

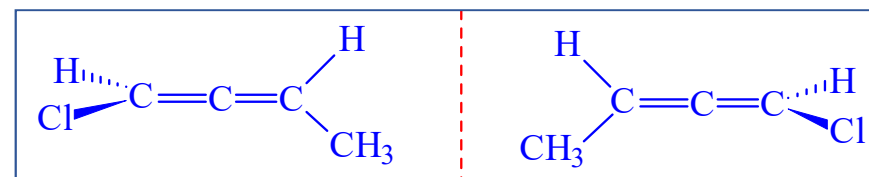
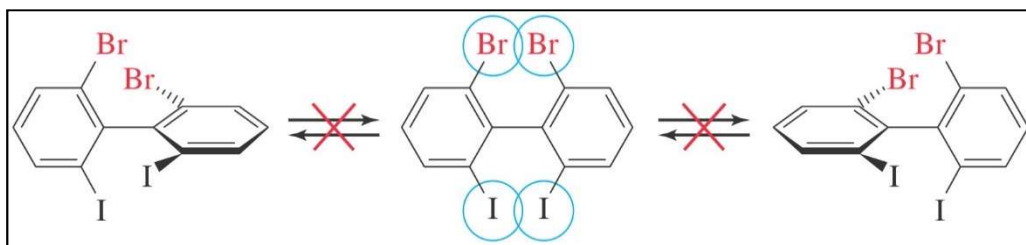


CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture 35 (16-04-2018)

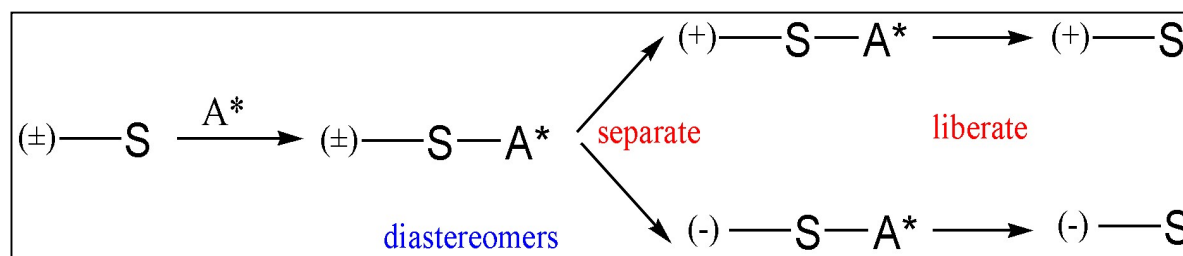
Summary of Lecture 36



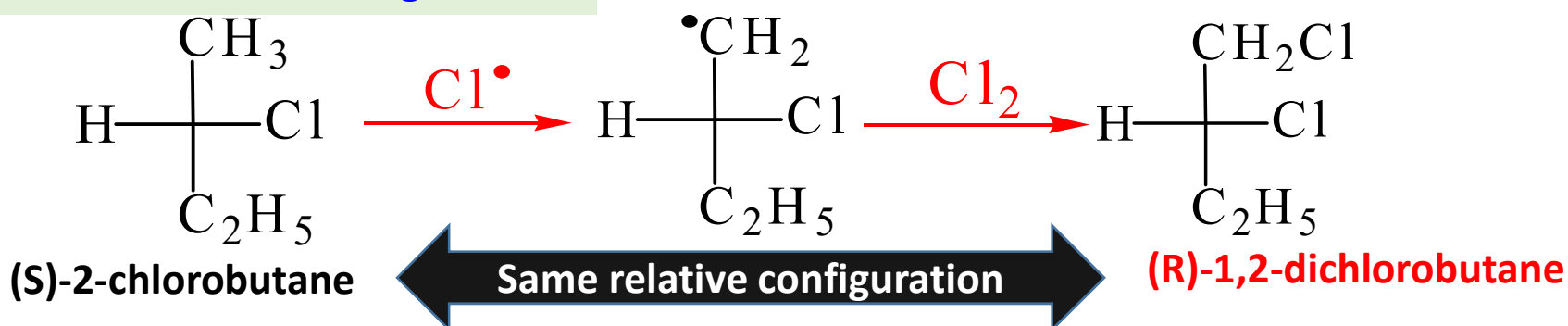
Resolution of Enantiomers:

- Two methods:
 - Chemical resolution
 - Chromatographic resolution

Resolution: Separating enantiomers by make environment chiral so that enantiomers have different properties.



Relative and absolute configurations

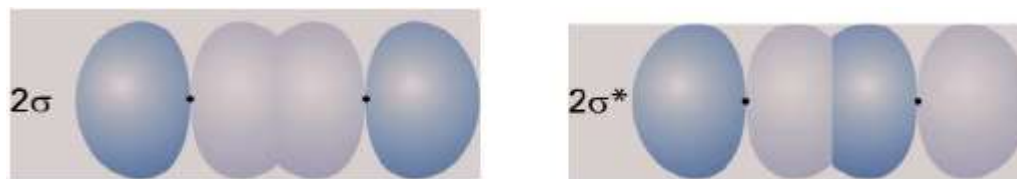


Molecular Orbitals using p-Atomic Orbitals



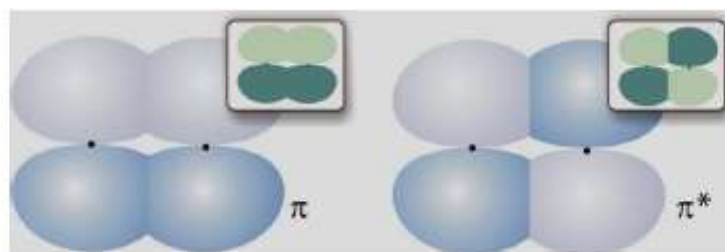
According to molecular orbital theory, σ orbitals are built from all orbitals that have the appropriate symmetry.

If we take molecular axis as Z-axis then Overlap of p_z orbitals leads to σ and σ^*



The bonding orbital is given the notation σ_g , where the g stands for *gerade*, or **symmetric around the bond axis** and anti-bonding orbitals given the notation σ_u , where the u stands for *ungerade*, or asymmetric around the bond axis.

Overlap of $2p_x$ and $2p_y$ orbitals lead to a pair of π and a pair of π^* orbitals.



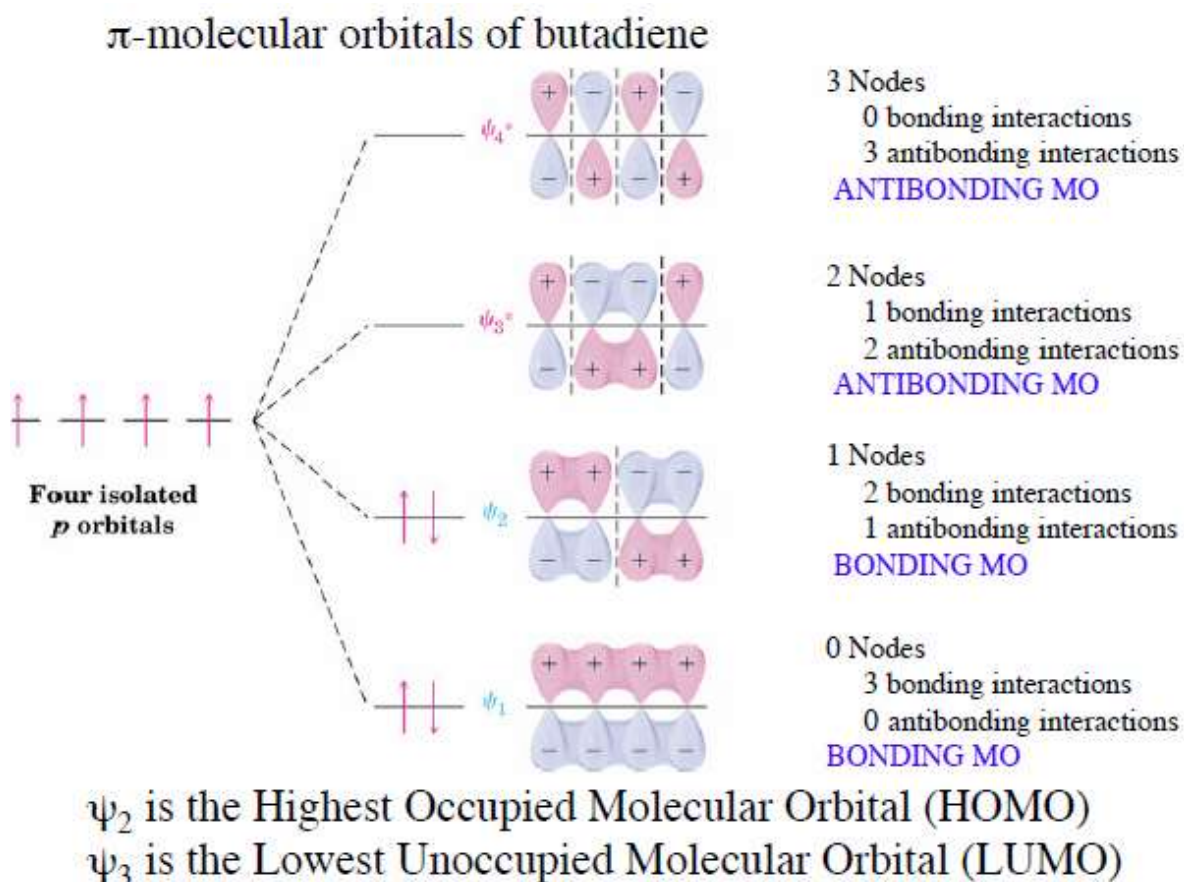
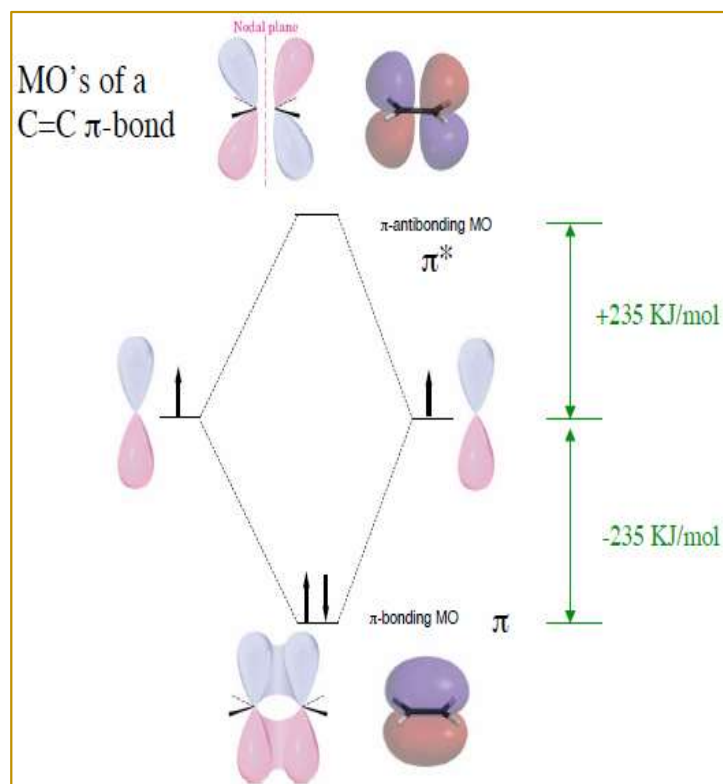
π -bonding orbitals are asymmetric about a **center of symmetry** or it is *ungerade* and anti-bonding orbital is *gerade*, or symmetric about a center of symmetry.

Note that the designations of u or g do not correlate with bonding or anti-bonding.

Construction of molecular orbitals



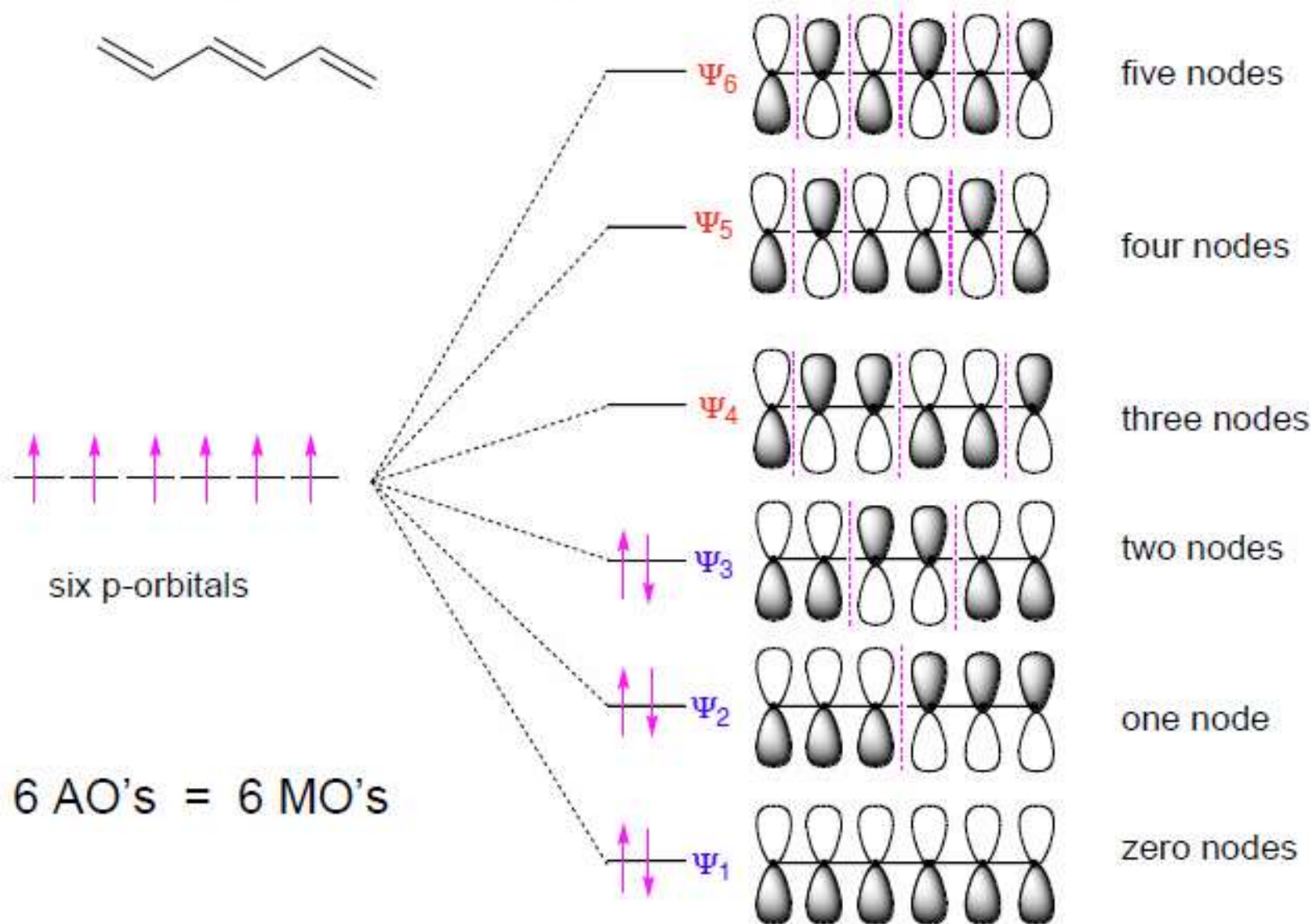
- ❑ Use of available valence orbitals from atoms
- ❑ Classify according to symmetry (σ/π) with respect to axis
- ❑ From N_σ AO's build N_σ MOs for σ symmetry
- ❑ Similar N_π MO's of π -symmetry. These occur in degenerate pairs.
- ❑ In general, the energy of each type of orbitals increases with the number of inter-nuclear nodes



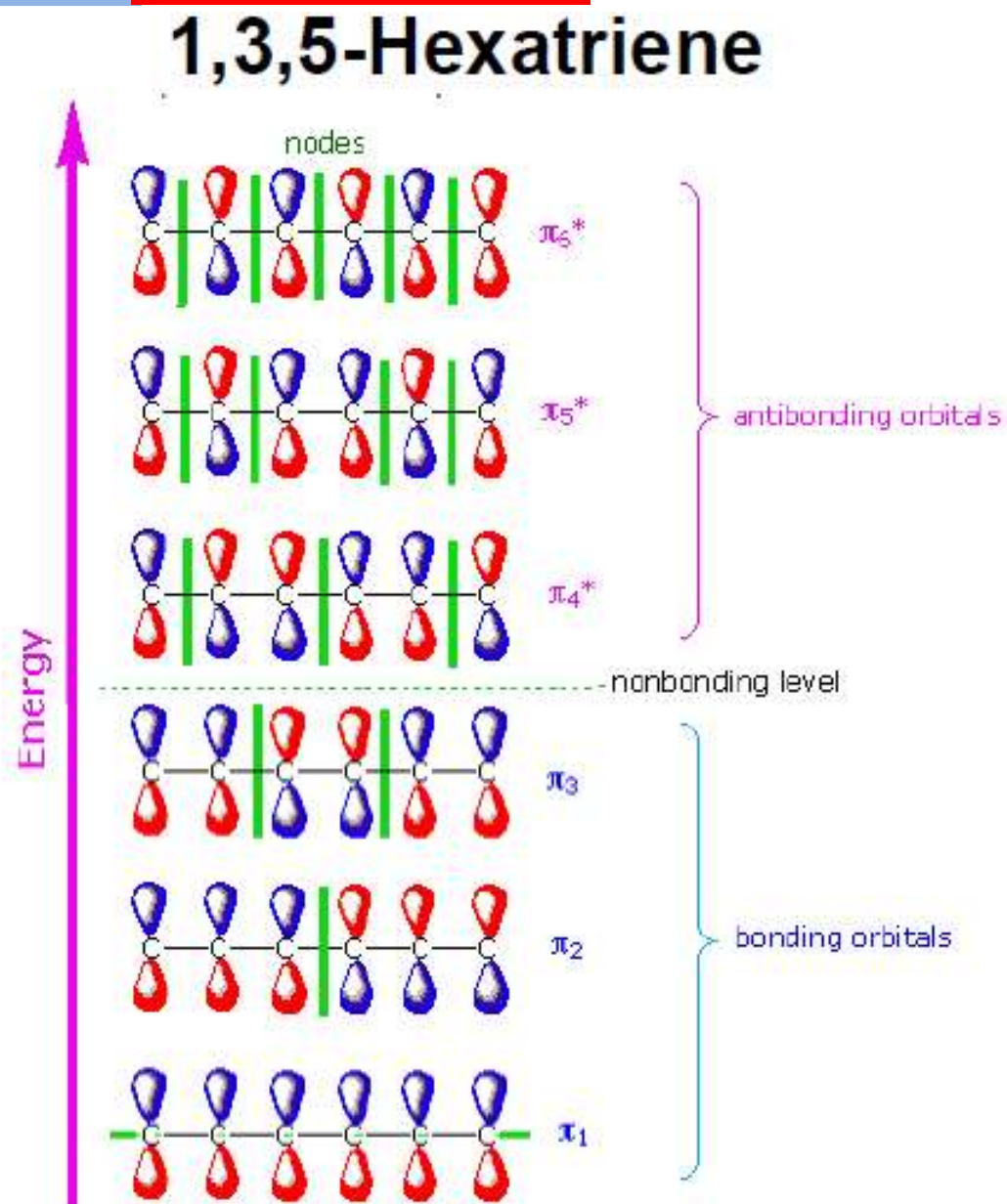
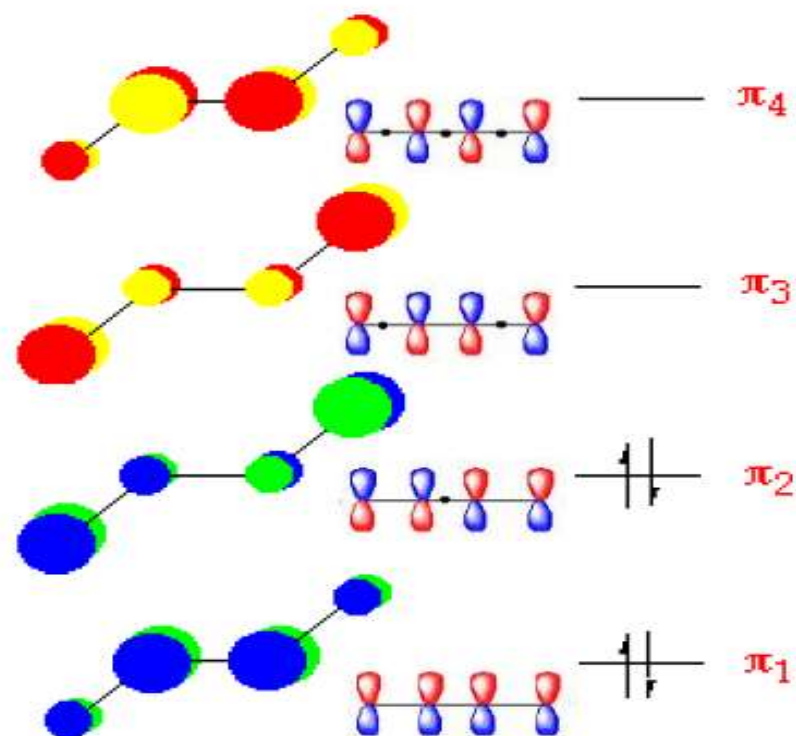
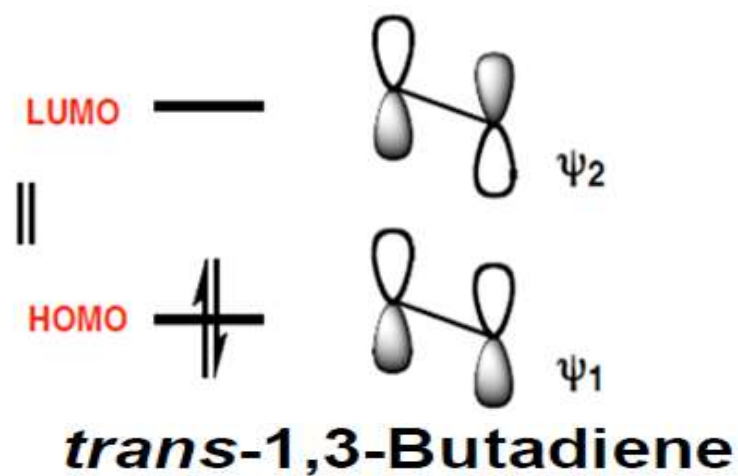
Construction of molecular orbitals



π -molecular orbitals of hexatriene



π -Mos of conjugated Molecules



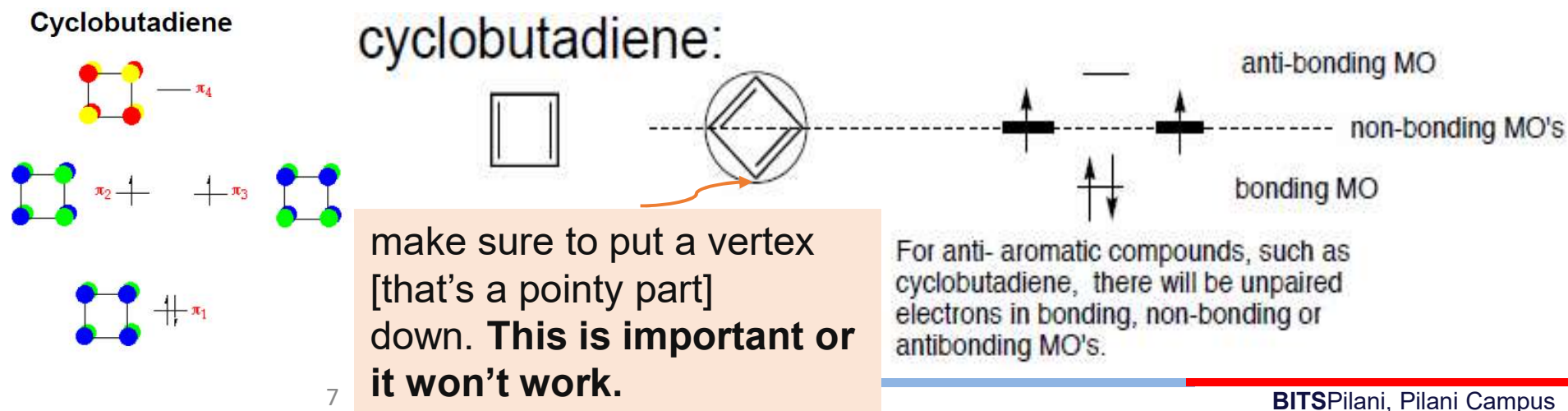
π -MOs of cyclic conjugated: Frost-Musulin diagrams



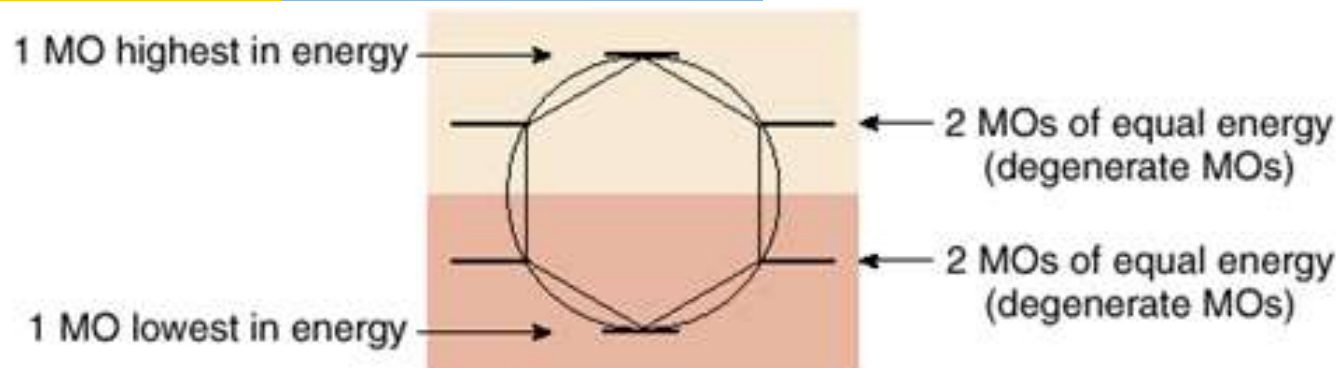
Draw the molecular framework of a cyclic system of overlapping p-orbitals, making sure you put an atom at the bottom. Atomic positions (positions of p-orbitals) then map on to the energy level diagram!

Draw a horizontal line through the center of the circle and label MOs as bonding, antibonding and nonbonding.

- MOs below the line are bonding, and lower in energy than p-orbitals from which they are formed.
- MOs above the line are anti-bonding, and higher in energy than p-orbitals from which they are formed.
- MOs on the line are non-bonding, and equal in energy to the p-orbitals from which they are formed.



Frost-Musulin diagrams of benzene



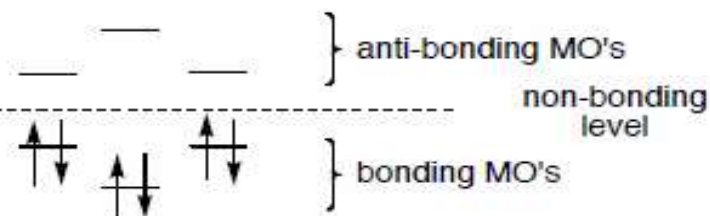
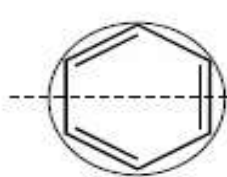
Frost Circles: relative energies of the molecular orbitals of cyclic, conjugated systems

Inscribe the cyclic, conjugated molecule into a circle so that a vertex is at the bottom. The relative energies of the MO's are where the ring atoms intersect the circle

benzene:



Benzene
6 π -electrons

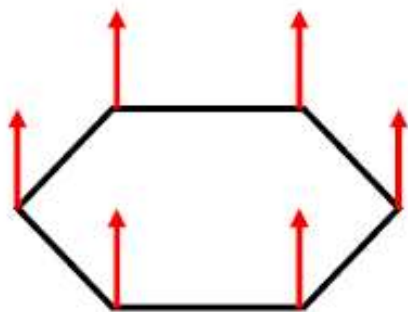


For aromatic compounds, such as benzene, the bonding MO's will be filled.

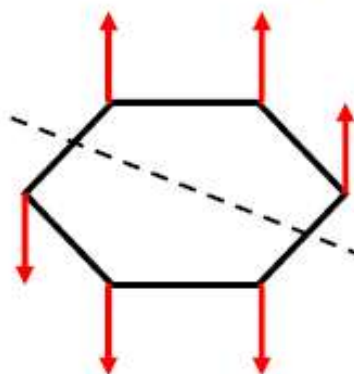
π -Mos of Benzene



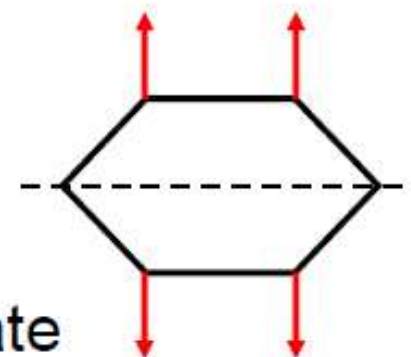
Fully bonding orbital with no node



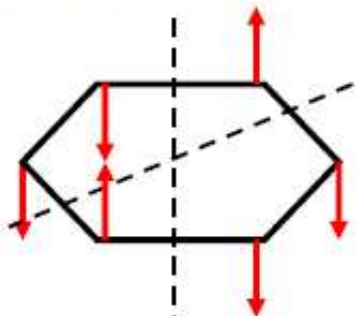
Bonding orbitals with one node



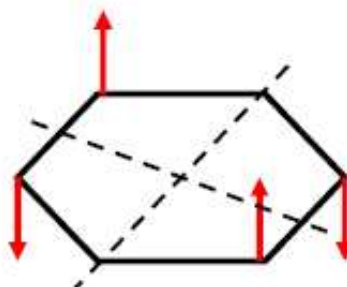
degenerate



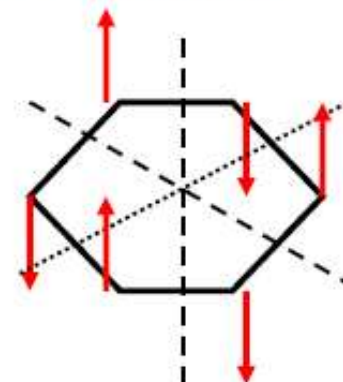
Anti-bonding orbitals with two nodes



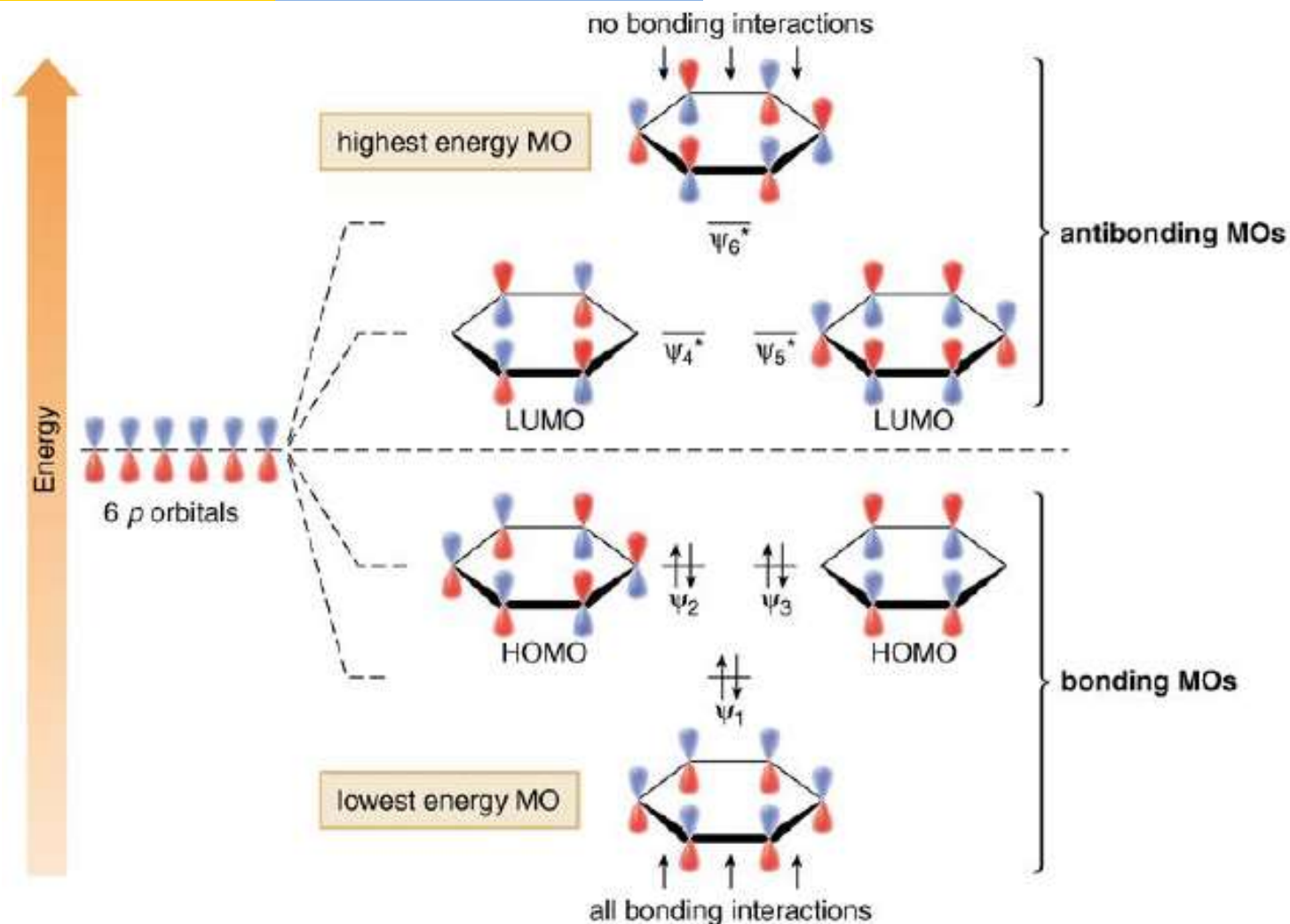
degenerate



Fully anti-bonding orbital with three nodes



π -Mos of Benzene



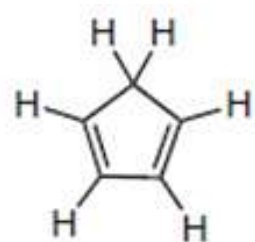
The relative energies of MOs for cyclic conjugated molecules can be determined by Polygon Method of Predicting (Frost-Musulin diagrams).

π -Mos of cyclic conjugated Molecules



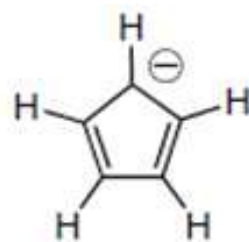
Cyclopentadiene anion

$4n+2=6$
 $n=1$
 aromatic



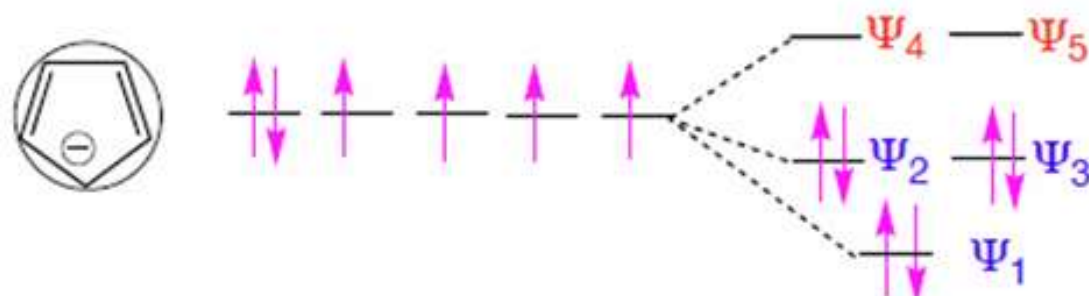
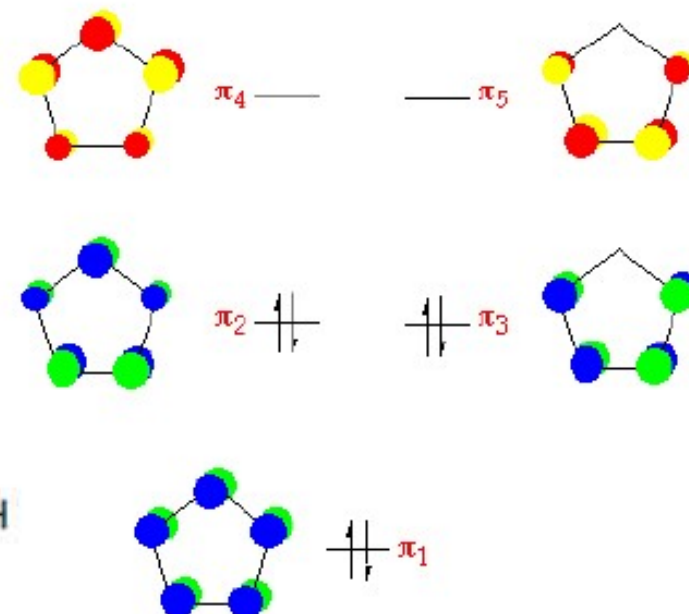
$pK_a \sim 15$

+ B:



+ B:H

cyclopentadienyl anion
 6π -electrons

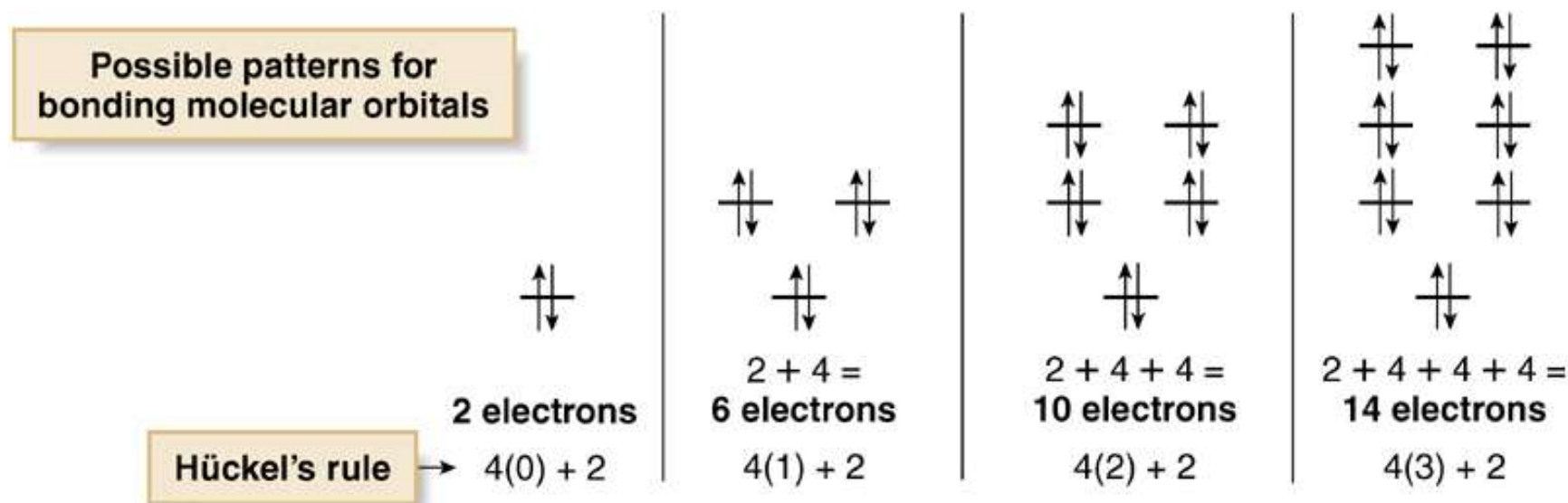


Hückel's Rule: The $(4n+2)p$ Electron Rule & MO



For **monocyclic planar compounds** in which each atom has a p orbital, Hückel showed that compounds with $(4n+2)$ p-electrons, where $n = 0, 1, 2, 3$ etc, would have closed shells of delocalised p electrons and should show exceptional stability (high resonance energy “aromatic”). i.e. planar monocycles with 2, 6, 10, 14....delocalised p electrons should be “aromatic”.

For the compound to be aromatic, bonding MOs must be completely filled with electrons, so the “magic numbers” for aromaticity fit Hückel's $4n + 2$ rule.

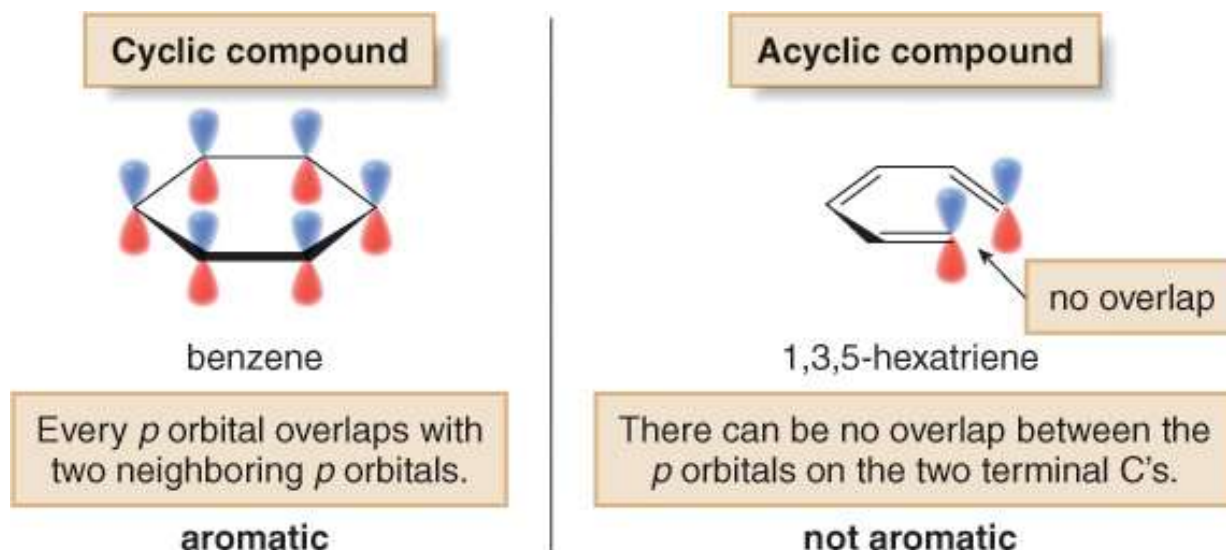


Criteria for Aromaticity—Hückel's Rule

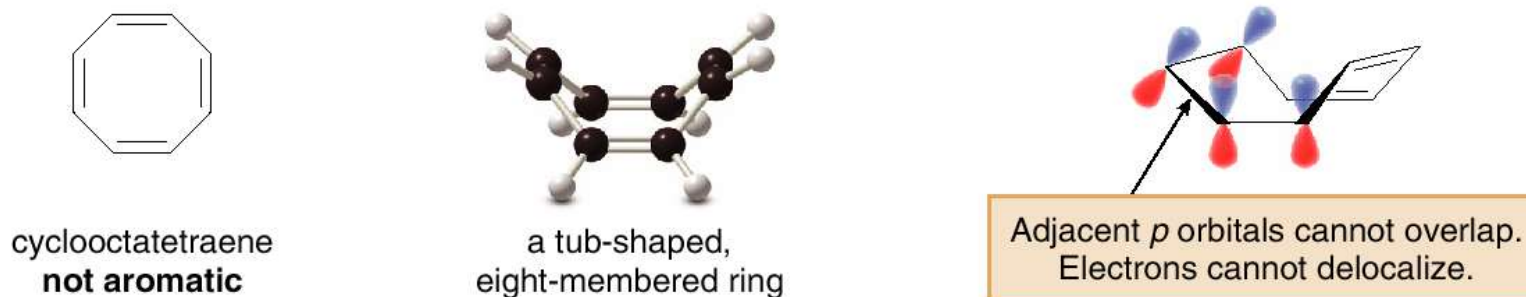


Four structural criteria must be satisfied for a compound to be aromatic.

[1] A molecule must be cyclic.



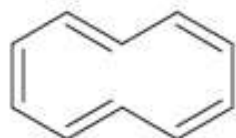
[2] A molecule must be planar. All adjacent p orbitals must be aligned so that the π electron density can be delocalized.



Criteria for Aromaticity—Hückel's Rule



[10]-Annulene fits Hückel's rule, but it's **not planar**.



[10]-annulene
10 π electrons
not aromatic

=

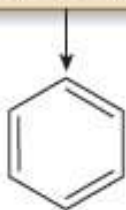


3-D representation

The molecule puckers to keep these H's further away from each other.

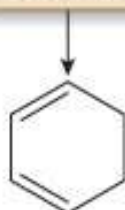
[3] A molecule must be completely conjugated. Aromatic compounds must have a p orbital on every atom.

A completely conjugated ring



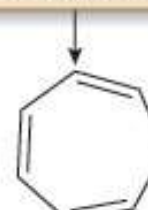
benzene
a p orbital on **every C**
aromatic

These rings are not completely conjugated.



1,3-cyclohexadiene
not aromatic

no p orbitals



1,3,5-cycloheptatriene
not aromatic

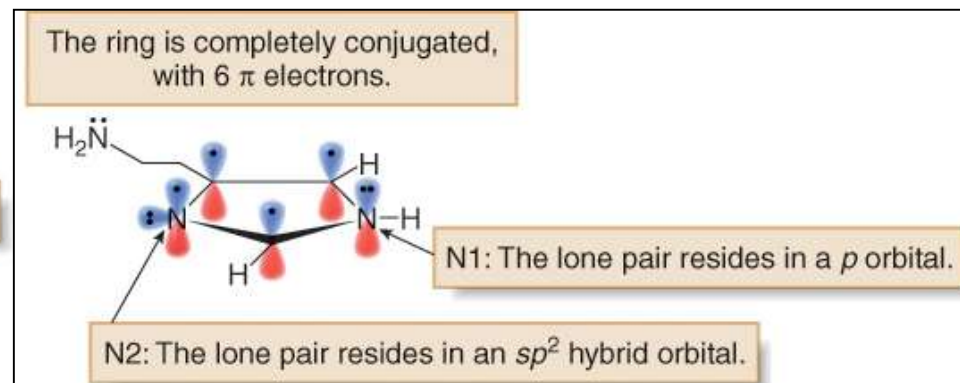
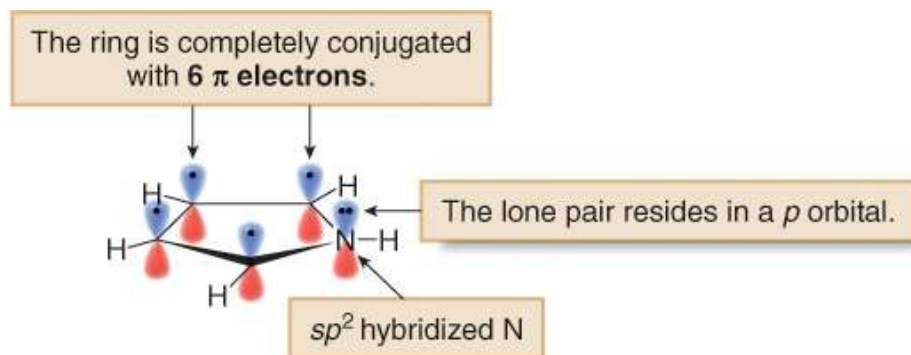
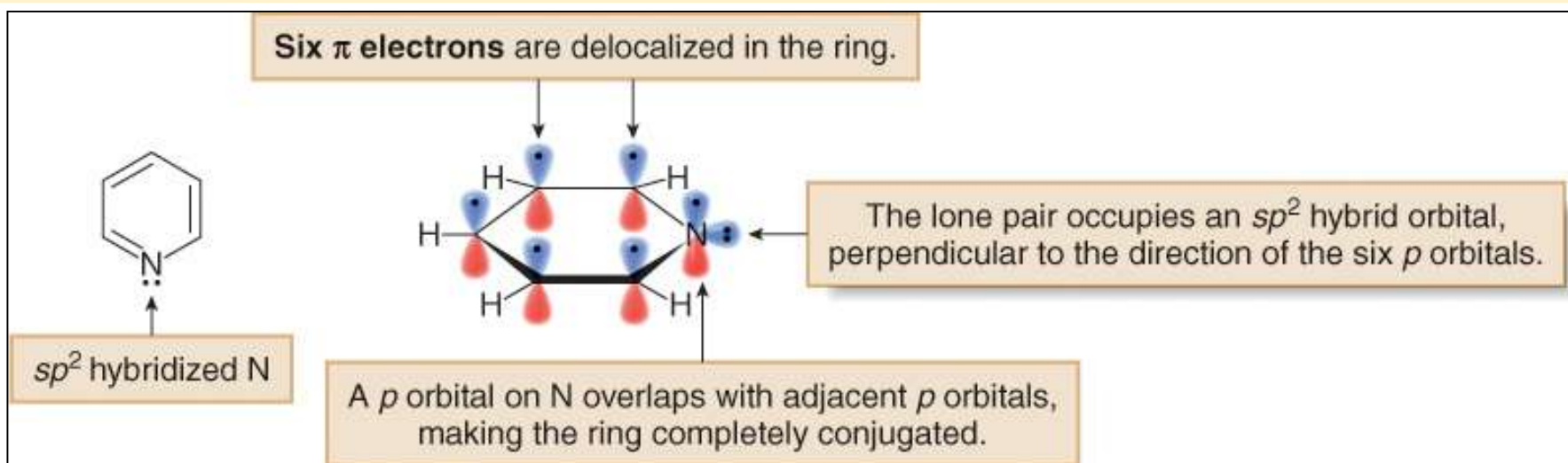
no p orbital

[4] A molecule must satisfy Hückel's rule, and contain a particular number ($4n+2$) of π electrons.

Aromatic compound with heteroatom



- Heterocycles containing oxygen, nitrogen or sulfur, can also be aromatic.
- With heteroatoms, we must determine whether the lone pair is localized on the heteroatom or part of the delocalized π system.
- An example of an aromatic heterocycle are pyridine, pyrrole etc.

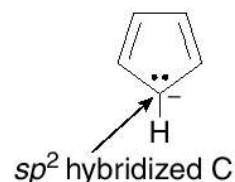


Ions as Aromatic compound

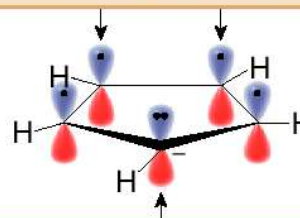


Both negatively and positively charged ions can be aromatic if they possess all the necessary elements.

The cyclopentadienyl anion



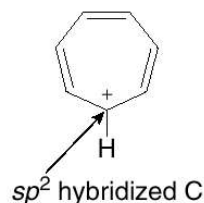
The ring is completely conjugated with **6 π electrons**.



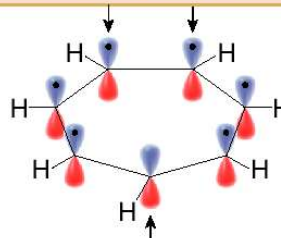
The lone pair resides in a *p* orbital.

- The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.

The tropylium cation



The ring is completely conjugated with **6 π electrons**.



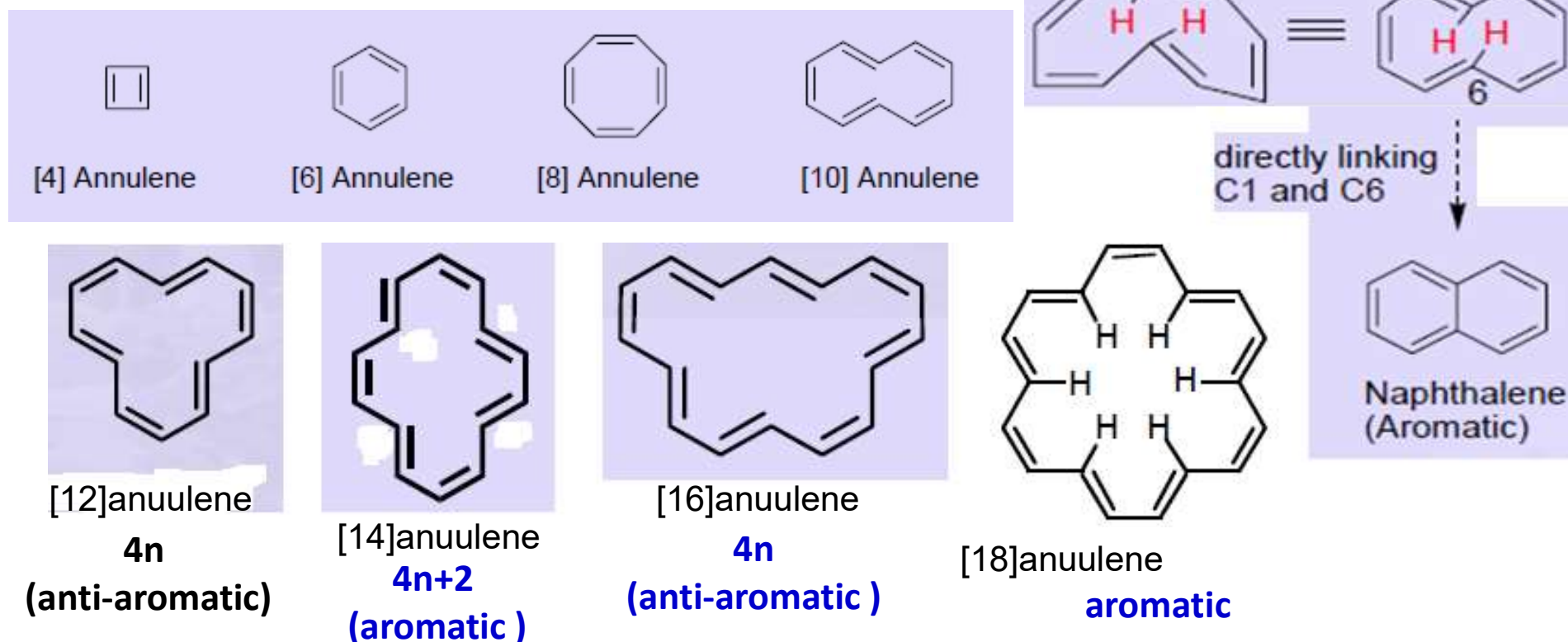
One *p* orbital is vacant.

- The tropylium cation is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons delocalized over the seven atoms of the ring.

Non-benzenoid Aromatics



Annulenes: Hydrocarbons containing a single ring with alternating double and single bonds are called annulenes. To name an annulene, indicate the number of atoms in the ring (usually, the number of π electrons) in brackets and add the word annulene.



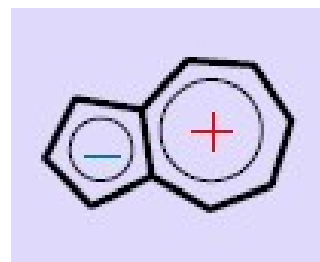
[18]annulene is a planar, fully aromatic compound. The ring is just large enough that the hydrogens sticking into the middle of the ring do not interact to twist the molecule out of planarity.

Non-benzenoid Aromatics

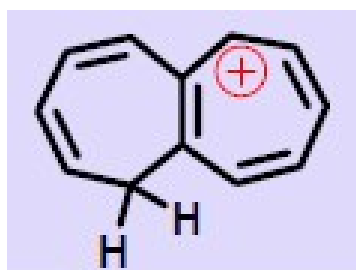
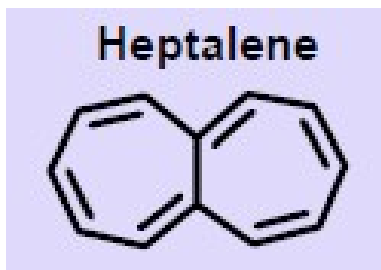


Azulene is one of the few non-benzenoids that appears to have significant aromatic stabilization. It has a noticeable dipole moment (0.8 D).

It acts like a combination of cyclopentadienyl anion and cycloheptatrienyl cation.



In contrast, Pentalene and heptalene which possess fused five and seven membered rings, respectively, are not stable but conjugate acid of heptalene is very stable, reflecting the stability of resulting Tropylium cation.



Unstable

The large measured dipole moments and reduced barrier of rotation of the unsymmetrical fulvalene (x) analog are manifestations of aromatic stabilization.

