Conjugated Systems
- Conjugated systems have alternating single and double bonds.
  For example: C=C−C=C−C=C and C=C−C=O
- This is not conjugated because the double and single bonds do not alternate: C=C−C=C
- Triple bonds (C≡C and C≡N) can be included in place of double bonds.
  For example: C≡C−C=C−C≡N
- All of the conjugated atoms are sp² or sp.
- Atoms with sp³ are not part of the conjugated system.

Preparation
- Conjugated systems are typically prepared either by
dehydrohalogenation of allyl halides (C=C−CX−C) with base in alcohol,
or by dehydration of 1,3-diols (HOC−C−COH−C) with Al₂O₃ and heat.

Stability
- Conjugated dienes are more stable than non-conjugated alkenes.
- This is known because conjugated dienes release less heat than non-conjugated alkenes
  when hydrogenated. That is, hydrogenation of conjugated molecules is less exothermic.
- Stability results from the alternating \( \pi \) bonds interacting with each other.

Valence Bond Description
- The sp² orbitals have more s character than the sp³ orbitals have.
- The sp² orbitals are shorter and rounder than the sp³ orbitals.
- C−C \( \sigma \) bonds involving sp³ orbitals are stronger and shorter and than those that do not.
- In 1,3-butadiene, C=C−C=C, all three \( \sigma \) bonds are sp² - sp².
- In 1-butene, C=C−C=C, the first \( \sigma \) bond is sp² - sp² (strongest), the
  second is sp² - sp³ (less strong), then the third is sp³ - sp³ (weakest).

Molecular Orbital (MO) Description
- When p orbitals bond to form \( \pi \) bonds, each p atomic orbital
  becomes a \( \Pi \) molecular orbital.
- The \( \Pi \) MO’s in adjacent conjugated bonds interact together as a single \( \Pi \) system.
- In 1,3-butadiene, C=C−C=C, all four C’s have one \( \Pi \) MO each.
  So, there are four \( \Pi \) MO’s total.
- Two are bonding orbitals (stabilizing), and the other two are anti-bonding (destabilizing).
- Each C has one \( \Pi \) e⁻¹. So, there are four \( \Pi \) e⁻¹’s total.
  They fill the two bonding MO’s, while the antibonding MO’s are left empty.
- The lowest energy MO (\( \Psi 1 \)) has no nodes and is a completely continuous system,
  involving all four C’s with no separation.
- The next to lowest MO (\( \Psi 2 \)) has one node, between C2 and C3, and acts like two separate \( \Pi \) bonds.
- The next highest energy MO ($\Psi^3*$) is antibonding. It has two nodes, one between C1 and C2, the other between C3 and C4. So, it acts like there is only one $\Pi$ bond. This would destabilize the molecule if occupied with $e^-$’s.
- The highest energy MO ($\Psi^4*$) has three nodes, one between each C. This completely isolates the $\Pi$ orbitals. It is very destabilizing (antibonding) if occupied with $e^-$’s.

Electrophilic Additions and Allyl Cations
- When a conjugated diene reacts with HBr, the first step is addition of an H to the least substituted C in the $\Pi$ system. In 1,3-butadiene, C=C−C=C, this would be an end carbon.
- The C with the positive charge will be adjacent to the one that got the H, and that C will be allylic because it is next to another double bond.
- Allylic cations, like allylic free radicals, have resonance forms, where the + charge and the adjacent $\Pi$ bond trade places.
  \[ C^-C^+=C=C \leftrightarrow C=C^+\ !C^+ \]
- The H added to C1, now the Br can add to either C2 (1,2 addition) or C4 (1,4 addition). So, the two products are $\text{H}_3\text{C}^-\text{CHBr}^-\text{CH}=\text{CH}_2$ and $\text{H}_3\text{C}^-\text{CH}=\text{CH}^-\text{CH}_2\text{Br}$.

Kinetic Control (Low T)
- At low T, less energy is available for $E_a$, and the reactions are less reversible.
- The 1,2 addition has a lower $E_a$, and forms primarily.
- The 1,2 addition does not need to switch to the 2nd carbocation resonance form. Therefore, it forms faster and predominates.

Thermodynamic Control (High T)
- At high T, more energy is available to be used as activation energy for reactions. The system is fully reversible at high T, and it can therefore achieve equilibrium.
- The more stable 1,4 product (more substituted alkene) forms primarily.
- Since more $E_a$ is available, the 1,2 product can revert back to the carbocation, and also the 2nd resonance form has enough $E_a$ to form the 1,4 product.
Diels Alder Cycloaddition
- Cycloaddition is one of the few general methods to create cyclic organic compounds.
- A conjugated diene (4 C’s) reacts with a dienophile (2 C’s) to form a cyclohexene ring (6 C’s).
- The mechanism is neither polar, nor radical. It is pericyclic.
- The six $\pi$ e$^{-1}$’s act in concert (simultaneously) to form a cyclic transition state.
- The diene’s two inside $\pi$ e$^{-1}$’s form a new $\pi$ bond, and the other four $\pi$ e$^{-1}$’s form two new $\sigma$ bonds, which create the new ring.

![Diels Alder Cycloaddition Diagram](https://via.placeholder.com/150)

**Dienophile**
- Needs to have an e$^{-1}$ withdrawing group (EWG) that is attached to at least one of the $\Pi$ bonded C’s.
- The most typical EWG’s are carbonyls ($\text{C}=\text{O}$) and nitriles ($\text{C}=\text{N}$).
- Alkyl groups are not EWG’s.
- An EWG will pull e$^{-1}$’s toward itself, so that the $\Pi$ bond C’s become $\delta^+$, and can react with the e$^{-1}$ rich diene.

**Diene**
- Must have “s-cis” at the $\sigma$ bond between the two $\Pi$ bonds.
- Not exactly cis because it involves only the $\sigma$ bond, but the two $\Pi$ bonds face each other.
- Note that $\sigma$ bonds can rotate, and s-trans is more stable because there is less steric strain between the $\Pi$ bonds.
- For the reaction to occur, the s-trans must typically rotate to the higher $\Sigma$ s-cis state.
Diene Rubbers
- Formed from repeated 1,4 addition of diene molecules to a growing chain.
- Intermediates can be cationic, like the 1,4 cation in 1,4 addition of HBr. This occurs if an acid catalyst is used.
- Intermediates can also be free radicals, with an initiation, propagation, and termination, as in section 8.10. Here a free-radical initiator is used to start the reaction.
- The original double bonds are broken to create new single bonds, which link the monomer units together.
- The polymers will have new double bonds for the C’s that were single bonded between two double bonds.
- The new double bonds can be Z (cis) or E (trans). For example, there are both cis and trans polybutadienes. Neoprene is a Z polymer made from chloroprene units.
- Rubbers polymers are initially soft and tacky when formed, but can be made firmer and non-sticky by vulcanization (heating with S). Essentially, S creates cross-linked disulfide bridges (R−S−S−R)

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UV Spectroscopy
- Absorptions have $\lambda = 200 – 400$ nm. Range is next to visible with $\lambda$ shorter than visible.
- Absorptions correspond to $\Pi \rightarrow \Pi^*$ transitions that are $\Pi$ to $\Pi^*$ (bonding to antibonding).
- For a single molecule and photon, $E = h\nu = hc/\lambda$. So, $E$ of UV is higher than visible.
- For a mole, we have $E = N_A h\nu = N_A hc/\lambda$.
- Spectra of samples are measured by their Absorbance:
  \[ A = -\log \left( \frac{I}{I_0} \right) = -\log(T) \]
  $I_0$ is incoming light, $I$ is transmitted thru the sample, and $T$ is transmittance.
- Beer’s Law is used to find absorptivity ($\varepsilon$), which is a constant for a particular molecule at a particular wavelength.
  \[ A = \varepsilon LC \]
  $L$ is the pathlength (cm) and $C$ is concentration (mol/L)
- Spectra are $A$ vs $\lambda$, and are usually a simple curve with one $\lambda_{\text{max}}$.
- $\lambda_{\text{max}}$ is the wavelength with the highest $A$ (and $\varepsilon$)

Effect of conjugation on $\lambda_{\text{max}}$
- $\lambda_{\text{max}}$ is a function of the $E$ gap between the highest occupied bonding MO ($\Psi$) and the lowest unoccupied antibonding MO ($\Psi^*$).
- As the extent of conjugation (number of conjugated $\Pi$ bonds) increases, the $E$ gap decreases. This causes $\lambda_{\text{max}}$ to increase, so that it becomes closer to the visible range.
- Different types of molecules, such as conjugated alkenes, enones ($\text{C}=\text{C}−\text{C}=\text{O}$), and aromatic compounds (benzene rings) have characteristic $\lambda_{\text{max}}$ and $\varepsilon$ that can be used to identify them.

Conjugation, Color, and Vision
- With extended conjugation systems, the $\lambda_{\text{max}}$ extends into the visible range.
- The molecule then absorbs blue-violet, and it appears as the complementary color, which is yellow-orange, like $\beta$-carotene (from carrots).
- $\beta$-carotene is converted to all-trans retinol (vitamin A) by the body, which then converts it to 11-cis retinal. This molecule is attached to a protein called opsin, and becomes rhodopsin.
- Rhodopsin is also 11-cis, and is the light sensor in our rod cells. It is isomerized to all-trans metarhodopsin II by light.
- The isomerization would practically never happen without the presence of light.