

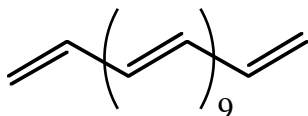
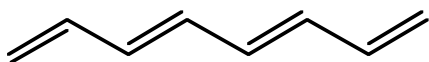
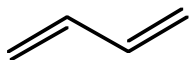
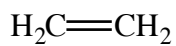
**Lecture outline**

3. Conjugation — for a given chromophore, increasing conjugation increases  $\lambda_{\max}$  for the lowest-E transition.

This implies that inc. conjugation has what effect on the HOMO-LUMO gap?

e.g., polyene chromophores

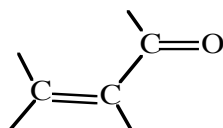
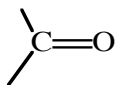
$\lambda_{\max}$  for HO-LU transition



carbonyl-based chromophores

$\text{n} \rightarrow \pi^*$

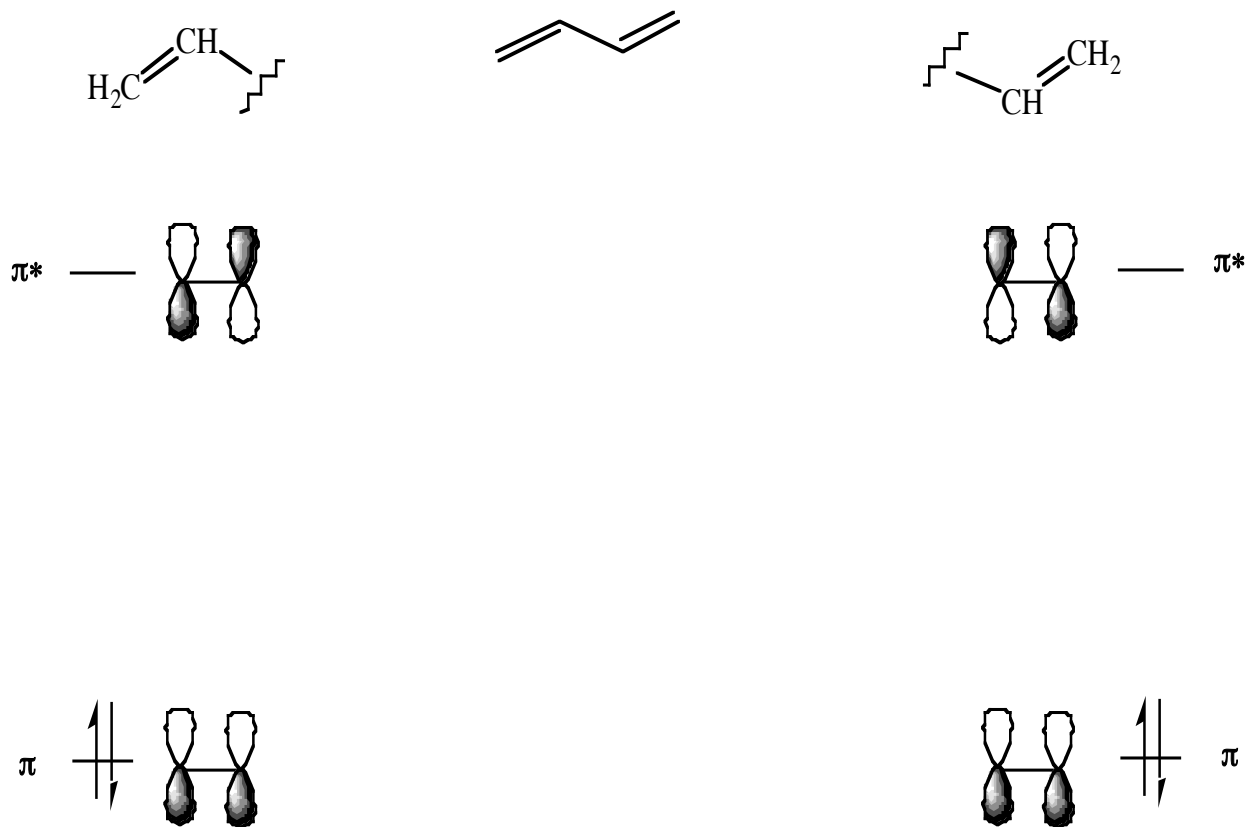
$\pi \rightarrow \pi^*$



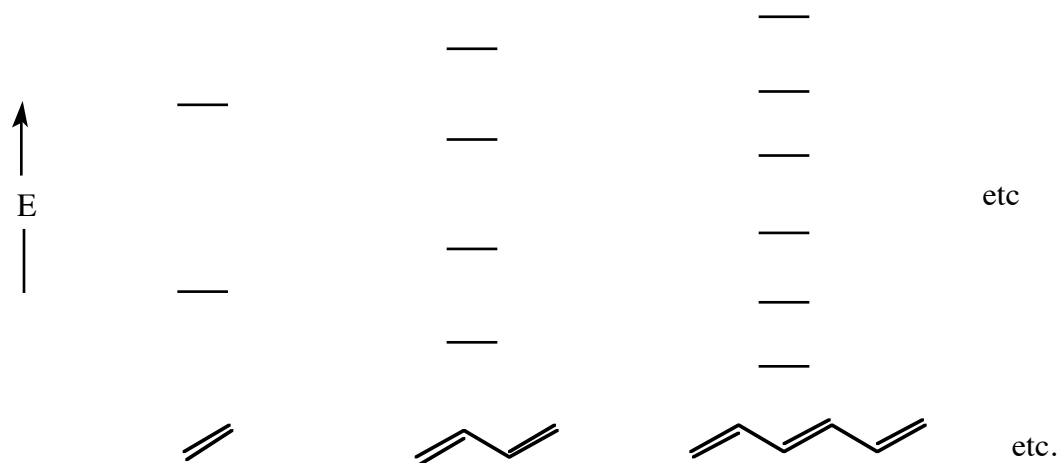
Increasing conjugation decreases  $\Delta E$  (HOMO - LUMO) because  $\pi$ -MOs are not really localized to individual  $\pi$ -bonds, but *delocalized* over the entire conjugated  $\pi$ -system.

(in fact, *all* MOs are really delocalized over the entire molecule, rather than localized to individual bonds. Our localized bonding models are easy to understand and serve us well enough for as a basis for understanding most aspects of structure and reactivity. But now we need to consider a property that depends on *orbital energies*, so we need a more correct description of the orbitals involved.)

Let's see why by building the  $\pi$ -system of butadiene from two isolated  $\pi$ -bonds...



Extending this idea to longer  $\pi$ -systems, we see the following patterns of  $\pi$ -MO energy levels.



### Color —

The transmitted or reflected color we see is the *complement* of the color absorbed...  
(e.g., if a compound *absorbs red* light, it *appears green*)

Here's a simple way to remember wavelengths that correspond to various colors.  
Each 50-nm section of the visible corresponds *roughly* to one of six colors.  
Fill them in (refer to a rainbow if necessary), and mark the complementary pairs.

