

Molecular Orbitals and Huckel Theory For Conjugated Systems

In this topic we will discuss

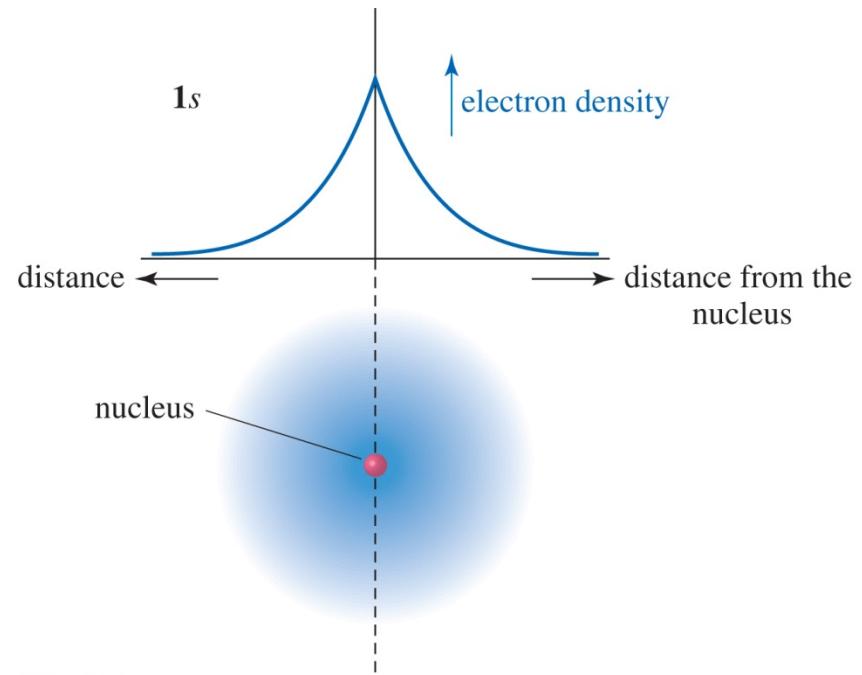
- What are Molecular orbitals? How are they formed? HOMO and LUMO? Why MOT?
- About empty cups and FMO approach
- How to construct MO diagrams of conjugated polyenes?
- How to calculate the energy of MOs of polyenes?
- Huckel Theory for conjugated systems
- Stability of Benzene
- Aromaticity and its effect on properties
- How do we use MOs for rationalizing and predicting the course of organic reactions?

Wave nature of electrons

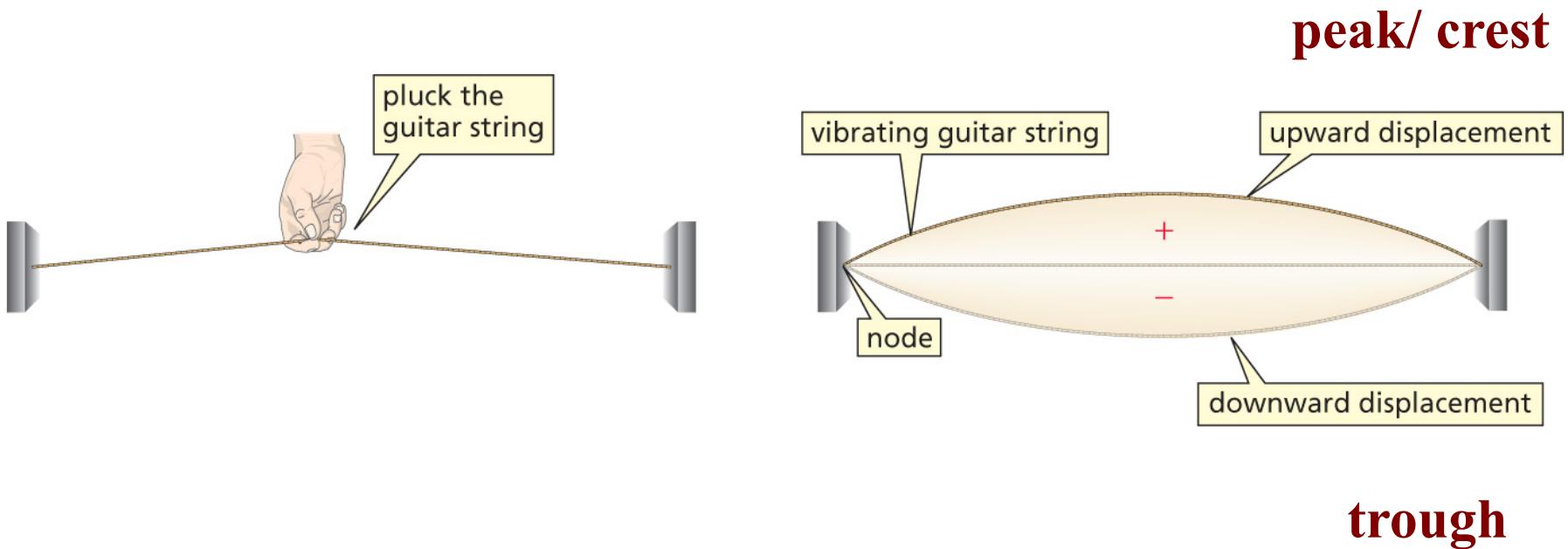
- Dual nature : Particle (Charge, mass), wave (diffraction)
- Quantum mechanics invokes that in submicroscopic world, there is no real distinction between particles and waves.
- *Heisenberg's uncertainty principle*
The exact position and momentum of the electron cannot be specified; only the probability of finding an electron in a certain region of space can be specified.
- An atomic orbital is a three-dimensional region around the nucleus where there is a high probability of finding an electron. It is a description of wave properties of electron in an atom. It is described by a mathematical function called a wave function (ψ).

Electronic Structure of the Atom

- An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.
- The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.

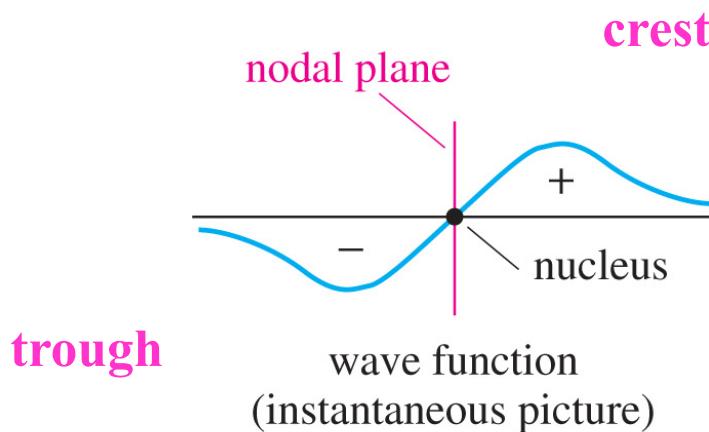


A Standing Wave

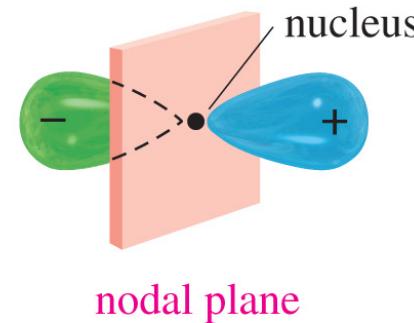


Electron behaves like a standing wave
But it is more like a 3 Dimensional surface

Wave Properties of Electrons/Orbitals



represented by



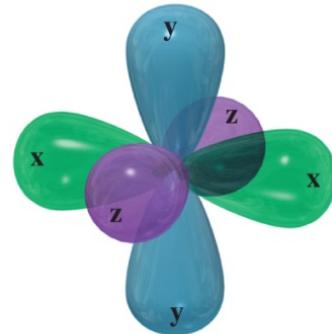
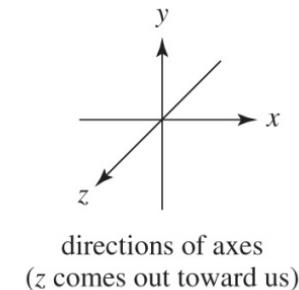
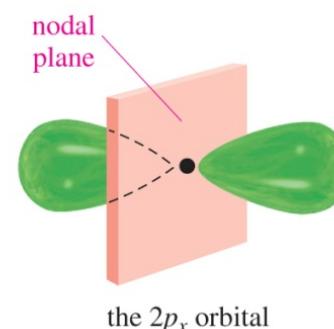
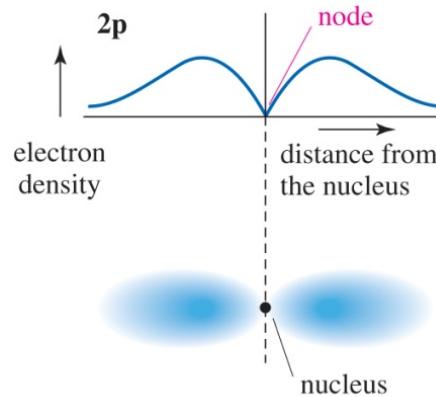
- Standing wave vibrates in fixed location.
- Wave function, ψ , is a mathematical description of size, shape, and orientation.
- Amplitude may be positive or negative.
- Node: Amplitude is zero.
- (+) & (-) do not indicate charges but just the phase
- ψ^2 denotes the electron density probability.



computer-generated
2p atomic orbital

The 2p Orbitals

- There are three 2p orbitals, oriented at right angles to each other.
- Each p orbital consists of two lobes.
- Each is labeled according to its orientation along the x, y, or z axis.



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<http://winter.group.shef.ac.uk/orbitron>

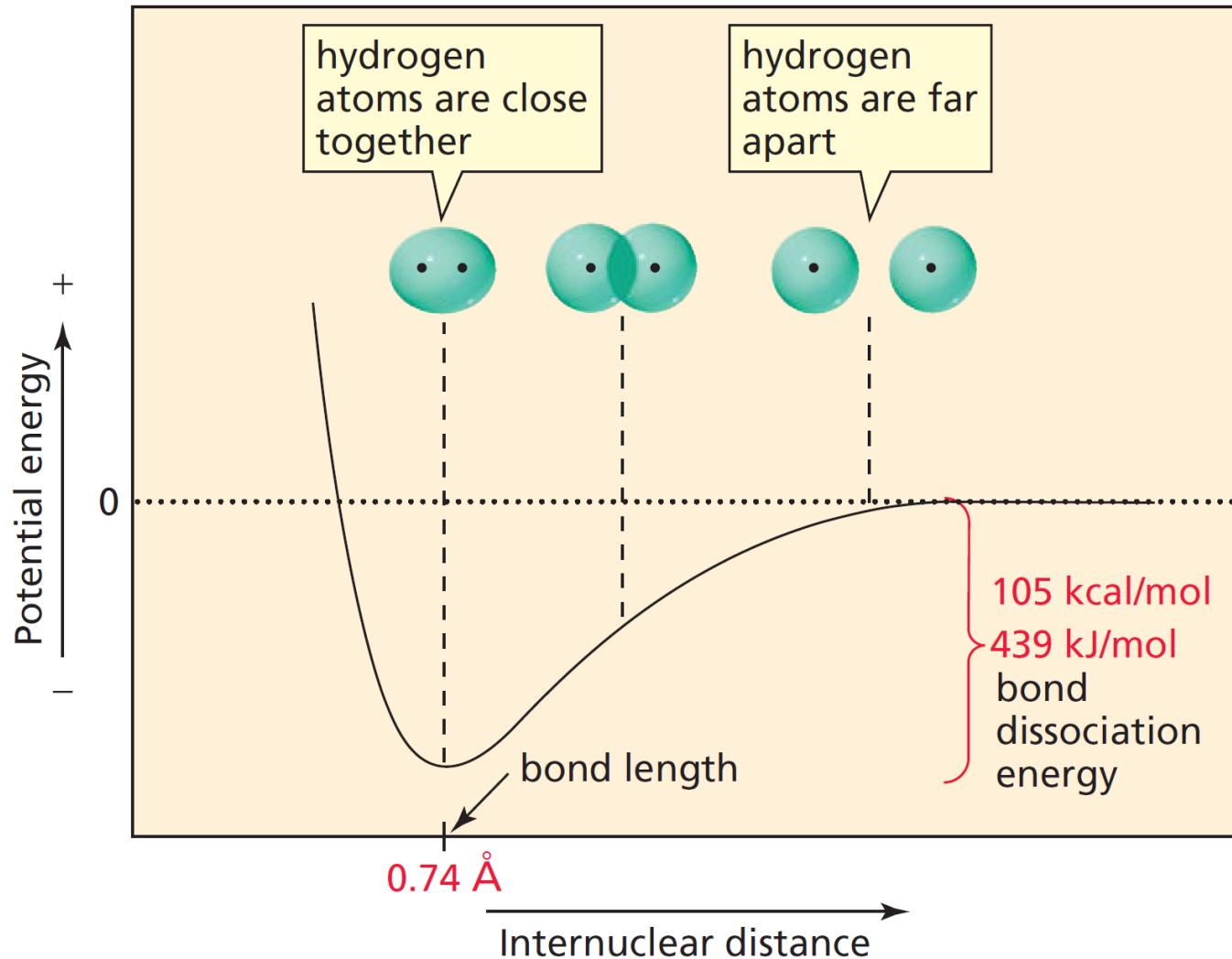
Molecular Orbital Theory

- How a covalent bond is formed?
- The Lewis model treats electrons like particles and not like waves
- MOT combines their wave like properties and the tendency to complete the octet by sharing electrons – complete picture
- Covalent bonds form when AOs combine to form MOs

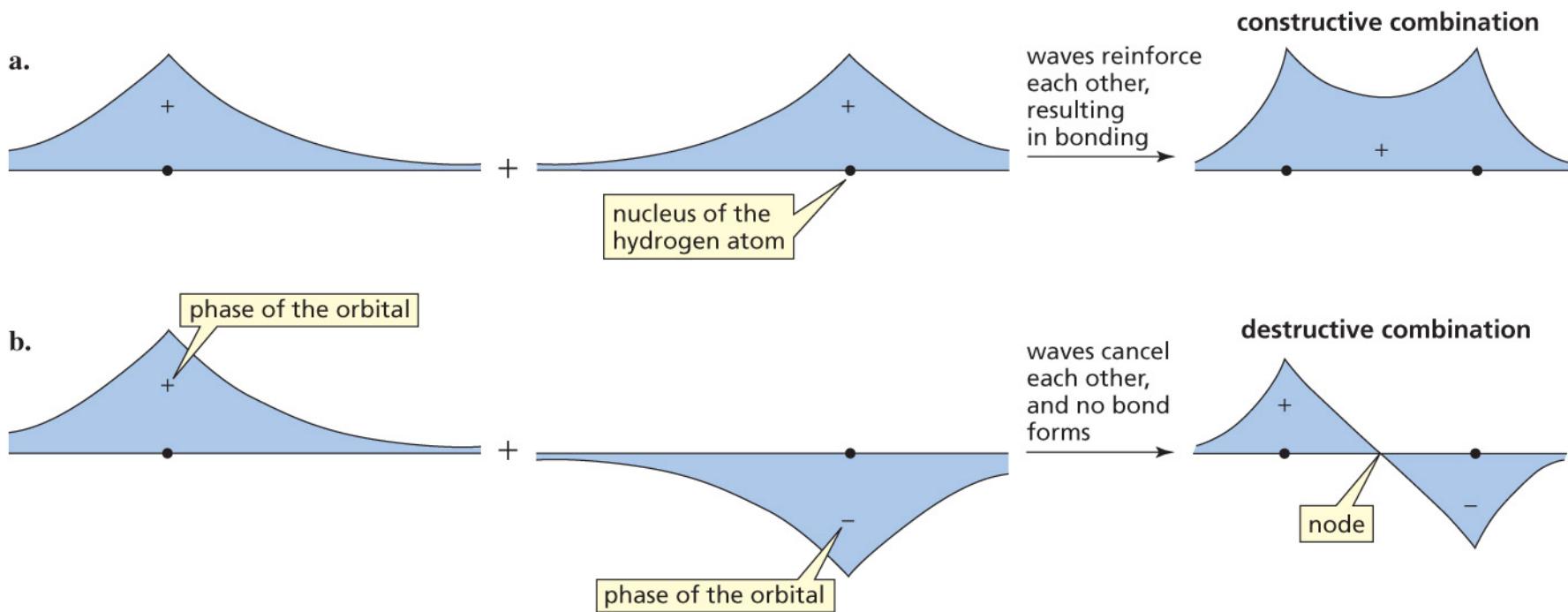
Linear Combination of Atomic Orbitals

- Combining orbitals on the same atom is *hybridization*.
- Combining orbitals between two different atoms is *bond formation*. – M. O. Theory
- Description of the electron distribution over the whole molecule
- Molecular orbitals are formed by LCAO
- MOs belong to the whole molecule
- MOs have specific sizes, shapes & energy
- Conservation of orbitals – 2 AOs give 2 MOs
- Waves that are in phase add together
- Waves that are out of phase cancel out.

MO Theory : H₂ molecule



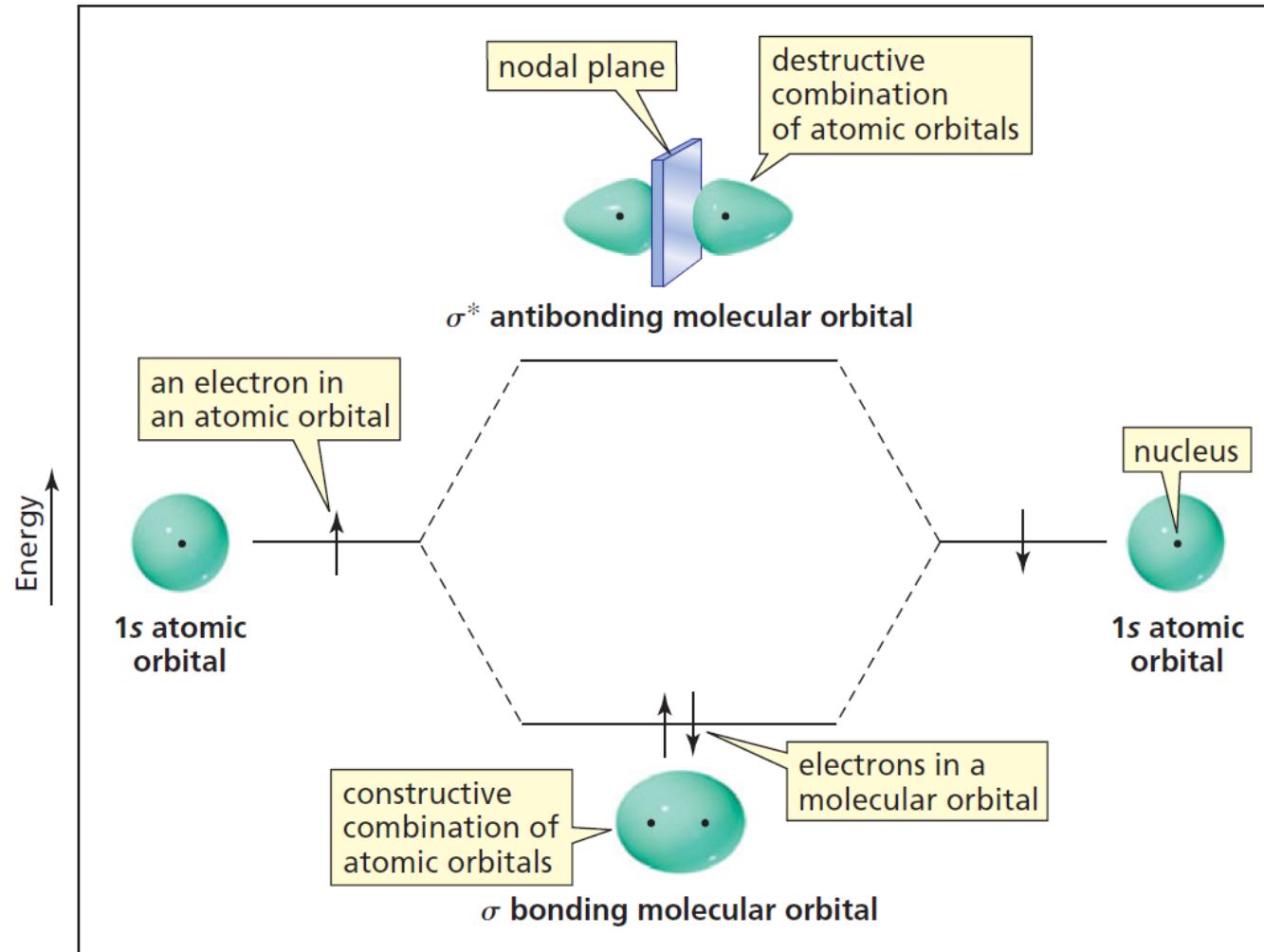
Waves Can Reinforce Each Other; Waves Can Cancel Each Other



Constructive combination = bonding

Destructive combination = antibonding

Molecular orbitals of H₂



Electrons are assigned based on aufbau principle, Pauli exclusion principle and Hund's rule. Lowest energy first and no more than two electrons per MO

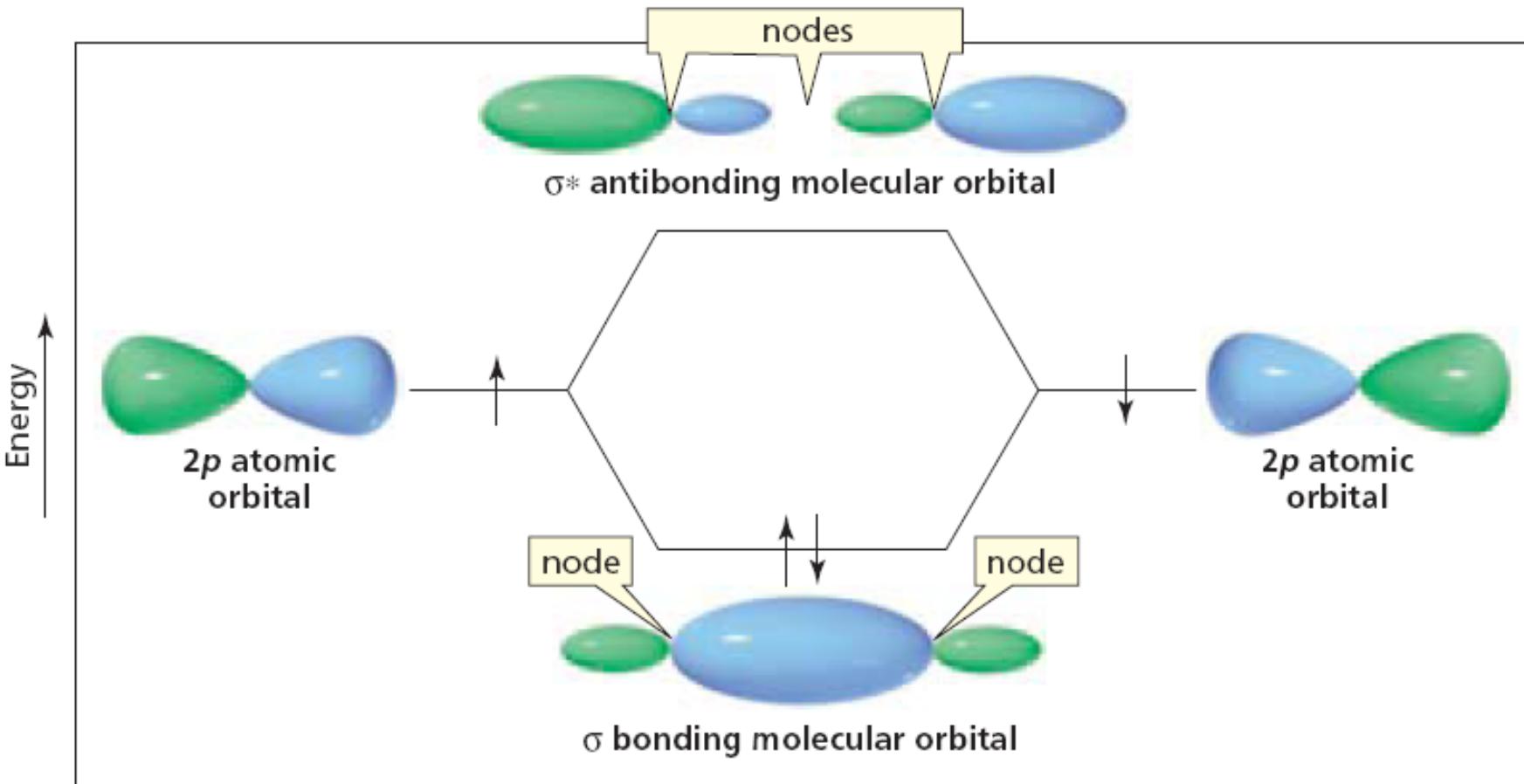
Bonding and antibonding orbitals

Electrons in a Bonding MO assist in bonding – Bond formation

Electrons in an antibonding MO detract from bonding – Bond breaking

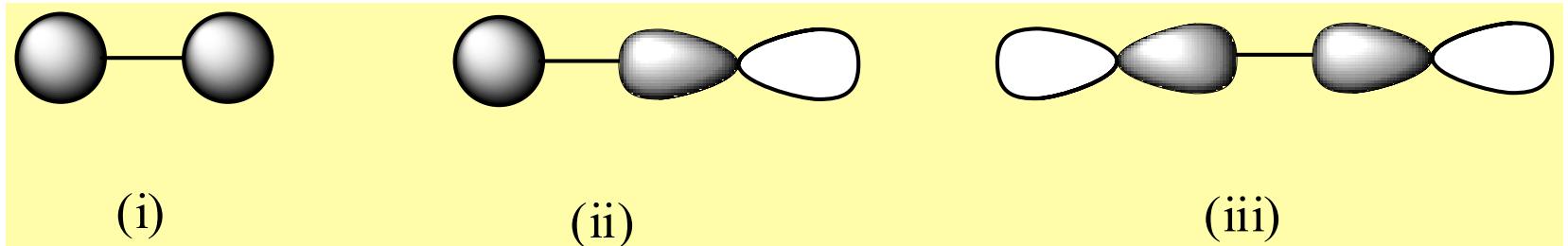
Covalent Bond strength increases as the atomic overlap increases

End on overlap of two p AOs



**Sigma bonding MO are cylindrically symmetrical
i.e. along inter-nuclear axis**

More on sigma orbitals

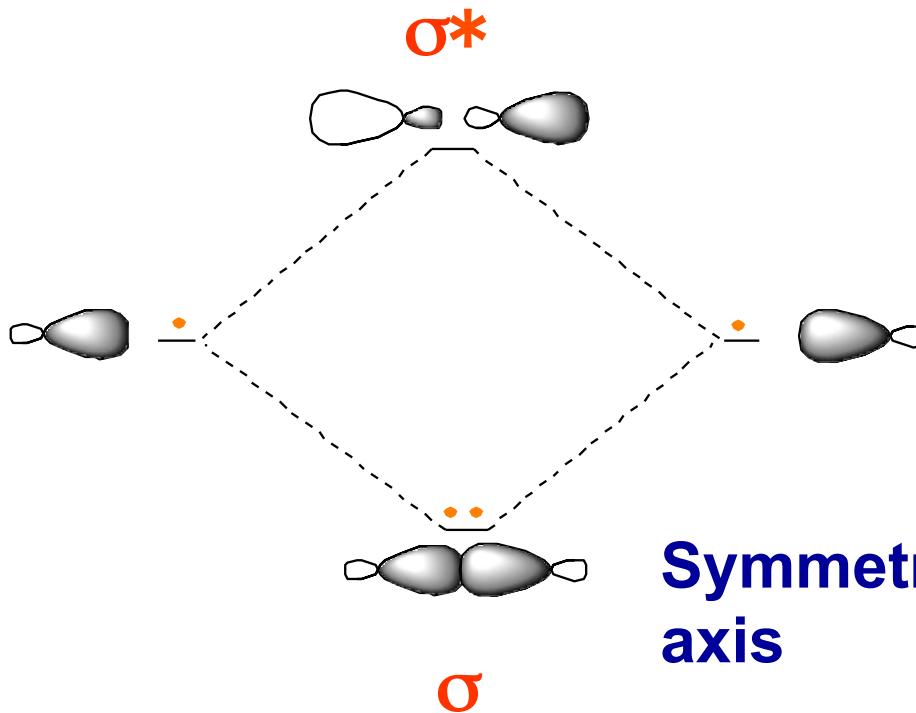
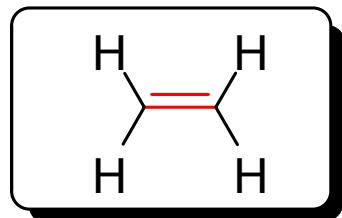


σ

sigma-type overlaps contain no nodes along the internuclear region/axis.

Symmetric along the axis

Orbital Symmetry in ethylene



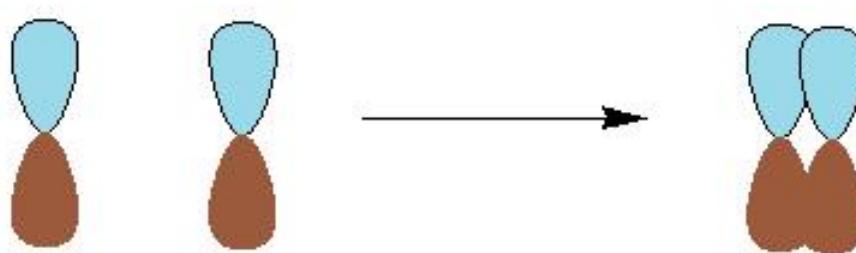
For any bonding molecular orbital (BMO) there should be a corresponding antibonding molecular orbital (ABMO)

Because the π -bonding portion of a molecule is perpendicular to the σ -bond framework, the π -bonds can be treated independently.

Types of overlap between orbitals

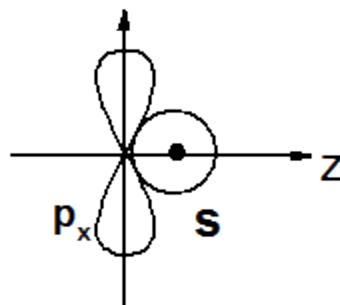
lateral overlap of atomic orbitals

(iv)

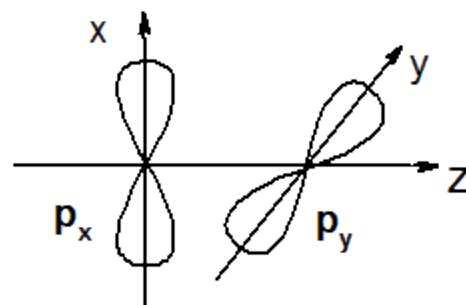


p-p orbital overlapping

Sideways overlapping of p orbitals produces a pi covalent bond



No overlap between s and P_x



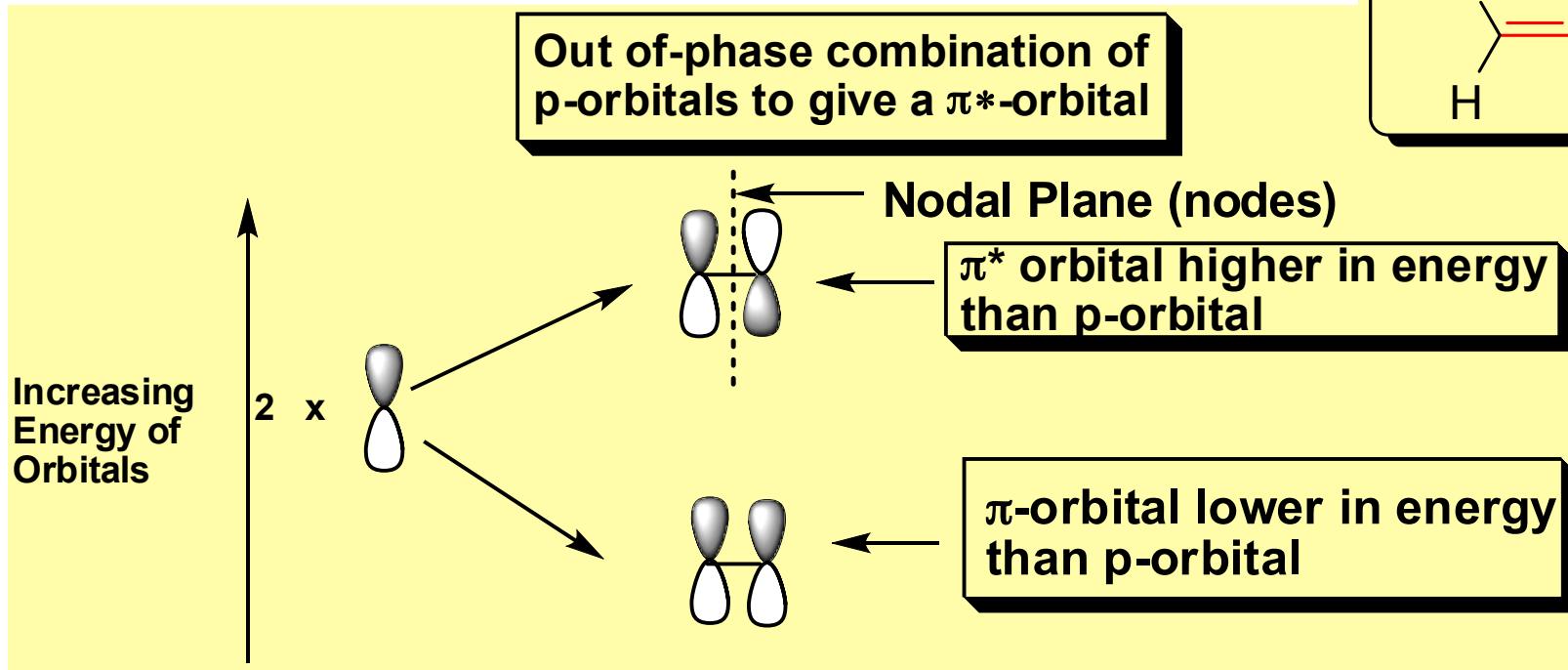
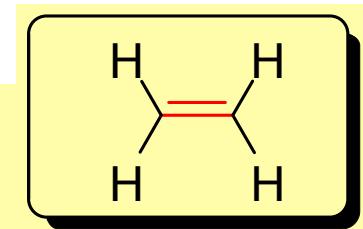
No overlap between P_x and P_y

Ethylene MOs

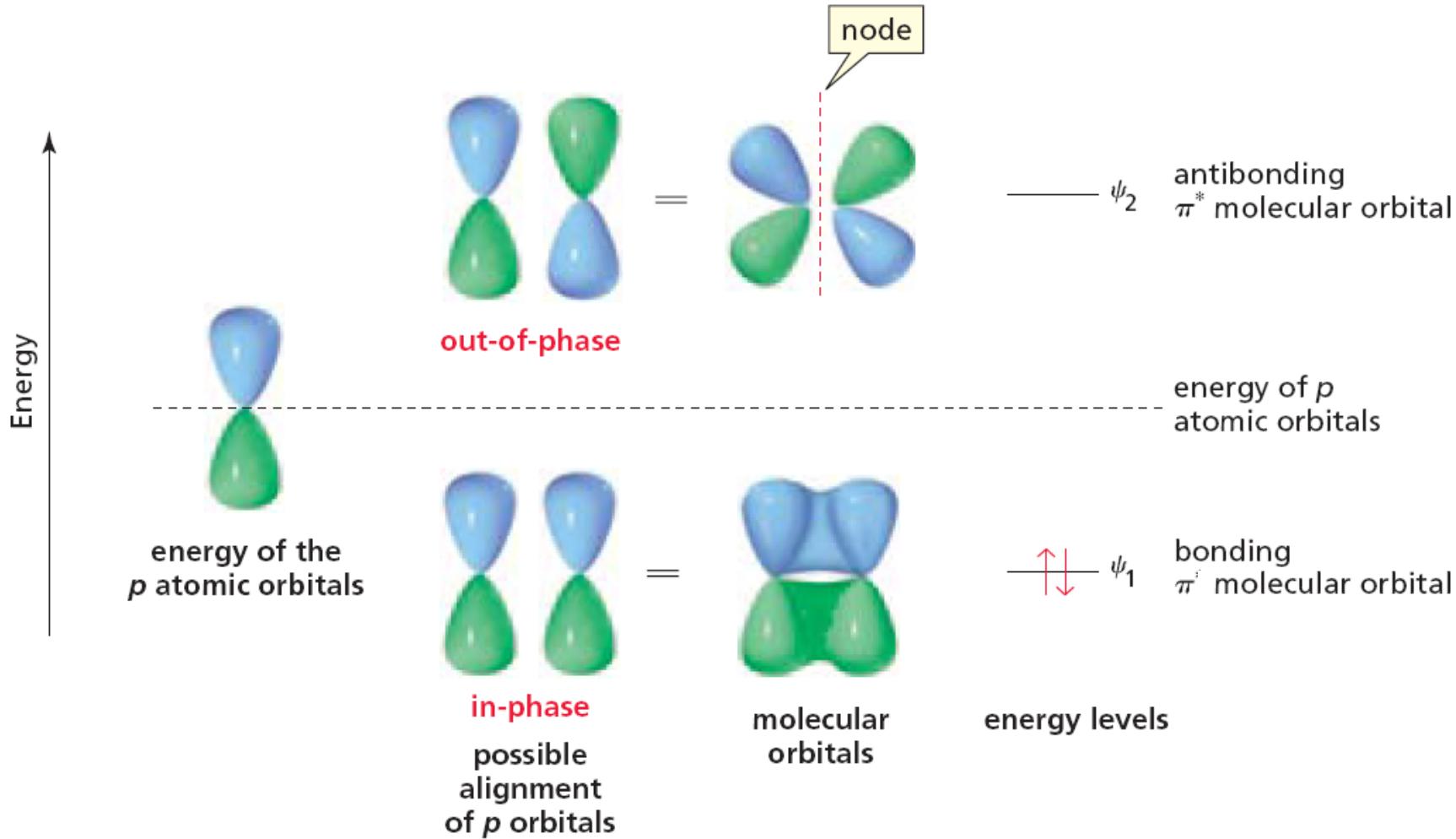
Ethylene shows interesting properties due to the presence of a π -bond

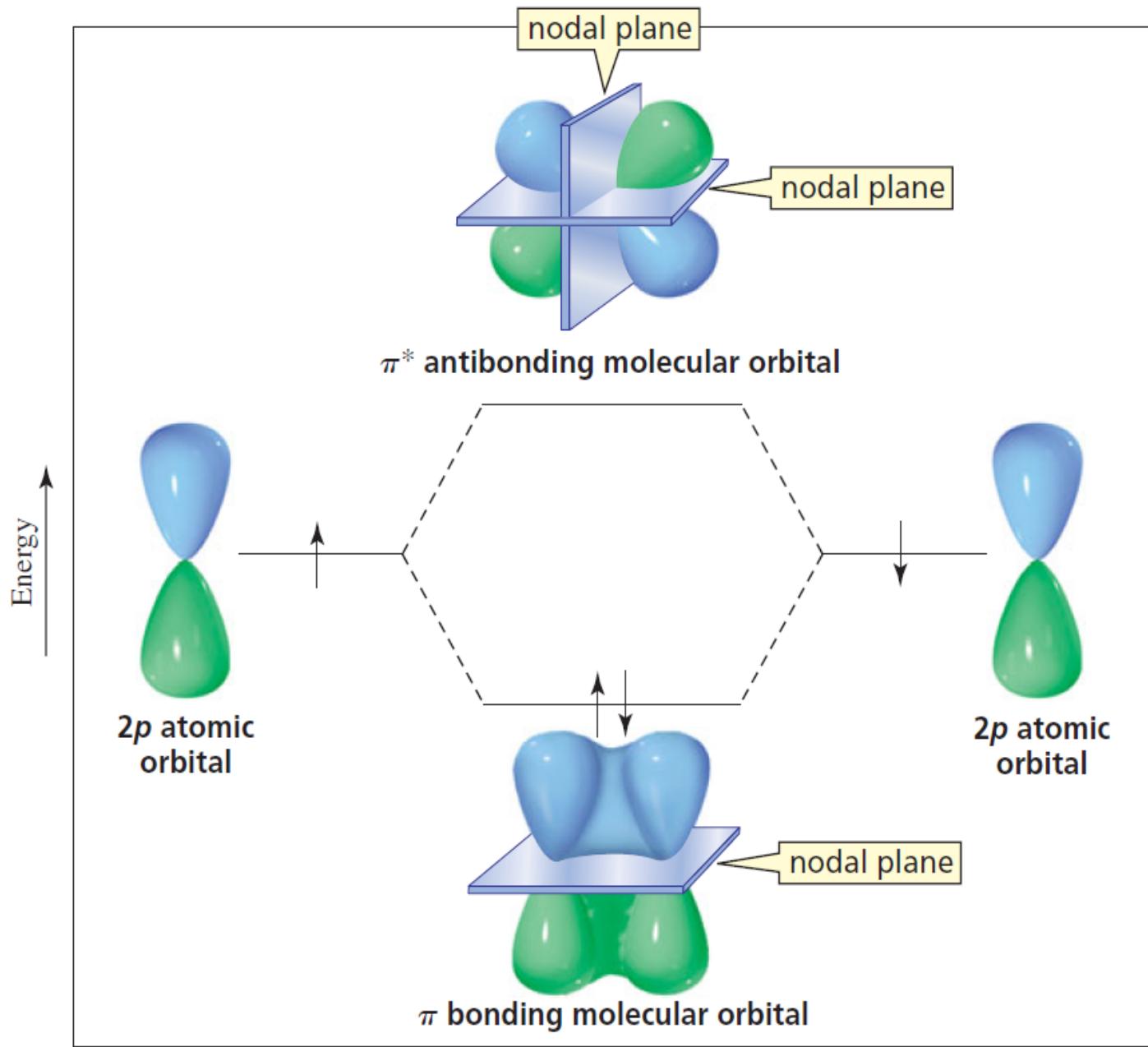
The C-C π -orbital is the **Highest Occupied Molecular Orbital (HOMO)** of the alkene

Linear Combination of p-orbitals, leading to C-C π -orbital can be represented as,



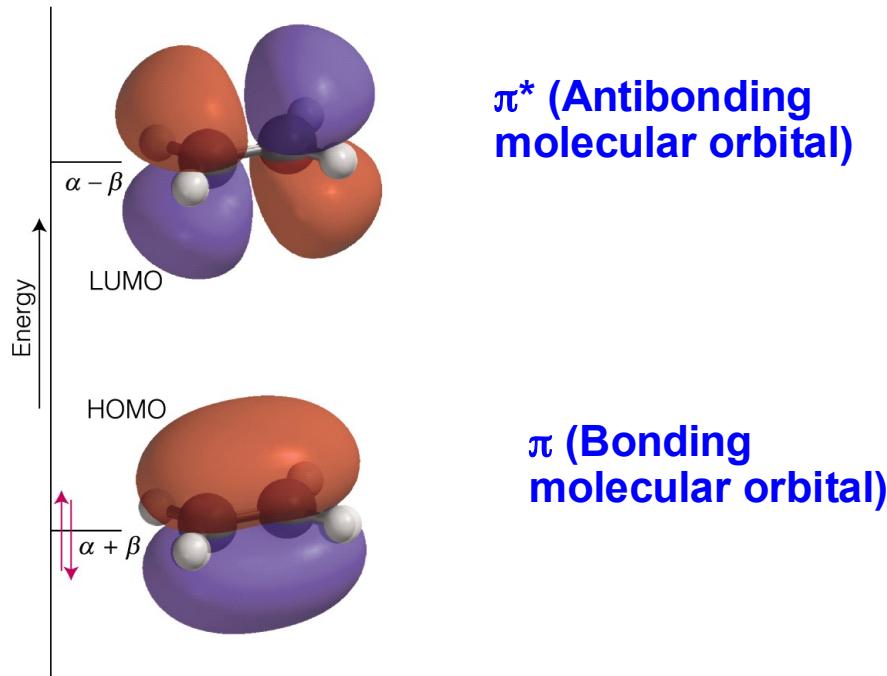
Side-to-side overlap of two p AOs





Ethylene MOs

Increasing
Energy of
Orbitals

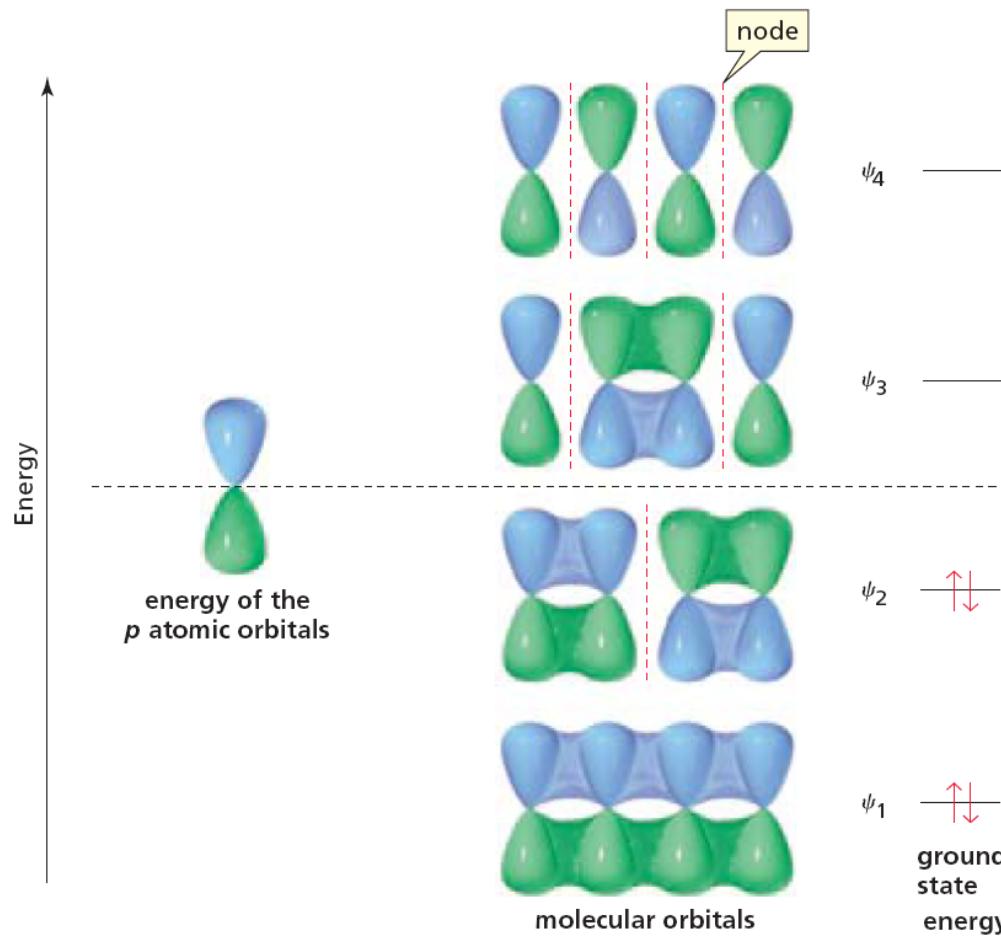


Total Number of π -electrons = 2

Total Number of π -orbitals = 2

Both electrons will occupy the lowest energy MO, i.e., BMO

Butadiene MOs

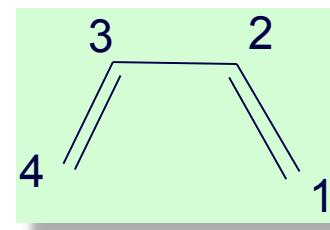
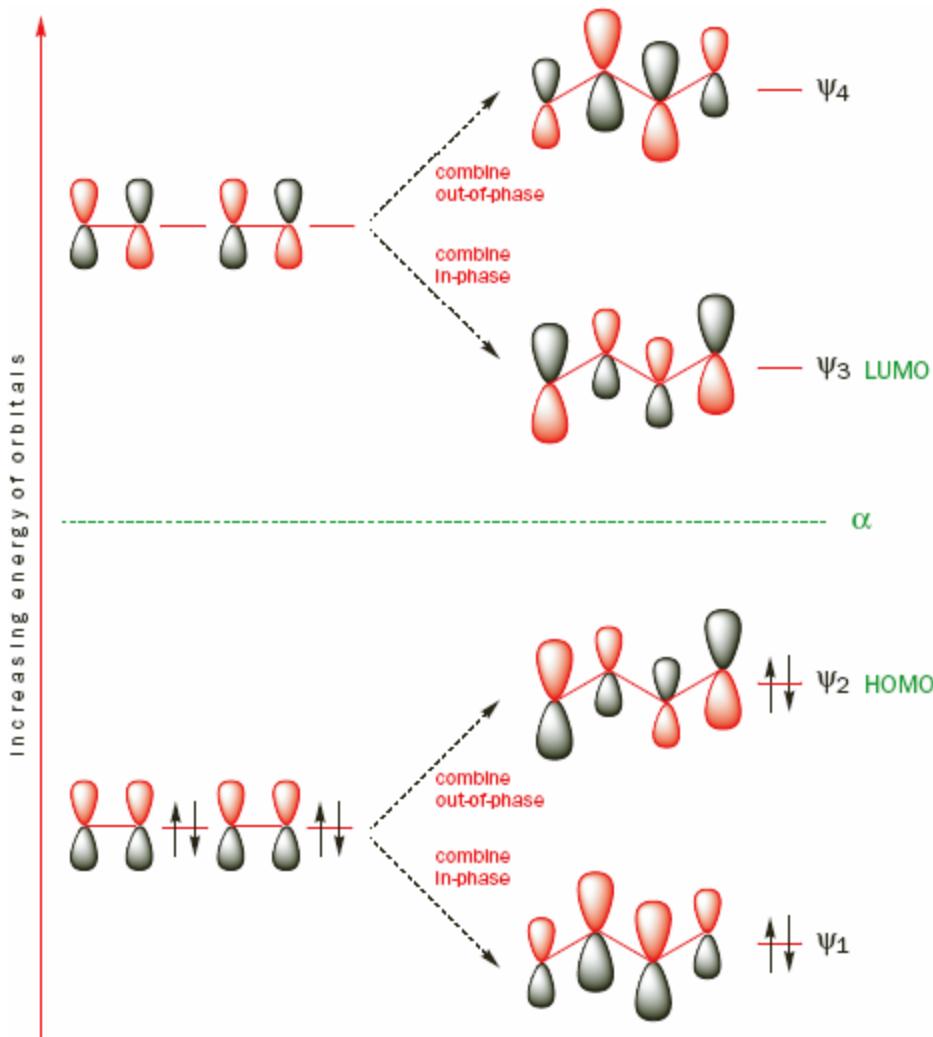


Although MOs have different energies, they all coexist
No. of bonding interactions > no. of nodes = bonding MO
No. of bonding interactions < no. of nodes = anti-bonding MO

Butadiene MOs

Total number of $\text{p}\pi$ -orbitals = 4

Total number of π -electrons = 4



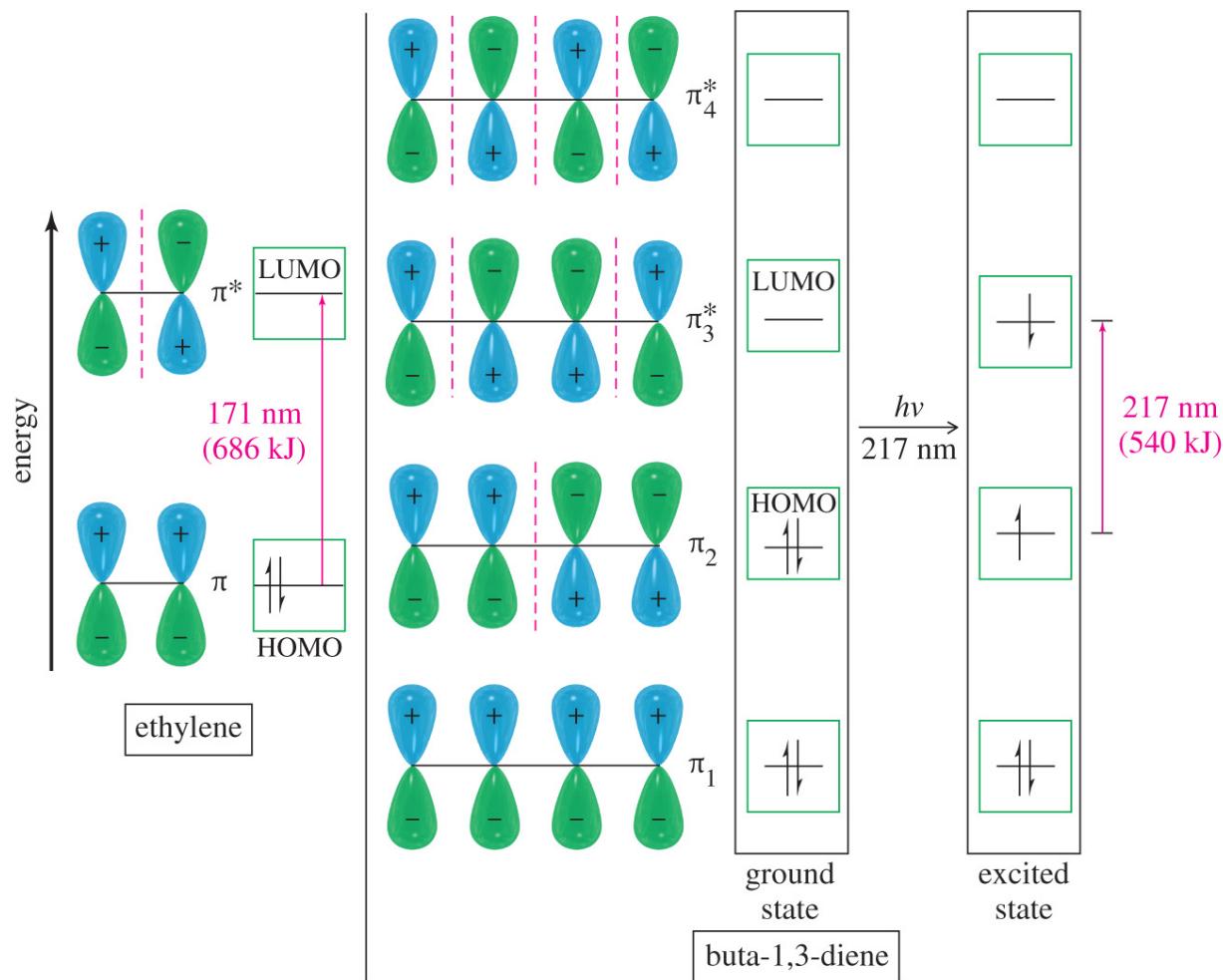
LUMO is lower in energy than the LUMO of ethylene

Butadiene is more reactive than ethylene

HOMO is higher in energy than the HOMO of ethylene

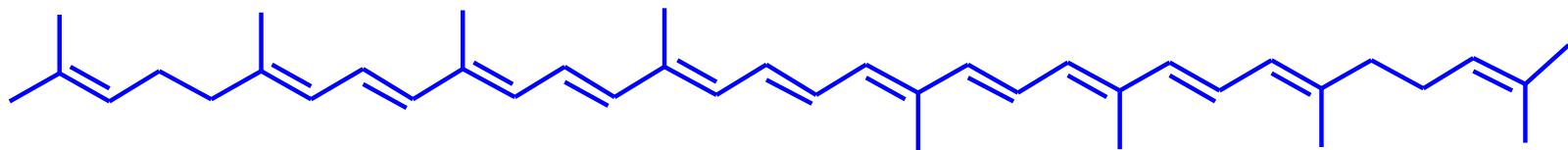
HOMO-LUMO Gap

$\pi \rightarrow \pi^*$ for Ethylene and Butadiene



Extended Conjugation and Colour (E.g. 1)

If the conjugation is extended further, the gap between HOMO and LUMO will decrease to allow the compound to absorb visible light and hence be COLOURED.



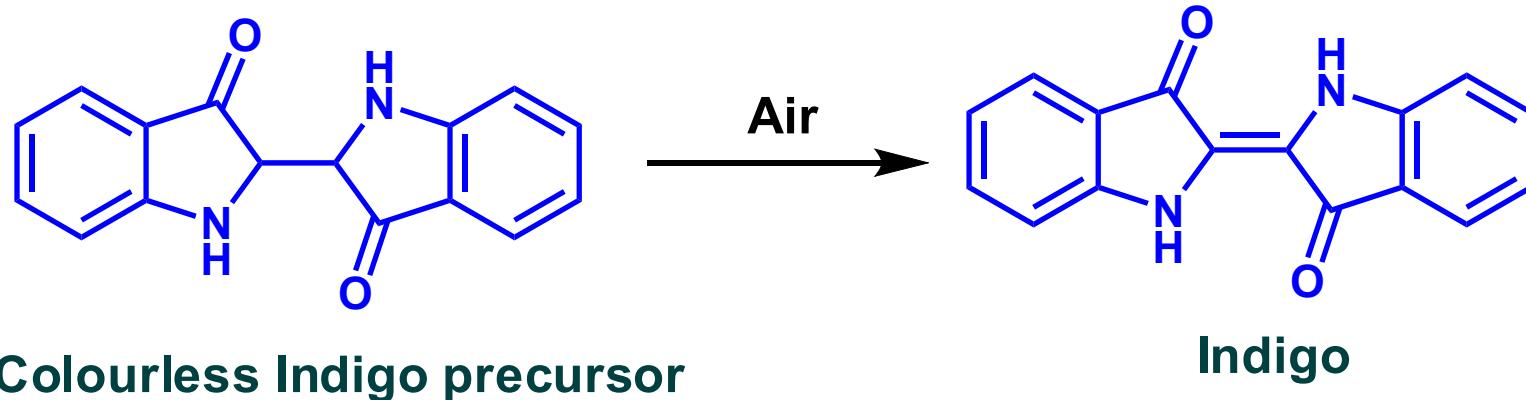
Lycopene, the red pigment present in tomatoes and other berries



β -carotene, the red pigment present in carrots and other vegetables

Extended Conjugation and Color (E.g. 2)

The colour of the blue jeans come from the pigment indigo



Jeans are generally dyed by immersion in a vat of reduced indigo, which is colourless since there is no conjugation.

When the cloth is hung up to dry, the oxygen in the air oxidizes the pigment to indigo and the jeans turn blue.

Generalizations for Acyclic Polyenes

The lowest energy orbital is always symmetric with respect to the principal mirror plane

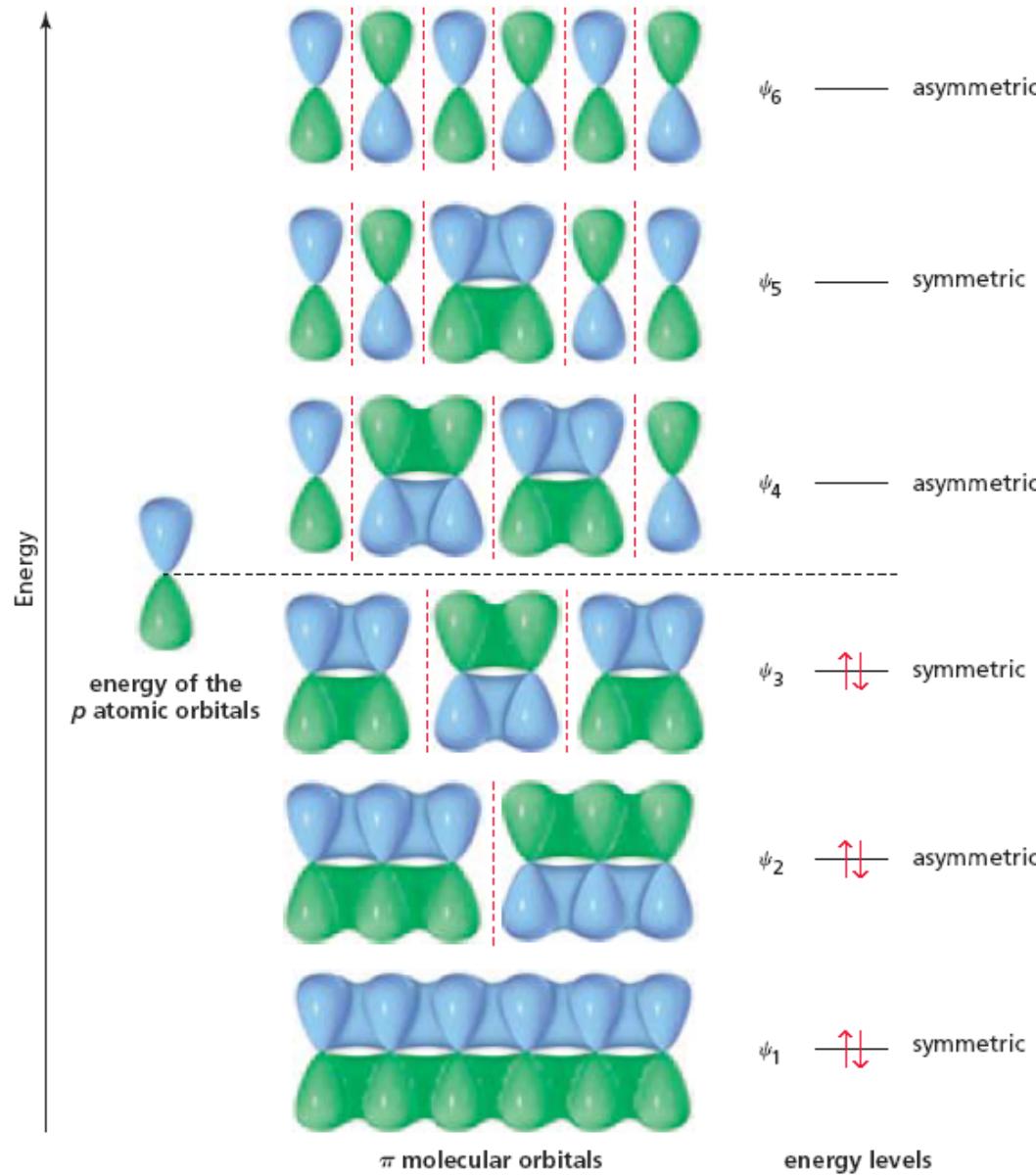
The number of nodes increases by ONE on going from one orbital to the next higher energy orbital

Nodes must be symmetrically located with respect to the central mirror plane

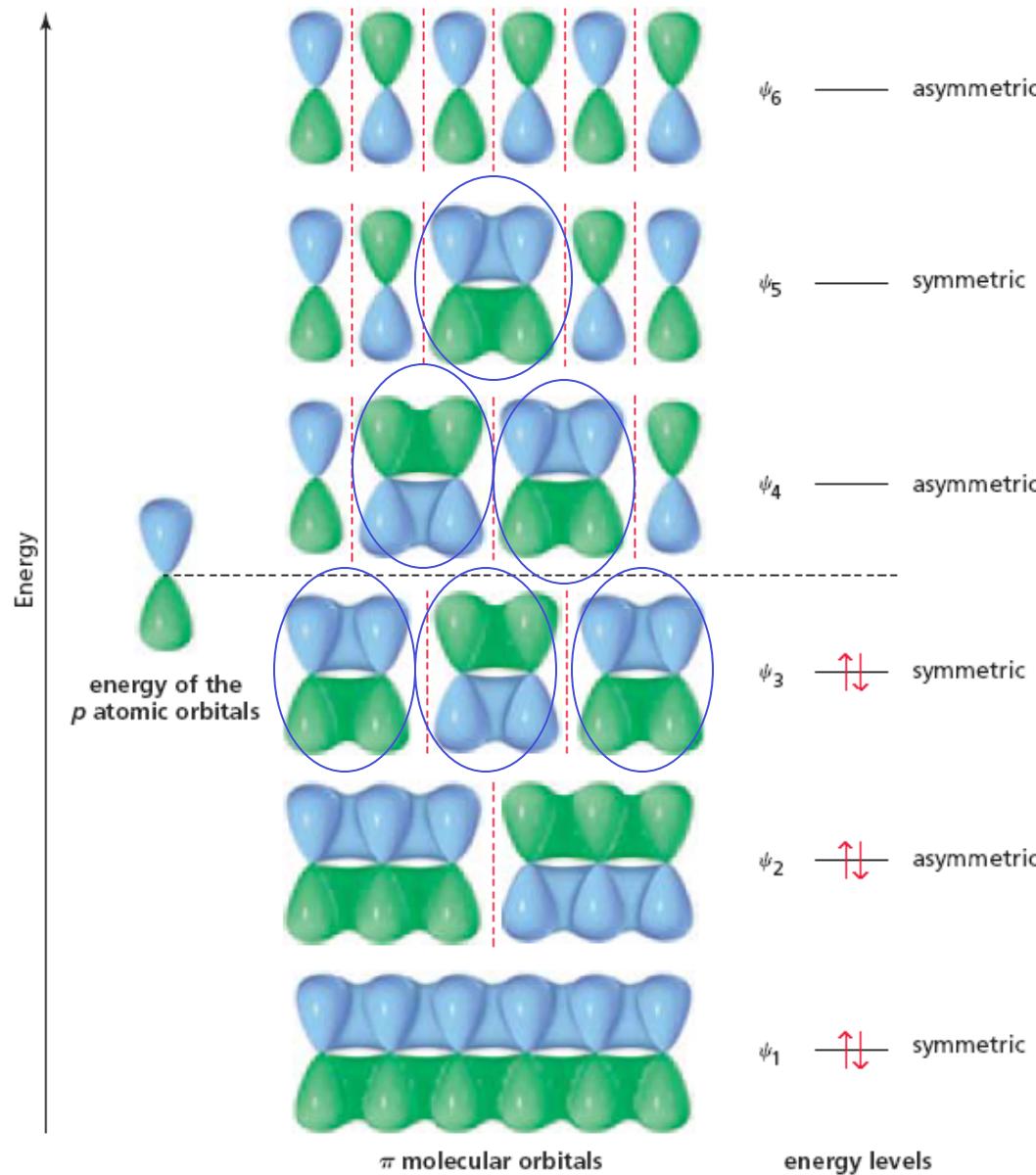
In systems with an odd number of atoms, the levels can have node/nodes at the carbon atoms. (**homework: penta dienyl cation**)

MOs alternate from symmetric to asymmetric as the MOs increase in energy (check it in 1,3,5-hexatriene)

MOs of 1,3,5-hexatriene



MOs of 1,3,5-hexatriene



Generalizations for Acyclic Polyenes

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Acyclic Polyenes with Odd no. of atoms

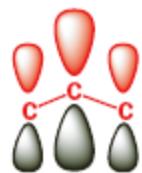
In an acyclic pi system the no of BMO = no. of ABMO

In systems with an **odd number of atoms**, odd no. of Mos will be there and one of the Mos has to be **non bonding MO**

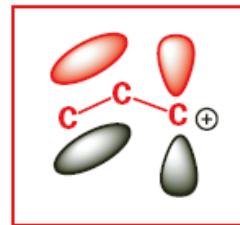
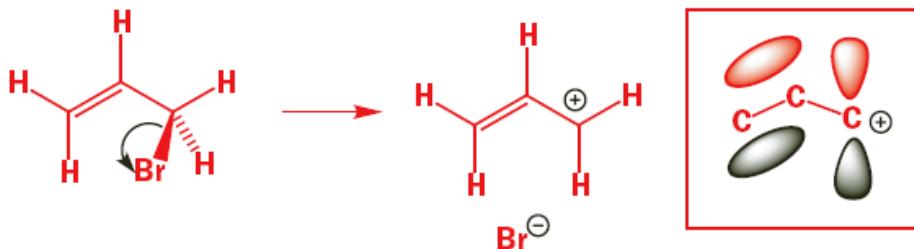
The levels can have **node/nodes at the carbon atoms.**

MOS alternate from symmetric to asymmetric as the MOS increase in energy

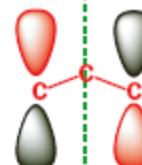
How about MOs for allyl system?



the p orbital has the correct symmetry to combine with the π bond to form a new molecular orbital for the allyl system

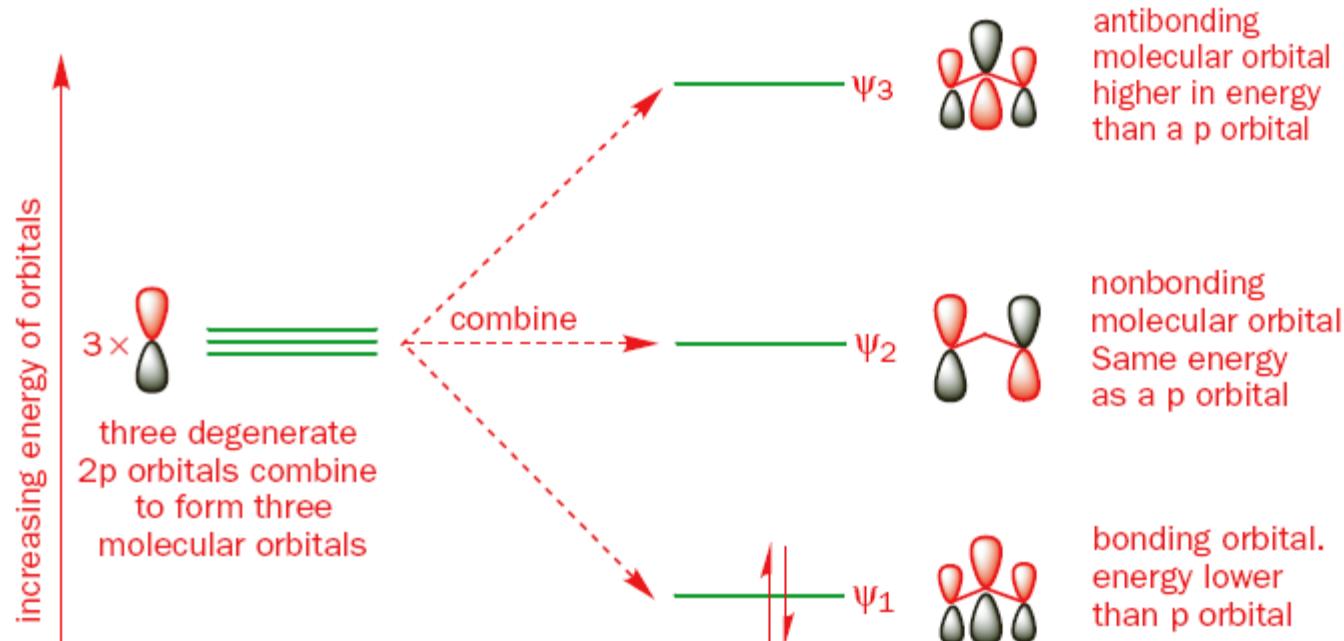


the bonding molecular orbital of the allyl system, Ψ_1



nodal plane through the middle atom
nonbonding Ψ_2

the π molecular orbitals of the allyl system: the allyl cation



antibonding molecular orbital higher in energy than a p orbital

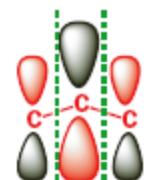
nonbonding molecular orbital Same energy as a p orbital

this is the Lowest Unoccupied Molecular Orbital (LUMO)

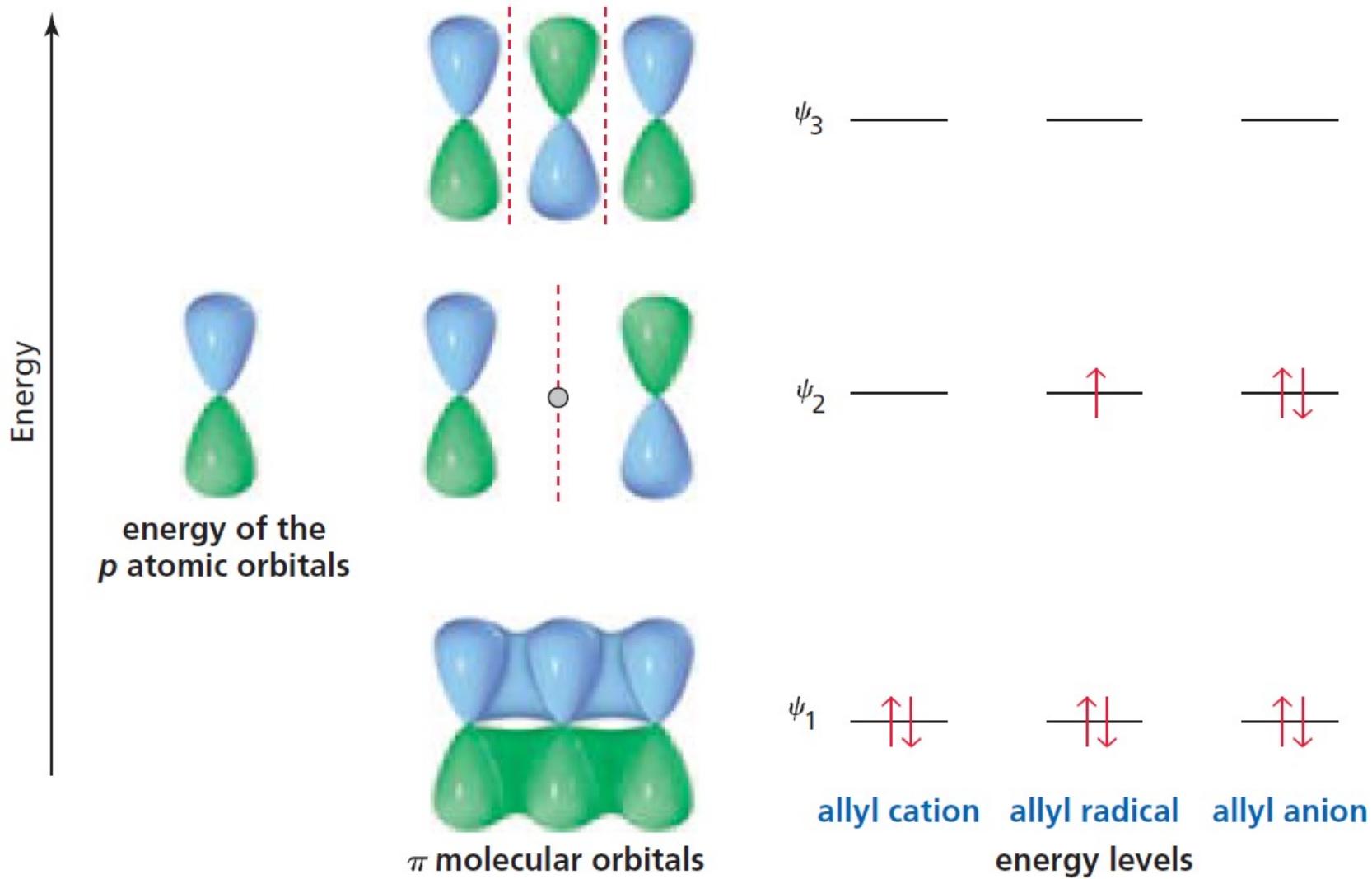
bonding orbital. energy lower than p orbital

this is the Highest Occupied Molecular Orbital (HOMO)

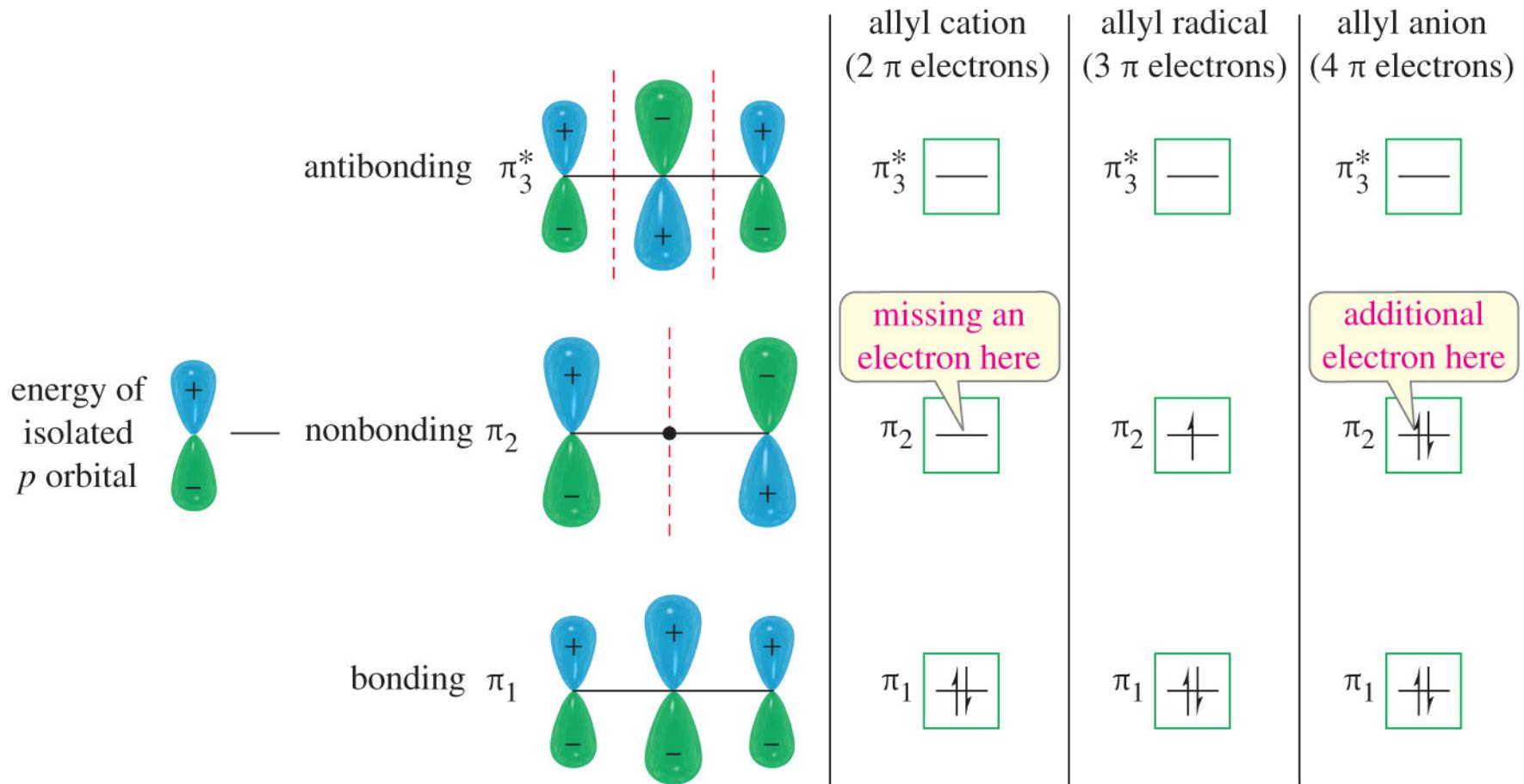
three molecular orbitals resulting from the combinations of the three atomic orbitals the energies are now different



two nodal planes antibonding Ψ_3



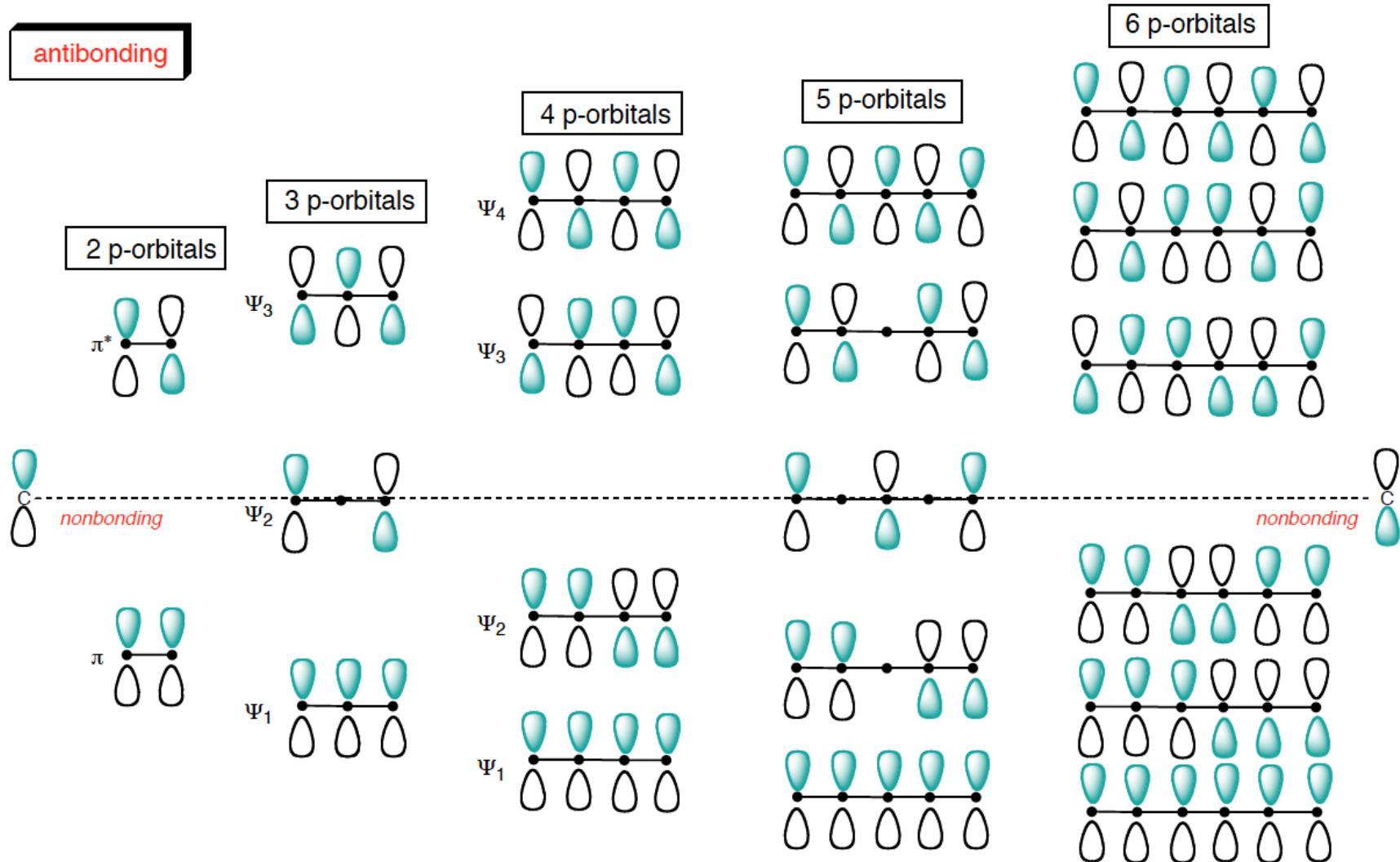
MOs for the Allylic Species



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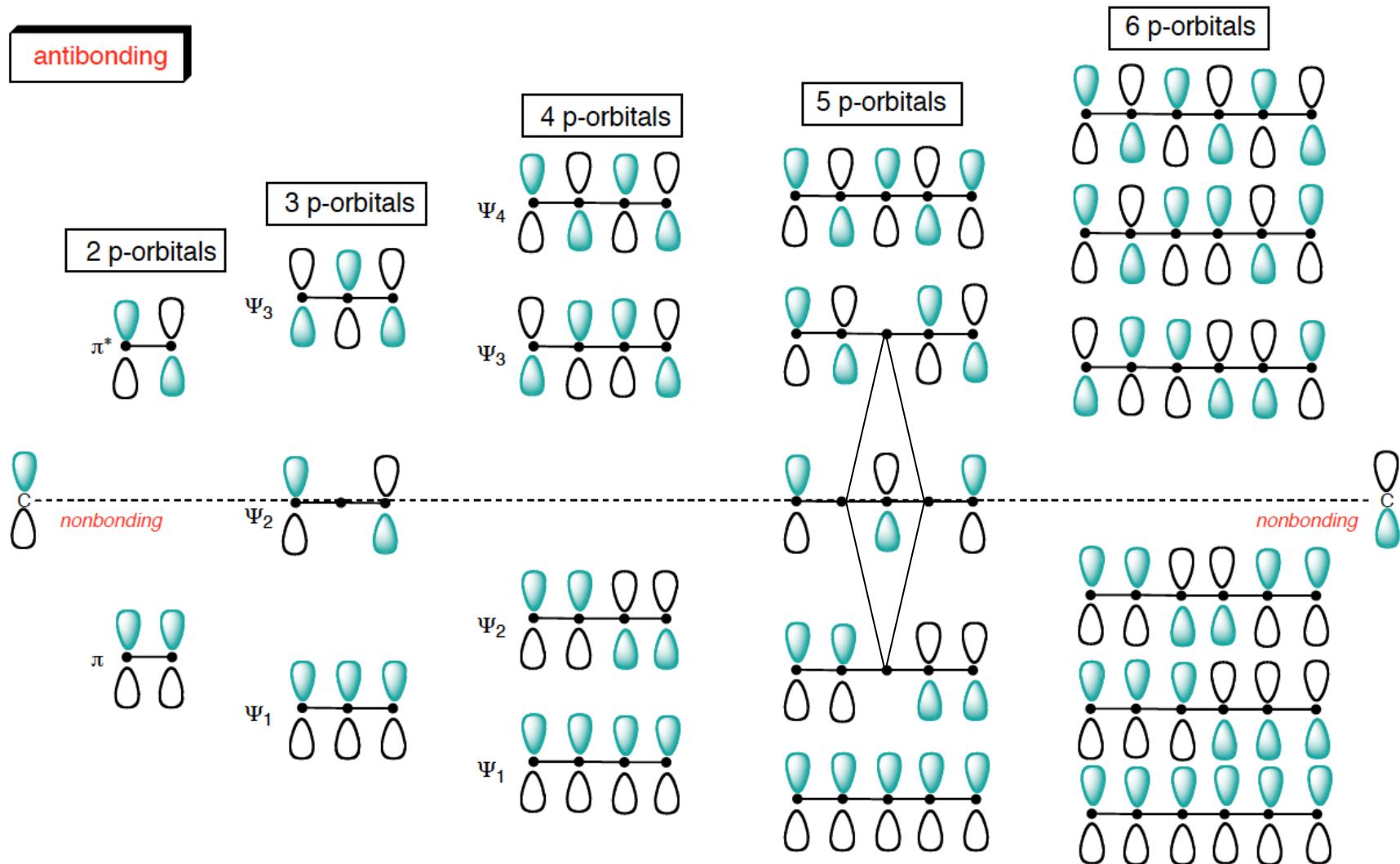
Lets draw MOs for pentadienyl system

Conjugated pi systems



There are no nodal planes in the most stable bonding MO. With each higher MO, one additional nodal plane is added. The more nodes, the higher the orbital energy.

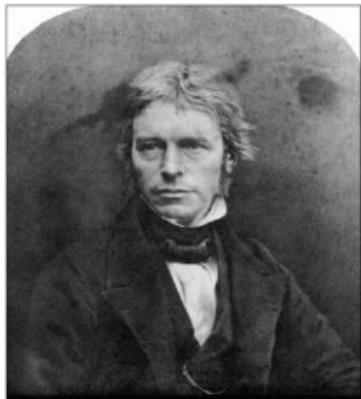
Conjugated pi systems



bonding

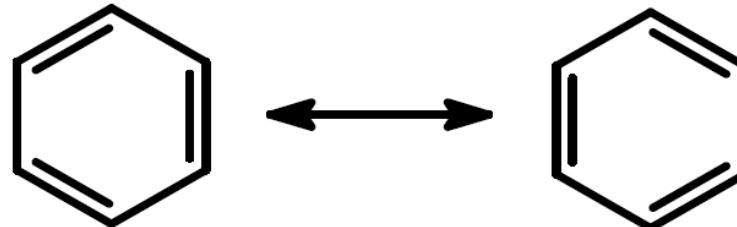
There are no nodal planes in the most stable bonding MO. With each higher MO, one additional nodal plane is added. The more nodes, the higher the orbital energy.

Aromaticity: Benzene



Michael Faraday
(1825): first isolated
benzene

BENZENE

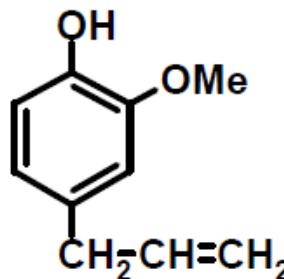


Mitscherlich (1834) C₆H₆

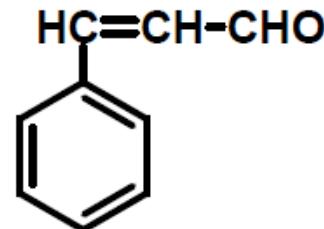


Friedrich Kekulé (1866)

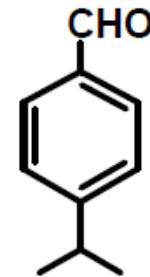
Aroma = Characteristic Odour



eugenol
(cloves)



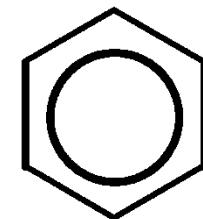
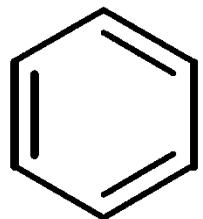
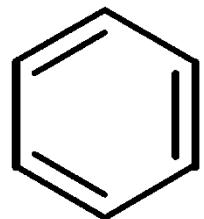
cinnamaldehyde
(cinnamon)



cuminaldehyde
(cumin)

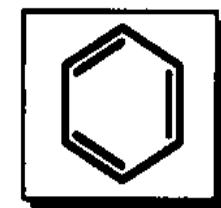
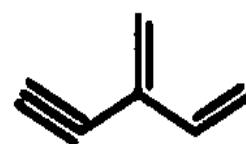
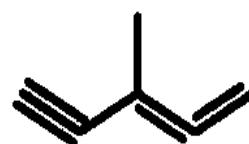
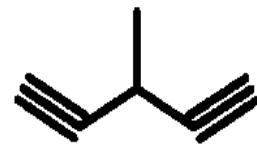
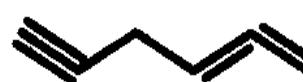
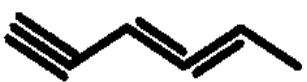
IN TODAY'S CONTEXT "AROMATIC" IS A MISNOMER!!³⁷

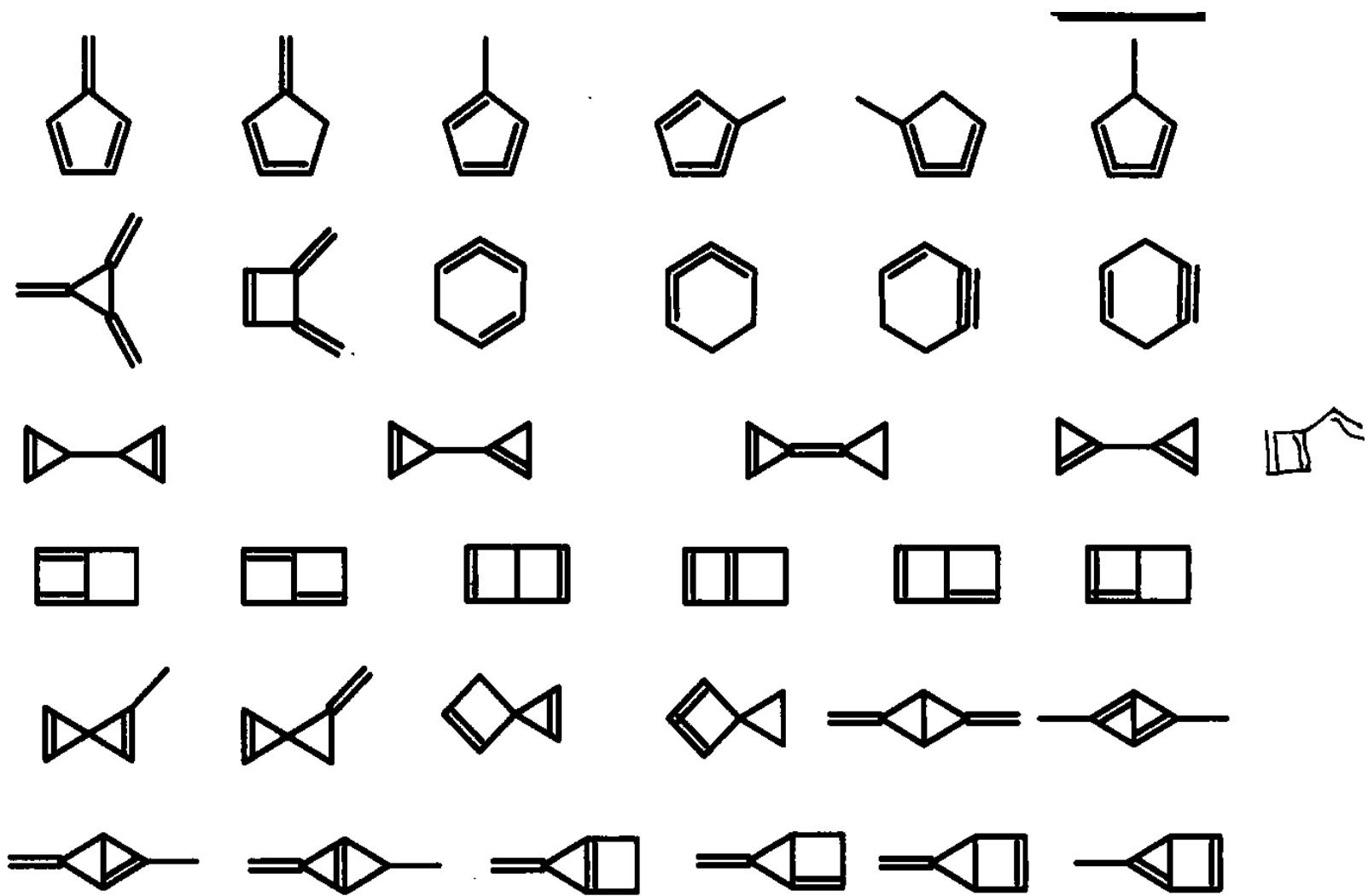
C_6H_6 : How many isomers??

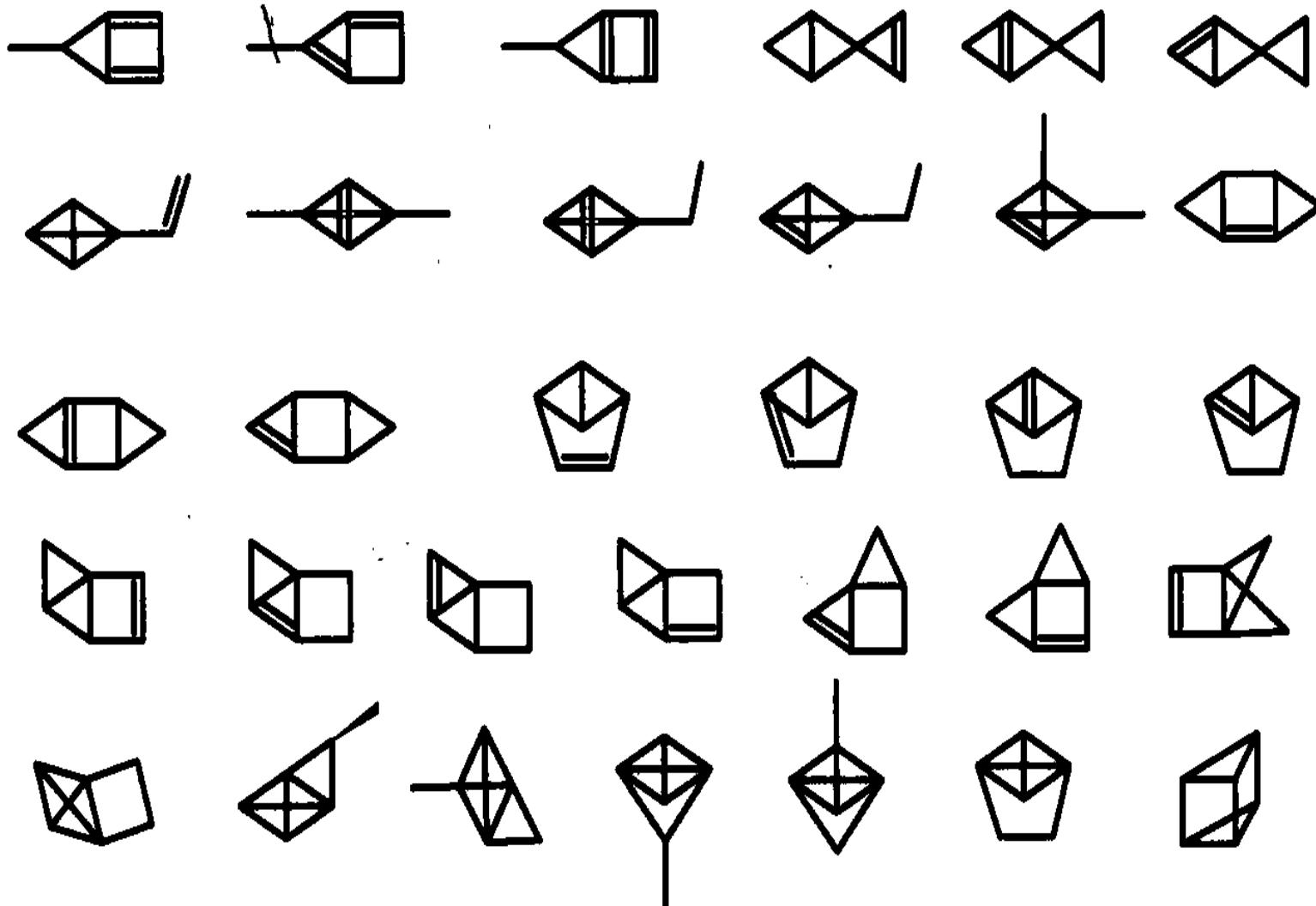


???

Isomers of Benzene (C_6H_6)



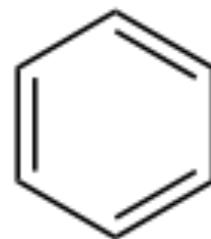
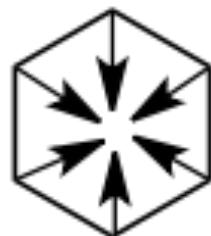
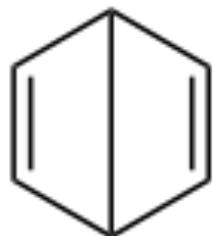




Totally 217 isomers are possible!
Only benzene is aromatic!!

Structure of benzene

- Benzene has a molecular formula C₆H₆.
- Its polyunsaturated structure was difficult to determine especially without spectroscopy.



Claus
(1867)

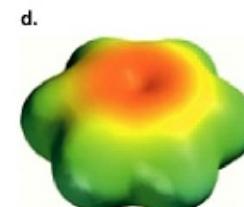
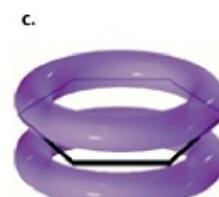
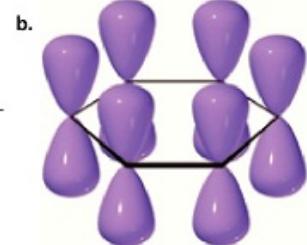
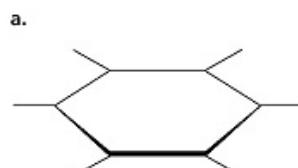
Dewar
(1867)

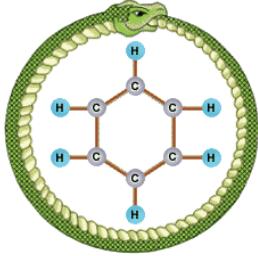
Ladenburg
(1869)

Armstrong
(1887)

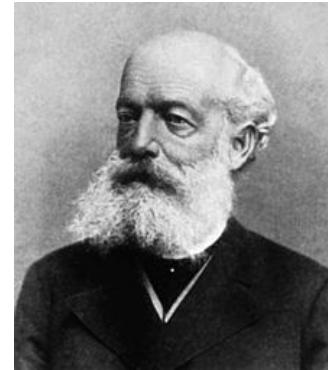
Thiele
(1899)

Kekulé
(1865)





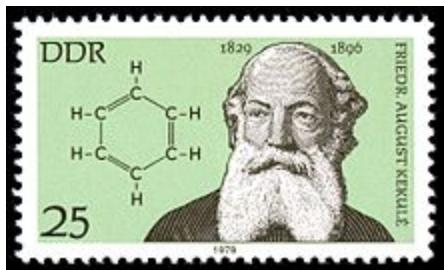
Kekule's dream



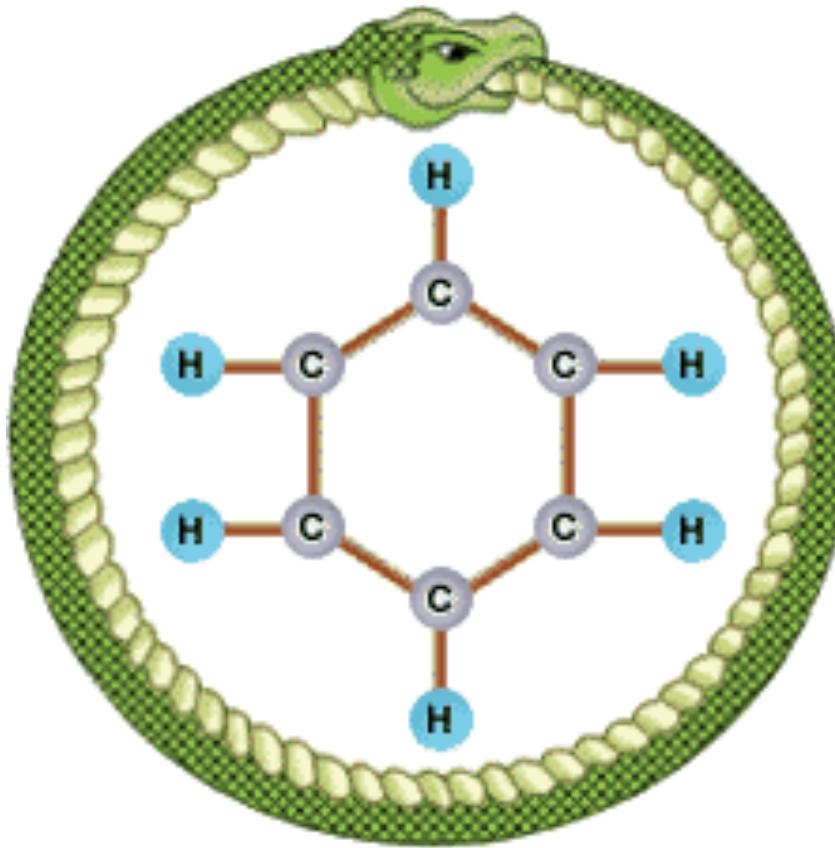
- "I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. ... My mental eye... could not distinguish larger structures, of manifold conformation; long rows, sometimes more closely fitted together; all twining and twisting in snakelike motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lighting I awoke..."

*From "**Creativity, Beyond the Myth of Genius**" by Robert Weisberg
published by W. H. Freeman 1992.*

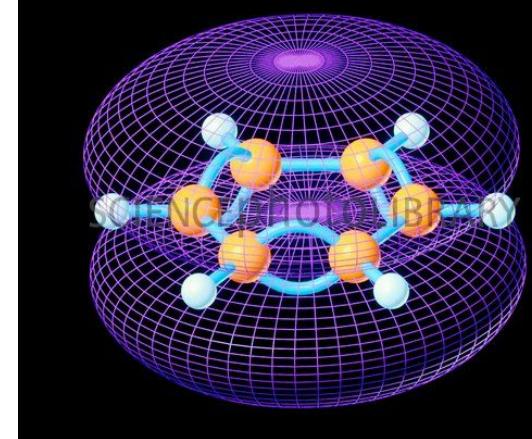
Friedrich August Kekulé von Stradonitz



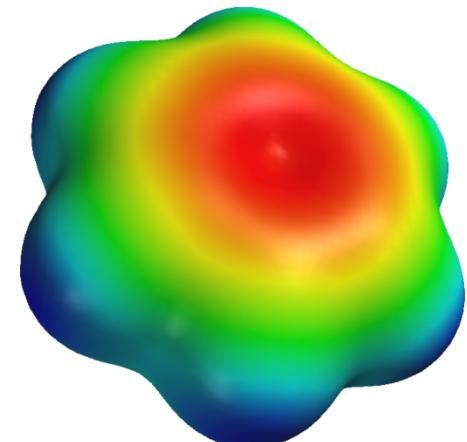
1979 East German stamp of Kekulé, in honor of the sesquicentennial of his birth.



1964 West German centenary stamp for the discovery of the molecular formula of benzene



Of the first five Nobel Prizes in Chemistry, Kekulé's students won three: van 't Hoff in 1901, Fischer in 1902 and Baeyer in 1905.



Some questions of significance

Most of the reactivities of conjugated systems (say, butadiene, or a carbonyl compound) primarily arise due to the π -molecular orbitals.

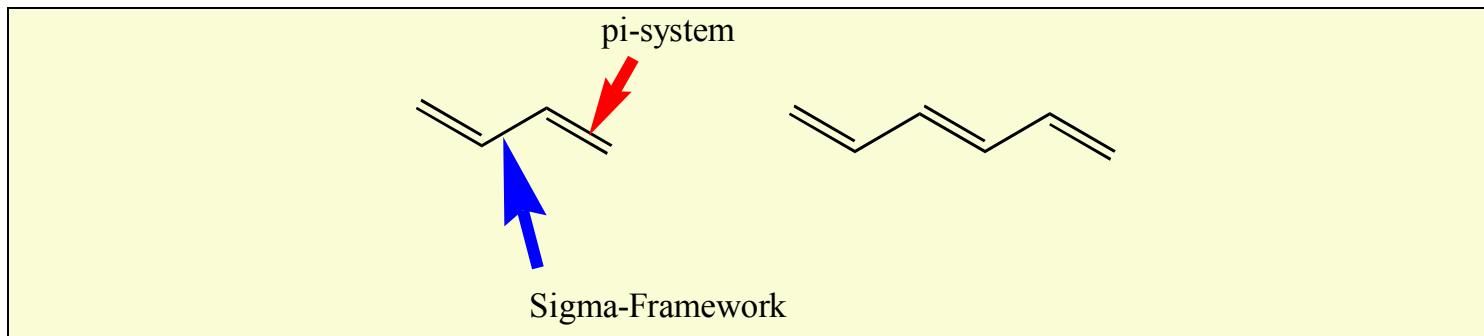
Is it possible to estimate the energies of the π -molecular orbitals?

Huckel MO Theory

Basic Approximations

- Used for the treatment of conjugated systems
- The π -system is treated independently of the σ -framework in planar conjugated molecules
- Or π -system do not interact with the σ -skeleton
- Interactions between $\pi\pi$ orbitals located on atoms which are not directly linked is zero

π -electron approximation: π -electrons move in some fixed effective potential of σ framework



Energies of MOs in terms of Integrals

The energy of each $p\pi$ -orbital before interaction is set equal to α , (**Coulomb integral**)

[refers to energy of an electron in the field of its own nucleus]

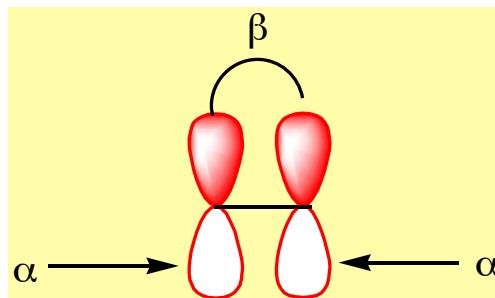
[can be taken as valence state ionization potential]

The interaction energy between two adjacent $p\pi$ orbitals equals to β (**Resonance integral**)

[refers to energy of i^{th} electron in the field of j^{th} nucleus]

[can be taken as the interaction between atomic orbitals i and j]

[energy of an electron in the field of two or more nuclei]



Energies of MOs

- The energy of the j^{th} MO for a linear unbranched conjugated polyene with $N \text{ p}\pi$ orbitals (or N number of carbon atoms) is given by

$$e_j = \alpha + 2\beta \cos \frac{\pi}{N+1} j \quad j = 1, 2, \dots, N$$

- The energy of the j^{th} MO for a cyclic polyene with $N \text{ p}\pi$ orbitals is given by

$$e_j = \alpha + 2\beta \cos \frac{2\pi}{N} j \quad j = 0, 1, 2, \dots, N$$

Note: α and β are negative (attractive !) by definition

The α and β are not calculated as numerical values, but the energies are expressed in terms of these quantities

Energies of MOs

Linear polyenes

For ethylene

Energy of LUMO = $\alpha - \beta$

Energy of HOMO = $\alpha + \beta$

For Butadiene

Energy of LUMO = $\alpha - 0.62\beta$

Energy of HOMO = $\alpha + 0.62\beta$

$$e_j = \alpha + 2\beta \cos \frac{\pi}{N+1} j$$

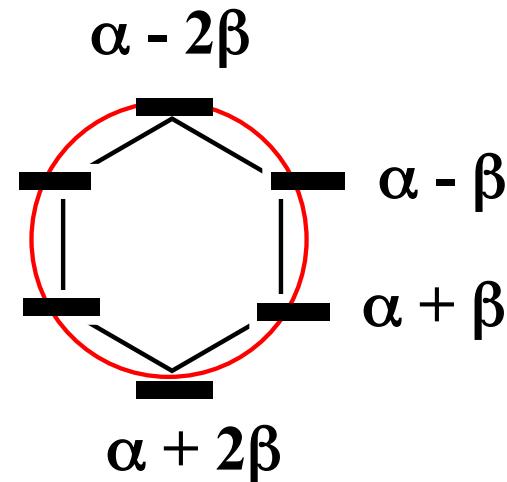
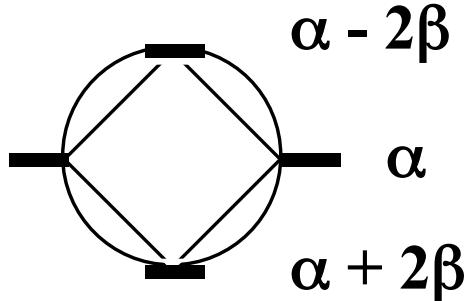
$$j = 1, 2, \dots, N$$

Energies of MOs

Cyclic polyenes

Draw a circle of radius 2β and inscribe an N-vertex polygon such that two vertices are in the six o' clock position. The points of contact between the circle and the polygon defines the energy levels

Frost Diagram



The energy level α is at the same level as that of the center of the circle

$$e_j = \alpha + 2\beta \cos \frac{2\pi}{N} j$$

$$j = 0, 1, 2,..N-1$$

Energies of MOs

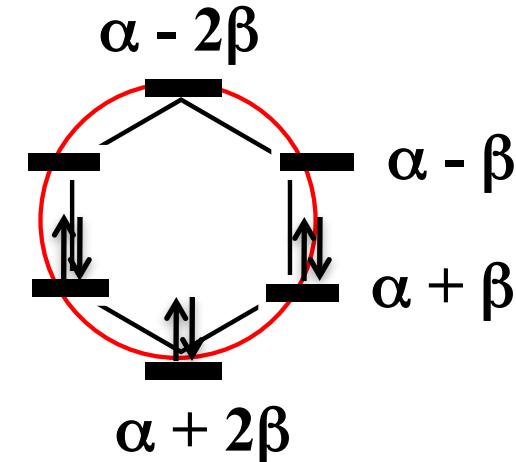
Calculate the total energy of π -electrons in benzene?

Total number of π -electrons = 6

Total energy = $2 \times (\alpha + 2\beta) +$

$4 \times (\alpha + \beta)$

 $6\alpha + 8\beta$



If the double bonds were localized (not conjugated)!

Equivalent to three ethylenes

Total energy = $6 \times (\alpha + \beta)$

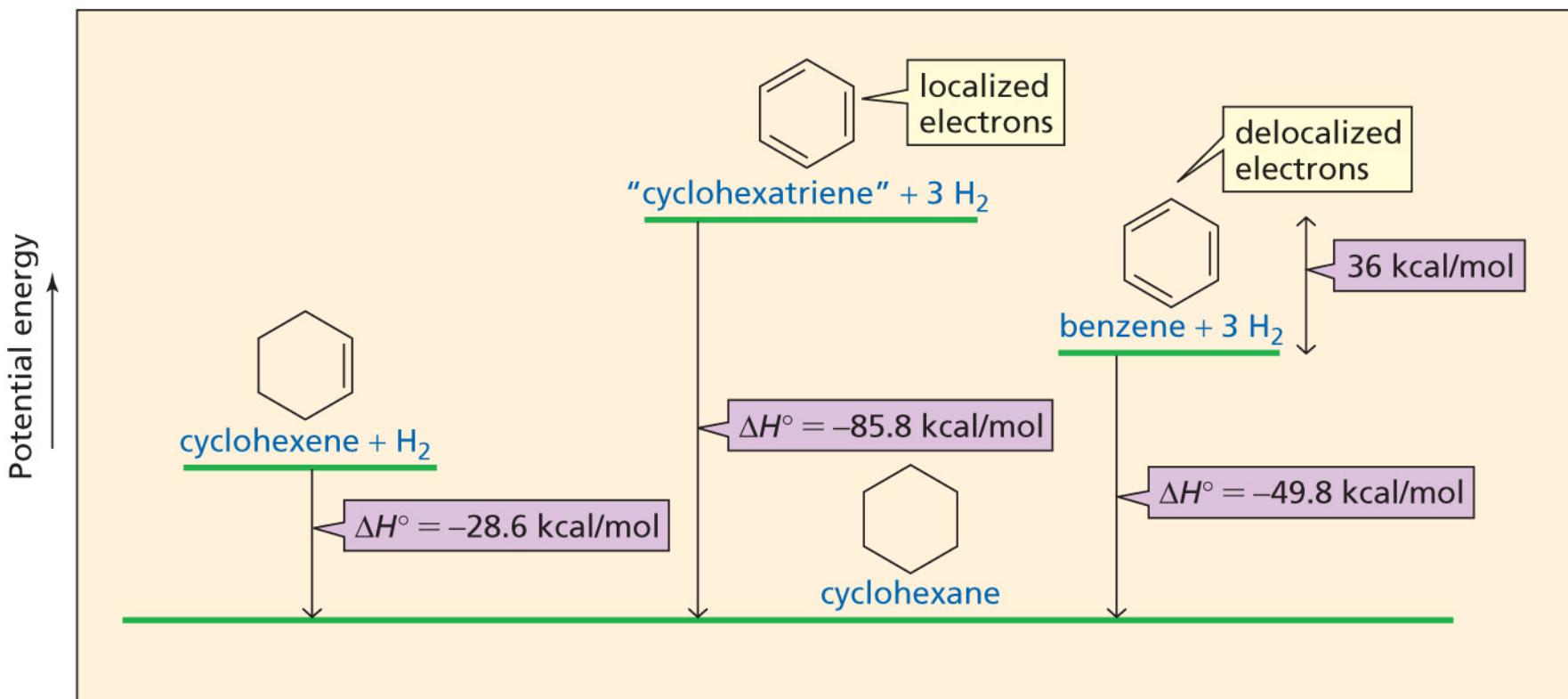
Additional Stabilization in Benzene (fully delocalized) = 2β

What is the resonance stabilization energy in benzene?

Can we calculate the energy of electrons in cyclobutadiene?

Benzene is unusually unreactive. Does this mean that it is also especially stable thermodynamically? Look at ΔH° hydrogenation:

(Quantity of heat released when 1 mole of an unsaturated compound is hydrogenated)

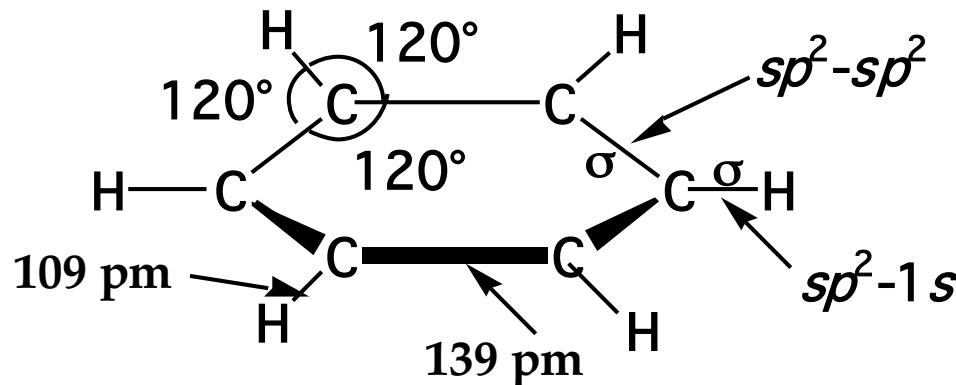


Special stability is now called **aromaticity**. All cyclic 6e arrangements are aromatic, including transition states.

Benzene: Structure

The concepts of hybridization of atomic orbitals and the theory of resonance, developed in the 1930s, provided the first adequate description of benzene's structure.

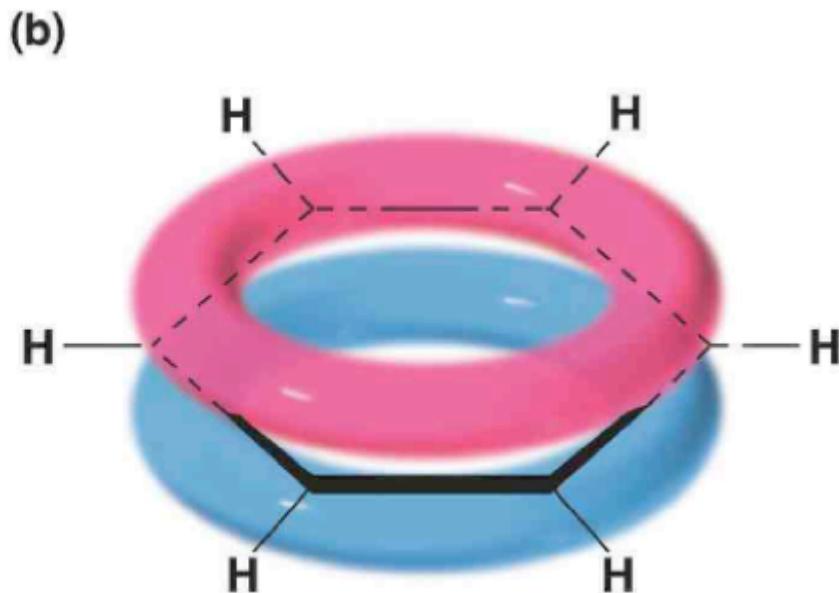
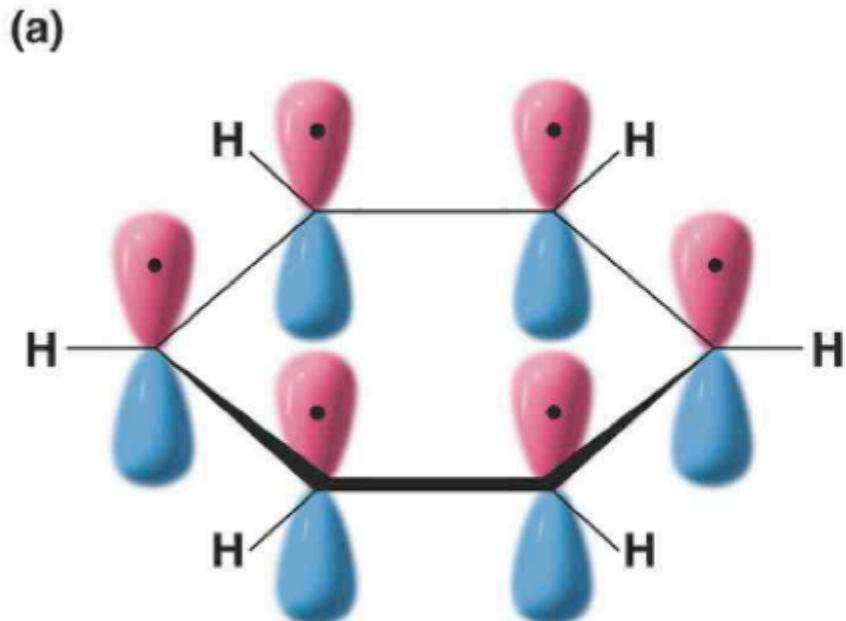
- The carbon skeleton is a planar regular hexagon.
- All C-C-C and H-C-C bond angles 120°.



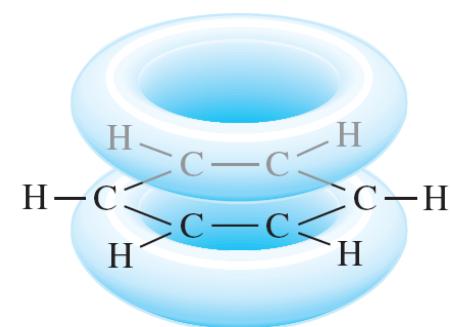
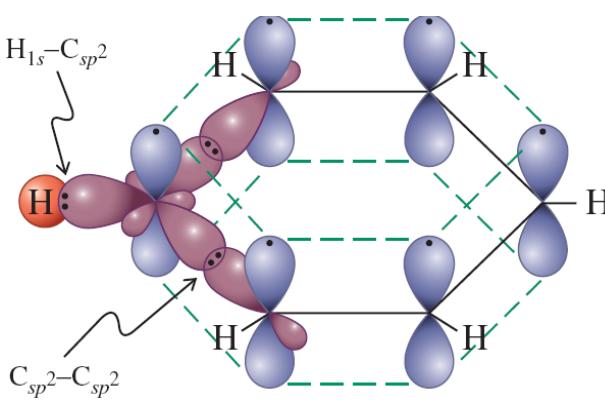
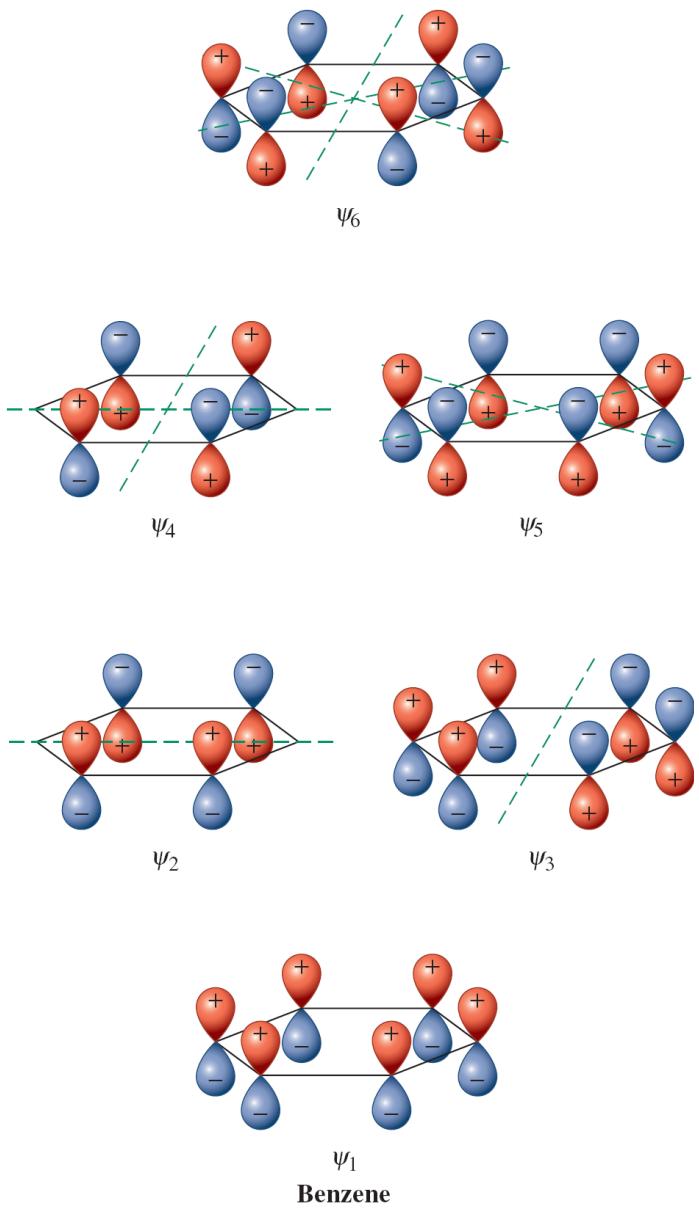
All C-C bonds 1.39 \AA
All C-H bonds 1.09 \AA

Benzene: Structure

- (a) The carbon framework with the six $2p$ orbitals.
- (b) Overlap of the parallel $2p$ orbitals forms one torus above the plane of the ring and another below it
- this orbital represents the lowest-lying pi-bonding molecular orbital.



π Molecular Orbitals of Benzene



Huckel's Rule of Aromaticity

- Planar, fully conjugated, **monocyclic systems with $(4n+2)\pi$ electrons** having a **closed shell of electrons all in bonding orbitals** are exceptionally stable. Such compounds are said to be aromatic
- Analogous systems with $4n \pi$ electrons are described as **anti-aromatic**

i

Modern definition of aromaticity:

Compounds that possesses the ability to sustain induced ring current when subjected to magnetic field

Huckel's Rule and Aromaticity

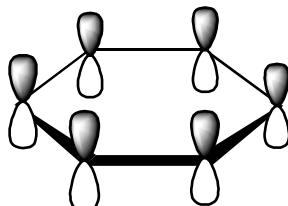
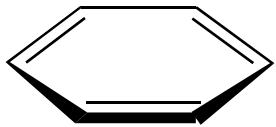
The compound must have an uninterrupted cyclic π -cloud of electrons

For the π -cloud to be cyclic, the molecule must be **cyclic**.

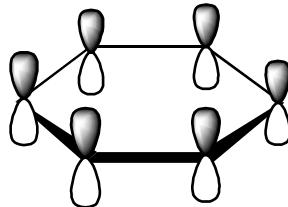
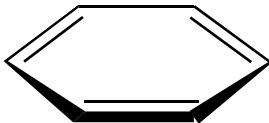
For the π -cloud to be uninterrupted, every atom in the ring must have a **p-orbital**

For the π -cloud to form, each p-orbital must be able to overlap with the p-orbitals on either side of it. This means that the molecule must be **planar**.

E.g., 1

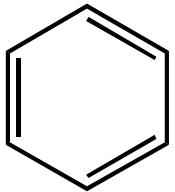


Huckel's Rule and Aromaticity



- It must have an **uninterrupted cloud of π electrons**.
(cyclic, planar, every ring atom must have a p orbital).
- The π cloud must have an **odd number of pairs of π electrons**. Have a closed loop of $(4n + 2)$ pi electrons in the cyclic arrangement of p orbitals.

Huckel's Rule of Aromaticity



Number of π electrons = 6

**Satisfies Huckel' rule,
where $n = 1$**

Aromatic

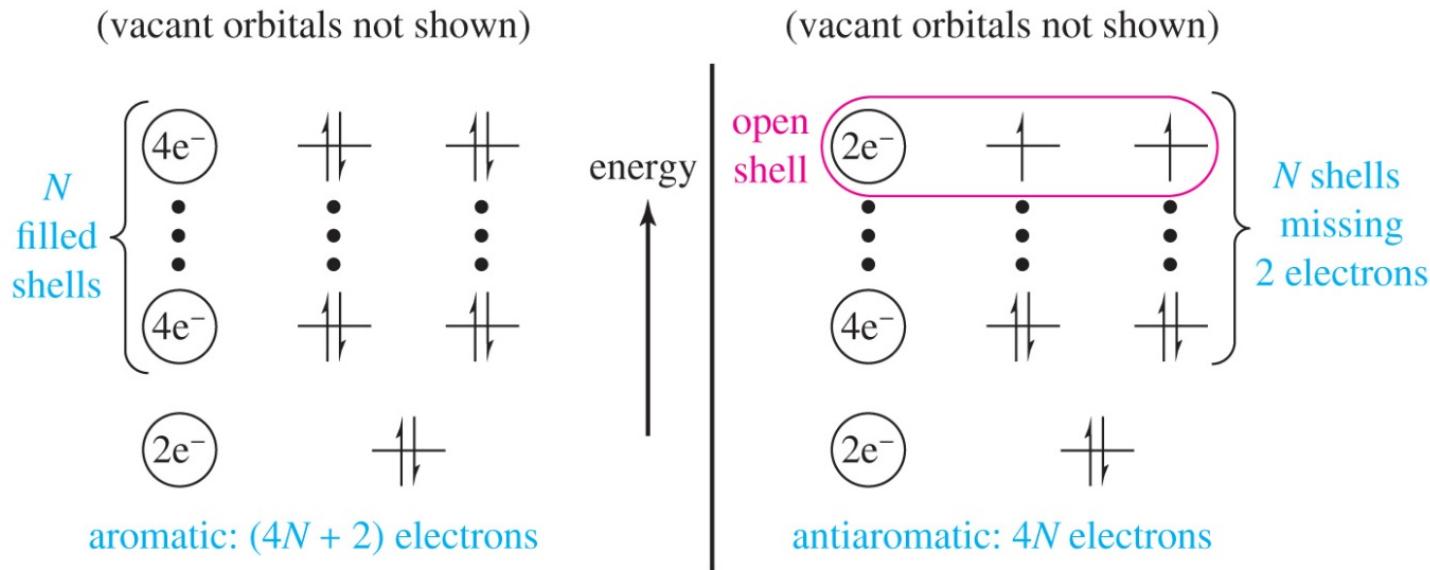


Number of π electrons = 4

Where $n = 1$

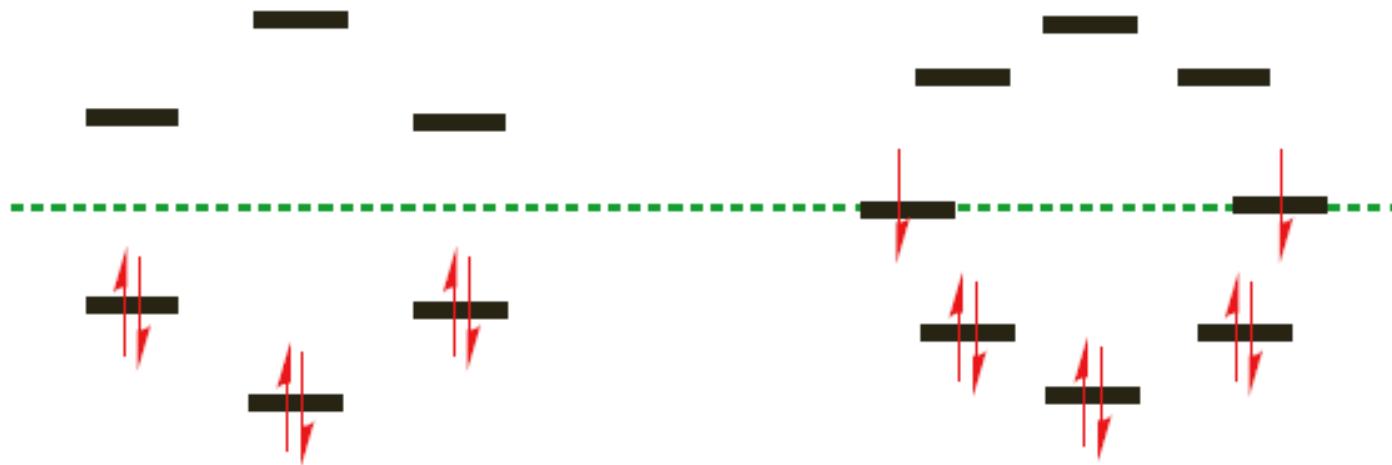
Anti-aromatic

MO Derivation of Hückel's Rule



- **Aromatic compounds have $(4N + 2)$ electrons and the orbitals are filled.**
- **Antiaromatic compounds have only $4N$ electrons and have unpaired electrons in two degenerate orbitals.**

Why $4n\pi$ Compounds are Unstable?



MO level diagram for benzene

MO level diagram for *planar* cyclooctatetraene



cyclooctatetraene

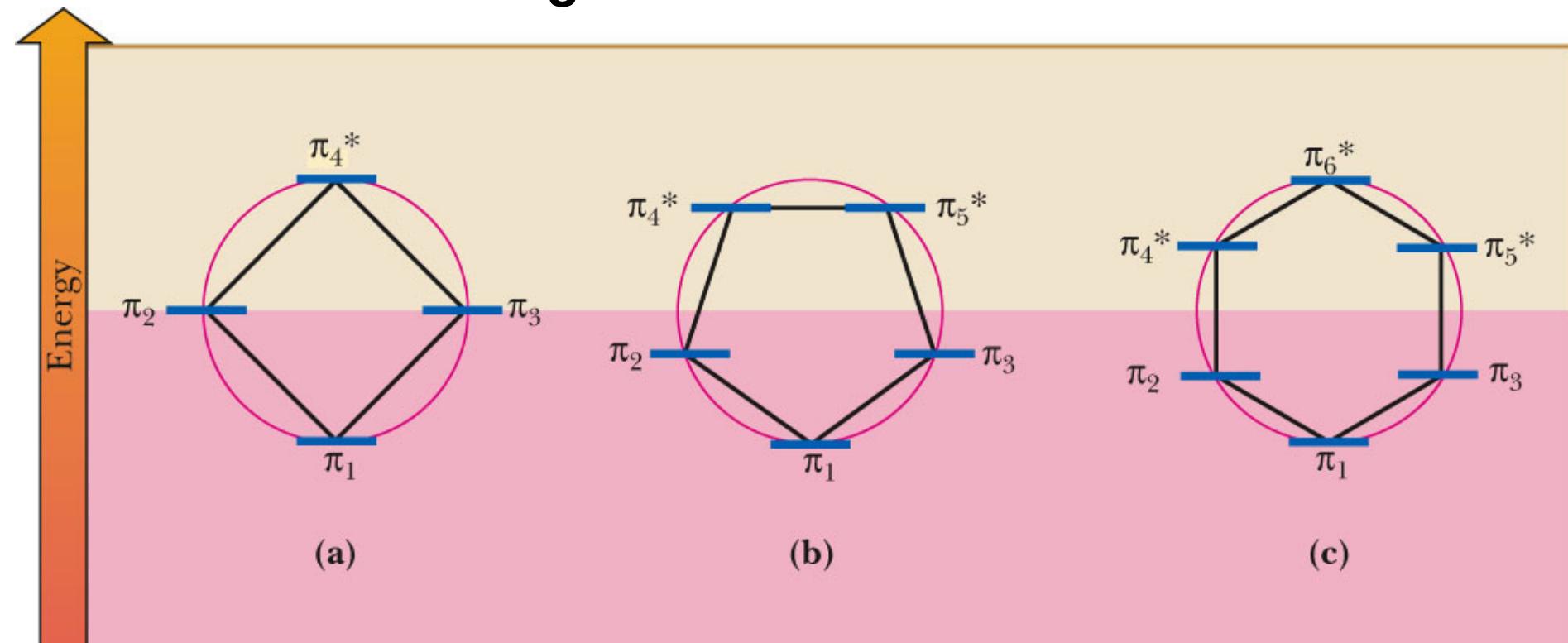
**But I don't know MO! What do I do? Use
Frost Circle**

Frost Circle

- ◆ **Frost circle:** A graphic method for determining the relative order of pi MOs in planar, fully conjugated monocyclic compounds.
 - Inscribe in a circle a polygon of the same number of sides as the ring to be examined such that one of the vertices of the polygon is at the bottom of the circle.
 - The relative energies of the MOs in the ring are given by where the vertices of the polygon touch the circle.
- ◆ Those MOs
 - Below the horizontal line through the center of the ring are **bonding MOs**.
 - on the horizontal line are **nonbonding MOs**.
 - above the horizontal line are **antibonding MOs**.

Frost Circle

- Frost circles describing the MOs for monocyclic, planar, fully conjugated four-, five-, and six-membered rings.

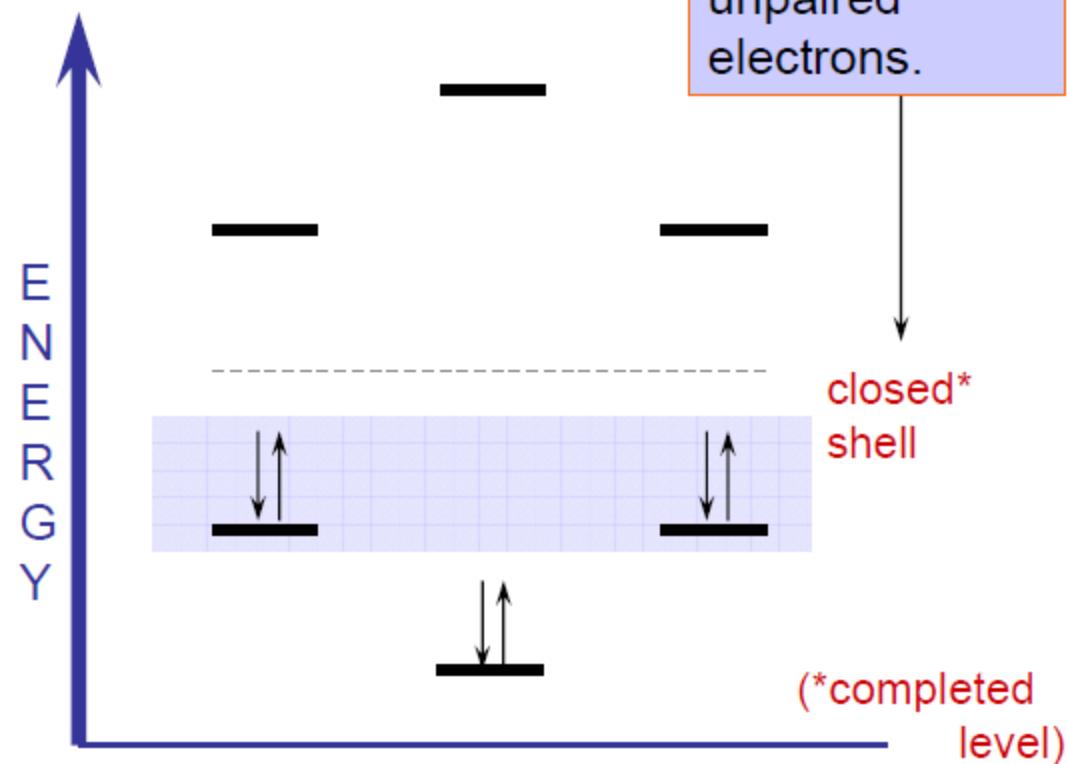
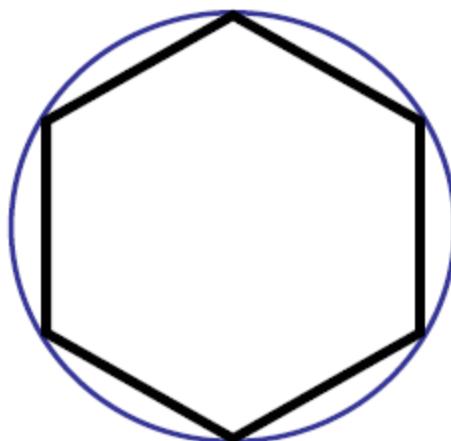


BENZENE



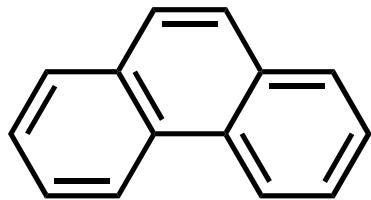
6π electrons

AROMATIC

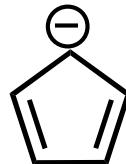


Aromatic compounds will have all of the occupied π M.O. levels completely Filled, with **no** unpaired electrons.

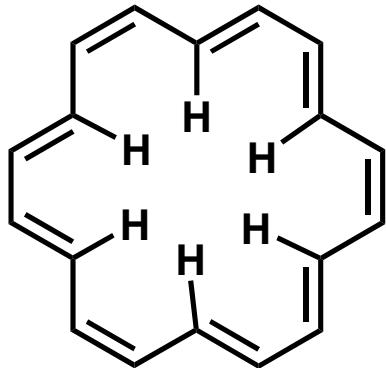
Examples for Aromatic Compounds



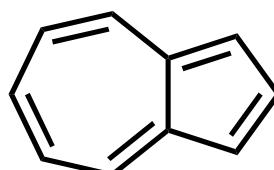
Phenathrene



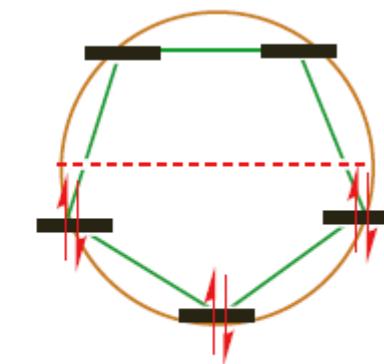
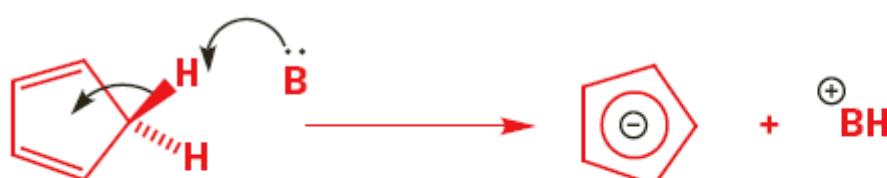
cyclopentadienyl anion



[18]-annulene

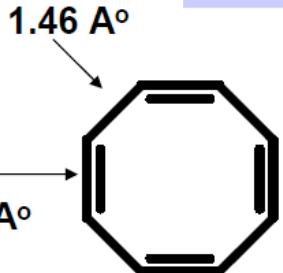


Azulene

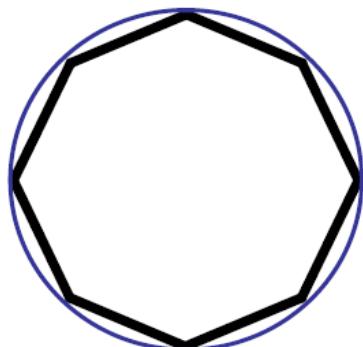


the anion has 6π electrons completely filling the bonding MOs

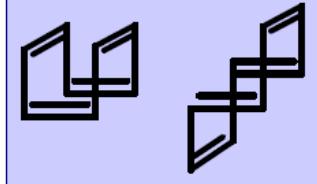
CYCLOOCTATETRAENE



8π electrons



not planar



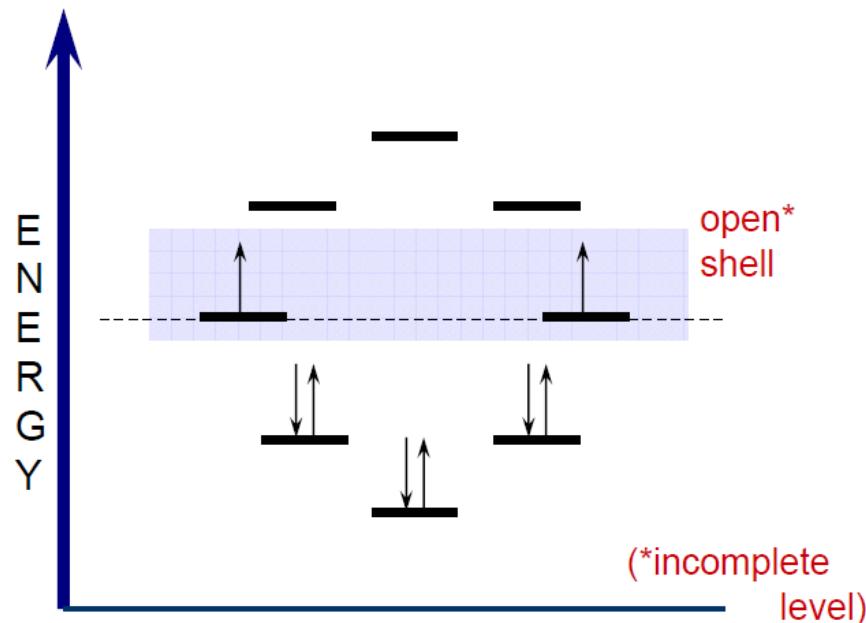
ANTI-AROMATIC

Does not have a completed shell and has unpaired electrons.

Does not have $4n+2 \pi$ electrons.

1.46 Å

1.33 Å

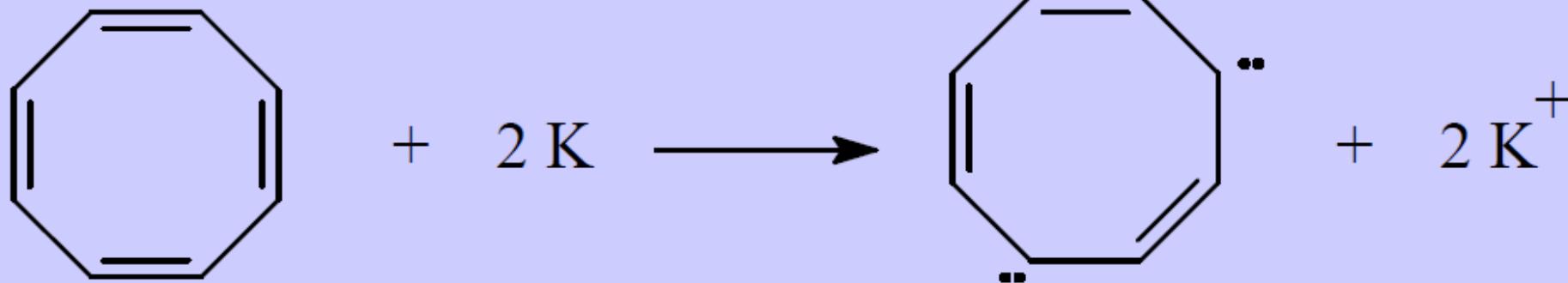


Planar cyclooctatetraene would be antiaromatic (Bond angle = 135°). To avoid it, the ring goes out of plane - possible as it is a larger ring.

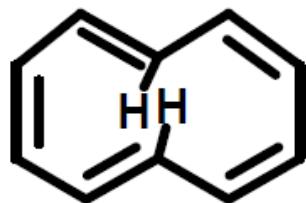
It is Non-aromatic.

Dianion of [8]Annulene

Cyclooctatetraene easily forms a -2 ion. Ten electrons; continuous overlapping of π orbitals,... so the dianion it is aromatic.

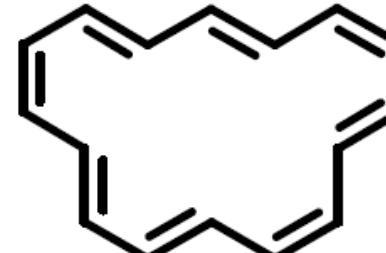


Some examples of Annulenes



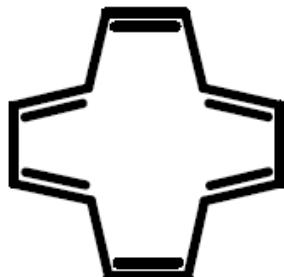
$10\pi = 4(2) + 2$
BUT CANNOT BE PLANAR
(see the hydrogens)

NON-AROMATIC [10]-annulene



16π

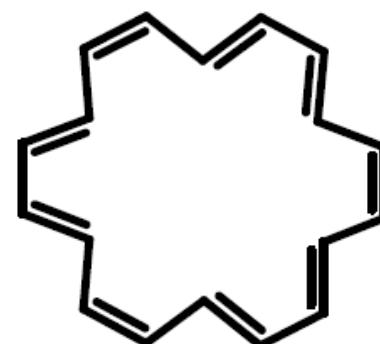
[16]-annulene



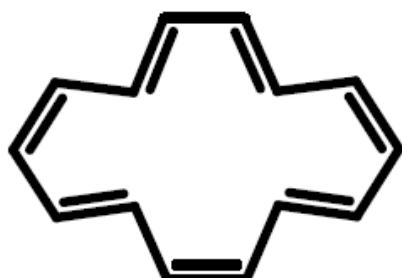
12π

ANTI/NON-AROMATIC

$18\pi = 4(4) + 2$
AROMATIC



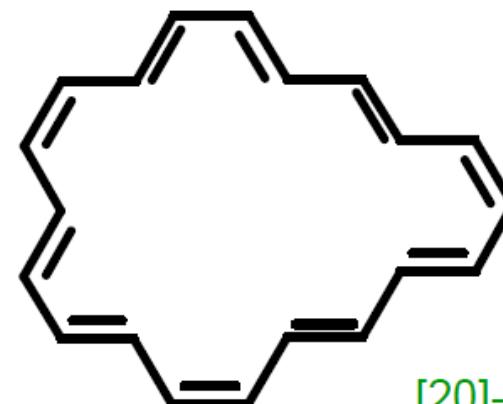
[18]-annulene



$14\pi = 4(3) + 2$

AROMATIC

[14]-annulene

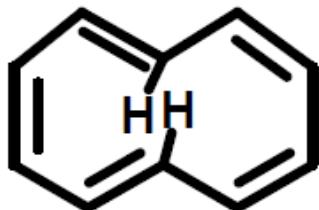


20π

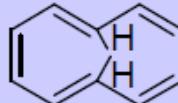
[20]-annulene

ANTi/ NON-AROMATIC

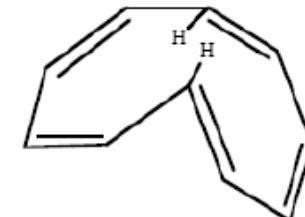
[10] Annulene



all cis
non-aromatic
(too strained
being planar)

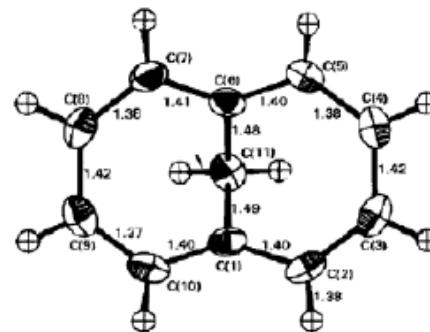
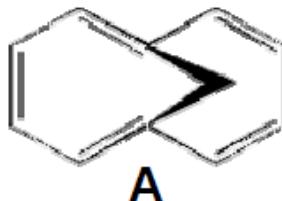


two trans
non-aromatic
(too sterically
crowded to be planar)



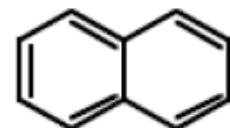
Becomes
nonplanar

A methylene bridge
Introduced to get a
planar pi system



X-ray structure of A.

It showed diamagnetic ring current in NMR
and a bond length pattern as in naphthalene



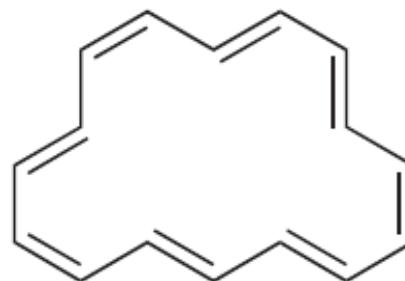
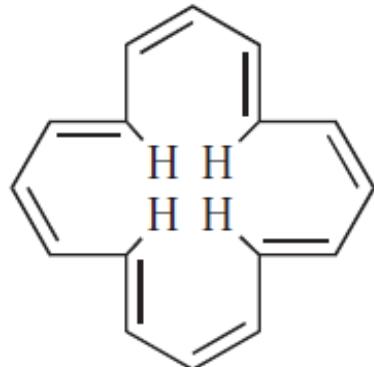
naphthalene

Directly connecting two Carbons in [10]annulene gives naphthalene
.....Again aromatic!

Temperature dependent behavior (Anti/ Non aromatic)



The [12] annulene has been prepared. In solution, it exhibits rapid conformational mobility (as do many other annulenes), and above $-150\text{ }^{\circ}\text{C}$. However, at $-170\text{ }^{\circ}\text{C}$ the mobility is greatly slowed and it shows antiaromatic behavior. Interaction of the ‘internal’ hydrogen atoms in annulene leads to nonplanarity. Above $-50\text{ }^{\circ}\text{C}$, it is unstable and rearranges to a bicyclic compound shown above.

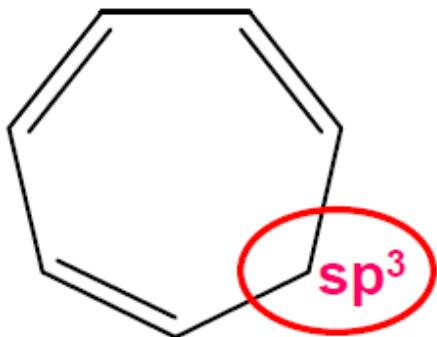


[20] annulene shows a similar behavior. It is Antiaromatic at $-105\text{ }^{\circ}\text{C}$ whereas it loses planarity above $-60\text{ }^{\circ}\text{C}$.

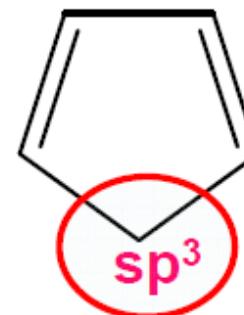
(16) annulene: In solution these two forms A and B are in equilibrium. Above $-50\text{ }^{\circ}\text{C}$ it shows conformational mobility. However, at $-130\text{ }^{\circ}\text{C}$ it shows antiaromatic behaviour. In the solid state, where the compound exists entirely as A, X-ray crystallography shows that the molecules are nonplanar with almost complete bond alternation: The single bonds are $1.44\text{--}1.47\text{\AA}$ and the double bonds are $1.31\text{--}1.35\text{\AA}$.

How about odd numbered rings?

Non-aromatics (with interrupted π cloud)



cycloheptatriene



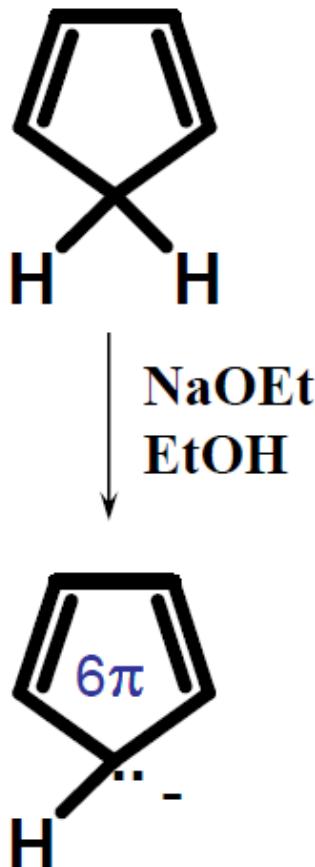
cyclopentadiene

A cyclic compound that does not have a continuous overlapping ring of p orbitals cannot be aromatic or antiaromatic. They are called non-aromatic

However, remove an H (H^+ or H^-) and you may have aromatic or aniaromatic behaviour!

CYCLOPENTADIENYL ANION AND CATION

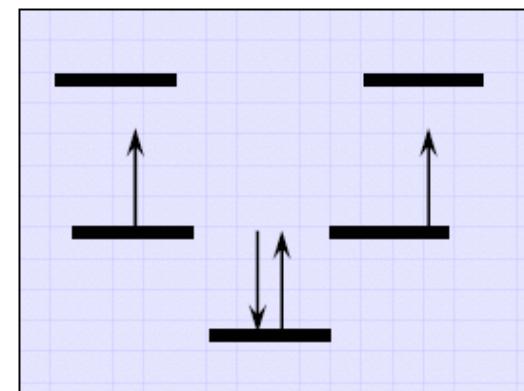
The methylene hydrogens are acidic.



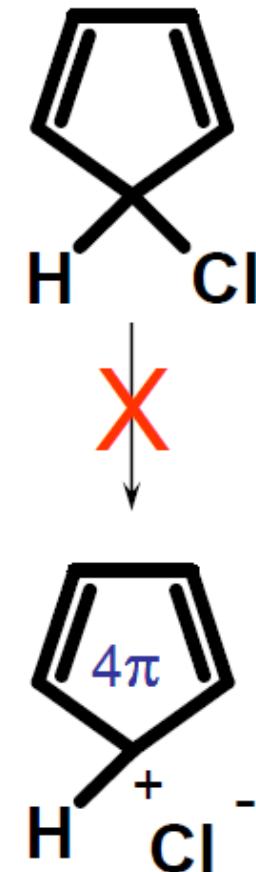
AROMATIC

The anion forms readily.

This compound does not dissolve in water.



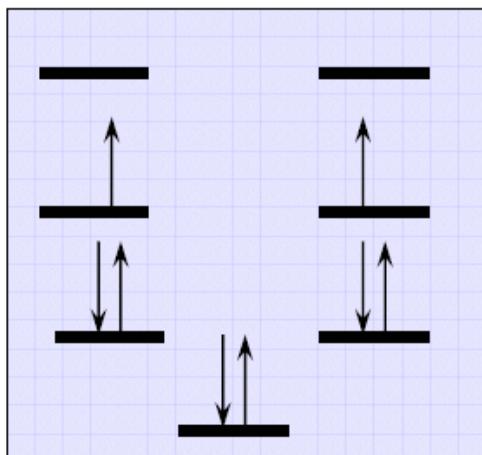
ANTI-AROMATIC



The cation does not form at all.

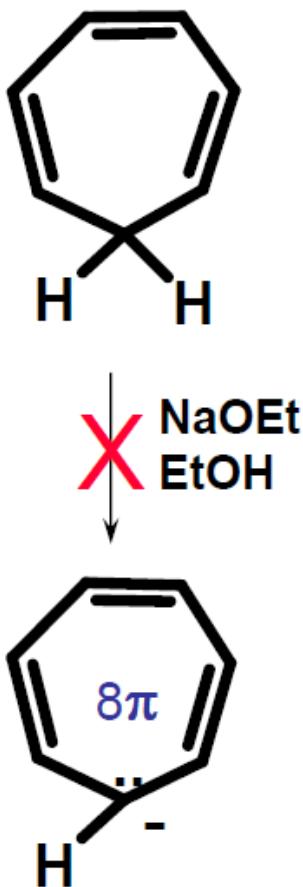
CYCLOHEPTATRIENYL ANION AND CATION

The methylene hydrogens are not acidic.

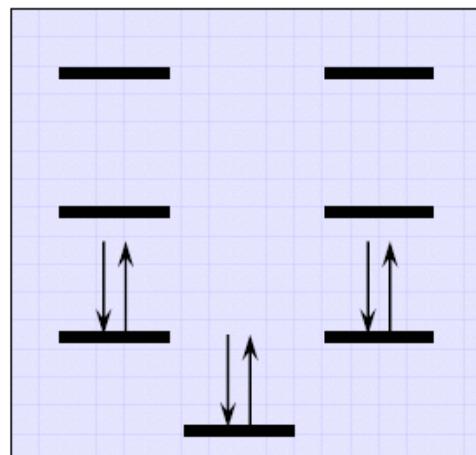


ANTI-AROMATIC

Doesn't form easily

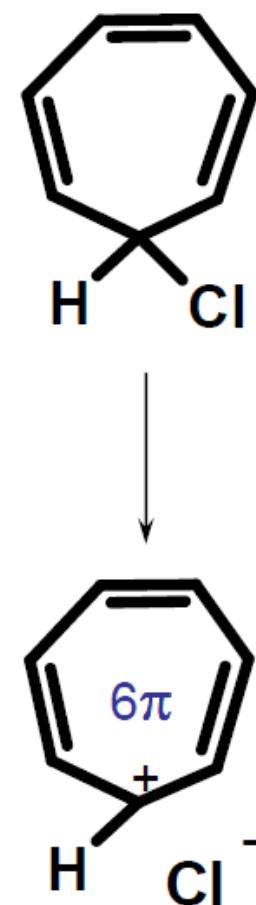


This compound ionizes easily in water.



AROMATIC

Stable; Dissolves in water!



POLYCYCLIC AROMATIC COMPOUNDS can follow HUCKEL 4n+2 RULE

Compounds that have $4n+2 \pi$ electrons in a cyclic array will be aromatic.

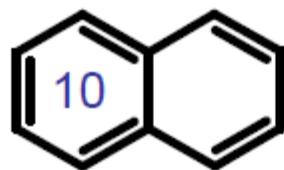
$4n+2$ series = 2, 6, 10, 14, 18, 22, 26, 30 etc.

The rule was formulated by analyzing various benzene and Polycyclic aromatic hydrocarbons

5 pairs
 $(4x2+2)$

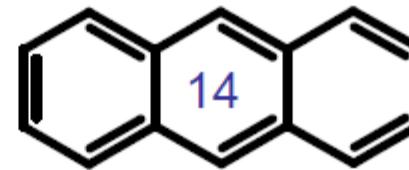


benzene



10

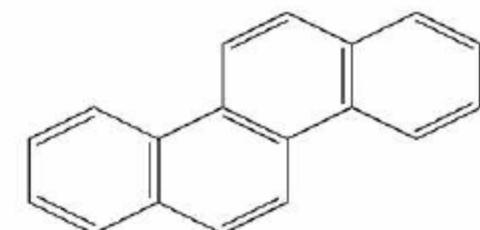
naphthalene



14

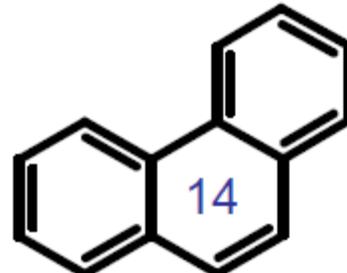
anthracene

9 pairs
 $(4x4+2)$



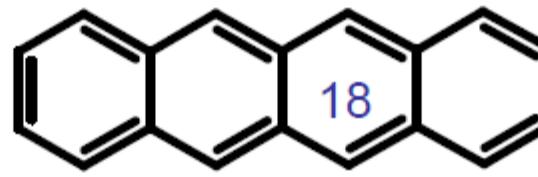
chrysene

7 pairs
 $(4x3+2)$



14

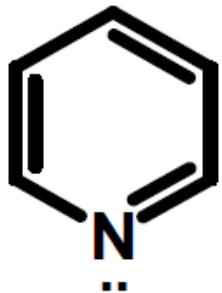
Phenanthrene



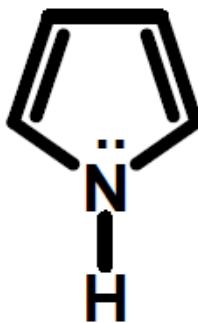
18

tetracene

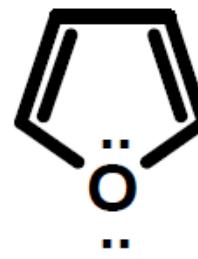
HETEROCYCLIC COMPOUNDS



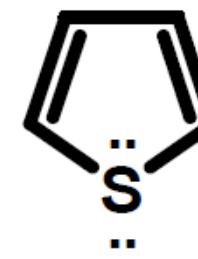
pyridine



pyrrole

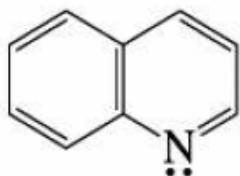


furan

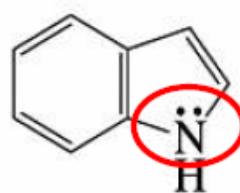


thiophene

Other Heterocyclic Aromatic Compounds



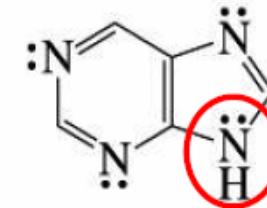
quinoline



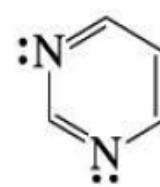
indole



imidazole



purine

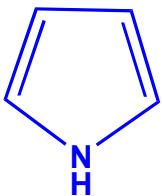


pyrimidine

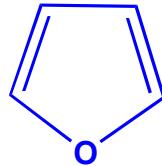
Apply **Hückel's rule** to these systems; See how the basicity of nitrogens (pK_b) in a heterocyclic framework is affected by aromaticity (delocalization); See the orientations (hybridization of atoms) of lone pairs on hetero atoms when
a) they are part of delocalization and b) when they are not; in the case of
b) heterocycles having more than one nitrogen, find out which nitrogen is more basic.

Aromatic Heterocyclic Compounds

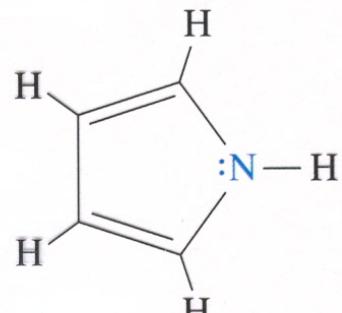
Lone pair is part of the aromatic system



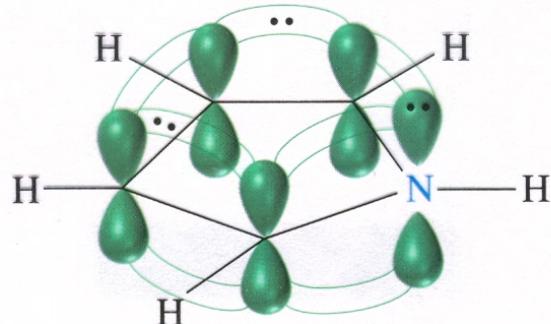
pyrrole



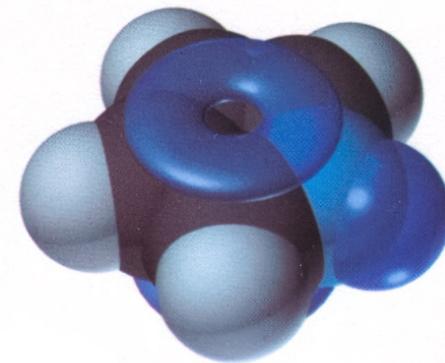
furan



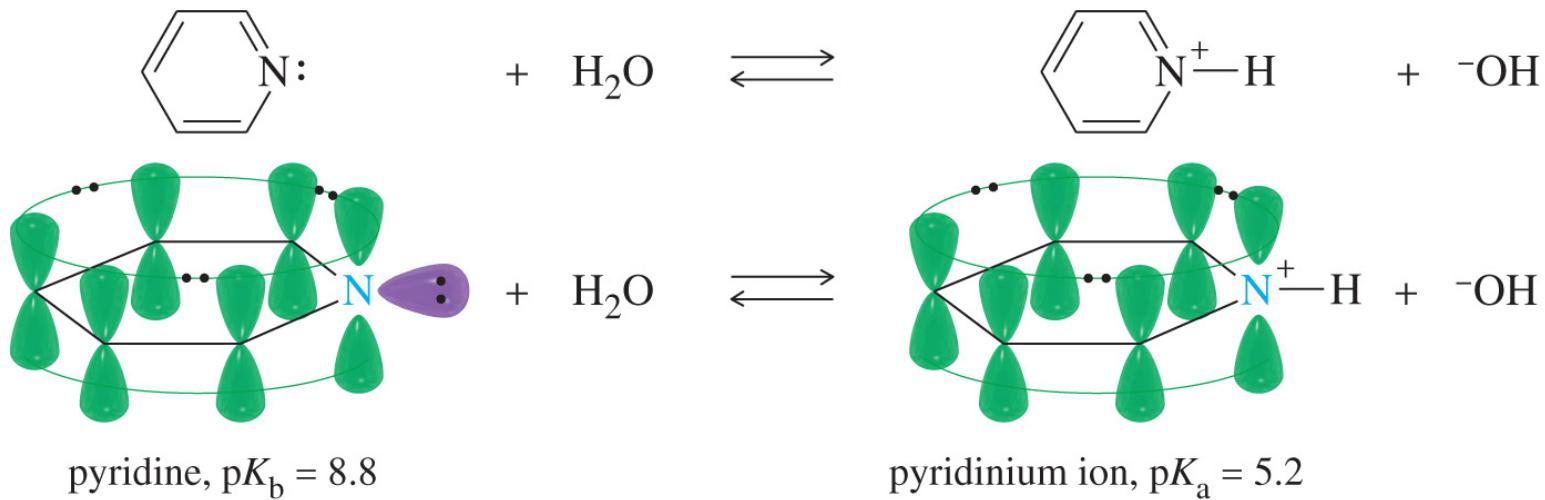
pyrrole



orbital structure of pyrrole
(six pi electrons, aromatic)



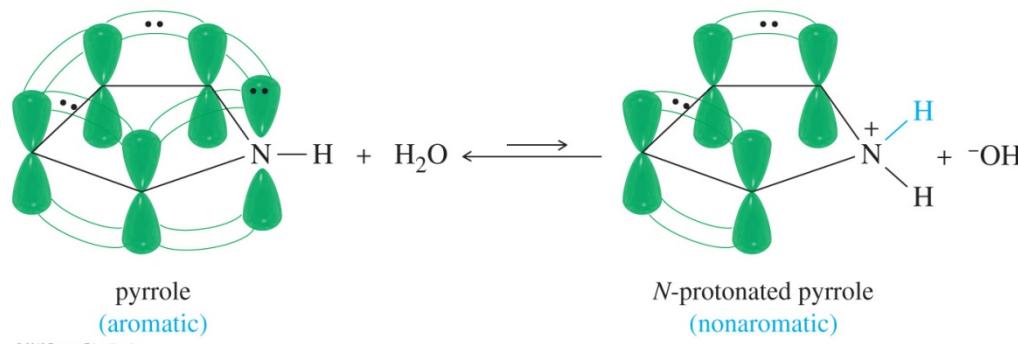
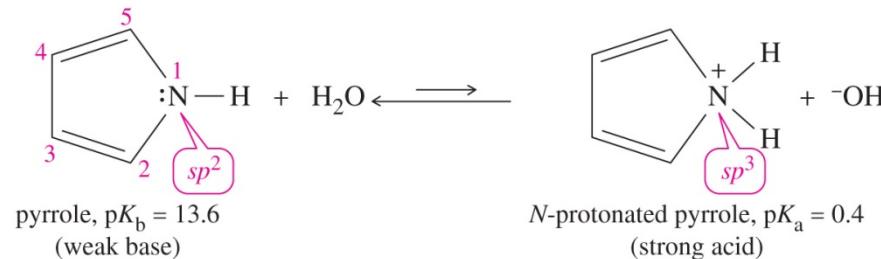
Pyridine is a Base



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- Pyridine is basic, with a pair of nonbonding electrons available to abstract a proton.
- The protonated pyridine (the pyridinium ion) is still aromatic.

Pyrrole is a weak base

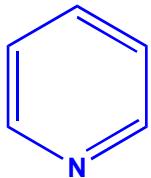


- Pyrrole is aromatic because the lone pair on nitrogen is delocalized.
- *N*-protonated pyrrole is nonaromatic because the nitrogen is sp^3 .

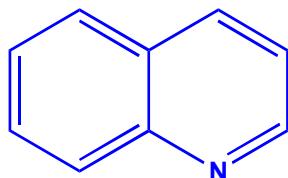
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Aromatic Heterocyclic Compounds

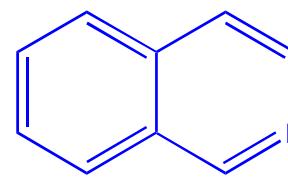
Lone pair not involved in aromatic system



6π electrons



10π electrons



$$4n + 2 = 6, \text{ with } n=1$$

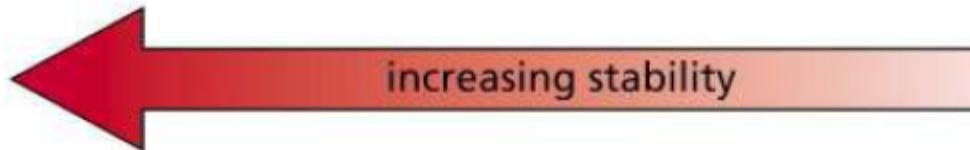
Antiaromaticity

A compound is anti-aromatic if it :

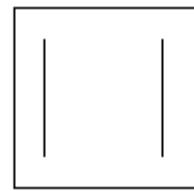
- (1) is Planar and cyclic
- (2) Has Uninterrupted ring of π cloud
- (3) Contains even number of pairs of π electrons ($4n$)

relative stabilities

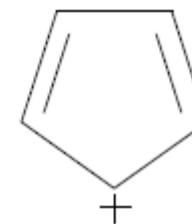
aromatic compound > cyclic compound with localized electrons > antiaromatic compound



Examples



Cyclobutadiene



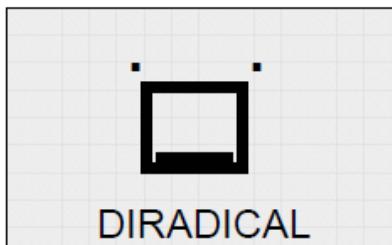
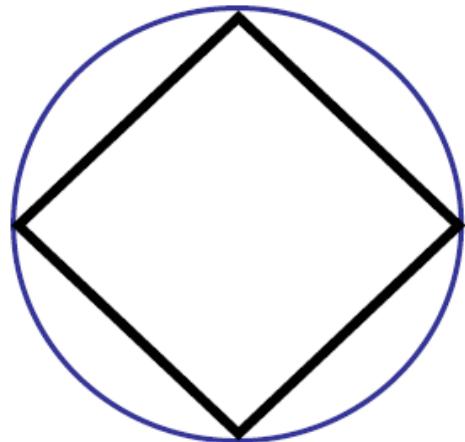
Cyclopentadienyl cation

Both are antiaromatic (4 pi-electrons)

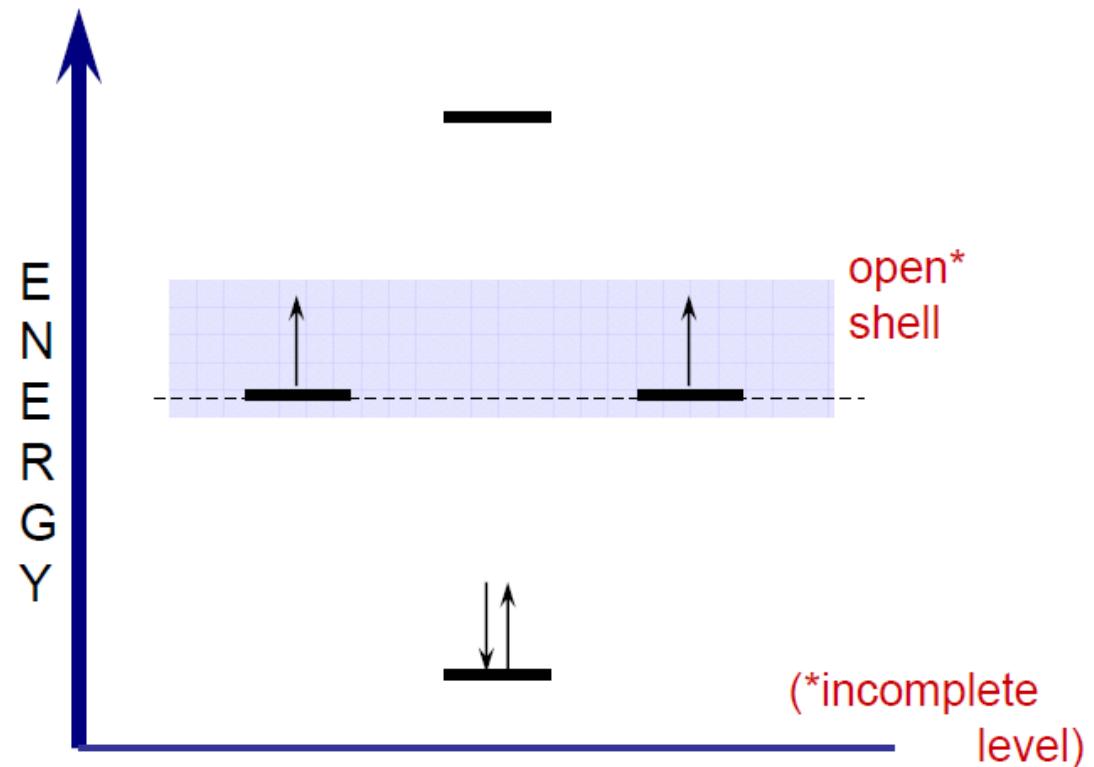
CYCLOBUTADIENE

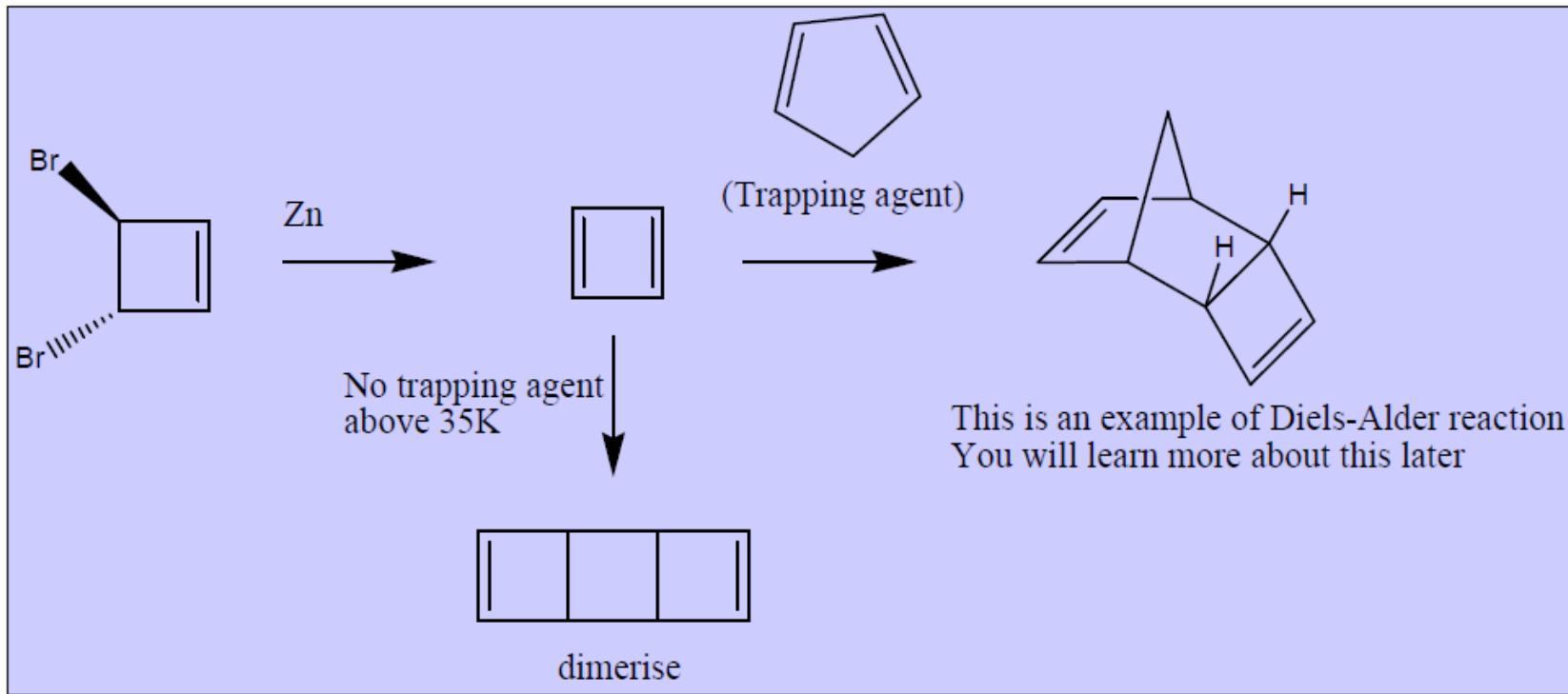


4π electrons

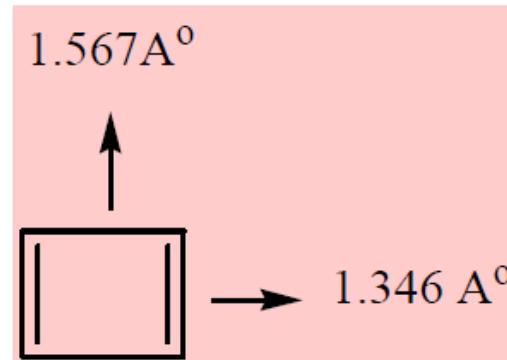


DIRADICAL





Cyclobutadiene is unstable; it can be isolated under controlled conditions such as in Ar matrix or can be trapped with suitable dienes. Studies show that it has a rectangular structure rather than a square.

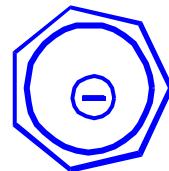
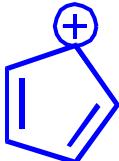


Jahn-Teller Distortion

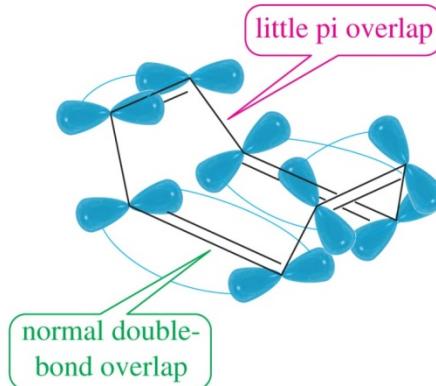
Examples of Antiaromatic Compounds

Cyclic planar molecules with conjugated $4n \pi$ -electrons (where n is an integer) are antiaromatic

Antiaromatic compounds are less stable than the open chain counterpart



eight pi electrons



Azepine

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A cyclic compound that does not have a continuous conjugated p orbitals are known as nonaromatic

e.g., 1,3,5-cycloheptatriene

Effect of aromaticity on properties



- Cyclopentadiene pKa is 15 whereas that of cycloheptatriene is 46.
- Azulene has dipole moment of 0.8 D.
- Tropylium bromide is actually ionic compound.
- Pyrrole is much weaker base than pyridine.
- 1,2,3,4,5-penta(trifluoromethyl)cyclopentadiene is stronger acid than nitric acid!
- Ferrocene (Cp_2Fe) undergoes electrophilic aromatic substitution.
- When 3-chlorocyclopropene is treated with SbCl_5 , it forms a stable salt. (This chemical behavior is to be contrasted with that of 5-chloro-1,3-cyclopentadiene, which cannot be made to form a stable salt.)

Think about it!

Significance of Orbital Energies

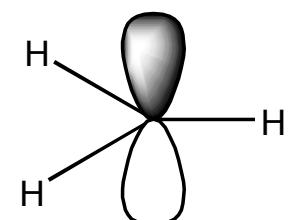
Donors and Acceptors

**Nucleophiles have higher energy filled nonbonding orbitals
(Ready to donate electrons to suitable electrophiles)**

e.g., nonbonding MO in NH_3 that contains the lone pair of electrons is responsible for the nucleophilic nature of the molecule

Electrophiles are characterized by lower energy unfilled nonbonding orbitals

e.g., empty nonbonding MO in BF_3 or CH_3^+



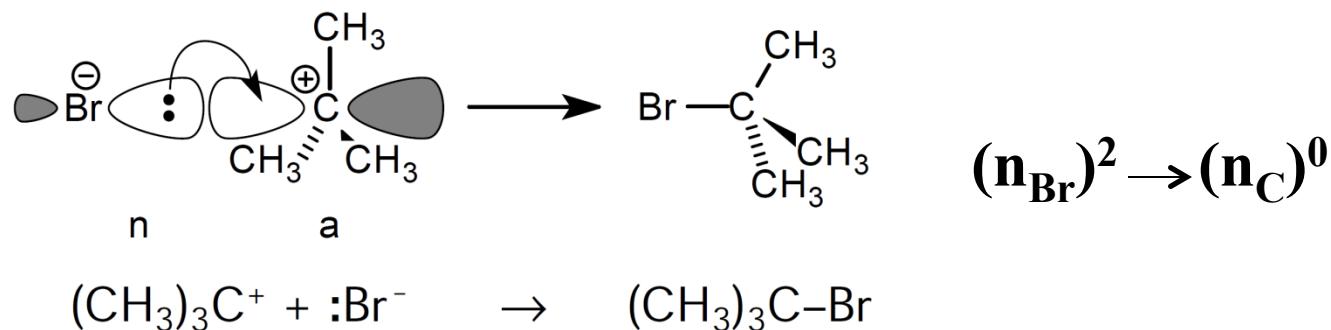
Electron Rich to Electron poor

Possible HOMO-LUMO Combinations

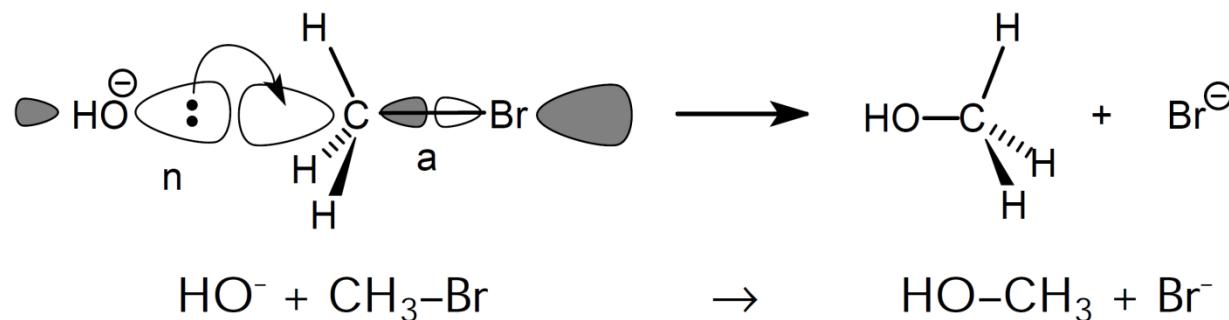
HOMO	LUMO	Result
an occupied n orbital	an empty a orbital	bond formation only
an occupied n orbital	a σ^* orbital	bond formation and bond rupture
an occupied n orbital	a π^* orbital	bond formation and bond rupture
a π orbital	an empty a orbital	bond formation and bond rupture
a π orbital	a σ^* orbital	bond formation and bond rupture
a π orbital	a π^* orbital	bond formation and bond rupture
a σ orbital	an empty a orbital	bond formation and bond rupture
a σ orbital	a σ^* orbital	bond formation and bond rupture
a σ orbital	a π^* orbital	bond formation and bond rupture

Explanation of Reactions Through Molecular Orbitals

1. non bonding orbital + atomic orbital: S_N1



2. non bonding orbital + antibonding orbital (σ^*): S_N2

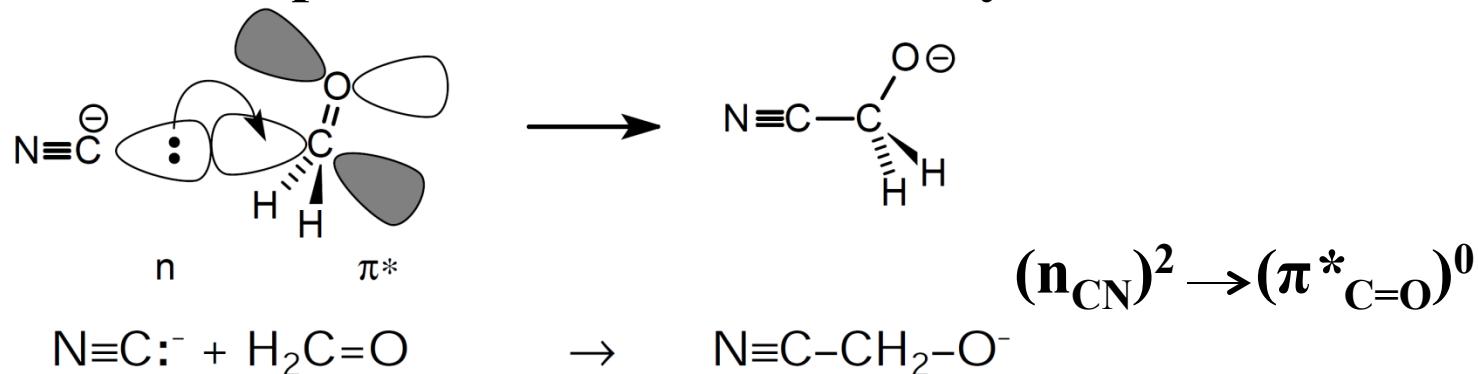


“Back-side attack”

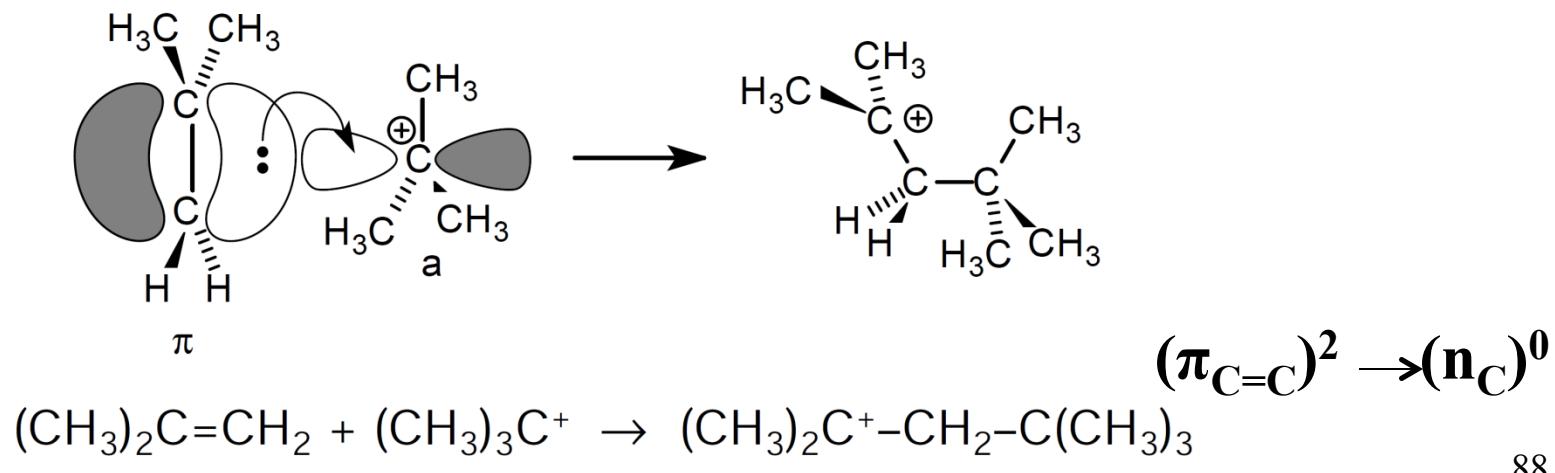
$(n_O)^2 \rightarrow (\sigma^*_{C-Br})^0$

Explanation of Reactions Through Molecular Orbitals

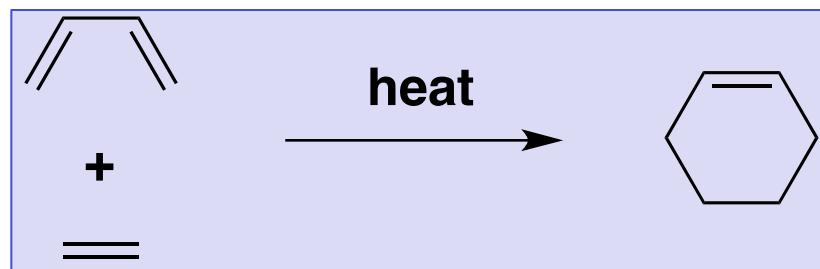
3. $n + \pi^*$: Nucleophilic addition on carbonyls



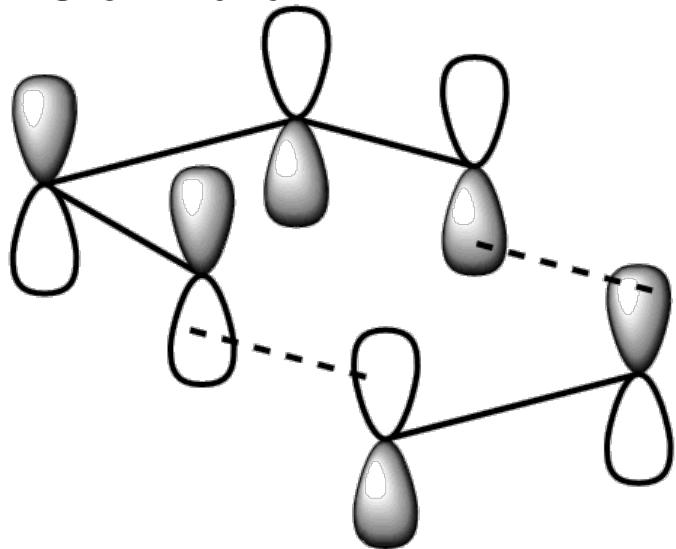
4. $\pi + n$: addition on olefins



FMO Treatment of [4+2] Cycloaddition reaction

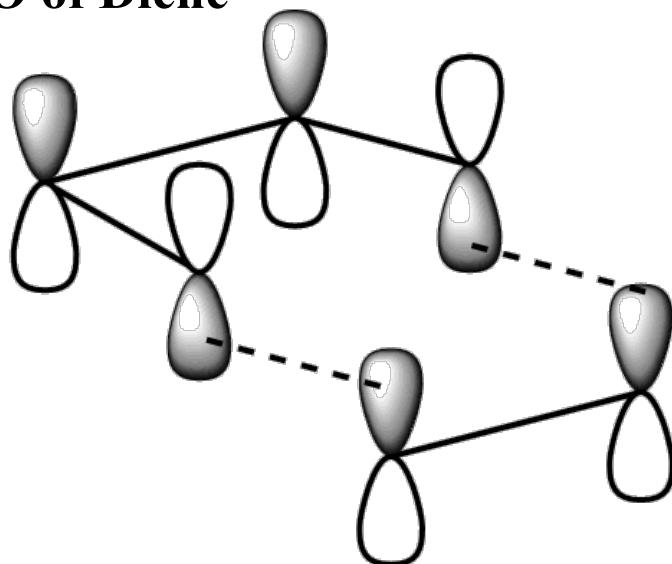


HOMO of Diene



LUMO of Dienophile

LUMO of Diene

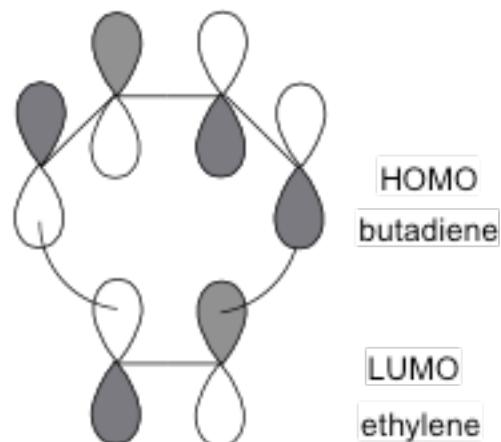
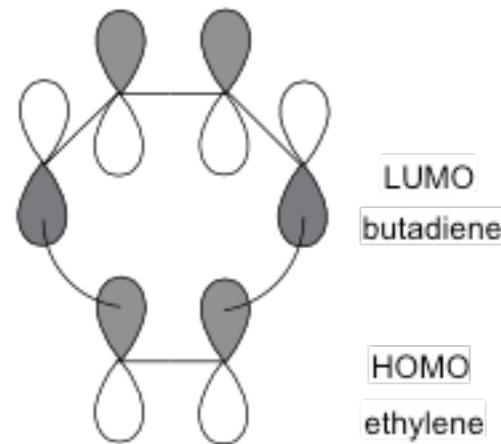


HOMO of Dienophile

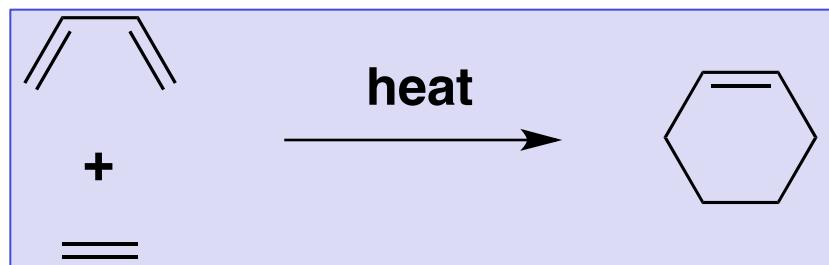
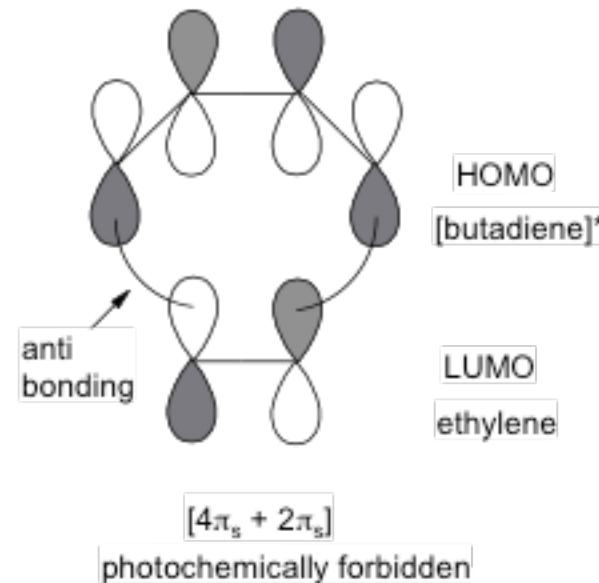
Phases match – leads to bond formation

What will be outcome with light as source of energy?!

FMO Treatment of [4+2] Cycloaddition reaction



$[4\pi_s + 2\pi_s]$
thermally allowed



THANK YOU