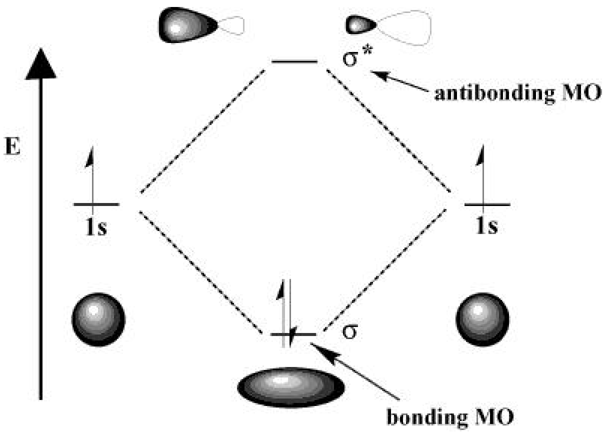
Basics of Molecular Orbital Theory

Valence Bond theory, as we saw in the last section, is based on the notion that electrons are *localized* to specific atomic orbitals. Molecular orbital theory asserts that atomic orbitals no longer hold significant meaning after atoms form molecules. Electrons no longer "belong", in a sense, to any particular atom but to the molecule as a whole. Molecular orbital theory holds, as its name suggests, that electrons reside in molecular orbitals that are distributed over the entire molecule.

Quantum mechanics specifies that we can get molecular orbitals through a *linear combination* of atomic orbitals; that is, by adding and subtracting them. How do we add and subtract orbitals? The best way to picture this process is to recall the wave-like nature of electrons. Recall from physics that two waves can interact either through *constructive interference,* in which the two waves reinforce each other, and *destructive interference,* in which the two waves cancel each other out. Mathematically, constructive interference corresponds to addition and destructive interference corresponds to subtraction. When atomic orbitals interact, we can either add them to obtain a bonding orbital or subtract them to obtain an antibonding orbital. Antibonding orbitals are denoted with an asterisk (*).



For instance, in the hydrogen molecule, the atomic 1*s* orbitals can overlap in a *σ* (head-on) fashion to form a *σ*-bonding molecular orbital and a *σ*-antibonding molecular orbital. The bonding molecular orbital is "bonding" in the sense that it is lower in energy than its component atomic orbitals. Forming a bond and moving electrons into the bonding orbital lowers the total energy of the system, which is favorable. On the other hand, moving electrons into the antibonding orbital raises the energy of the system, which disfavors bond formation. The total number of orbitals is conserved; the number of molecular orbitals equals the number of original atomic orbitals.

Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms.

Both theories provide different, useful ways of describing molecular structure.

Valence Bond Theory	**Molecular Orbital Theory**
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s, p, d…*) and hybrid orbitals (sp, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behaviour of an electron in a molecule is still described by a wave function, Ψ, analogous to the behaviour in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a **molecular orbital (Ψ^2)**. Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals (LCAO)**. The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (*Figure below*). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

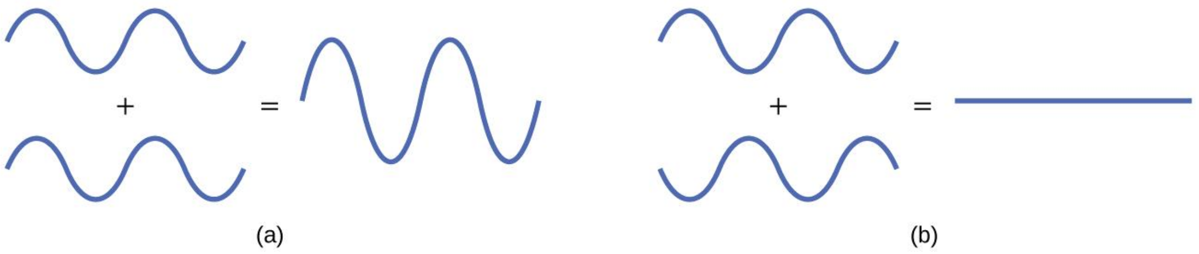
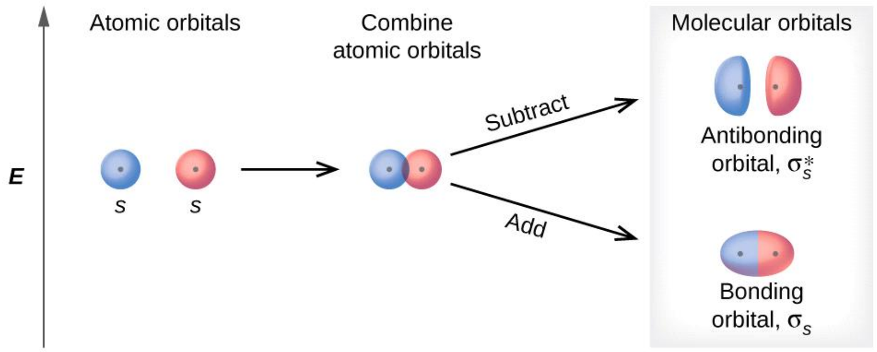
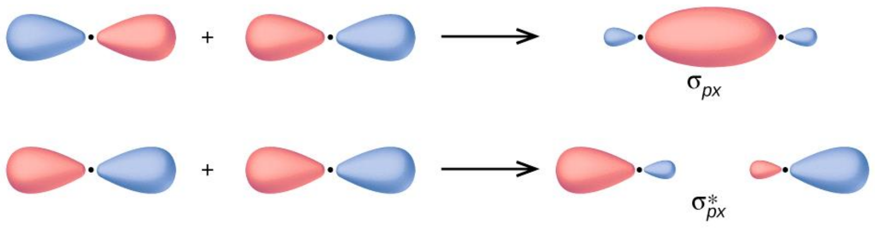


Figure *(a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.*

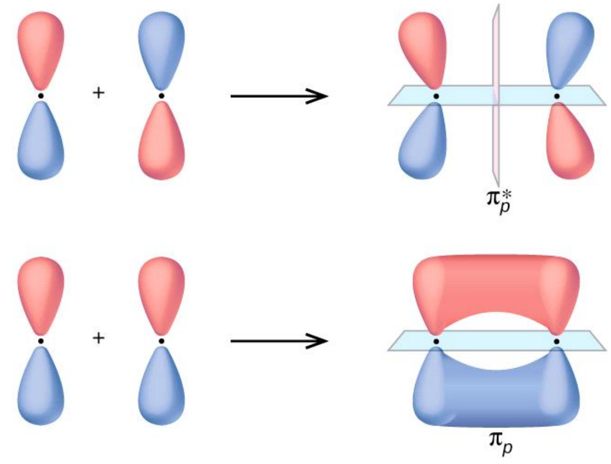
There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure below. The in-phase combination produces a lower energy **σ_s molecular orbital** (read as “sigma-s”) in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy **$\sigma^{ð}_{s}$ molecular orbital** (read as “sigma-s-star”) molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**. Electrons in the orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called **antibonding orbitals**. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.



In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colours. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure below). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and σ^*_{px} (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



The side-by-side overlap of two *p* orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibonding molecular orbital**, as shown in Figure below. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.



Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from the filling of the molecular orbitals by electrons

The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\textbf{Bond order} = \frac{\textbf{(number of bonding electrons) – (number of antibonding electrons)}}{\textbf{2}}$$

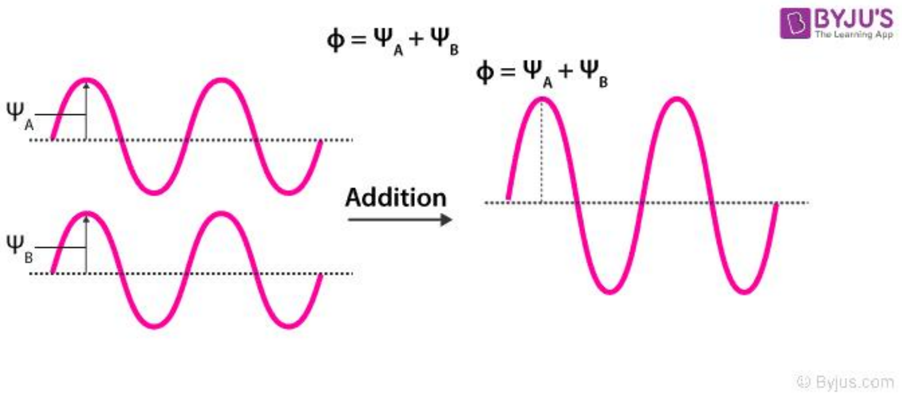
The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases.

The key features of the molecular orbital theory are listed below.

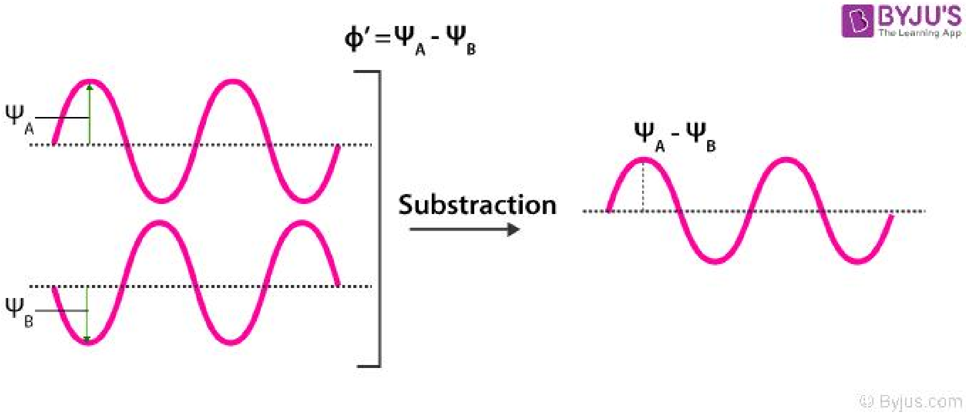
- The total number of molecular orbitals formed will always be equal to the total number of atomic orbitals offered by the bonding species.
- There exist different types of molecular orbitals: bonding molecular orbitals, anti-bonding molecular orbitals and non-bonding molecular orbitals. Of these, anti-bonding molecular orbitals will always have higher energy than the parent orbitals, whereas bonding molecular orbitals will always have lower energy than the parent orbitals.
- The electrons are filled into molecular orbitals in the increasing order of orbital energy (from the orbital with the lowest energy to the orbital with the highest energy).
- The most effective combinations of atomic orbitals (for the formation of molecular orbitals) occur when the combining atomic orbitals have similar energies.

An atomic orbital is an electron wave; the waves of the two atomic orbitals may be in phase or out of phase. Suppose Ψ_A and Ψ_B represent the amplitude of the electron wave of the atomic orbitals of the two atoms A and B.

Case 1: When the two waves are in phase so that they add up and the amplitude of the wave is $\Phi = \Psi_A + \Psi_B$



Case 2: When the two waves are out of phase, the waves are subtracted from each other so that the amplitude of the new wave is $\Phi' = \Psi_A - \Psi_B$



According to the molecular orbital theory, the filling of orbitals takes place according to the following rules:

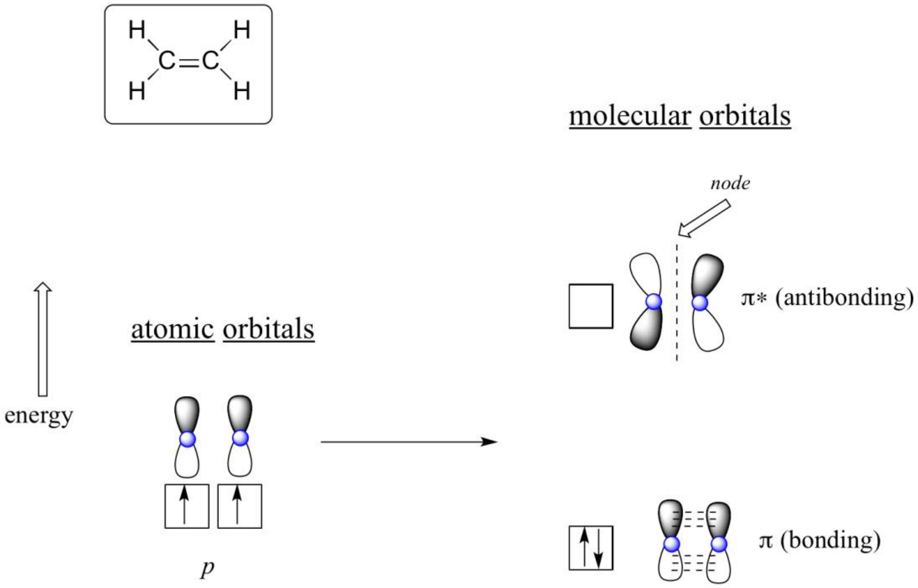
- Aufbau's principle: Molecular orbitals are filled in the increasing order of energy levels.
- Pauli's exclusion principle: In an atom or a molecule, no two electrons can have the same set of four quantum numbers.
- Hund's rule of maximum multiplicity: Pairing of electrons doesn't take place until all the atomic or molecular orbitals are singly occupied.

MO theory and conjugated pi bonds

The advantage of using MO theory to understand bonding in organic molecules becomes more apparent when we think about pi bonds.

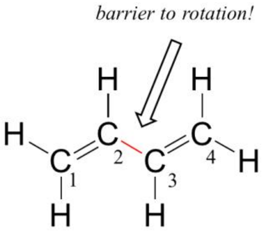
Let's first consider the pi bond in **ethene** from an MO theory standpoint (in this example we will be disregarding the sigma bonds in the molecule, and thinking *only* about the pi bond). We start with two atomic orbitals: one unhybridized 2p orbital from each carbon. Each contains a single electron. In MO theory, the two atomic combine mathematically to form two **pi (π) molecular orbitals**, one a low-energy pi bonding orbital and one a high-energy pi* (π*) antibonding orbital.

Molecular orbitals for ethene (ethylene)



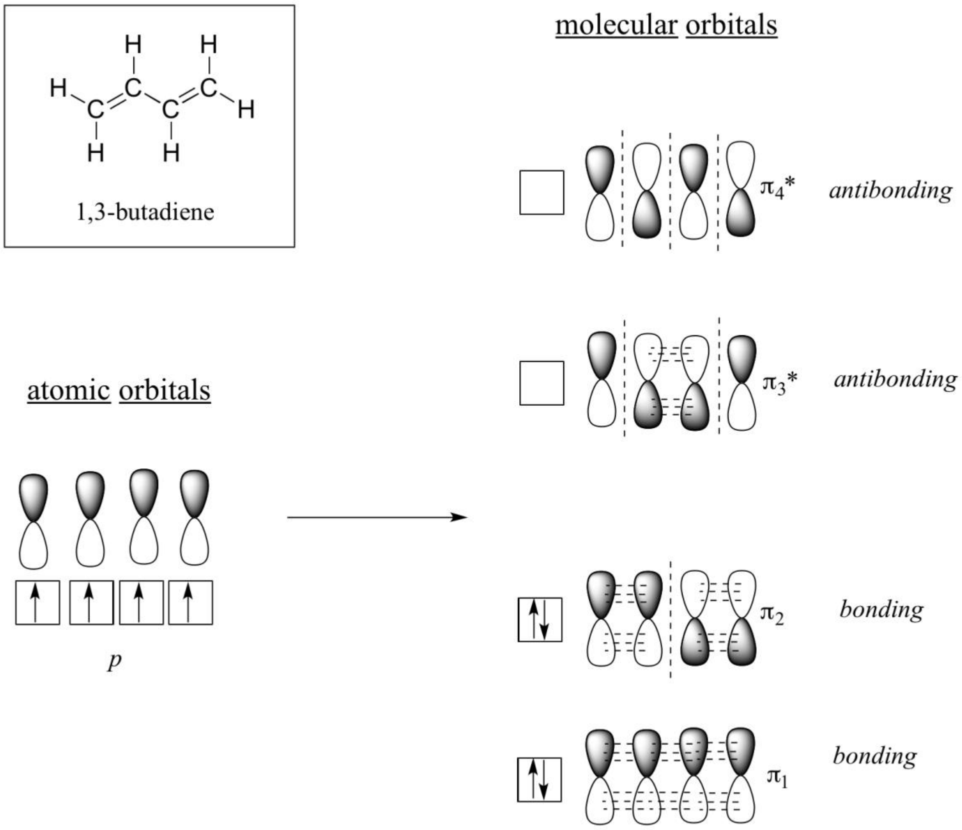
The 1, 3-butadiene molecule.

From valence orbital theory alone we might expect that the C_2-C_3 bond in this molecule, because it is a sigma bond, would be able to rotate freely.



Experimentally, however, it is observed that there is a significant barrier to rotation about the C_2-C_3 bond, and that the entire molecule is planar. In addition, the C_2-C_3 bond is 148 pm long, shorter than a typical carbon-carbon single bond (about 154 pm), though longer than a typical double bond (about 134 pm).

Molecular orbital theory accounts for these observations with the concept of **delocalized pi bonds**. In this picture, the four *2p* atomic orbitals combine mathematically to form four pi molecular orbitals of increasing energy. Two of these - the bonding pi orbitals - are lower in energy than the *p* atomic orbitals from which they are formed, while two - the antibonding pi* orbitals - are higher in energy.

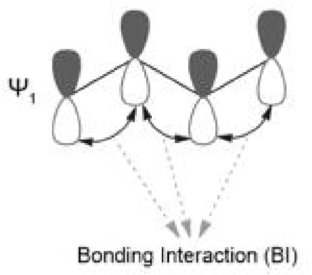


The lowest energy molecular orbital, pi$_1$, has only constructive interaction and zero nodes. Higher in energy, but still lower than the isolated *p* orbitals, the pi$_2$ orbital has one node but two constructive interactions - thus it is still a bonding orbital overall. Looking at the two antibonding orbitals, pi$_3$* has two nodes and one constructive interaction, while pi$_4$* has three nodes and zero constructive interactions.

By the *aufbau* principle, the four electrons from the isolated $2p_z$ atomic orbitals are placed in the bonding pi$_1$ and pi$_2$ MO's. Because pi$_1$ includes constructive interaction between C_2 and C_3, there is a degree, in the 1,3-butadiene molecule, of pi-bonding interaction between these two carbons, which accounts for its shorter length and the barrier to rotation. The valence bond picture of 1,3-butadiene shows the two pi bonds as being isolated from one another, with each pair of pi electrons 'stuck' in its own pi bond. However, molecular orbital theory predicts (accurately) that the four pi electrons are to some extent delocalized, or 'spread out', over the whole pi system

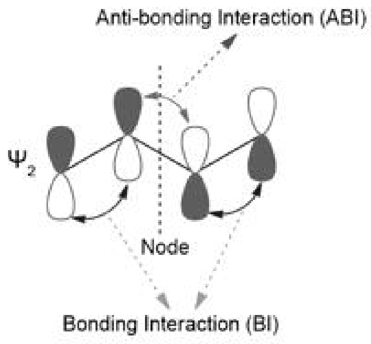
Bonding interactions

The interaction shown by the bonding orbitals (the orbitals participating in bonding) is referred to as the bonding interaction.



ψ_1 Orbital

There are three bonding interactions and zero nodes

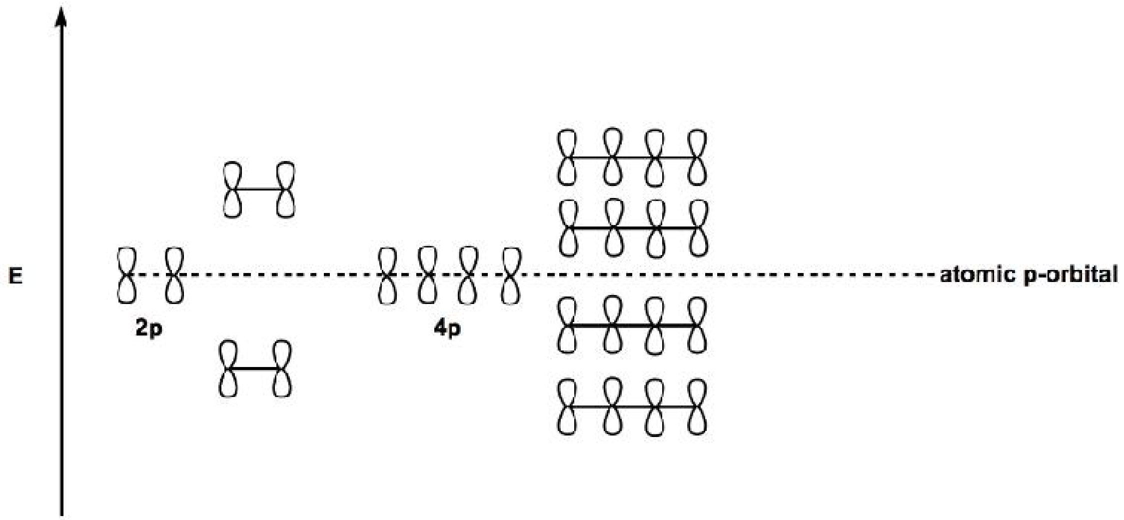


ψ_2 orbital

There are two bonding interactions: one antibonding interaction and one node.

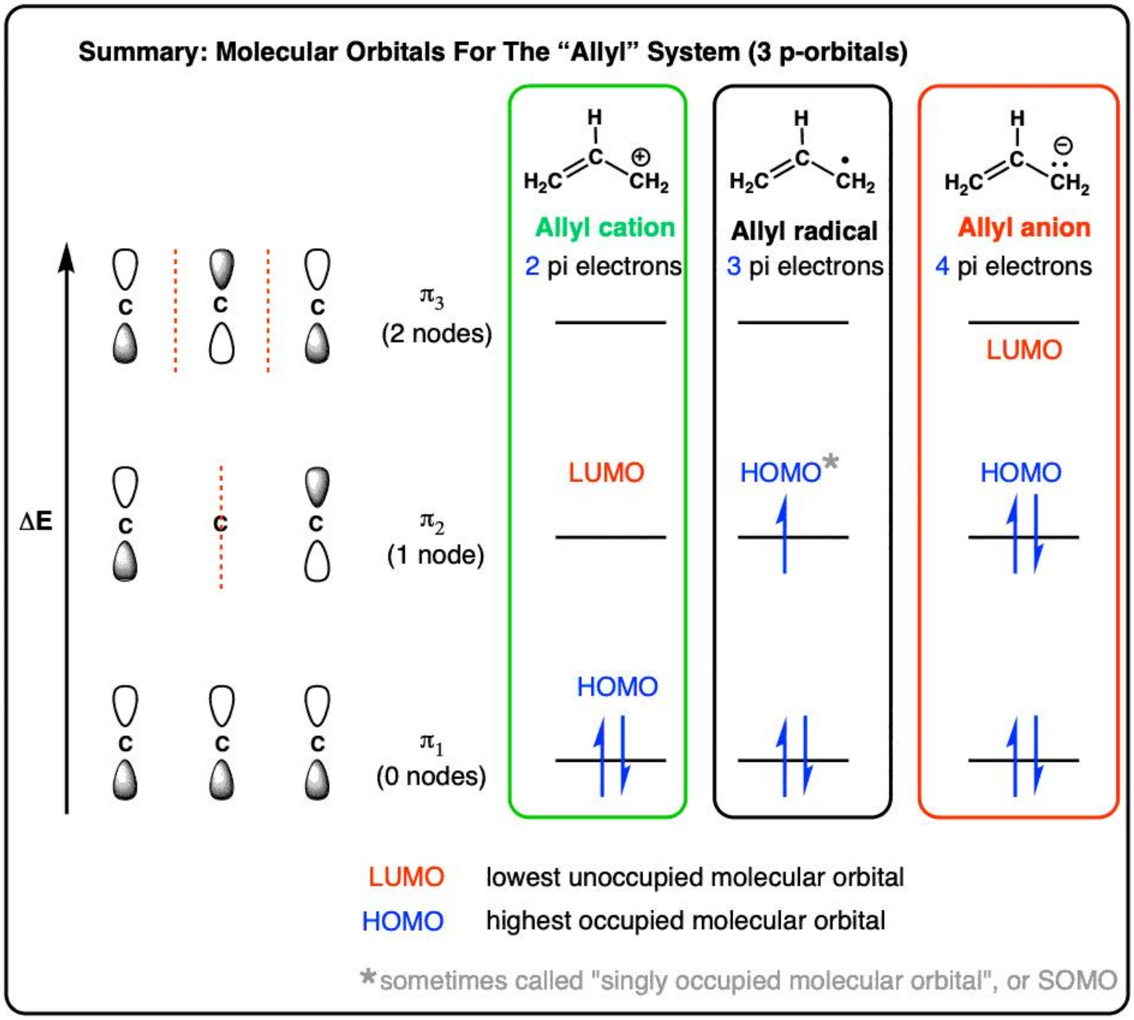
“Node" or **place of zero electron density between the atoms.** The higher in energy the MO, the more nodes it will have. In general, anti-bonding orbitals have higher energy and more nodes than their bonding counter parts.

MO energy comparison of localized with delocalized systems



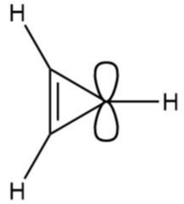
Molecular orbitals for delocalized acyclic vs cyclic systems

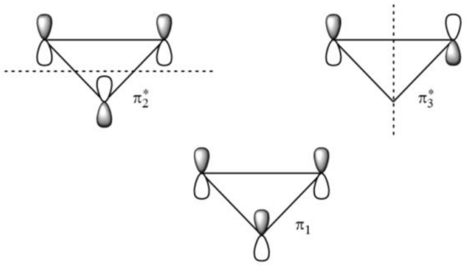
3 carbon acyclic…..…Allyl system



3 carbon cyclic…….cyclopropenyl system

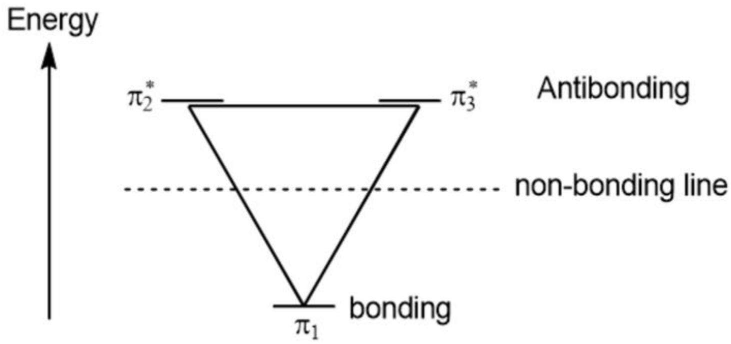
Cyclopropene is an organic three-membered cyclic ring compound with a molecular formula C_3H_4.It can exist as a cation which is an aromatic compound whereas cyclopropenyl anion is an antiaromatic compound depending upon the electrons.





MO diagram of cyclopropenyl

Representation of bonding, nonbonding and antibonding MO diagram of cyclopropenyl



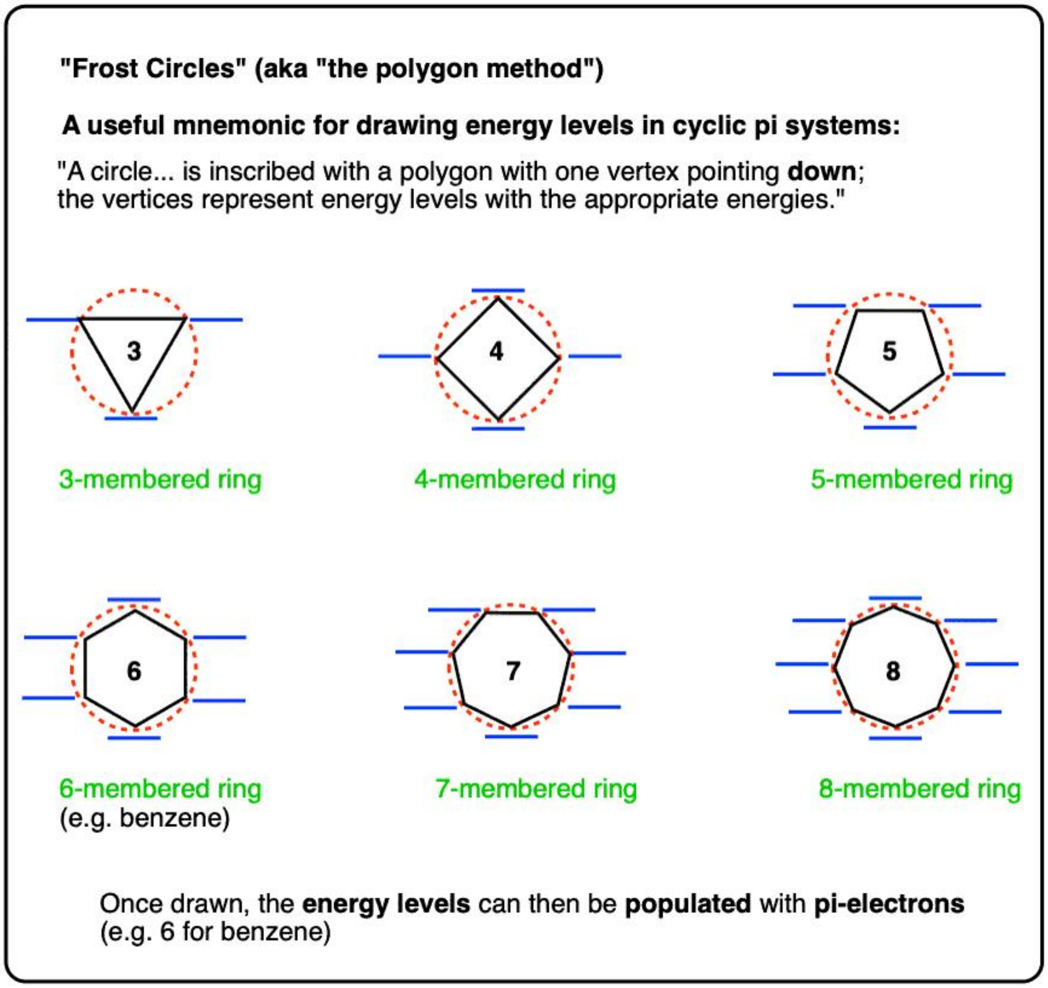
π_1 - Bonding molecular orbital

π_2^*, π_3^* - Antibonding molecular orbital

Frost Circles

A circle… is inscribed with a polygon with one vertex pointing down; the vertices represent energy levels with the appropriate energies".

Vertices below the halfway mark of the circle are considered **bonding orbitals**, and vertices above the halfway mark are considered **antibonding orbitals**. If vertices are exactly in the middle (as they are for 4- and 8- membered rings) they represent **non-bonding orbitals**.



"Frost Circles" (aka "the polygon method")

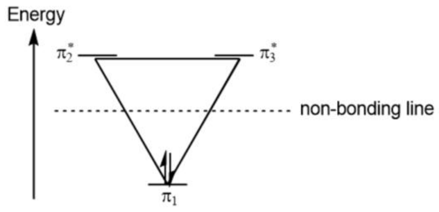
A useful mnemonic for drawing energy levels in cyclic pi systems:

"A circle... is inscribed with a polygon with one vertex pointing **down**;
the vertices represent energy levels with the appropriate energies."

Once drawn, the **energy levels** can then be **populated** with **pi-electrons**
(e.g. 6 for benzene)

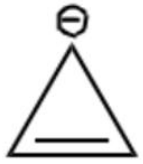
Thus, the cylopropenyl cation has two pi electrons. These two pi electrons are filled in the bonding molecular orbital.

Cylopropenyl cation

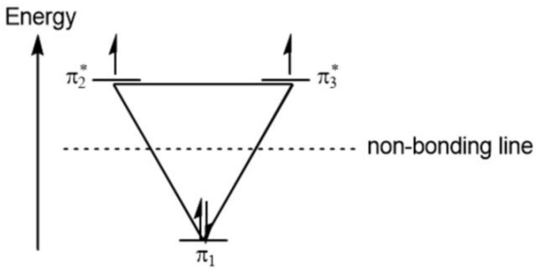


MO diagram of cylopropenyl cation

The cyclopropenyl anion has four pi electrons. These four pi electrons are filled in bonding molecular orbital and two degenerate antibonding molecular orbitals.

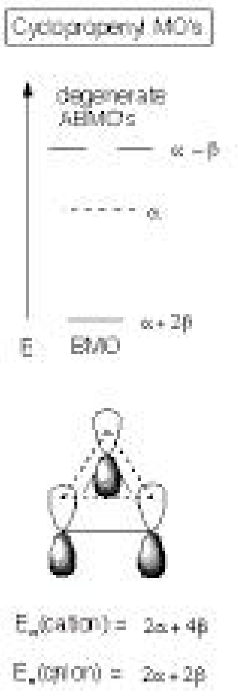


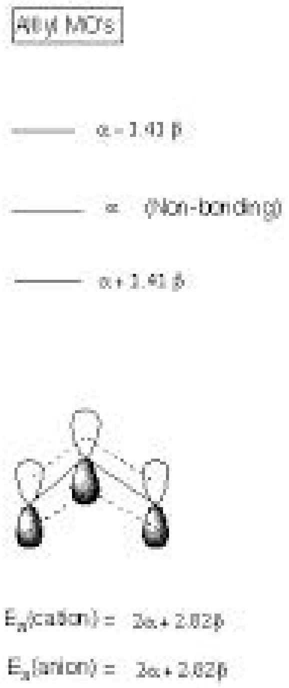
Cyclopropenyl anion



MO diagram of cylopropenyl anion

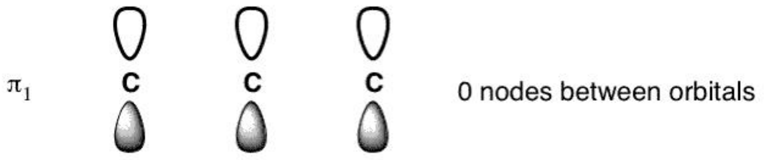
Allyl vs Cyclopropenyl Systems



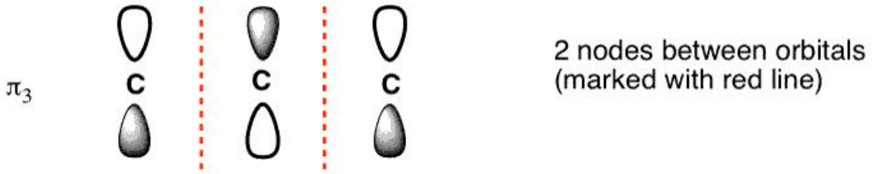


Remember the following points for drawing pi-MO’s

1. **The number of molecular orbitals (n) for a pi-system is equal to the number of contributing *p* orbitals.** For the allyl system, n=3. We had three contributing *p* orbitals and thus three pi molecular orbitals.
2. **The lowest-energy orbital always has zero nodes between the *p*-orbitals** *(note that we say “no nodes between the p-orbitals” because we’re not counting the node between the individual lobes, which is inherent to all p-orbitals).* That is, in the lowest-energy orbital, all phases of the contributing *p*-orbitals are aligned the same way.



3. **The number of nodes between *p*-orbitals increases by 1 for each successive energy level**, such that the highest-energy orbital has (n-1) nodes (all phases of contributing *p*-orbitals alternate).



4. **The lowest and highest energy orbitals are always the easiest pi molecular orbitals to draw.** It’s helpful to draw them first.

The trick to drawing the orbital(s) of intermediate energy is to understand where to put the node(s). Nodes are positioned in a way such that they are *symmetrical* relative to the centre. A system with 1 node has the node smack in the centre (right on the central atom, in fact). A system with 2 nodes will have the nodes at equal distance relative to the centre.

It’s helpful to draw out all the orbitals of the pi system first, and *then* add the pi-electrons to it.

Hückel Molecular Orbital Theory

An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of σ-bonds. This is, in fact, a more sophisticated version of a free-electron model. HMO theory is an approximate method which simplifies variation method to treat planar conjugated hydrocarbons. This theory treats the π electrons separately from σ electrons. Properties of the conjugated molecules are primarily determined by π-electrons.The

consideration of σ-π electro separation in a multi-electron molecule in HMO theory reduces the problem to the study of only π electrons. HMO calculations are carried out using variation method and LCAO(π)-MO approximation.

According to LCAO-MO approximation, the MO is written as,

$$\varphi_a = \sum_{i=1}^{n} c_i \psi_{2p_z i}$$

HMO theory approximates the π molecular orbitals as linear combination of atomic orbitals. For a planar conjugated hydrocarbon, the only atomic orbitals of π symmetry are the 2p π orbtials on carbon. In this module, we have consistently assumed the plane of the molecule as *x-y* plane with π orbital in the z axis, perpendicular to the molecular plane.

For a two π electron system φ_a becomes,

$$\varphi_a = c_1 \psi_{2pz1} + c_2 \psi_{2pz2}$$

Solving the energy of φa by using quantum mechanical calculation, we get

for *n*-π electron system leading to *n* energy levels and *n* molecular orbitals.

The energy of any a^{th} molecular orbital (MO) is given by

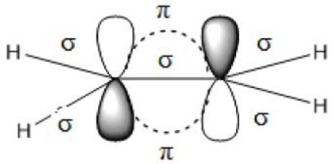
$$E_a = \alpha + x_a \beta$$

where x_a is the a^{th} root of the polynomial(in quantum mechanical calculations)

The values of the **coulomb integral α** and the **resonance integral β** are always negative. If the root x_a is positive, then the energy level corresponds to a more negative value and is more stable (Bonding molecular orbital) while a negative value of root gives antibonding molecular orbital.

Consider here the case of ethylene, C_2H_4 :--

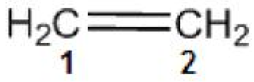
Ethylene is a 16 electron system but HMO theory reduces this to a two π electron system



Ethylene

HMO theory treats ethylene as a two electron problem, with one π electron on each carbon atom in p-orbital, perpendicular to the molecular plane. These two atomic orbitals (AOs) combine to form molecular orbitals (MOs).

Labeling the two carbons as 1 and 2,



$$\underset{1}{H_2C}=\underset{2}{CH_2}$$

We may write,

$$\varphi_a = c_1\psi_{2pz_1} + c_2\psi_{2pz_2}$$

So, the energies of the molecular orbitals are,(quantum mechanical calculations are done)

according to the formulas given :-

1. Linear system (polyene/polyenyl):

$$E_k = \alpha + 2\beta\cos\frac{(k+1)\pi}{N+1} \quad (k = 0, 1, \ldots, N-1).$$

here N = no. of atoms in the *pi*-system

2. Cyclic system (annulene/annulenyl):

$$E_k = \alpha + 2\beta\cos\frac{2k\pi}{N} \quad (k = 0, 1, \ldots, \lfloor N/2 \rfloor).$$

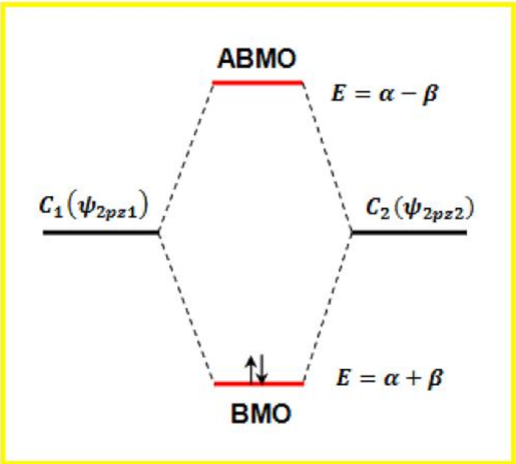
$k = 1, \ldots, \lceil N/2 \rceil - 1$ are each doubly degenerate.

N = no. of atoms in the *pi*-system

So, acoording to the linear system formula, the energies turn out to be:

$$E = \alpha + \beta \quad (Bonding\ Molecular\ Orbital \quad BMO)$$

$$E = \alpha - \beta \quad (Antibonding\ Molecular\ Orbital \quad ABMO)$$



HMO energy level diagram for ethylene

Total (π bond) energy = 2(α + β)
[As there are two electrons in the orbital with energy α+β]

The sum of the squares of the coefficients is always unity.

Molecular orbital	λ	E	c1	c2	Number of nodes
BMO	-1	α+β	$c = \frac{1}{\sqrt{2}}$	$c = \frac{1}{\sqrt{2}}$	0
ABMO	1	α-β	$c = \frac{1}{\sqrt{2}}$	$c = -\frac{1}{\sqrt{2}}$	1

Now consider 1,3,butadiene:---

Butadiene CH_2=CH-CH=CH_2. From four *p* atomic orbitals with nodes in the plane of the carbon skeleton, one can construct four π- molecular orbitals by an extension of the LCAO approach:

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4$$

Energies thus after calculation come out to be:

$$E = \alpha + 1.618\beta \quad (Bonding\ Molecular\ Orbital\ \ BMO)$$
$$E = \alpha - 1.618\beta \quad (Antibonding\ Molecular\ Orbital\ \ ABMO)$$
$$E = \alpha + 0.618\beta \quad (Bonding\ Molecular\ Orbital\ \ BMO)$$
$$E = \alpha - 0.618\beta \quad (Antibonding\ Molecular\ Orbital\ \ ABMO)$$

$$Total\ (\pi\ bond)ergy = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$
$$Total\ (\pi\ bond)ergy = 4\alpha + 4.472\beta$$

Now, we know that the sum of squares of coefficients is always 1,

So,

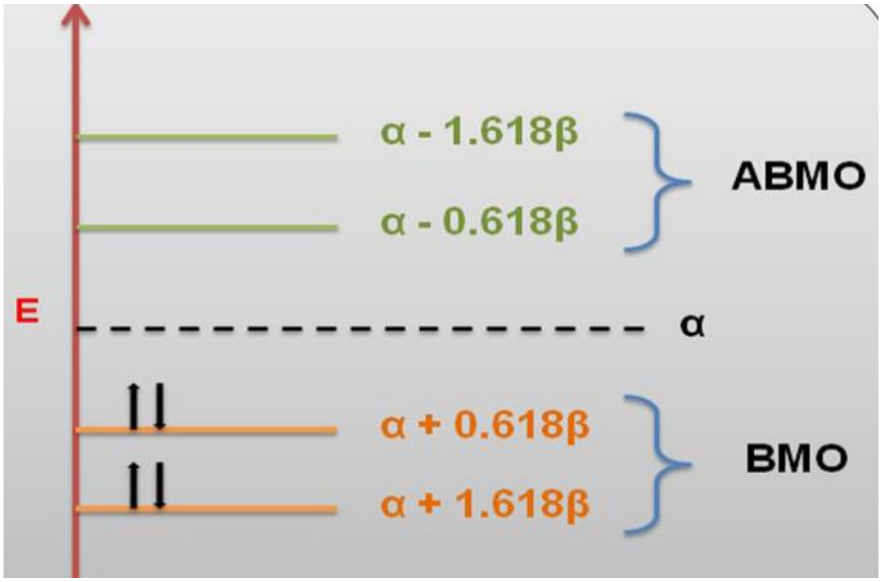
$$c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$$

$$\varphi_1 = 0.372\psi_{2p_{z1}} + 0.602\psi_{2p_{z2}} + 0.602\psi_{2p_{z3}} + 0.372\psi_{2p_{z4}}$$

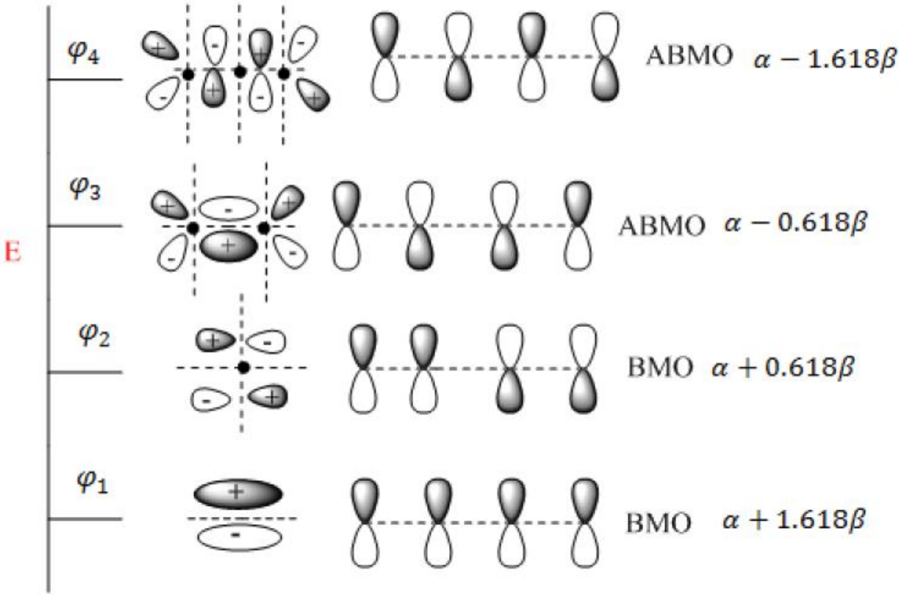
$$\varphi_2 = 0.602\psi_{2p_{z1}} + 0.372\psi_{2p_{z2}} - 0.372\psi_{2p_{z3}} - 0.602\psi_{2p_{z4}}$$

$$\varphi_3 = 0.602\psi_{2p_{z1}} - 0.372\psi_{2p_{z2}} - 0.372\psi_{2p_{z3}} + 0.602\psi_{2p_{z4}}$$

$$\varphi_4 = 0.372\psi_{2p_{z1}} - 0.602\psi_{2p_{z2}} + 0.602\psi_{2p_{z3}} - 0.372\psi_{2p_{z4}}$$



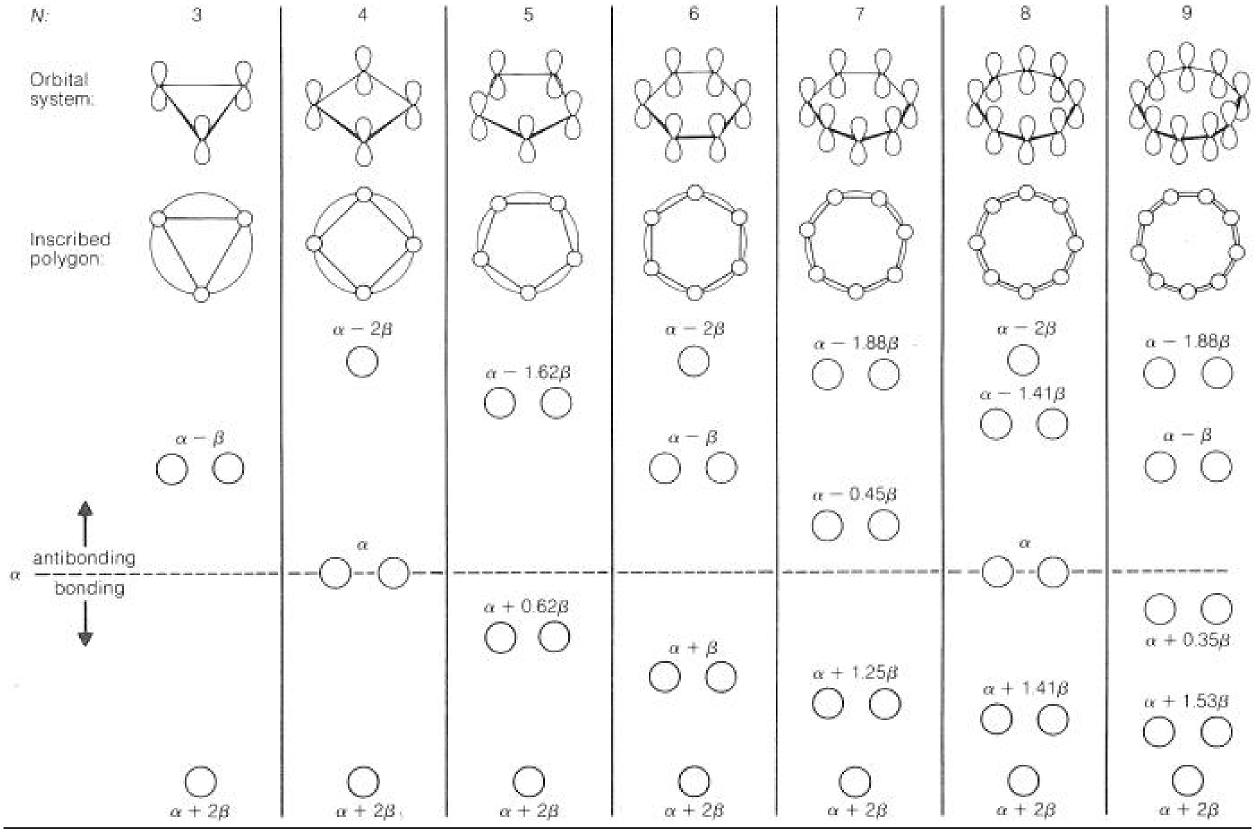
The MO's look like the following:



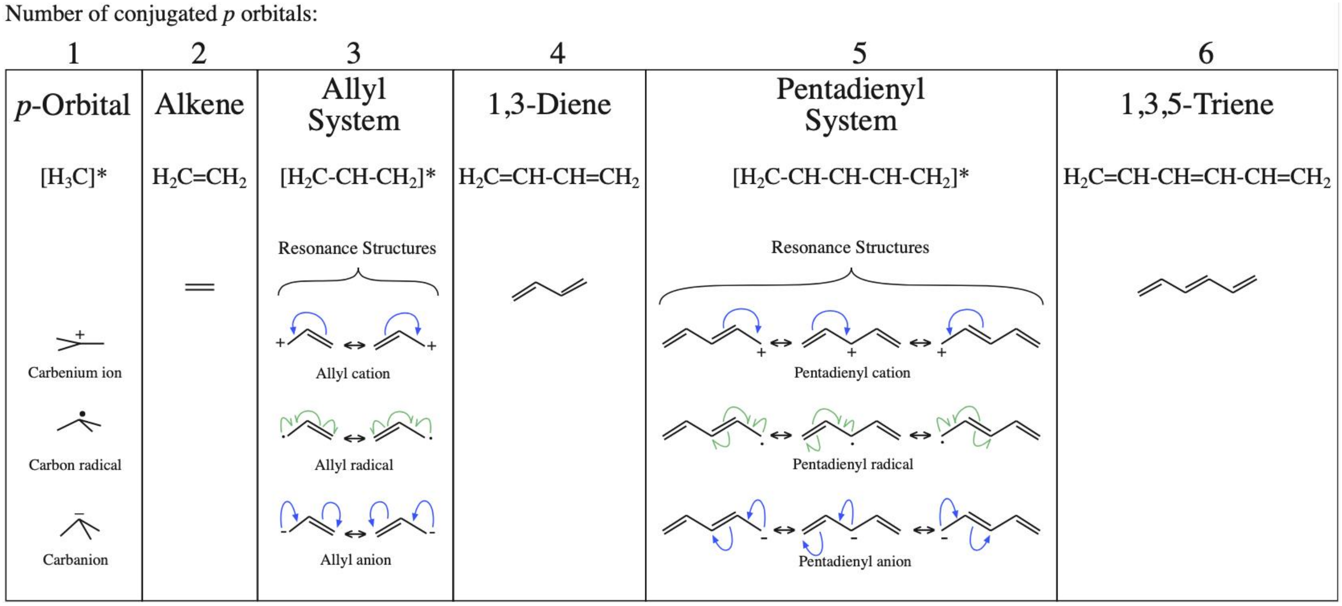
Resonance energy is defined as the difference in the energy of π electrons in a molecule and the sum of energies of isolated double bond

$$E_{\pi(resonance\ energy)} = E_{\pi} - E_{ethylene} = 4\alpha + 4.472\beta - 2(2\alpha + 2\beta) = 0.472\beta$$

Higher-energy molecular orbitals for cyclic conjugated polyenes are predicted to come in successive degenerate pairs:-



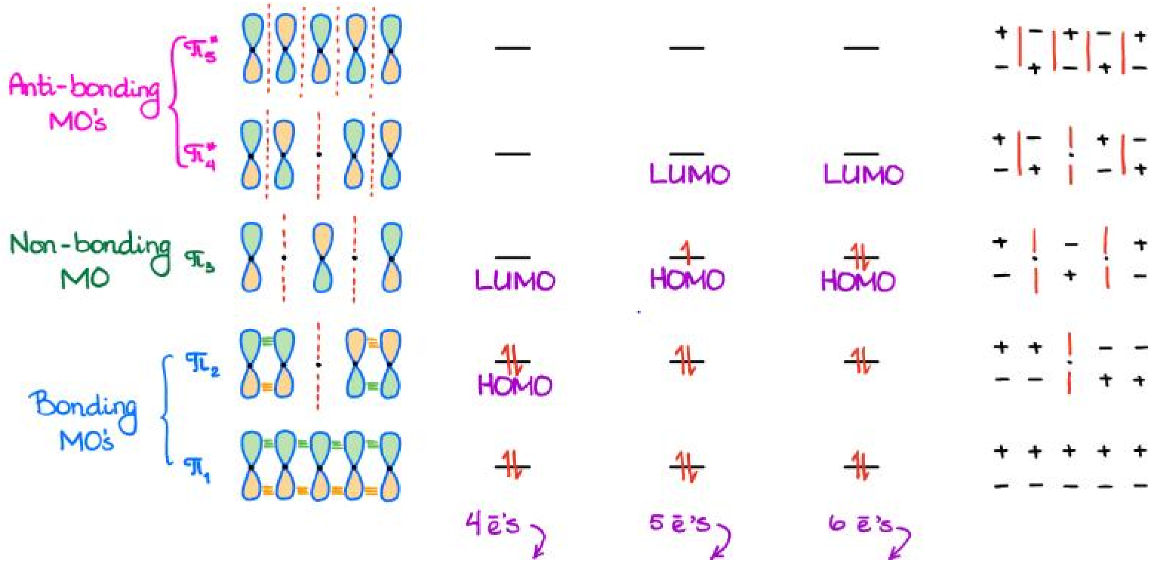
For acyclic systems



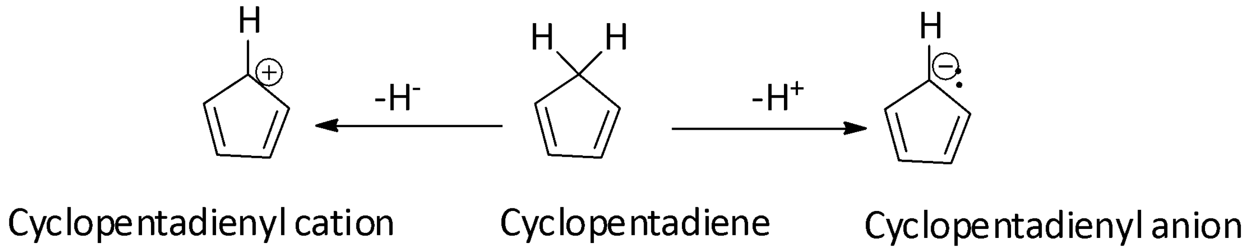
Number of conjugated *p* orbitals:

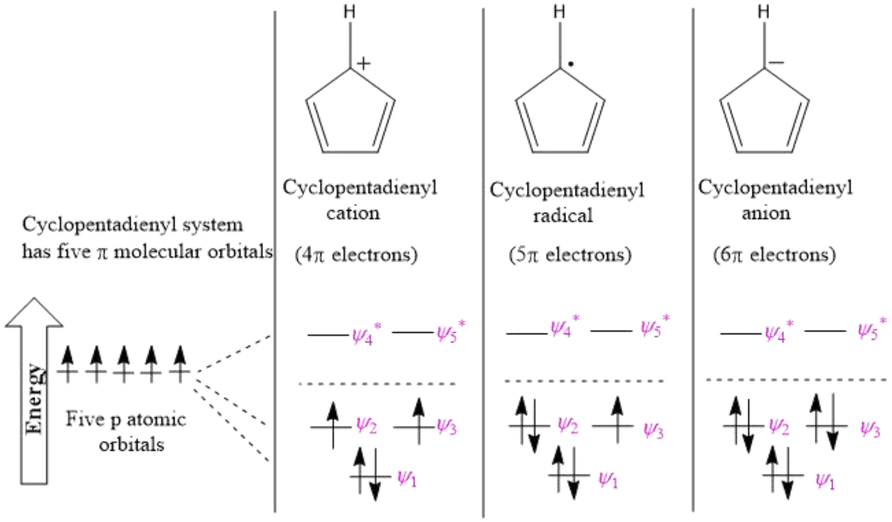
1	2	3	4	5	6
p-Orbital	Alkene	Allyl System	1,3-Diene	Pentadienyl System	1,3,5-Triene
$[H_3C]^*$	$H_2C{=}CH_2$	$[H_2C\text{-}CH\text{-}CH_2]^*$	$H_2C{=}CH\text{-}CH{=}CH_2$	$[H_2C\text{-}CH\text{-}CH\text{-}CH\text{-}CH_2]^*$	$H_2C{=}CH\text{-}CH{=}CH\text{-}CH{=}CH_2$
Carbenium ion Carbon radical Carbanion		Resonance Structures Allyl cation Allyl radical Allyl anion		Resonance Structures Pentadienyl cation Pentadienyl radical Pentadienyl anion	

Pentadienyl system:

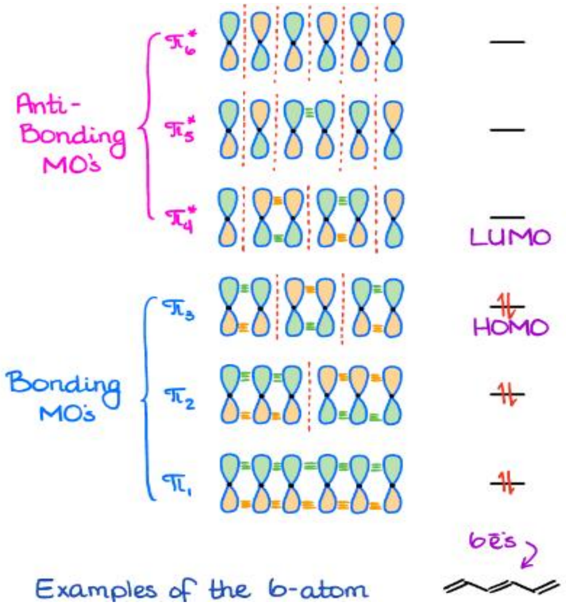


Cyclopentadienylic system

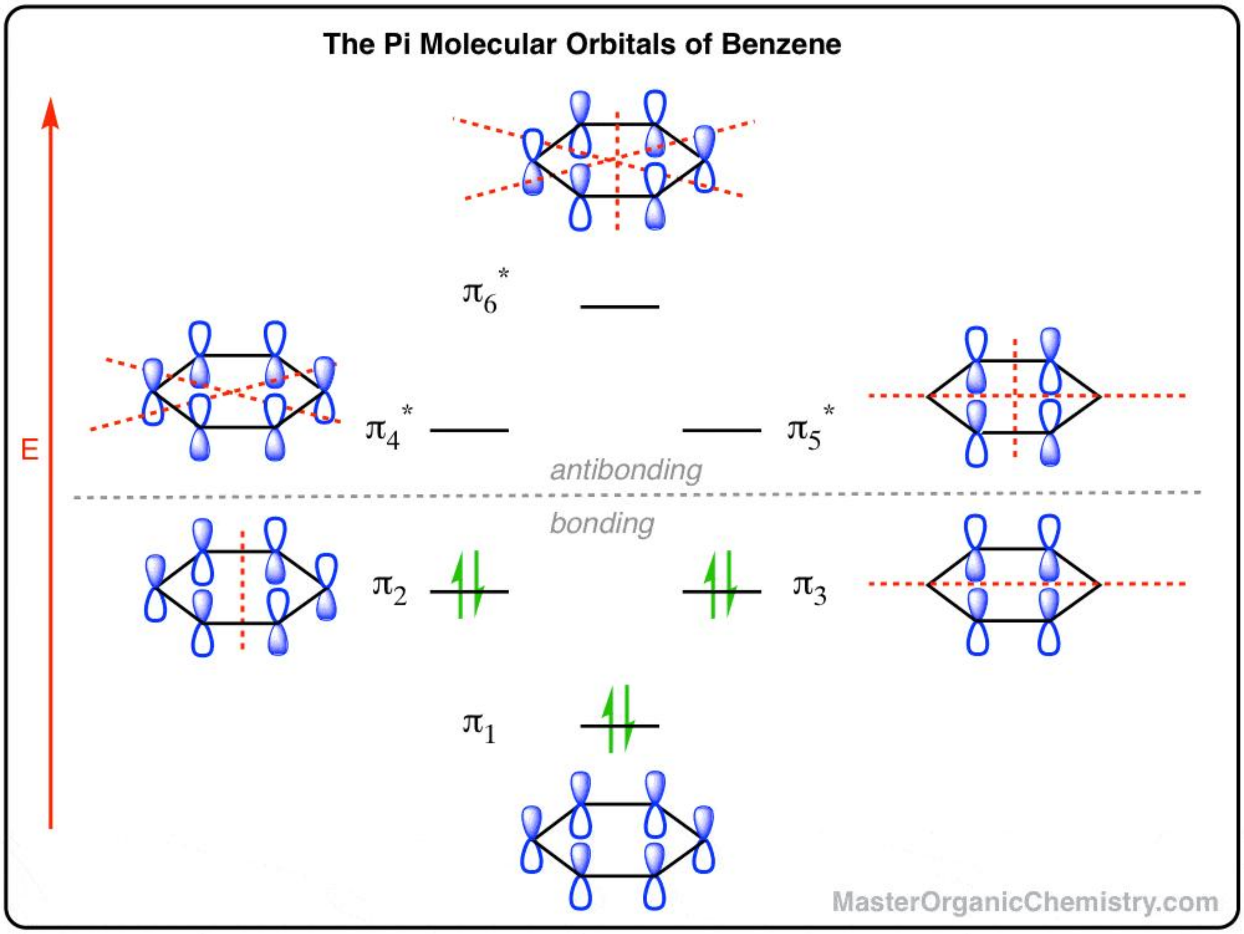


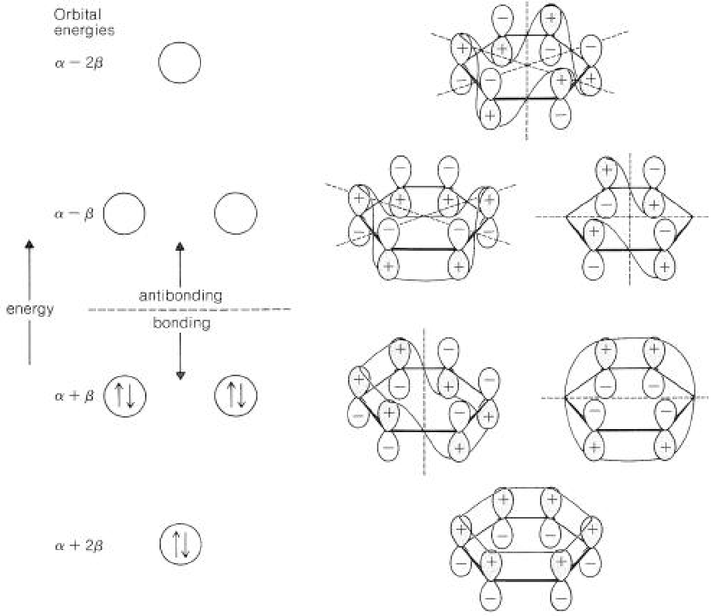


Hexatriene System:



Benzene


The Pi Molecular Orbitals of Benzene
E
π_6^*
π_4^*
π_5^*
antibonding
bonding
π_2
π_3
π_1
MasterOrganicChemistry.com


Orbital energies
$\alpha - 2\beta$
$\alpha - \beta$
energy
antibonding
bonding
$\alpha + \beta$
$\alpha + 2\beta$

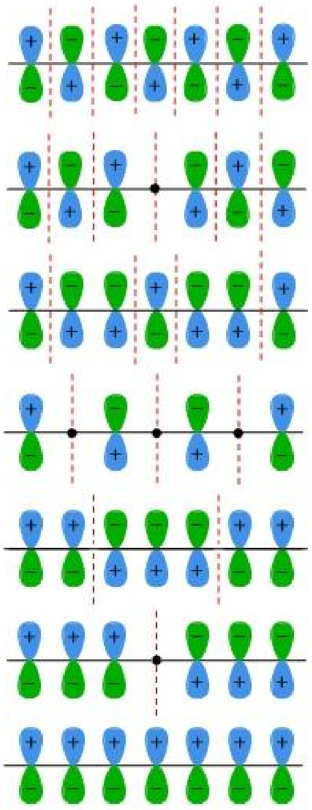
The calculated *delocalization energy* for benzene is the difference between these quantities

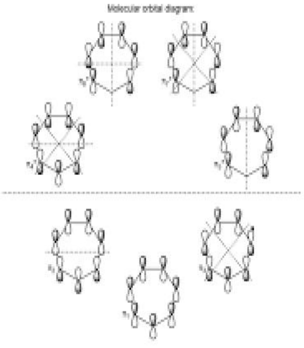
$(6\alpha+8\beta)-(6\alpha+6\beta)=2\beta(6\alpha+8\beta)-(6\alpha+6\beta)=2\beta$

That is to say, the calculated delocalization energy is the difference between the energy of benzene with full π bonding and the energy of 1,3,5-cyclohexatriene with alternating single and double bonds.

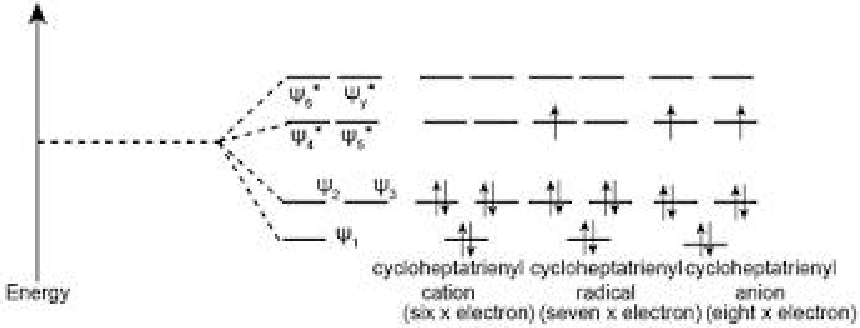
If the electron delocalization energy (2β) is equal to the stabilization energy (38kcal mol^{-1}), then β=19kcal $\text{mol}^{-1.}$. The results of the calculations do account for the fact that benzene is more stable than would be expected for 1,3,5-cyclohexatriene.

Heptatrienyl and cycloheptatrienyl System

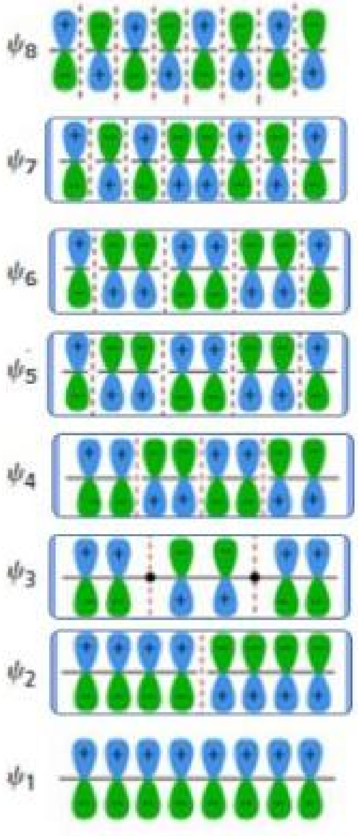


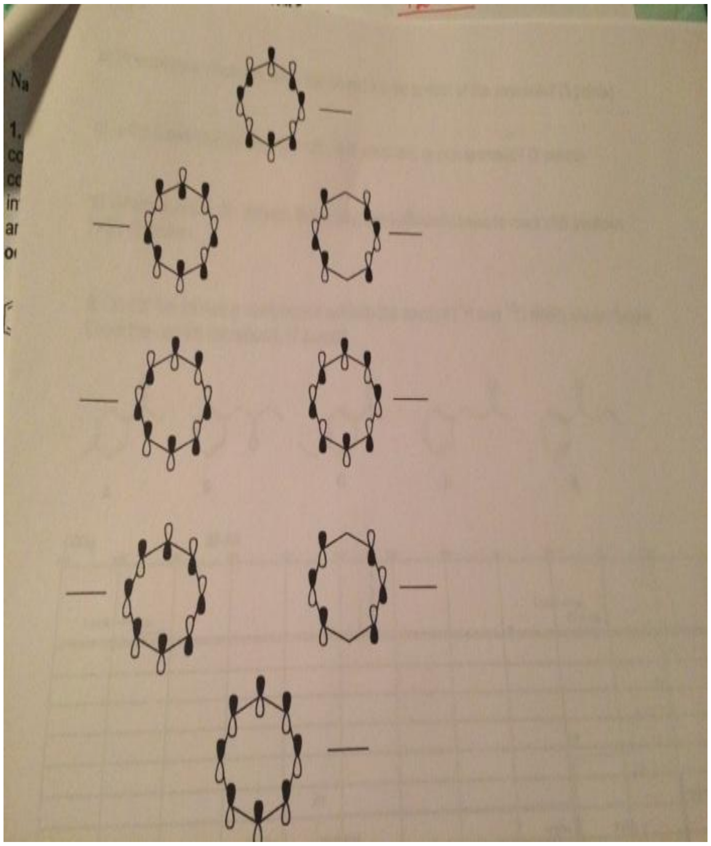


Cycloheptatrienyl cation is specially called ***tropylium ion***



Octatetraene and Cyclooctatetraene (COT)

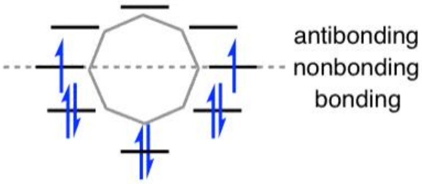




n = 8 Example of an 8-membered ring pi-system

Cyclooctatetraene

(8 pi electrons)



Predicted to be **antiaromatic**

(but is actually non-aromatic, since it can "escape" from antiaromaticity through twisting into a tub-like shape)