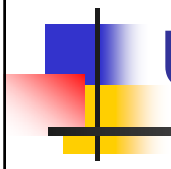


UV-Visible spectroscopy

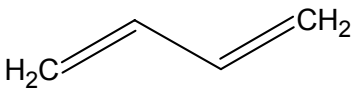
Conjugation and the values of electronic energy transitions

What's an "electronic energy transition"?

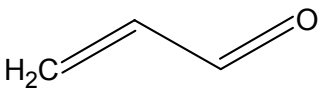
- When electrons move between energy levels ("orbitals") in an atom or molecule, they either emit or absorb energy.
- The jump is often called an "electronic energy transition" or just a "transition."
- The energy emitted or absorbed is in the UV/VIS range.

Electronic transitions in molecules with π-orbitals

- There are two types of transitions that are important in UV/VIS spectroscopy
  - $\pi \rightarrow \pi^*$ (bonding to antibonding)
  - $n \rightarrow \pi^*$ (non-bonding to antibonding)
  - Other transitions are possible but are typically so high-energy as to not be observed



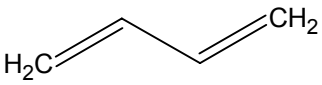
$\pi \longrightarrow \pi^*$



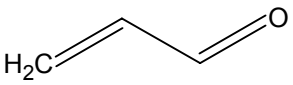
$n \longrightarrow \pi^*$

Electronic transitions in molecules with π-orbitals

- Non-bonding molecular orbitals will be higher in energy than bonding ones
  - Therefore $n \rightarrow \pi^*$ transitions will be lower in energy than $n \rightarrow \pi^*$ transitions in similar molecules
  - Therefore conjugated molecules with non-bonding electrons will be more highly colored than similar molecules without them

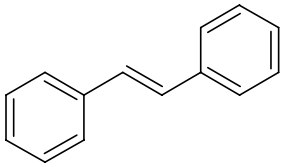


λ–max = 290 nm



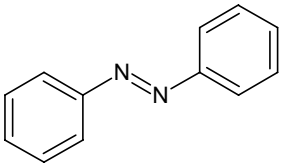
λ–max = 350 nm

Electronic transitions in molecules with π-orbitals



λ–max = 295

White in color



λ–max = 325 $\pi \longrightarrow \pi^*$

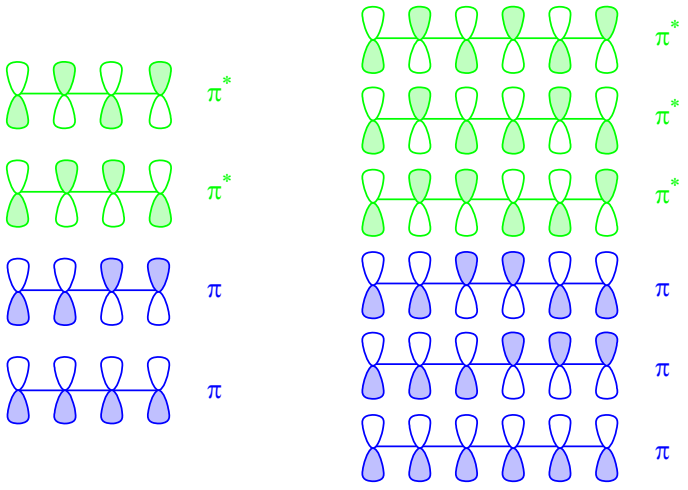
λ–max = 440 $n \longrightarrow \pi^*$

Yellow in color

Conjugation and λ-max

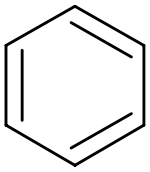
- The energy of light absorbed is a function of the energy distance between the HOMO (π or n) and the LUMO (π*)
- As we have seen, conjugation lowers that energy gap by providing more molecular orbitals to fit into a similar energy space

Compare butadiene and hexatriene



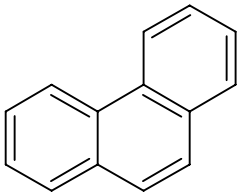
Conjugation in polycyclic aromatic compounds

- Adding rings gives a longer λ-max
- Arrangements that allow more "benzenoid" rings will have a shorter λ-max
  - This is because extra benzenoid rings means the molecule is more stable



a benzenoid ring

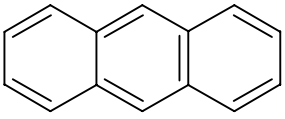
Compare phenanthrene with anthracene



Phenanthrene

2 benzenoid rings

λ-max = 250 nm



Anthracene

1 benzenoid ring

λ-max = 345, 360 nm