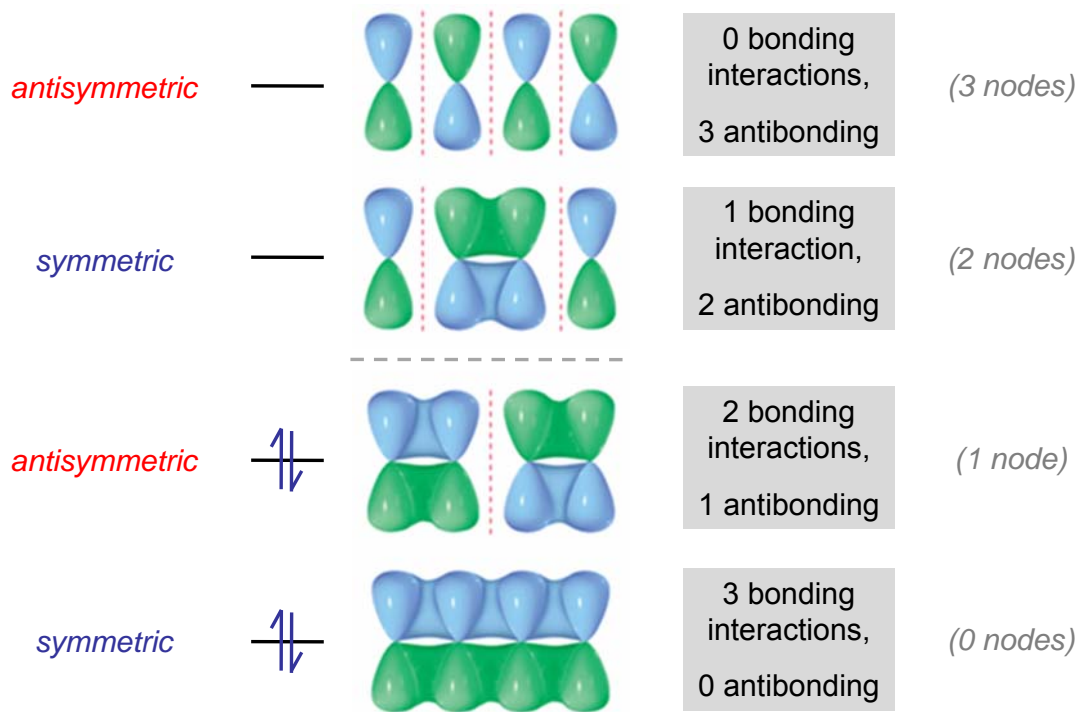
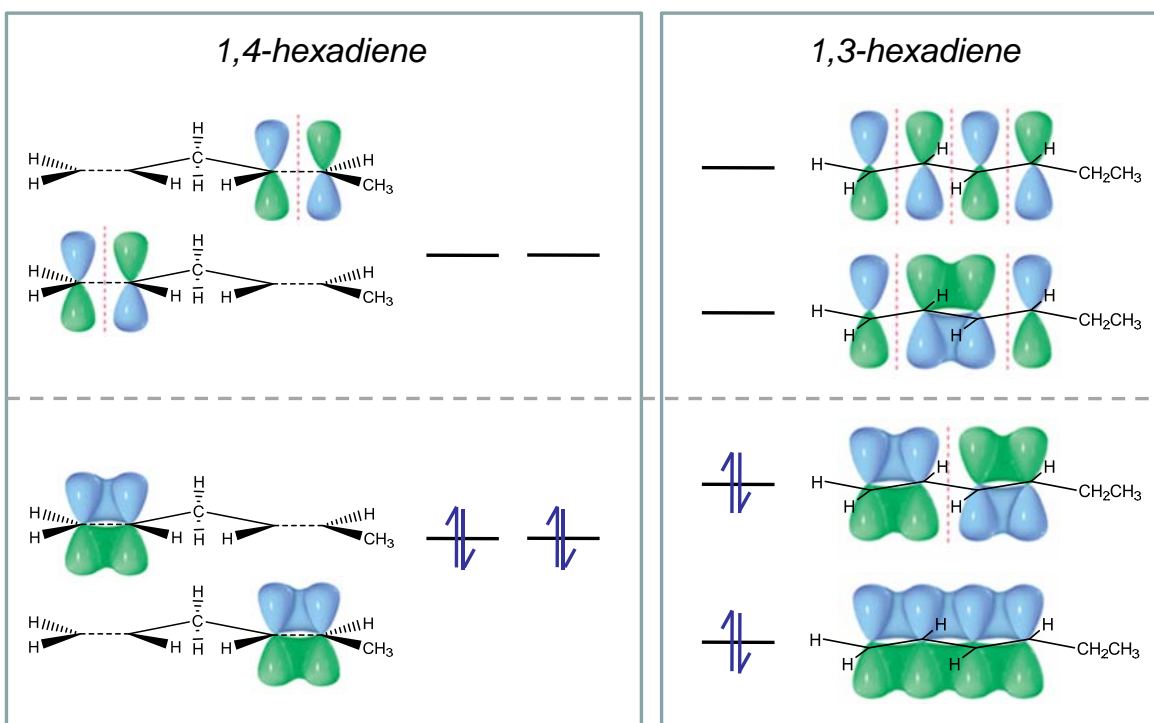


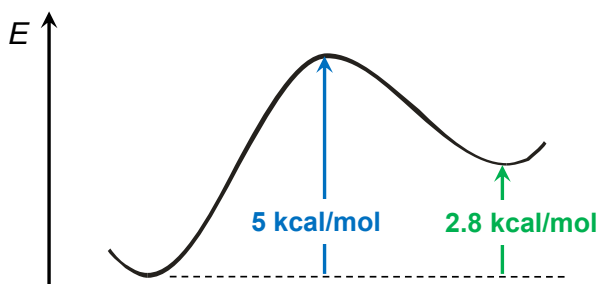
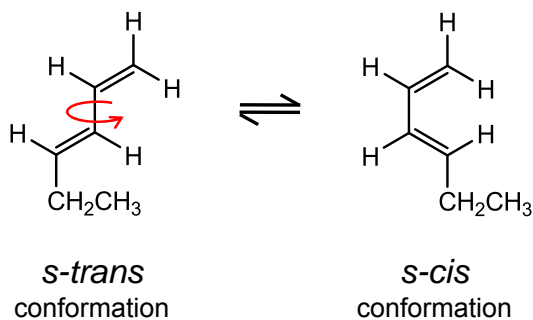
Conjugated Molecular Orbitals



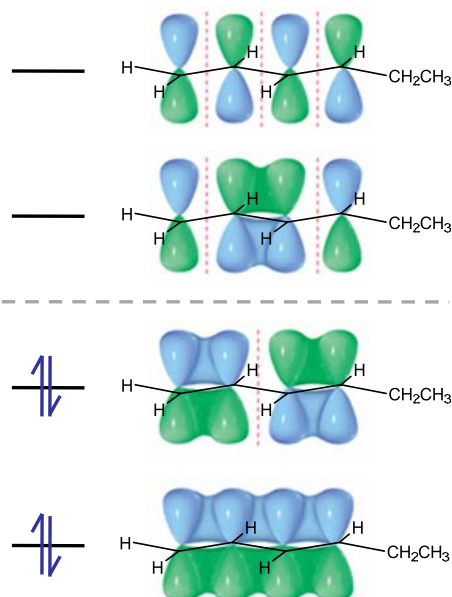
Conjugated Dienes Are More Stable Than Unconjugated Dienes



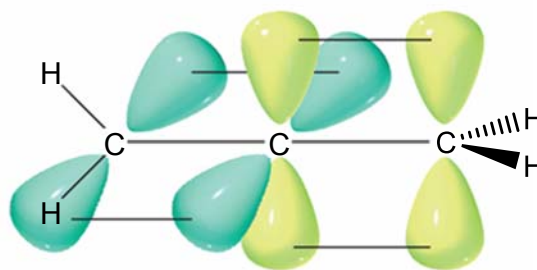
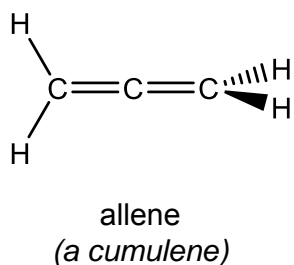
Diene Conformations



1,3-hexadiene



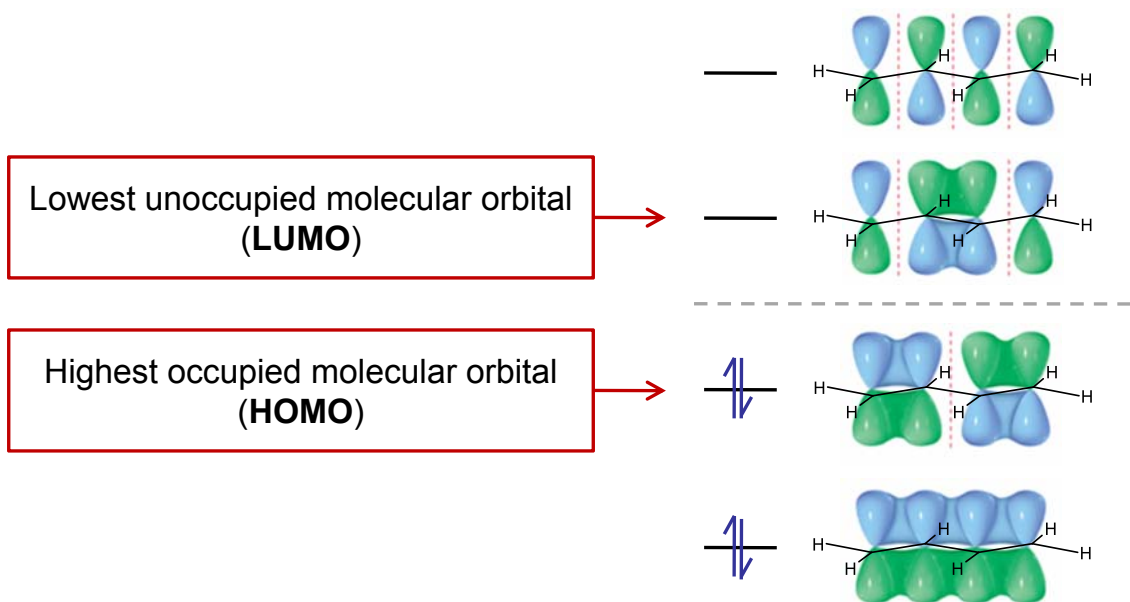
Cumulated Double Bonds Are Not Stabilized



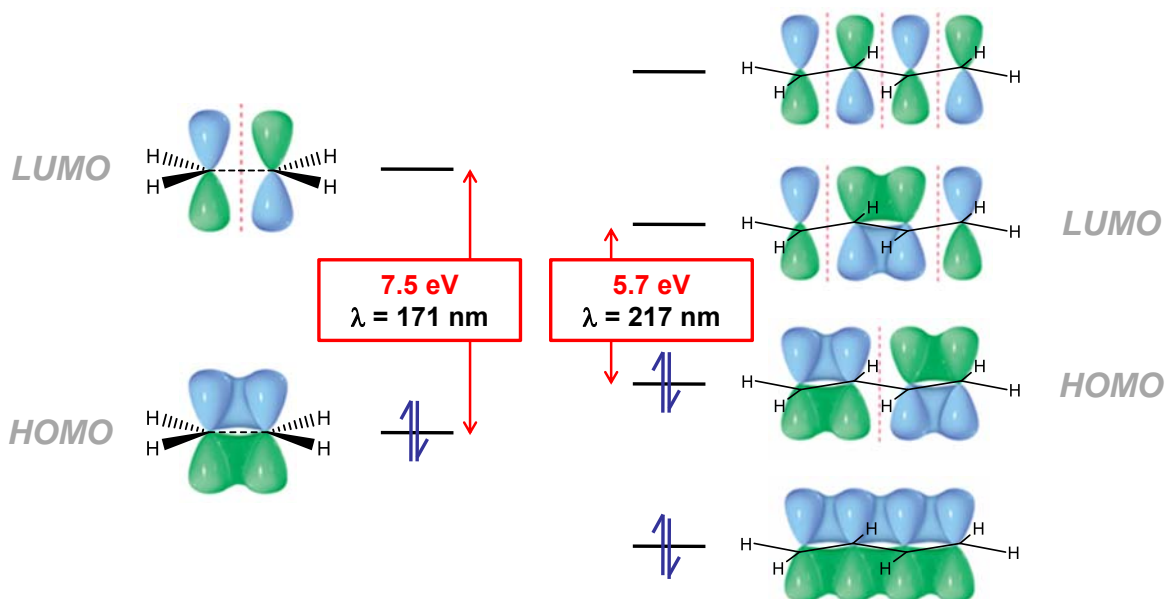
Central C is *sp*-hybridized, so it contributes 2 *p* orbitals to separate, perpendicular π -bonds.

No orbital overlap, so orbital mixing between π -systems is not possible.

Conjugation Reduces the “HOMO-LUMO Gap”



Conjugation Shifts UV-Vis Absorption to Longer Wavelengths



Electrons Can Be Promoted to Excited States By Light

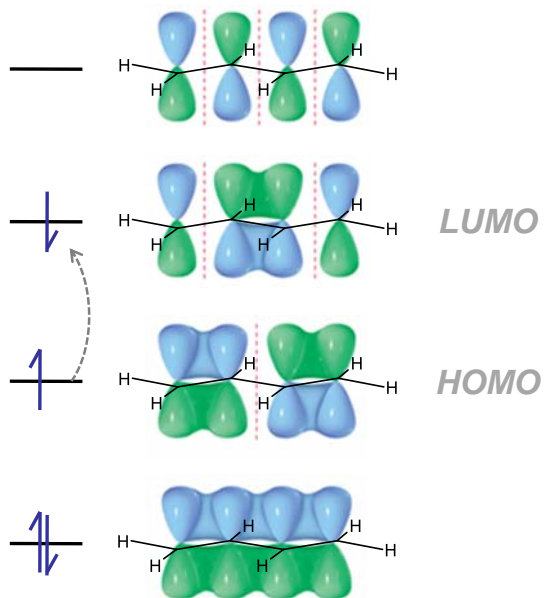
5.7 eV
(131 kcal/mol)

$$E = \frac{hc}{\lambda}$$

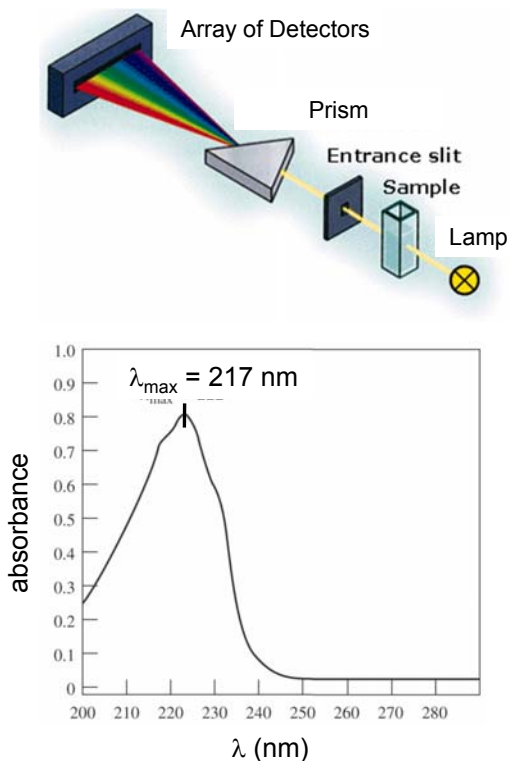
$$\lambda = 217 \text{ nm}$$

photon
($E = 5.7 \text{ eV}$,
 217 nm)

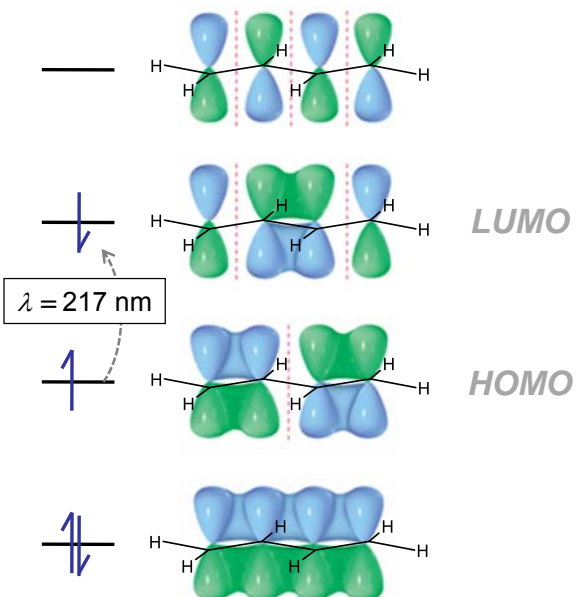
So, butadiene absorbs light at 217 nm (in the ultraviolet [UV] range).



UV/Vis Spectroscopy



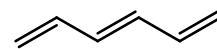
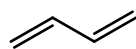
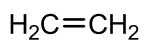
Used to measure how conjugated a molecule is.



Typical Absorption Maxima

λ_{\max} is increased by:

extent of conjugation

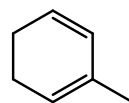
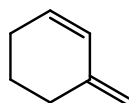


$$\lambda_{\max} = 171 \text{ nm}$$

$$217 \text{ nm}$$

$$258 \text{ nm}$$

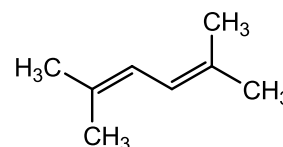
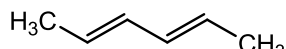
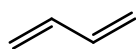
forced *s-cis*-arrangement of diene



$$\lambda_{\max} = 232 \text{ nm}$$

$$261 \text{ nm}$$

alkyl substitution

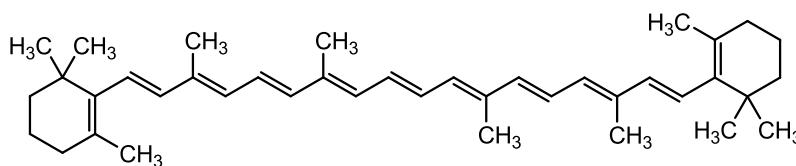


$$\lambda_{\max} = 217 \text{ nm}$$

$$227 \text{ nm}$$

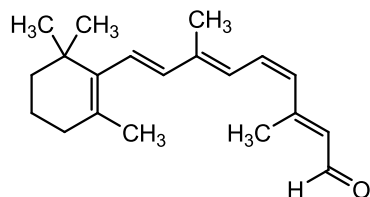
$$241 \text{ nm}$$

Typical Absorption Maxima



β -carotene
(one component of vitamin A)
 $\lambda_{\max} = 455 \text{ nm}$

is used by our eyes to synthesize

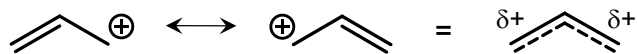


retinal
(absorbs light in our eyes' rods)
 $\lambda_{\max} = 370 \text{ nm}$ [in solution]
 $\lambda_{\max} = 500 \text{ nm}$ [complexed to rhodopsin]

Conjugation Stabilizes Allylic Systems

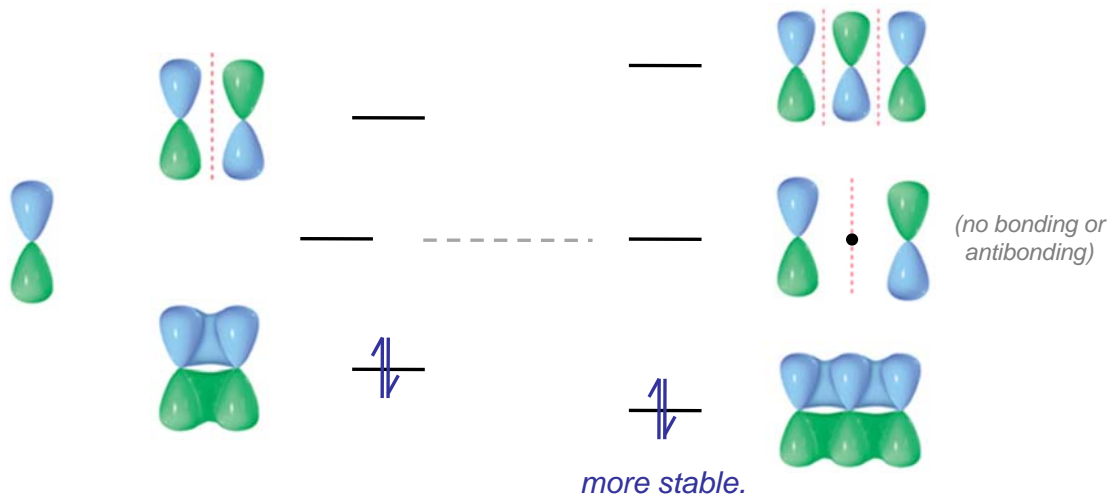
Resonance explanation:

Stabilization of allyl cation is due to distribution of charge.

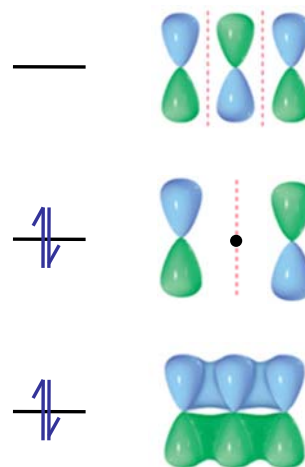
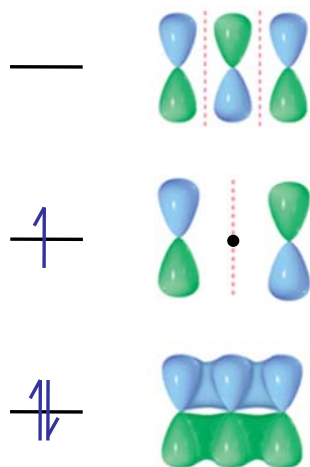
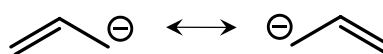
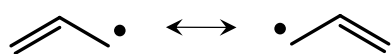


Molecular orbital explanation:

Stabilization also caused by orbital distribution.



Conjugation Stabilizes Allylic Systems



Reactions that go through allylic intermediates are usually accelerated (because the intermediates are more stable).