

Conjugated Systems
**1 - Nomenclature, Properties
and Applications**

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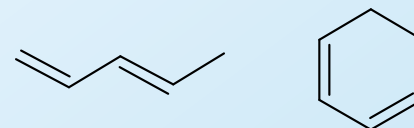
Introduction

Conjugated systems are usually alkenes with multiple double bonds. Where those double bonds are located is what can lead to conjugation (or not).

Conjugated

double bonds are separated by one single bond.

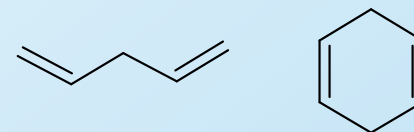
Example: 1,3-pentadiene.



Isolated

double bonds are separated by two or more single bonds (sp^3 carbon).

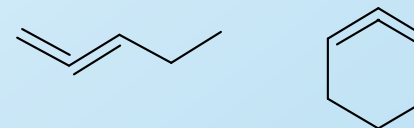
Example: 1,4-pentadiene.



Cumulated

double bonds are on adjacent carbons.

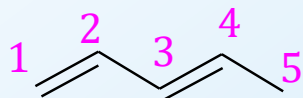
Example: 1,2-pentadiene.



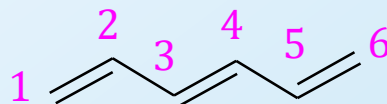
Nomenclature

Start the numbering from the alkene which is closest to the terminal carbon and in the longest chain.

- Two double bonds will be called diene; three: triene; four: tetraene etc.
- Where applicable you should use the cis/trans or E/Z configuration.
- Cis and trans can be used in cases where there are two hydrogens on the double bond.
- In case of substituents, give the double bond and the substituent lower numbers.

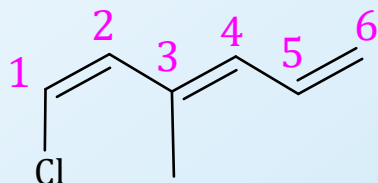


Trans-1,3-pentadiene
(E)-1,3-pentadiene

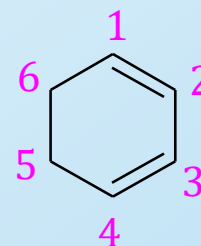


Trans-1,3,5-hexatriene
(E)-1,3,5-hexatriene

In the two compounds on the left we don't need to indicate the number on E because there is only one alkene with any configuration.



(1Z, 3E)-1-chloro-3-methyl-1,3,5-hexatriene

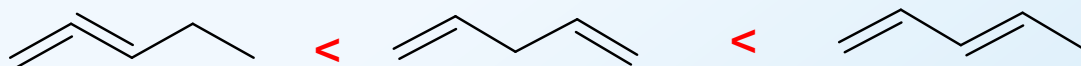


1,3-cyclohexadiene

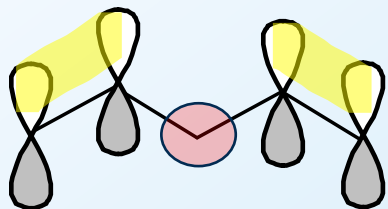
Stability of Alkenes

Stability of the alkene depends on location of double bonds.

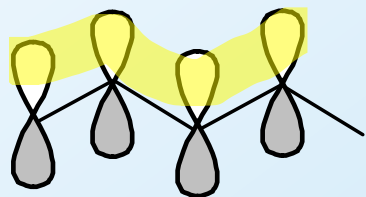
Conjugated are most stable and cumulated are the least stable.



Why are conjugated systems more stable? Each carbon with a double bond is sp^2 hybridized. Each sp^2 carbon has an unhybridized p orbitals. Below is a representation of what these orbitals would look like.



In the isolated system, the orbitals are separated by a sp^3 carbon (*circled*) which prevents the overlap of the p orbitals that form the pi bonds.

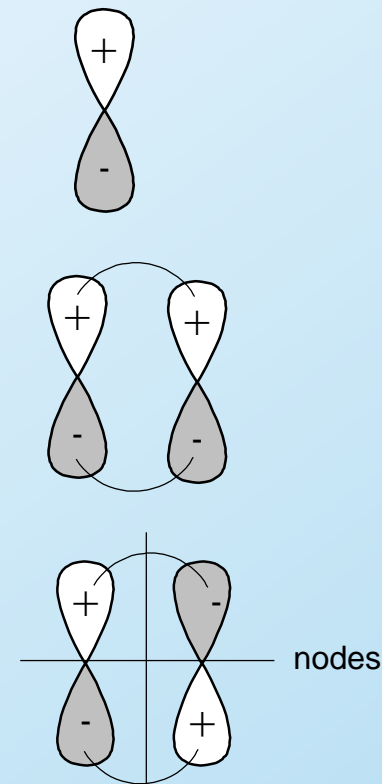


In the conjugated system, the orbitals are adjacent to other and overlap not only on the adjacent carbons by that conjugation is over all the sp^2 carbons. This leads to delocalization of electrons over many carbons, which leads to stability.

Using MO Theory to Understand Stability

As we know pi bonds are molecular orbitals (MO) that are the sideways overlap of p orbitals.

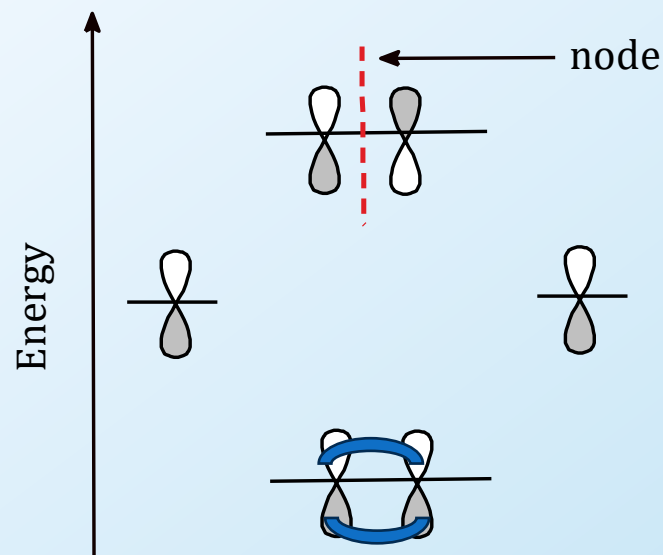
- p orbitals have 2 lobes. Plus (+) and minus (-) indicate the opposite phases of the wave function, not electrical charge.
- When lobes overlap constructively, (+ and +, or - and -) a bonding MO is formed.
- When + and - lobes overlap, waves cancel out and a node forms; antibonding MO.



MO Diagram of Ethene

Here is an example of the overlaps of orbitals in ethene – one pi bond.

- When + lobe overlaps with + is bonding MO.
- When + lobe overlaps with - is antibonding MO.
- Antibonding MOs will have one or more nodes in them. Nodes make the molecule have higher energy.

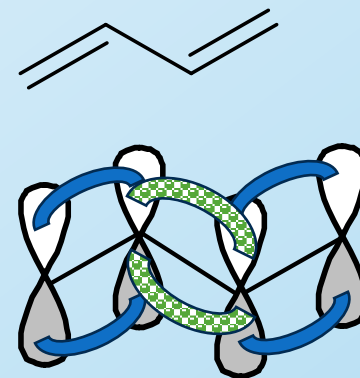


MO Diagram of 1,3-Butadiene

Most stable conformation of dienes is planar as it allows for maximum orbital overlap.

- Single bond is shorter than 1.54 Å. The green patterned curves show the overlap over the single bond.
- Electrons are delocalized all over molecule.
- Next slide shows all the variations possible for the MO diagram of butadiene.

The blue curves indicated overlap of similar wavefunction



π_4^* MO for 1,3-Butadiene

- All antibonding interactions.
- Highest energy.
- Vacant at ground state.

π_3^* MO for 1,3-Butadiene

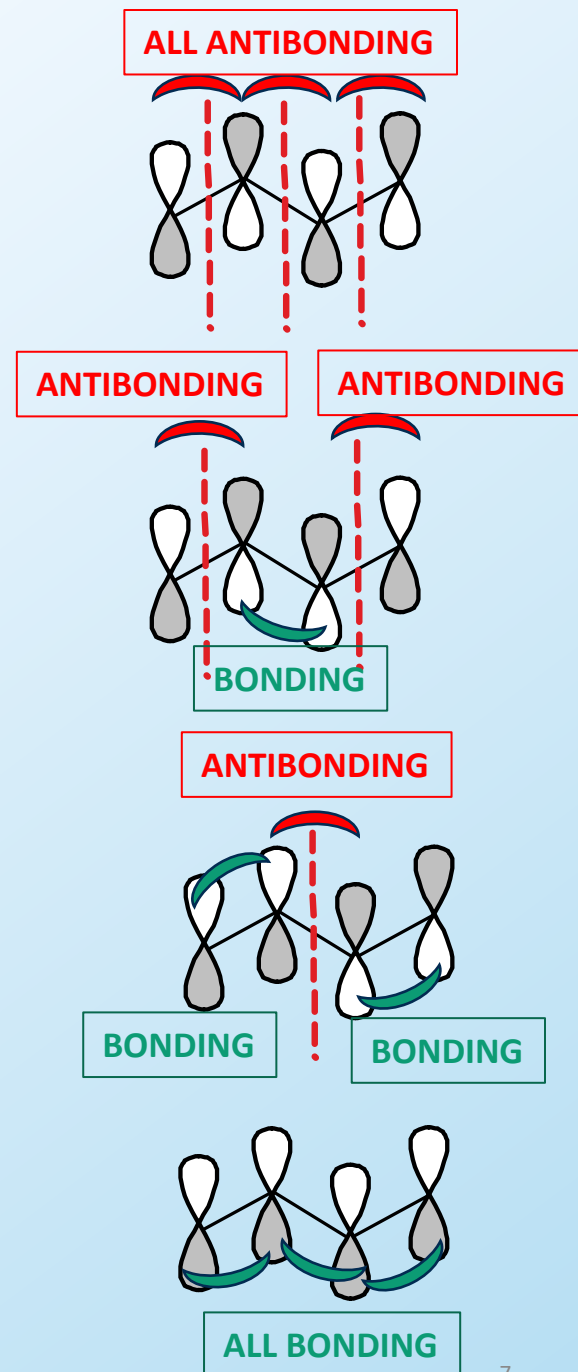
- Antibonding MO.
- Empty at ground state.
- Two nodes.

π_2 MO for 1,3-Butadiene

- 2 bonding interactions.
- 1 antibonding interaction.
- A bonding MO.

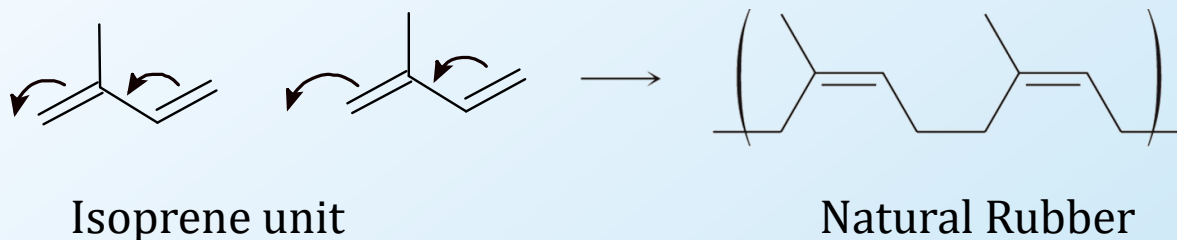
π_1 MO for 1,3-Butadiene

- Lowest energy.
- All bonding interactions.
- Electrons are delocalized over four nuclei.



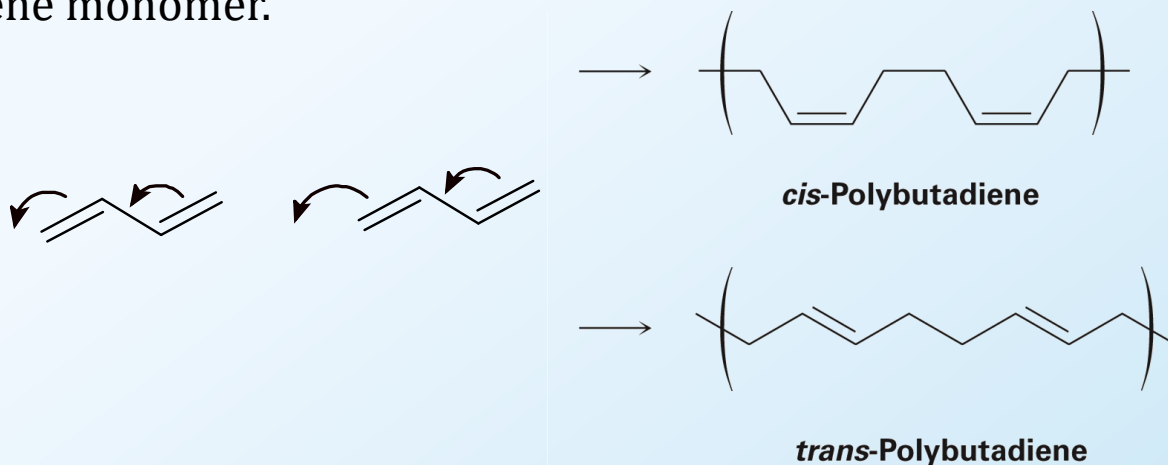
Applications - Natural Rubber

A material from latex, in plant sap in which the repeating unit has 5 carbons and **Z** stereochemistry of all C=C. The polymer looks like a head-to-tail polymer of isoprene. An isoprene unit is a 5 carbon fragment with two double bonds (2-methyl-1,3-butadiene). The 5 C skeleton is the key for isoprene.

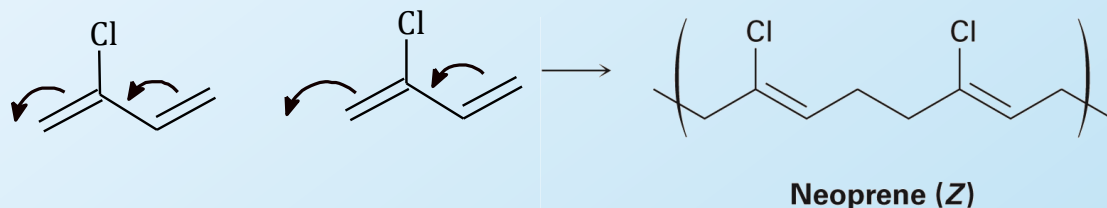


Diene Polymers: Natural and Synthetic Rubbers

Conjugated dienes can be polymerized to form long chains which is the basic structure of rubber. Polymerization: 1,4 addition of growing chain to conjugated diene monomer.

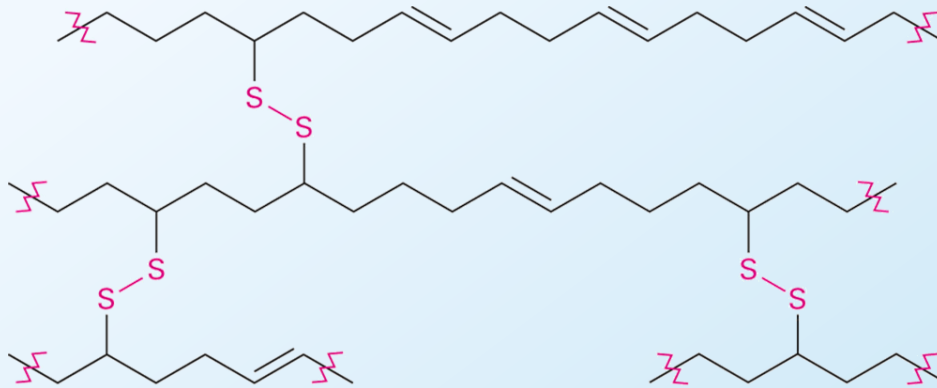


Chemical polymerization of isoprene does not produce rubber but using synthetic alternatives include neoprene, polymer of 2-chloro-1,3-butadiene can polymerize. This is also good as it resists weathering better than rubber.



Vulcanization

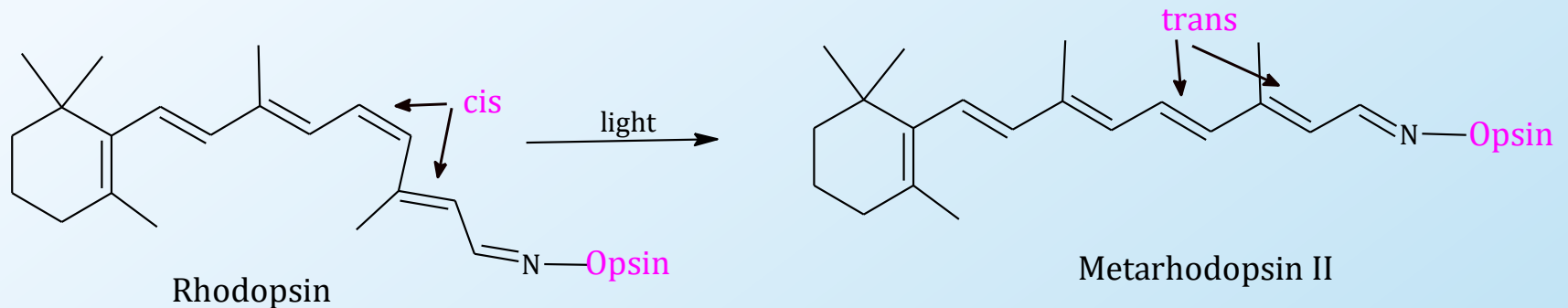
Natural and synthetic rubbers are too soft to be used in many products so Charles Goodyear discovered heating with small amount of sulfur produces strong material. Sulfur forms bridges between hydrocarbon chains (cross-links)



Conjugation, Color, and the Chemistry of Vision

Visual pigments are responsible for absorbing light in eye and triggering nerves to send signal to brain. Visible region is about 400 to 800 nm. Extended conjugation absorbs in visible region.

We have rhodopsin in our eyes, which when goes from cis to trans in presence of light will cause us to “see”.



Key Concepts

- Conjugated Systems
- Stability of alkenes
- MO orbitals