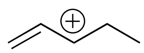
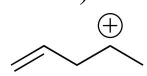
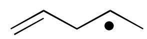
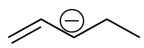
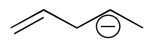
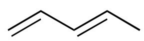
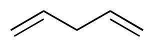
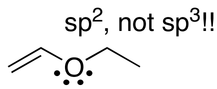
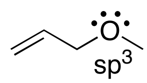
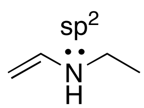
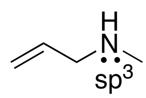
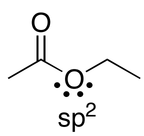
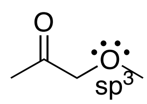
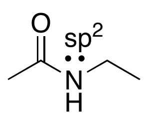
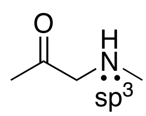
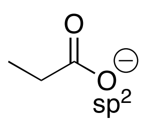
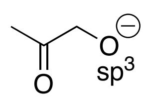
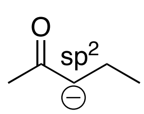
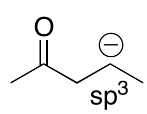
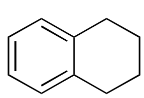
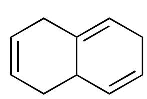
Ch. 15 Conjugated Systems

<u>The General Stabilization Effect of Conjugation (Section 15.1, 2, 3, 8, 9)</u>

		Conjugated (more stable)	Isolated (less stable)	Notes:
1	Cations			
2	Radicals			
3	Anions			
4	Dienes			
5	Ethers			An N or O next to a double bond becomes sp^2. An isolated N or O is sp^3
6	Amines			
7	Esters			
8	Amides			Very special, chapter 23, all of biochemistry, proteins, enzymes, etc.
9	Oxyanions (Carboxylates)			Very special, chapter 21
10	Carbanions (Enolates)			Very special, chapter 22
11	Aromatics			Very special, chapters 16 + 17

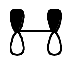
> Conjugation: Anything that is or can be sp^2 hybridized is stabilized when next to π bonds.
> - oxygens, nitrogens, cations, radicals, and anions

<u>Notes:</u>
1. Any atom that can be sp^2 will be sp^2 when next to a double bond
2. "Conjugation" is when sp^2 centers are joined in an uninterrupted series of 3 or more, such that an uninterrupted series of p-orbitals is possible
3. Any sp^2 center has one p orbital

Impact of Conjugation

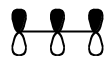
4. **Stability:** Conjugation is **stabilizing** because of p-orbital overlap (Sections 15.2, 4, 7)
   - Note: In the allyl family, **resonance = conjugation**

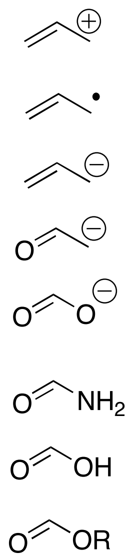

One p
Unstabilized
Isolated

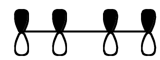

Two p's
π-bond
C=C

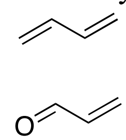
C=O

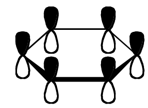
C=N

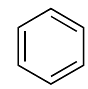

Three p's
Allyl type




Four p's
Butadiene type

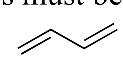



Six p's in circuit
Aromatic



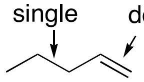
5. **Reactivity:** Conjugation-induced stability impacts **reactivity** (Sections 15.4-7)
   - If the **product** of a rate-determining step is stabilized, the reaction rate will go **faster** (product stability-reactivity principle)
     - Common when allylic cations, radicals, or carbanions are involved
   - If the **reactant** in the rate-determining step is stabilized, the reaction rate will go **slower** (reactant stability-reactivity principle)
     - Why aromatics are so much less reactive
     - Why ester, amide, and acid carbonyls are less electrophilic than aldehydes or ketones

6. **Molecular shape** (Sections 15.3, 8, 9)
   - The p-orbitals must be aligned in parallel for max overlap and max stability
   - The sp^2 centers must be coplanar

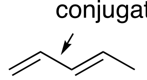

All four sp^2 carbons must be flat for the p's to align

7. **Bond Length:** Bonds that look like singles but are actually between conjugated sp^2 centers are **shorter** than ordinary single bonds

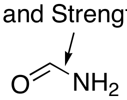
1.54 A normal single — 1.33 A normal double



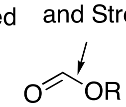
1.48 A = Shortened and Strengthened conjugated single



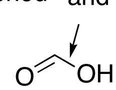
Shortened and Strengthened



Shortened and Strengthened



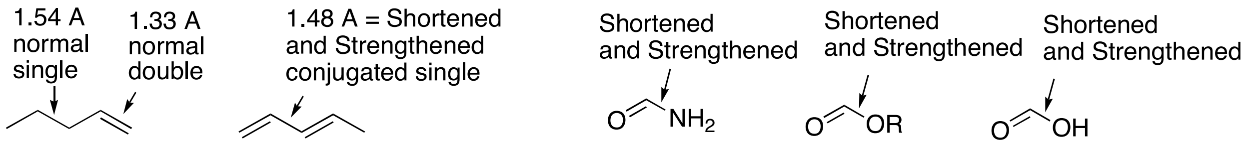
Shortened and Strengthened



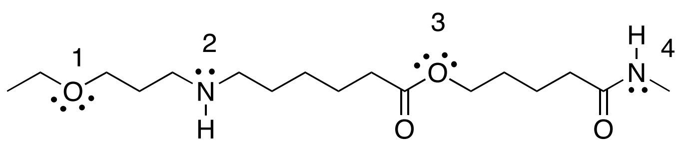
- In amides, esters, and acids, the bond between the carbonyl and the heteroatom is shortened
-

8. **Bond Strength:** Bonds that look like singles but are actually between conjugated sp^2 centers are **stronger** than ordinary single bonds

9. **Bond Rotation Barrier:** Bonds that look like singles but are actually between conjugated have much larger rotation barriers than ordinary single bonds
   - Because in the process of rotating, the p-overlap and its associated stability would be temporarily lost



10. **Hybridization:** Conjugated sp^2 atoms have both sp^2 and p orbitals. You should always be able to classify the hybridization of **lone pairs on nitrogen and oxygen**.
    - **Isolated** oxygens or nitrogens: sp^3 atom hybridization, sp^3 lone-pair hybridization, and tetrahedral, 109º bond angles
    - **Conjugated nitrogens**: sp^2 atom hybridization, **p lone-pair hybridization (needed for conjugation)**, and 120º bond angles
    - **Conjugated oxygens**: sp^2 atom hybridization, **one p lone-pair hybridization** (needed for conjugation), **one sp^2 lone-pair**, and 120º bond angles



Atom	O-1	N-2	O-3	N-4
Isolated vs. Conjugated				
Atom Hybridization				
Lone-Pair(s) Hybridization				
Bond Angles				