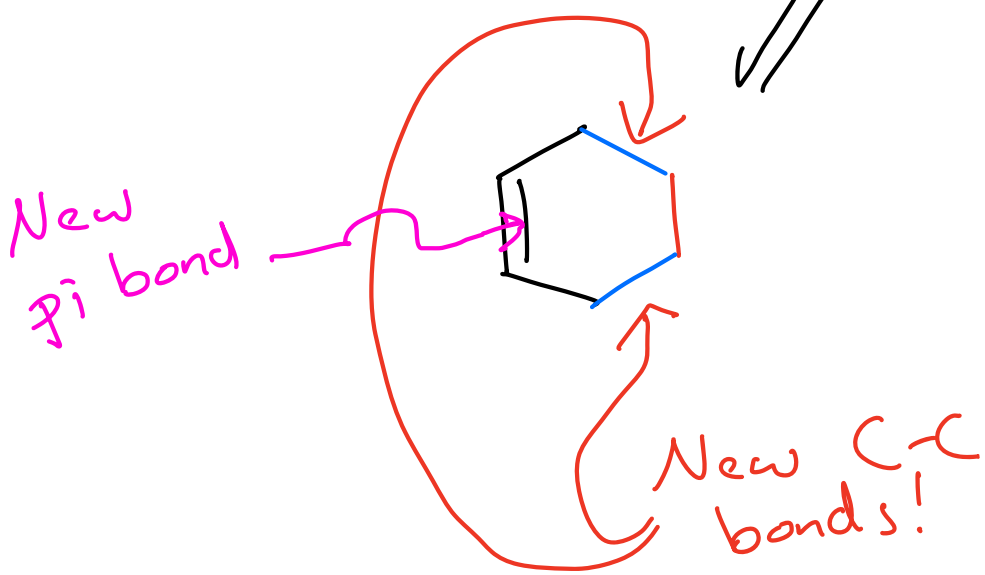
s-cis butadiene



‡

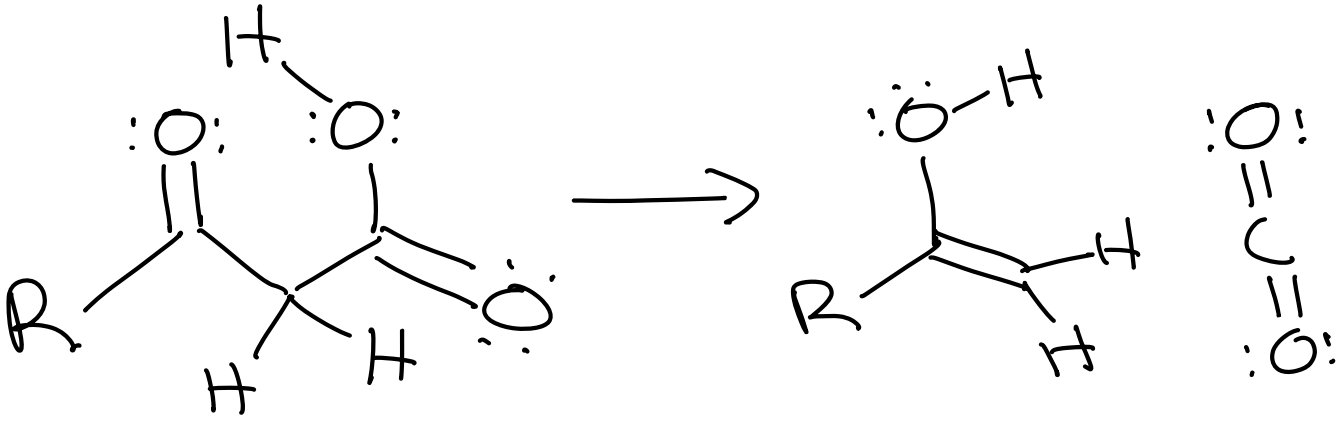
3 π bonds being made or used – all ring atoms are sp^2 hybridized to begin with

"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

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!

The Golden Rules of Organic Chemistry

Your goal should be to understand, not memorize, the material presented in your organic chemistry course. The following principles should be learned as you begin your study of organic chemistry, then used as a solid foundation for building your understanding throughout the course. These simple ideas explain a great deal about the structures and properties of organic molecules, as well as the characteristic ways in which they react. Thoroughly understanding the following three key principles and related ideas will allow you to develop an intuitive feel for organic chemistry that avoids the necessity of resorting to the far less effective use of extensive memorization.

A. Predicting Structure and Bonding

1. In most stable molecules, all the atoms will have filled valence shells.

2. Five- and six-membered rings are the most stable.

3. There are two possible arrangements of four different groups around a tetrahedral atom.

B. Predicting Stability and Properties

4. The most important question in organic chemistry is "Where are the electrons?"

5. Delocalization of charge over a larger area is stabilizing.

6. Delocalization of unpaired electron density over a larger area is stabilizing.

7. Delocalization of pi electron density over a larger area is stabilizing.

C. Predicting Reactions

8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough.

9. Functional groups react the same in different molecules.

10. A reaction mechanism describes the sequence of steps occurring during a reaction.

11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.

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

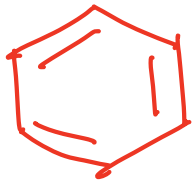
Aromatic Rings

1)

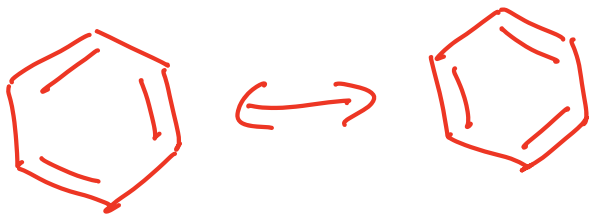
2)

3)

4)



Benzene



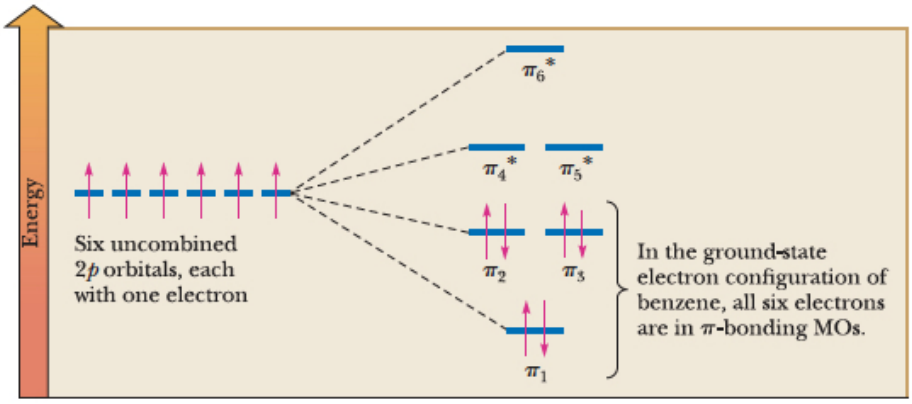


FIGURE 21.2 The molecular orbital representation of the π bonding in benzene.

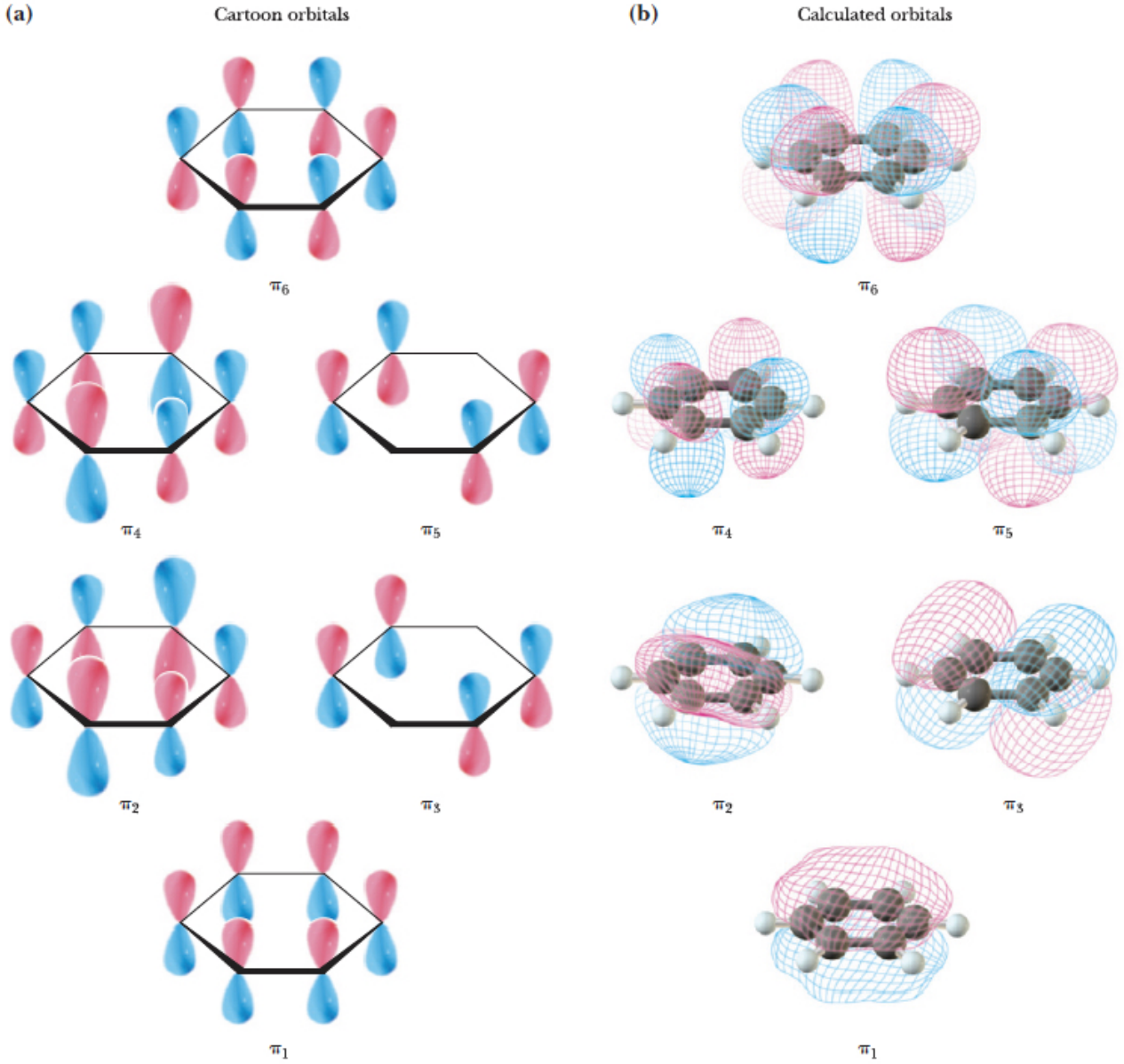


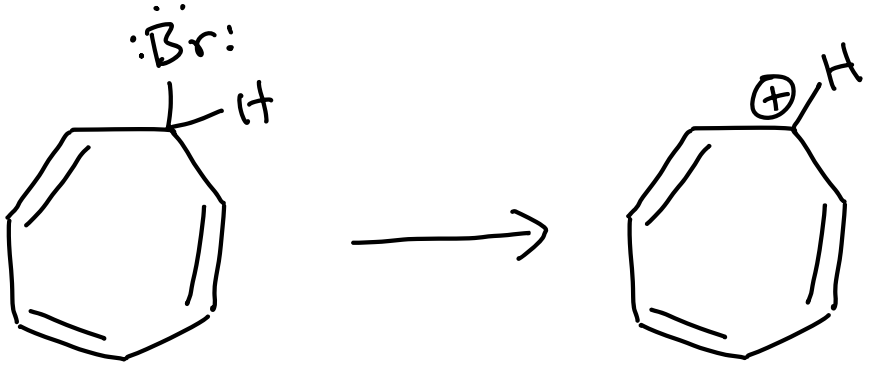
FIGURE 21.3 Orbitals for the π system of benzene. (a) Cartoon representations of the six calculated orbitals that chemists routinely draw. These pictures accentuate the fact that various combinations of parallel 2*p* orbitals lead to the π system of benzene. (b) Calculated orbitals. The three lowest 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.

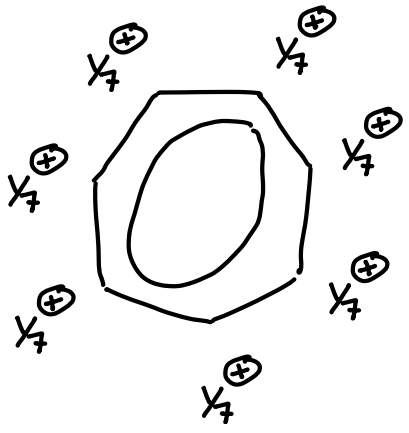
Two Important Consequences of Aromaticity

1) Aromaticity stabilizes ions

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

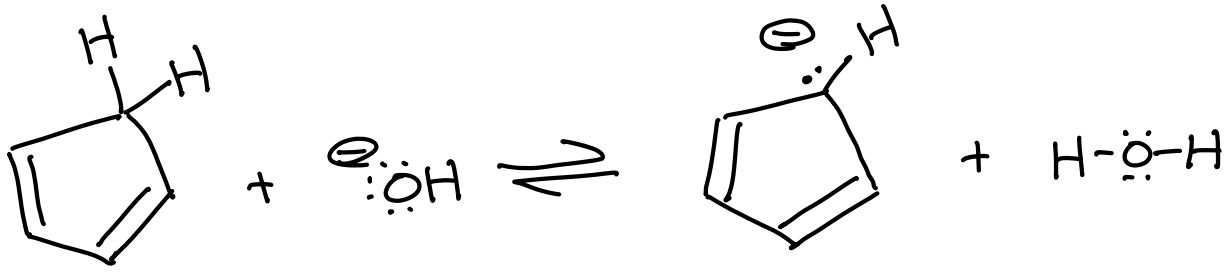
Tropylium Ion



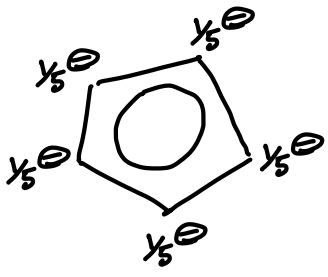


All atoms are equivalent → 7 equal contributing structures!

Cyclopentadienyl Anion



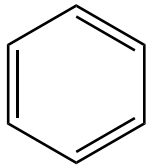
$pK_a = 16$



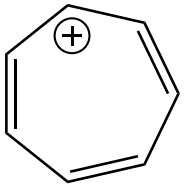
All atoms are equivalent → 5 equal contributing structures!

Hückel's Aromaticity Criteria

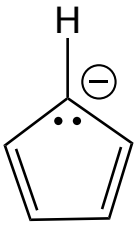
1)
2)
3)
4)



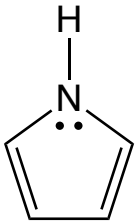
Benzene



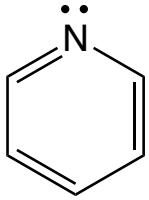
Tropylium Ion



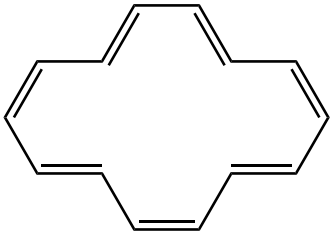
Cyclopentadienyl anion



Pyrrole

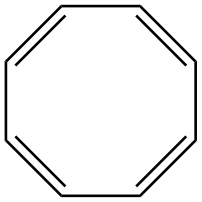


Pyridine

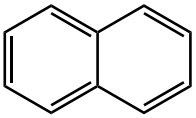


Annulene

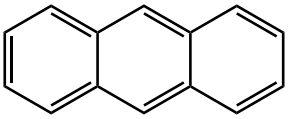
Cyclobutadiene



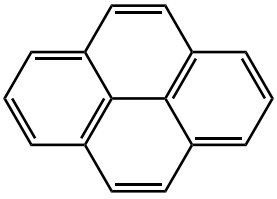
Cyclooctatetraene



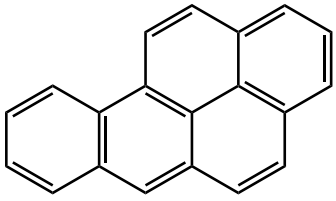
Naphtalene



Anthracene

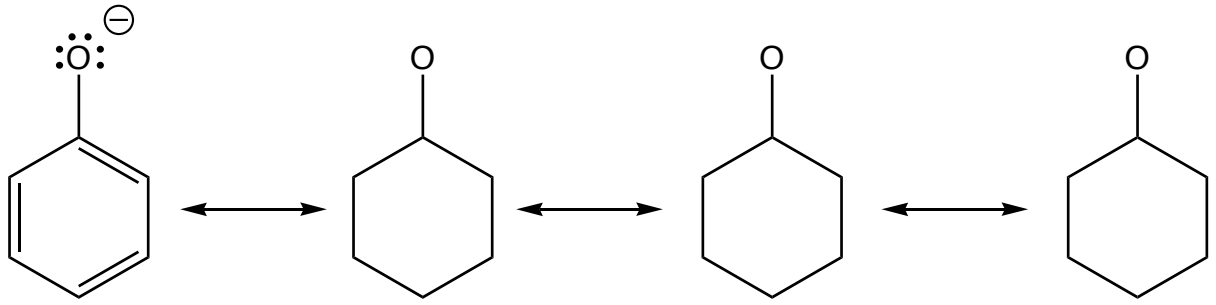


Pyrene

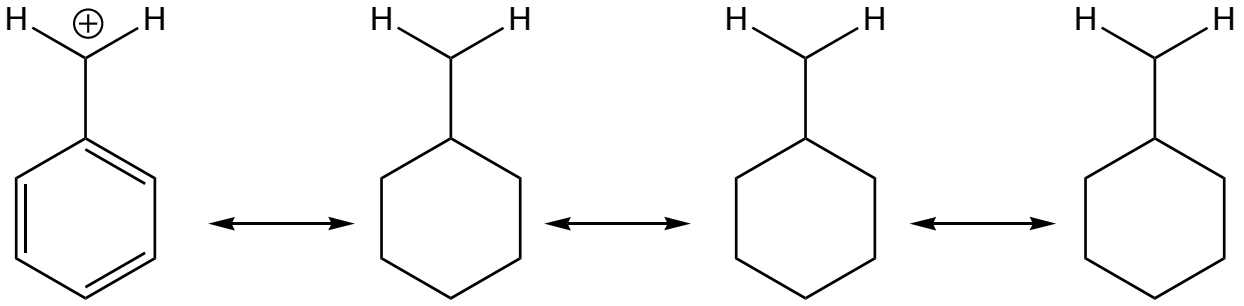


Benzo[α]pyrene

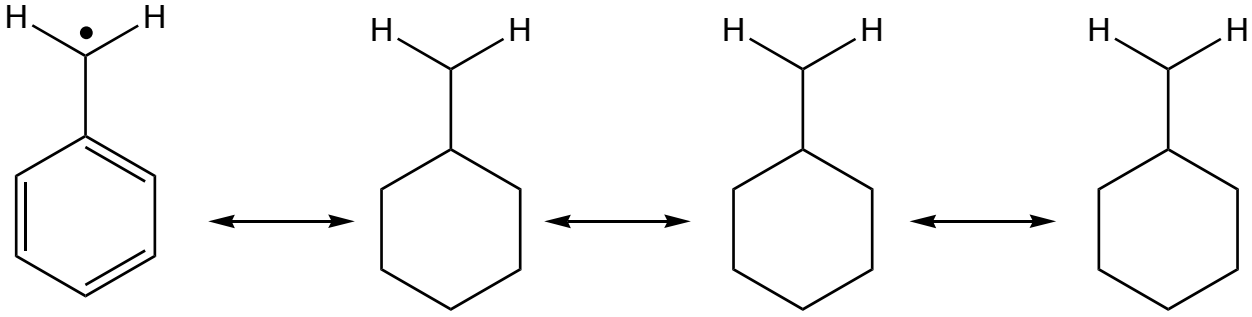
Aromatic resonance stabilization of charged species



Phenoxide anion



Benzyl cation



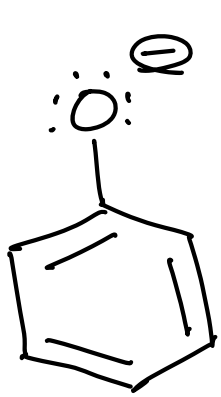
Benzyl radical

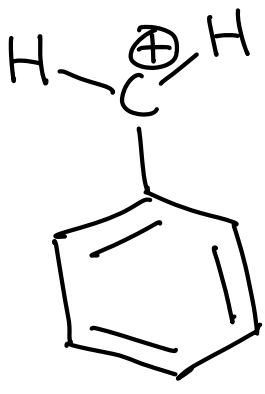
Important takeaways from the contributing structures

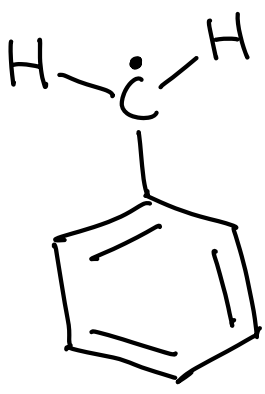
1) Benzene rings stabilize anions, cations and radicals

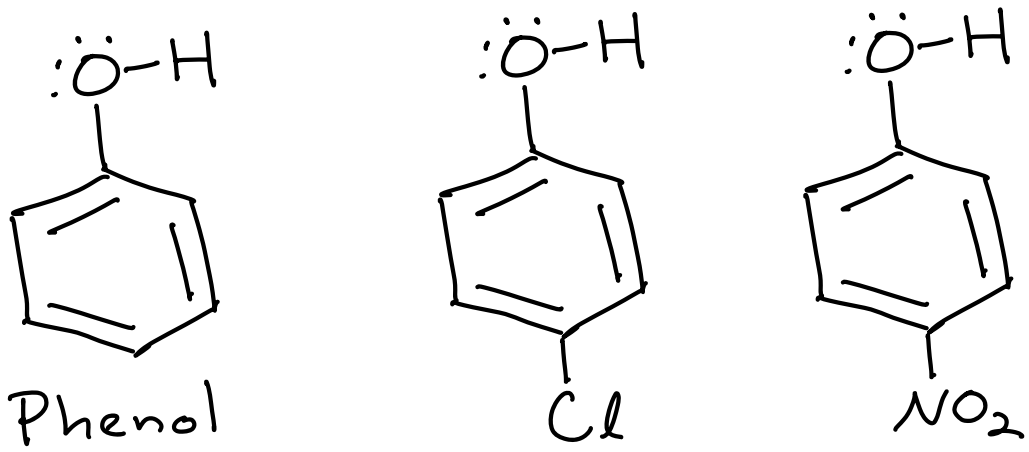
2) Molecules can have electrons on an atom outside the ring delocalized into the π system and the "extra" electrons do not count against the 4n+2 number of π electrons

Summary →









Electron withdrawing groups on the ring stabilize the deprotonated anion, making an OH group more acidic (Inductive effect)

Important terms