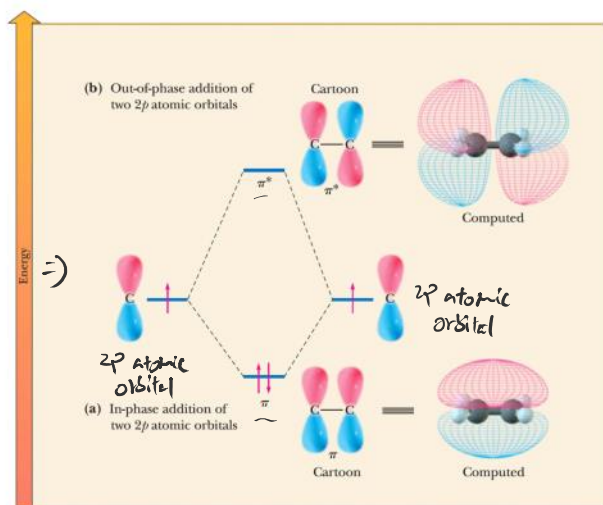




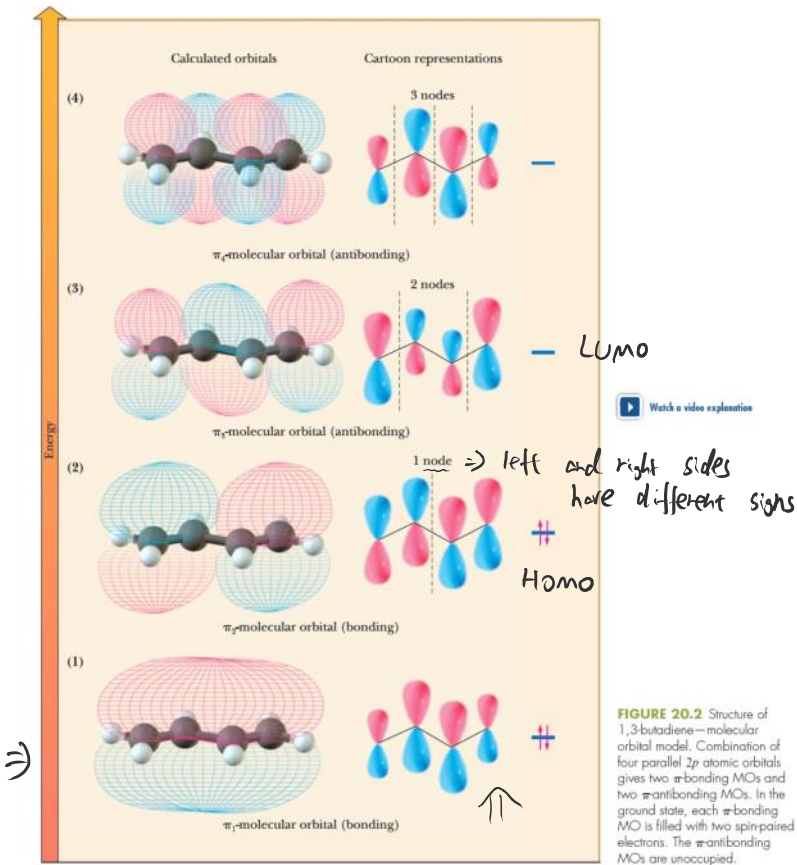
Week 11 Handouts



[Watch a video explanation](#)

**FIGURE 1.21** Molecular orbital mixing diagram for the creation of any C—C  $\pi$  bond. (a) Addition of two  $p$  atomic orbitals in phase leads to a  $\pi$  orbital that is lower in energy than the two separate starting orbitals. When populated with two electrons, the  $\pi$  orbital gives a  $\pi$  bond. (b) Addition of the  $p$  orbitals in an out-of-phase manner (meaning a reversal of phasing in one of the starting orbitals) leads to a  $\pi^*$  orbital. Population of this orbital with one or two electrons leads to weakening or cleavage of the  $\pi$  bond, respectively.





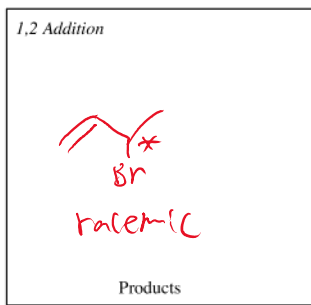
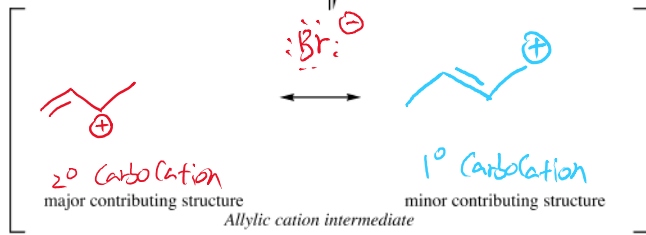
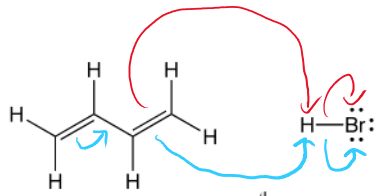
$\Rightarrow$



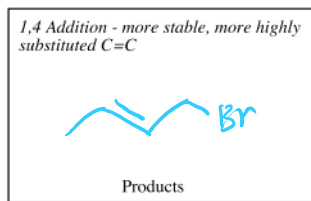
$\pi$ -way : conjugation  $\Rightarrow$   $\pi$  bonds that are one bond away from each other.



H-X reacting with conjugated dienes



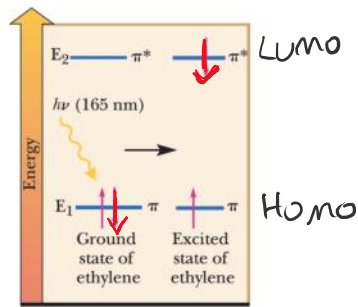
Kinetic product  
(formed faster)



thermodynamic  
product (more stable)

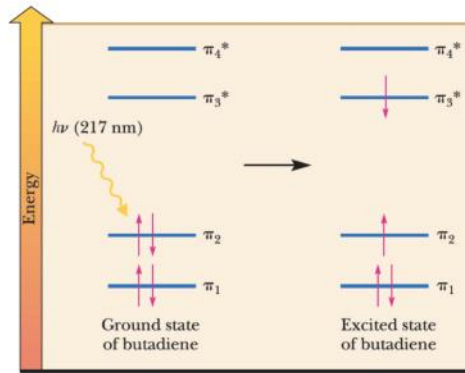


Ethere =



Homo-Lumo gap: 165nm

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

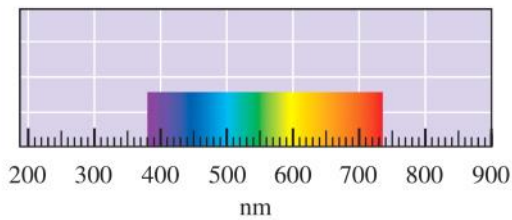


Homo-Lumo gap: 217nm

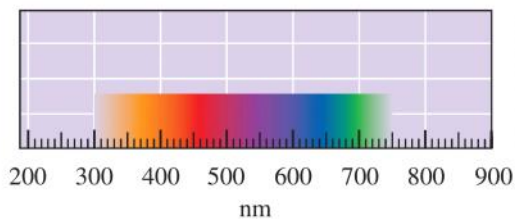
**FIGURE 20.7** Electronic excitation of 1,3-butadiene; a  $\pi \rightarrow \pi^*$  transition.

Conjugation lowers Homo-Lumo gap.

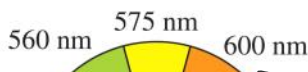
if we have a long enough/larger enough conjugated system:



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

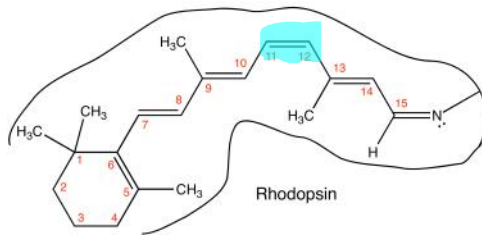
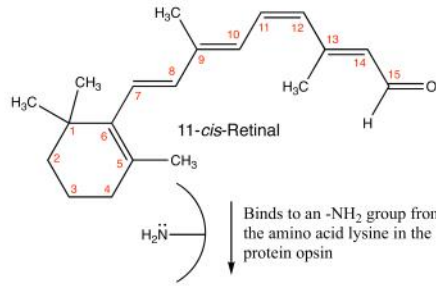


(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the x-axis) is absorbed.



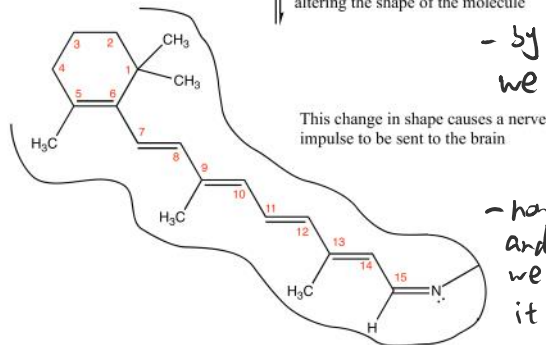


# How vision works



when excited  
 ( $\Rightarrow$  by light  $\Rightarrow$ )  
 one  $e^-$  was  
 moved from  
 $\pi$  bonding to  
 $\pi^*$  anti-bonding

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



- by exciting light  
 we "reduce"  $\pi$ -bond  
 between C11 and  
 C12 to a single bond  
 - now it can rotate,  
 and with equilibrium,  
 we can now trap  
 it in the trans form

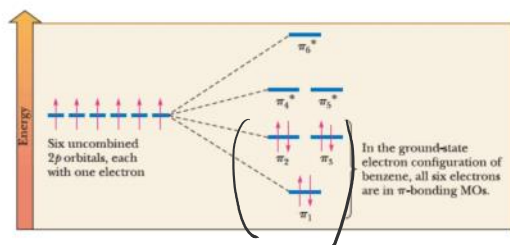


FIGURE 21.2 The molecular orbital representation of the  $\pi$  bonding in benzene.

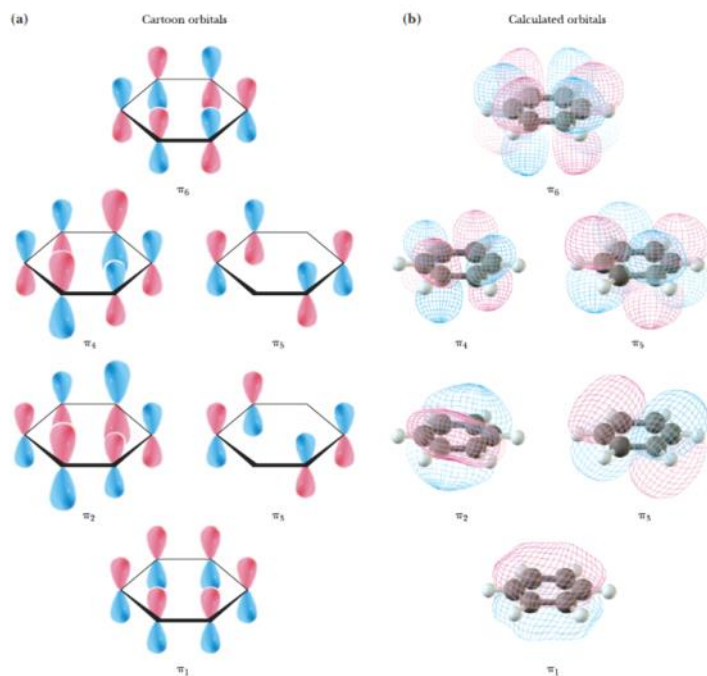
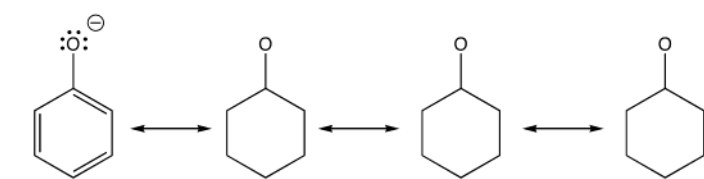
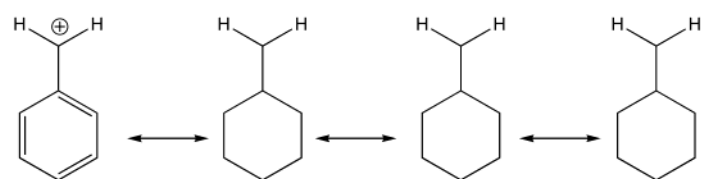


FIGURE 21.3 Orbitals for the  $\pi$  system of benzene. (a) Cartoon representations of the six calculated orbitals that chemists routinely draw. These pictures accentuate the fact that various combinations of parallel  $2p$  orbitals lead to the  $\pi$  system of benzene. (b) Calculated orbitals. The 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  $\pi$  system of benzene: a torus of electron density above and below the ring.

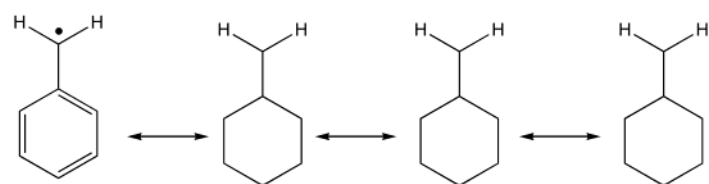
Aromatic resonance stabilization of charged species



Phenoxide anion

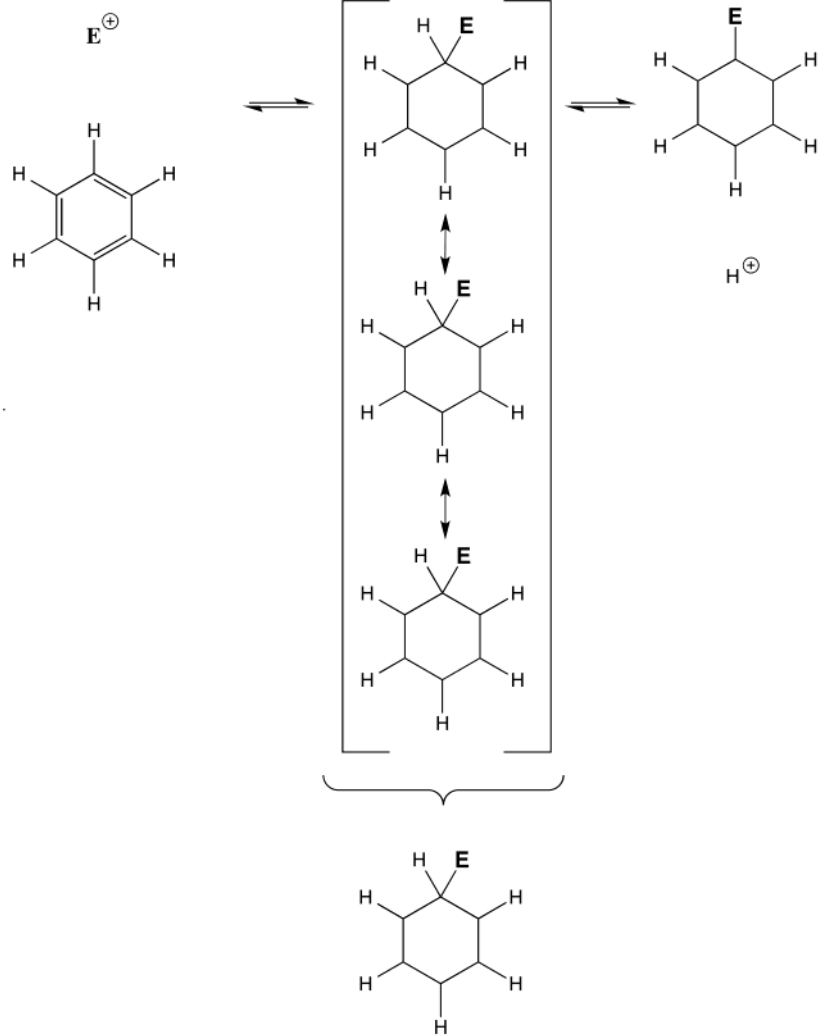


Benzyl cation



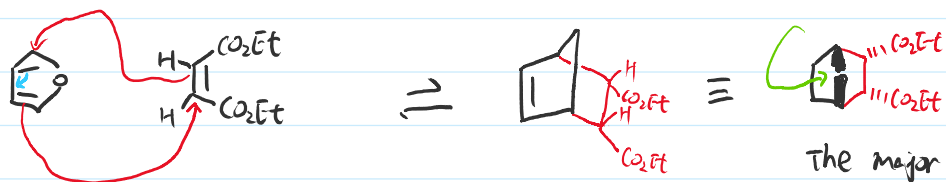
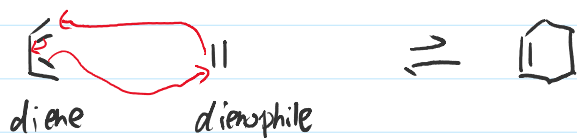
Benzyl radical





Pericyclic reactions:

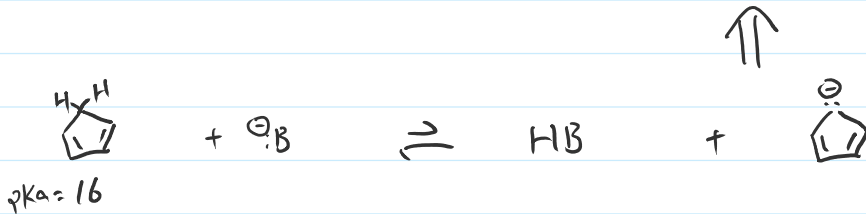
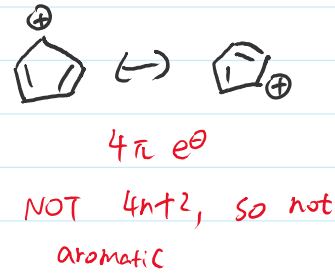
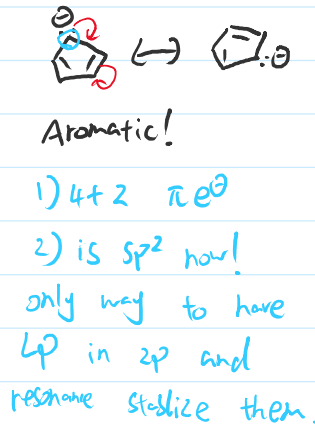
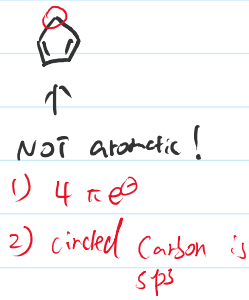
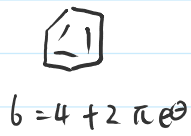
. Diels - Alder



Aromaticity (Huckels Rule)

- only applies to rings!

- 1) All atoms in the ring has to be  $sp^2$  hybridized
- 2) ring is flat
- 3) monocyclic
- 4)  $4n+2$   $\pi$  e<sup>-</sup>s in the systems



Counting  $\pi$  e<sup>-</sup> :

- In a ring,  $\pi$  e<sup>-</sup>s come from
  - 1)  $\pi$ -bonds
  - 2) lone pairs that are in  $2p$  orbitals

