

CH 105: Organic Chemistry

Molecular Orbital Theory



Santosh J. Gharpure
Room No. 440
Department of Chemistry,
IIT Bombay, Powai
Mumbai – 400076
e-mail: sjgharpure@chem.iitb.ac.in
sjgharpure@gmail.com
Phone: 2576 7171
Cell: 9167948171

TAs:
Dharmendra
Padmaja
Dipak
Sanyog

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Oxford University Press

Outline

- **Huckel Theory For Conjugated Systems**
- **Stereochemistry**
- **Conformational Analysis**
- **Chemistry of Carbonyl Compounds**

Text Book

- **Organic Chemistry : Structure and Function by Volhardt & Schore, 5th Edition**
<http://bcs.whfreeman.com/vollhardtschore5e/default.asp>

Additional Reading

- **Organic Chemistry, Clayden, Green, Warren and Wothers, Oxford University Press**

Animations

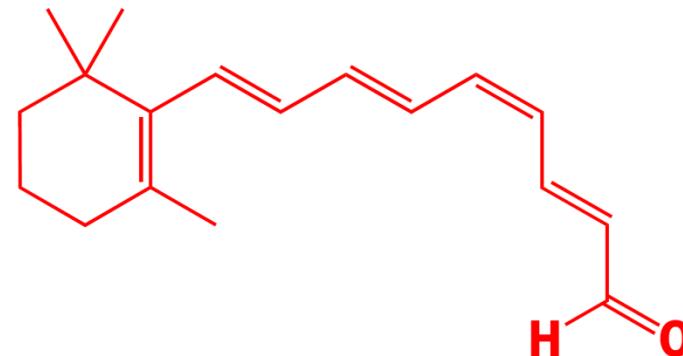
<http://www.chemtube3d.com/>

Course Outline and Evaluation

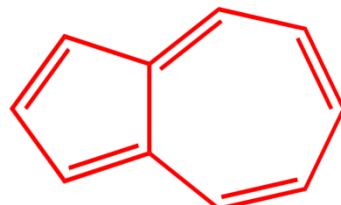
- **Organic Chemistry till Mid Sem (September 7)**
- **Evaluation: Organic + Inorganic (one grade)**
- **For Organic: One exam (Quiz) of 50% credit (It is final exam for Organic!) – Duration 2 hours**
- **Exam: During Mid-Sem period (exact date to be confirmed)**

Why Organic Chemistry?

Let's look at how our senses respond to molecules!!



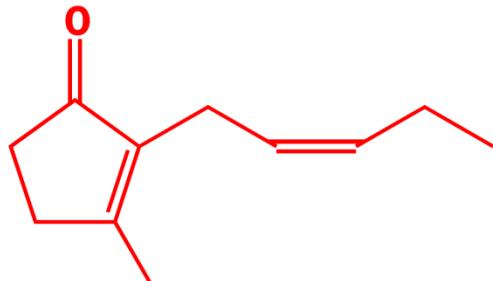
- **Sense of Sight:** 11 *cis*-retinal absorbs light when we see



Azulene, deep blue colour with pepper smell

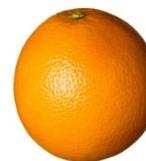
Why Organic Chemistry?

- **Sense of Smell:** *cis*-jasmone is responsible for jasmine smell.

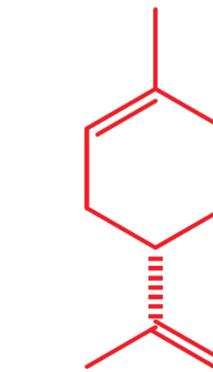


cis-jasmone

enantiomeric
smells



R(+)-limonene
smells of oranges



S(-)-limonene
smells of lemons



skunk spray contains:

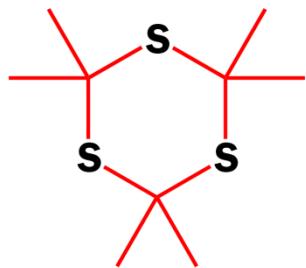


Why Organic Chemistry?



thioacetone

?



trithioacetone;
Freiburg was evacuated
because of a smell from
the distillation this compound

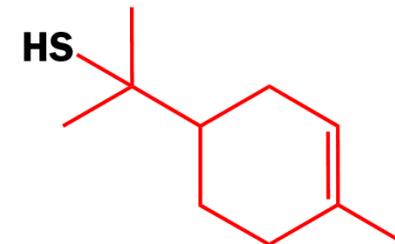
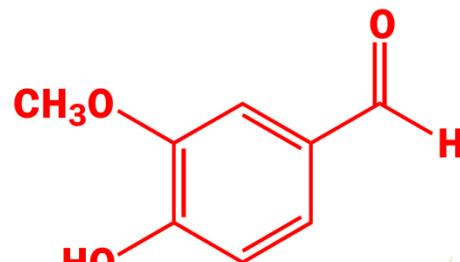


the divine smell
of the black truffle
comes from this compound

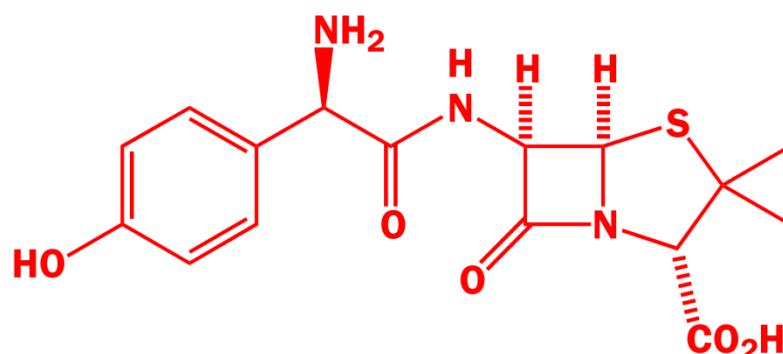


Why Organic Chemistry?

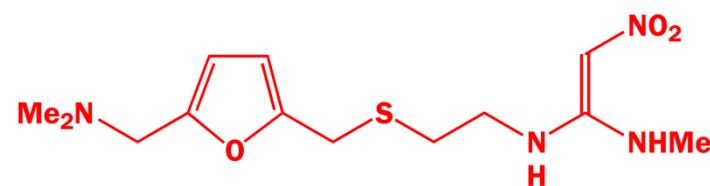
vanillin
found in vanilla pods;
manufactured
on a large scale



flavouring principle of grapefruit

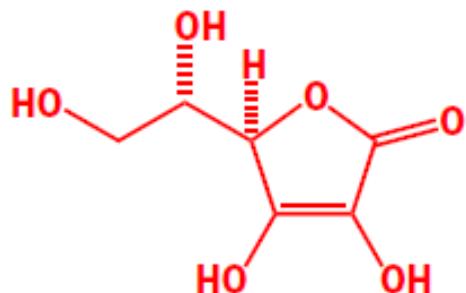


SmithKline Beecham's amoxycillin
β-lactam antibiotic
for treatment of bacterial infections



Glaxo-Wellcome's ranitidine
the most successful drug to date
world wide sales peaked >£1,000,000,000 per annum

Why Organic Chemistry?

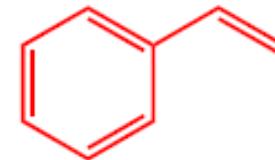


vitamin C (ascorbic acid)

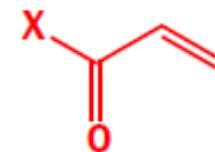


Plastics and
clothing fibres come
from their polymers.

monomers for polymer
manufacture



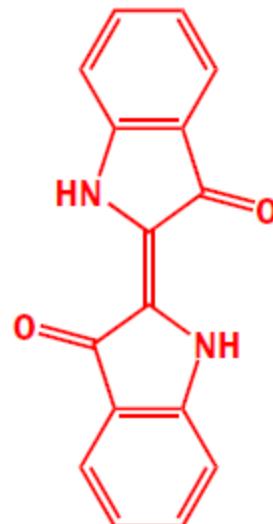
styrene



acrylates



vinyl chloride



indigo
the colour of blue jeans

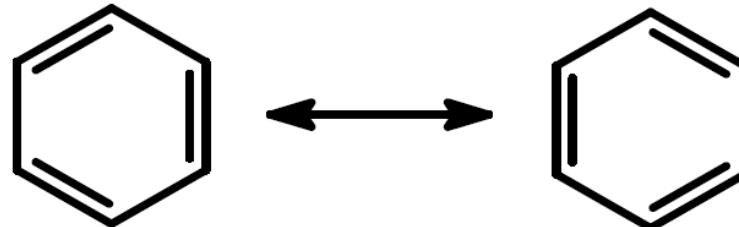
There is a necessity to
understand chemistry
and behaviour of
molecules

Aromaticity: Benzene



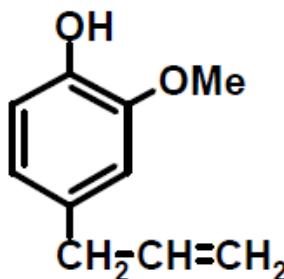
Michael Faraday
(1825): first isolated
benzene

BENZENE

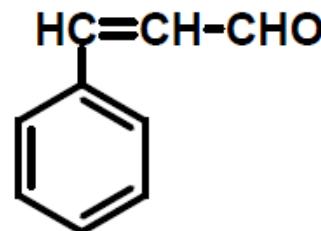


Friedrich Kekulé (1866)

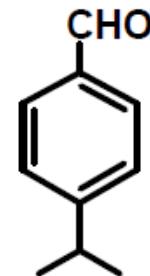
Aroma = Characteristic Odour



eugenol
(cloves)



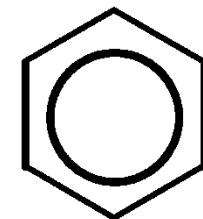
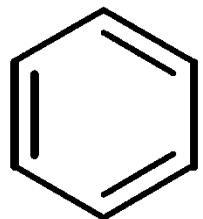
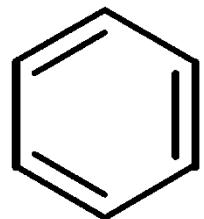
cinnamaldehyde
(cinnamon)



cuminaldehyde
(cumin)

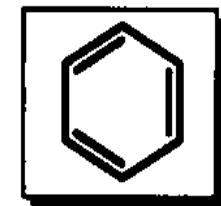
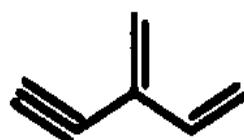
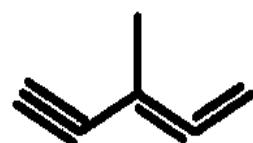
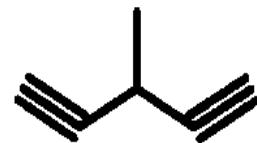
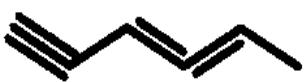
IN TODAY'S CONTEXT "AROMATIC" IS A MISNOMER!!¹¹

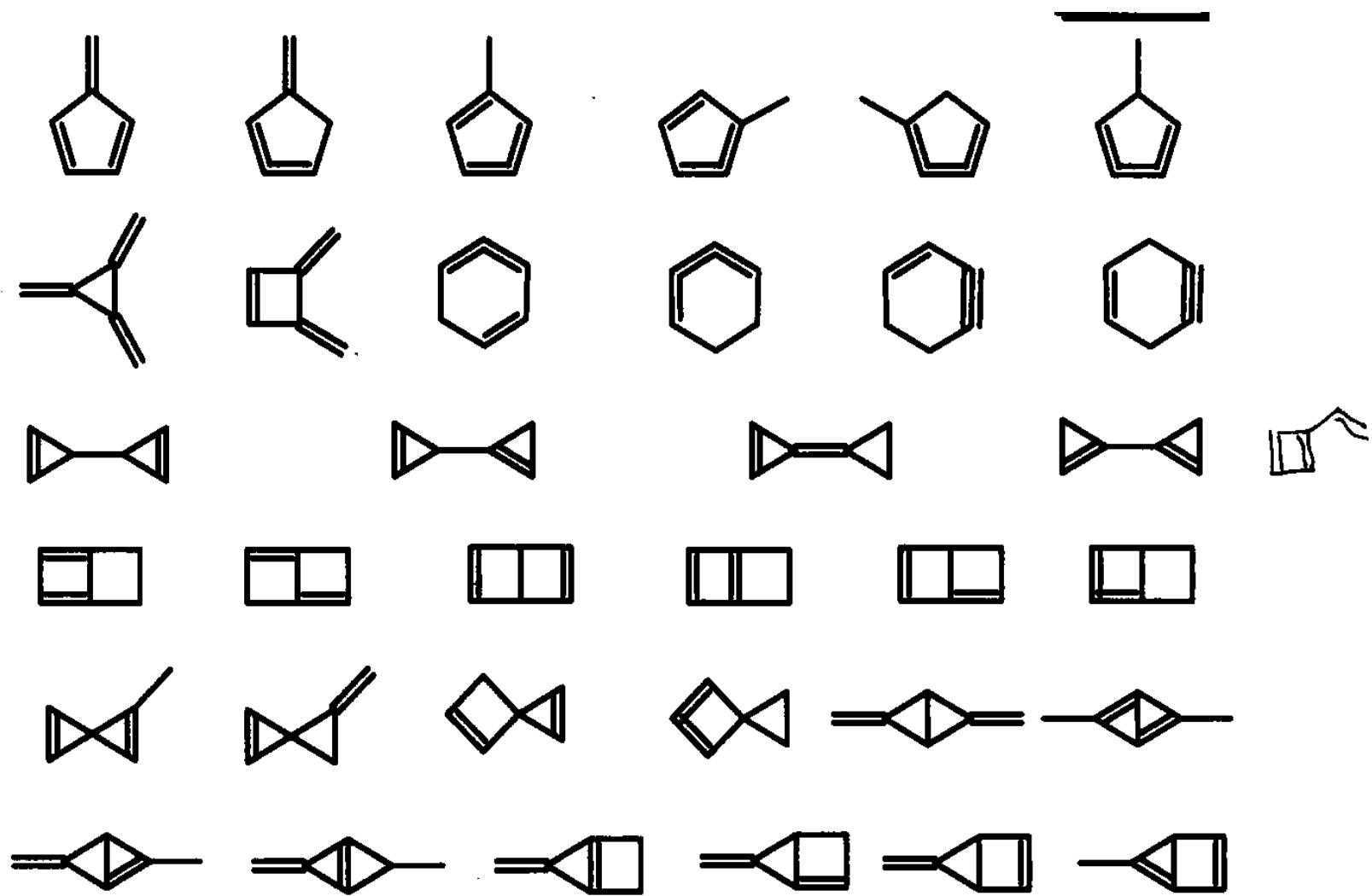
C_6H_6 : How many isomers??

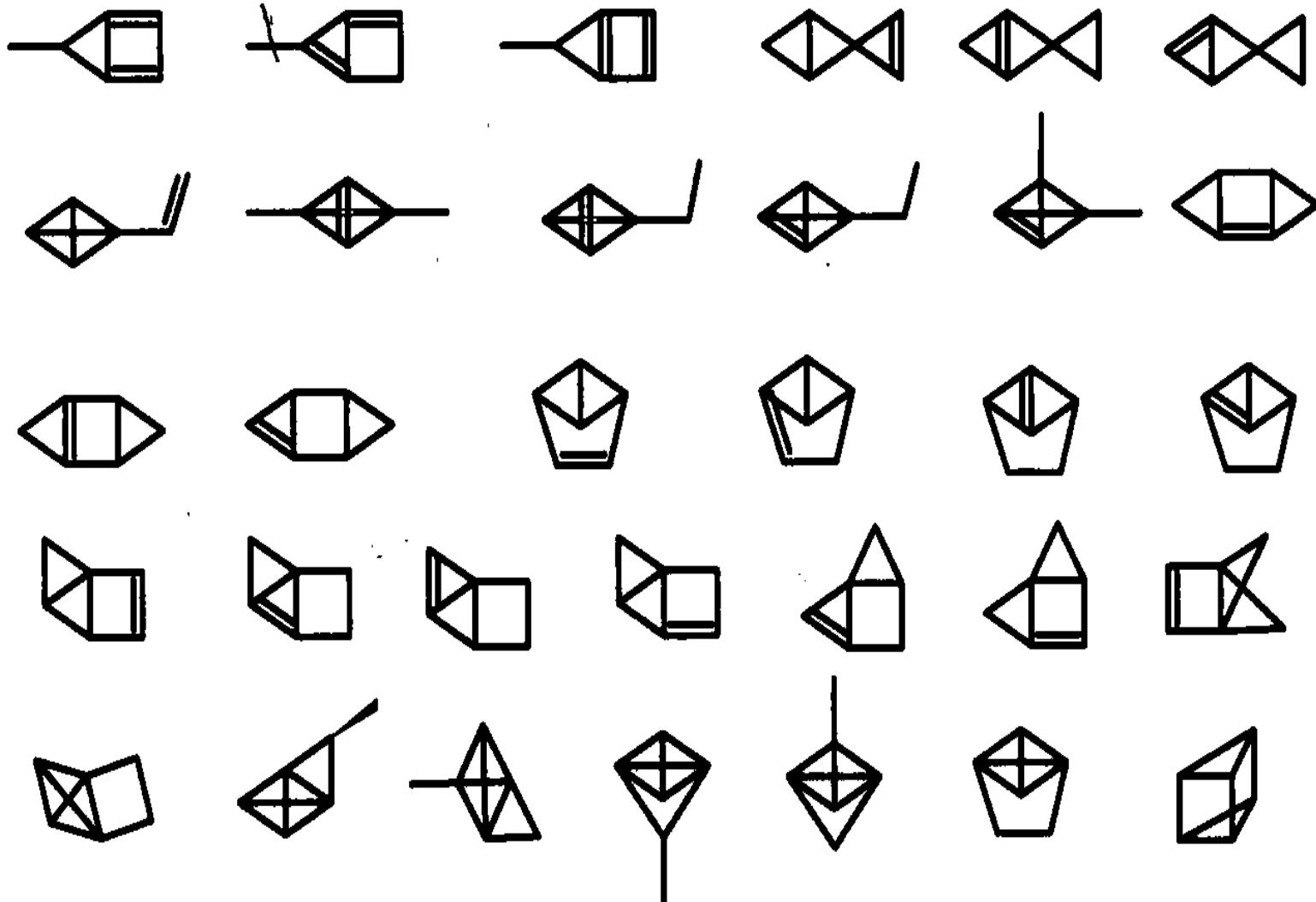


???

Isomers of Benzene (C_6H_6)





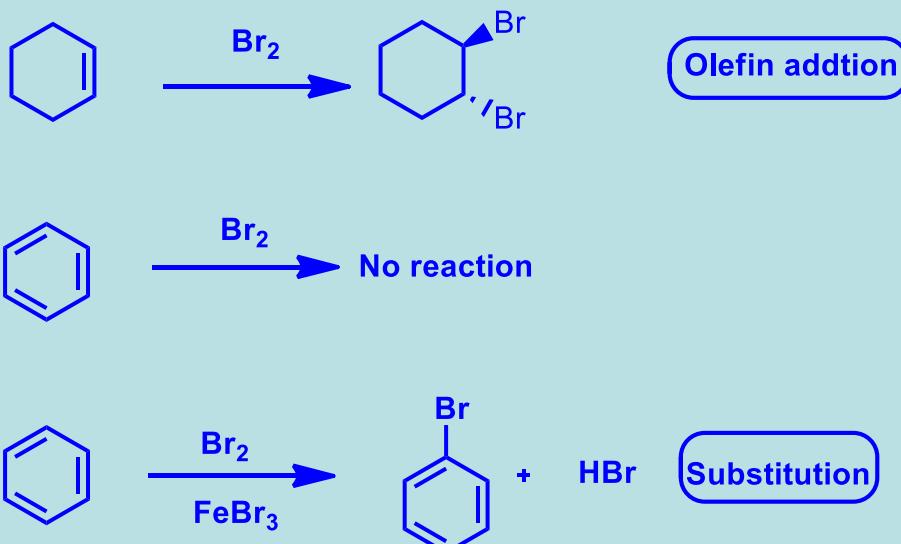


Totally 217 isomers are possible!
Only benzene is aromatic!!

So What is Aromatic? – Benzene Like Molecules

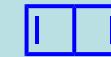
Benzene is special:

Reactions:

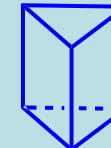


Structure:

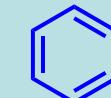
Several Proposed structure:



Dewar benzene



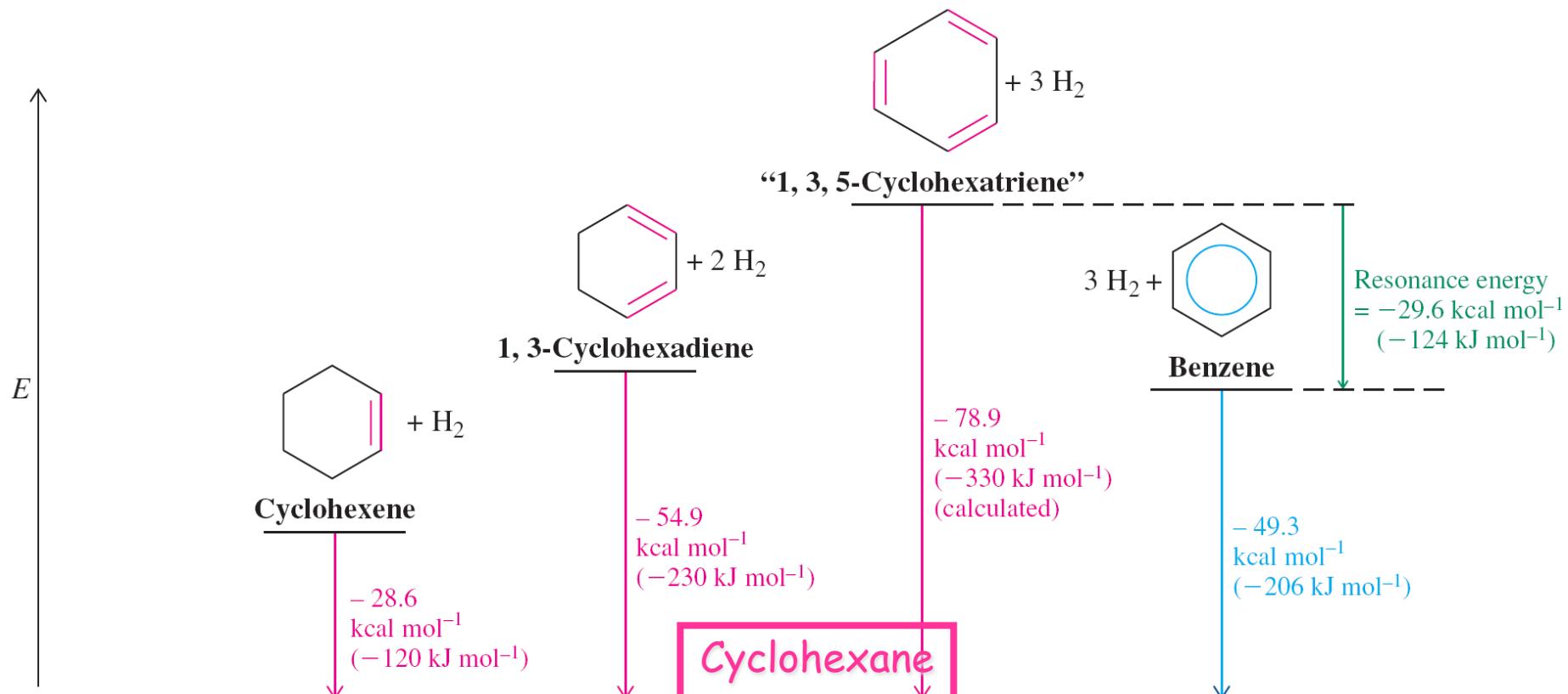
Prismane
(1879)



Kekulé benzene
(1865)

Kekulé suggested “rapid C=C oscillation feature”
What we call today as resonance

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

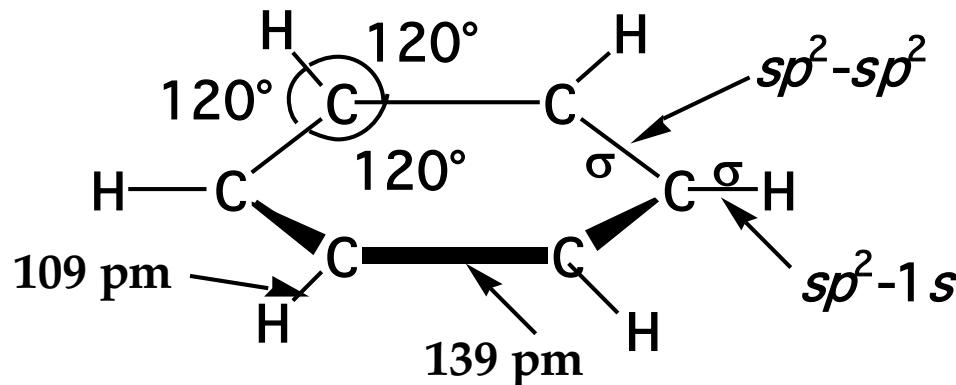


Special stability is now called **aromaticity**. All cyclic 6e¹⁶ arrangements are aromatic, including transition states.

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.

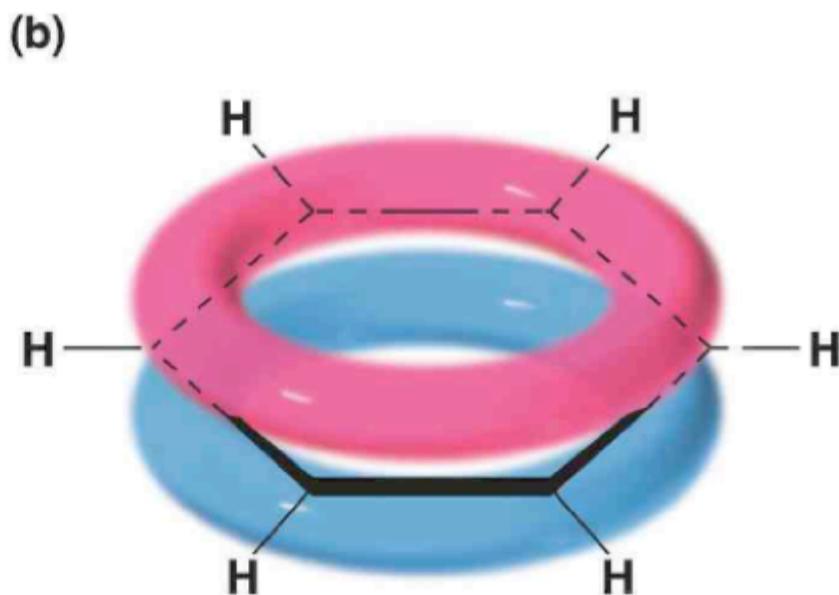
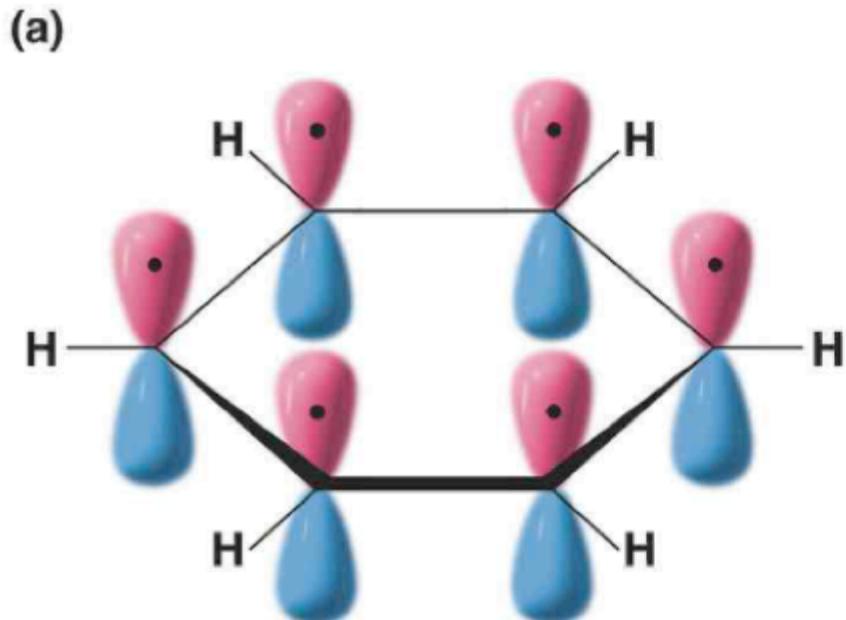
- The carbon skeleton is a planar regular hexagon.
- All C-C-C and H-C-C bond angles 120° .



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

Benzene: Structure

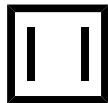
- (a) The carbon framework with the six $2p$ orbitals.
- (b) Overlap of the parallel $2p$ orbitals forms one torus above the plane of the ring and another below it
- this orbital represents the lowest-lying pi-bonding molecular orbital.



Is Benzene UNIQUE?

How about other Annulenes?

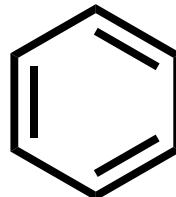
Annulenes: Monocyclic hydrocarbons with alternating single and double bonds



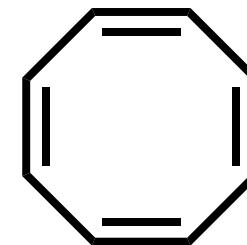
cyclobutadiene
[4]-annulene

Highly Unstable
Bonds are localized
Isolated in argon matrix

Just conjugation not
enough!

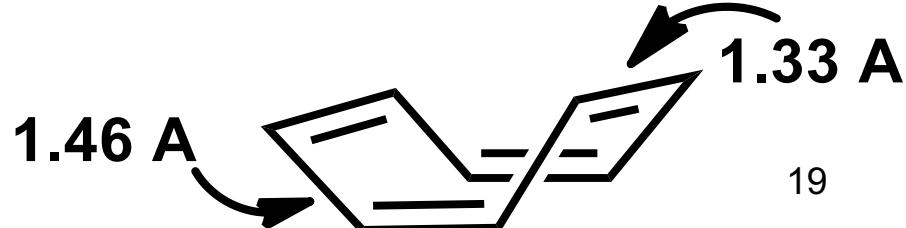


benzene
[6]-annulene



cyclooctatetraene
[8]-annulene

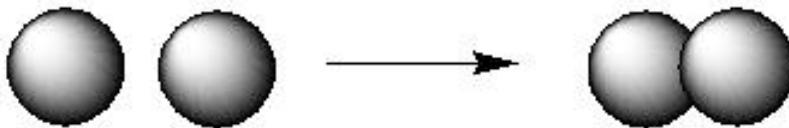
Not “Aromatic”
Tub shaped
Localized Bonds



Molecular Orbital Theory

Types of overlap between orbitals

Sideways overlap of atomic orbitals



s-s orbital overlapping

(ii)



s-p orbital overlapping

(iii)



p-p orbital overlapping

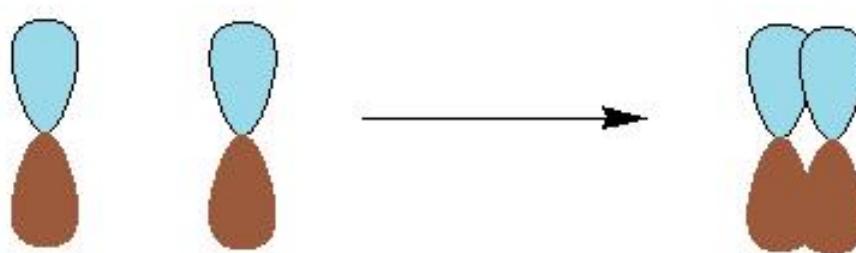
end to end overlapping of p orbitals produces a sigma covalent bond

σ -type overlap contain no nodes along the internuclear axis. (Ignore AO nodes e.g. of p orbital)

Types of overlap between orbitals

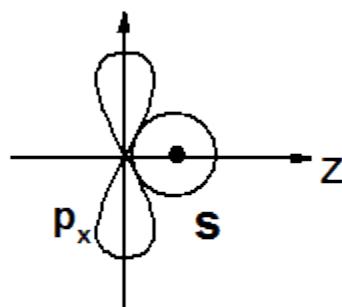
lateral overlap of atomic orbitals

(iv)

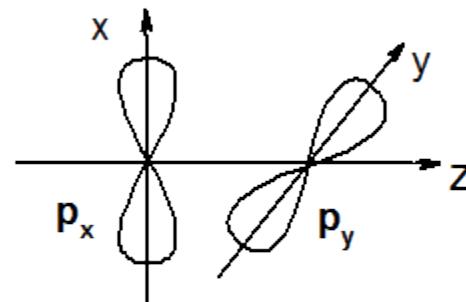


p-p orbital overlapping

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

Molecular Orbital Theory and LCAO

Molecular orbitals are obtained by combining the atomic orbitals on the atoms in the molecule.

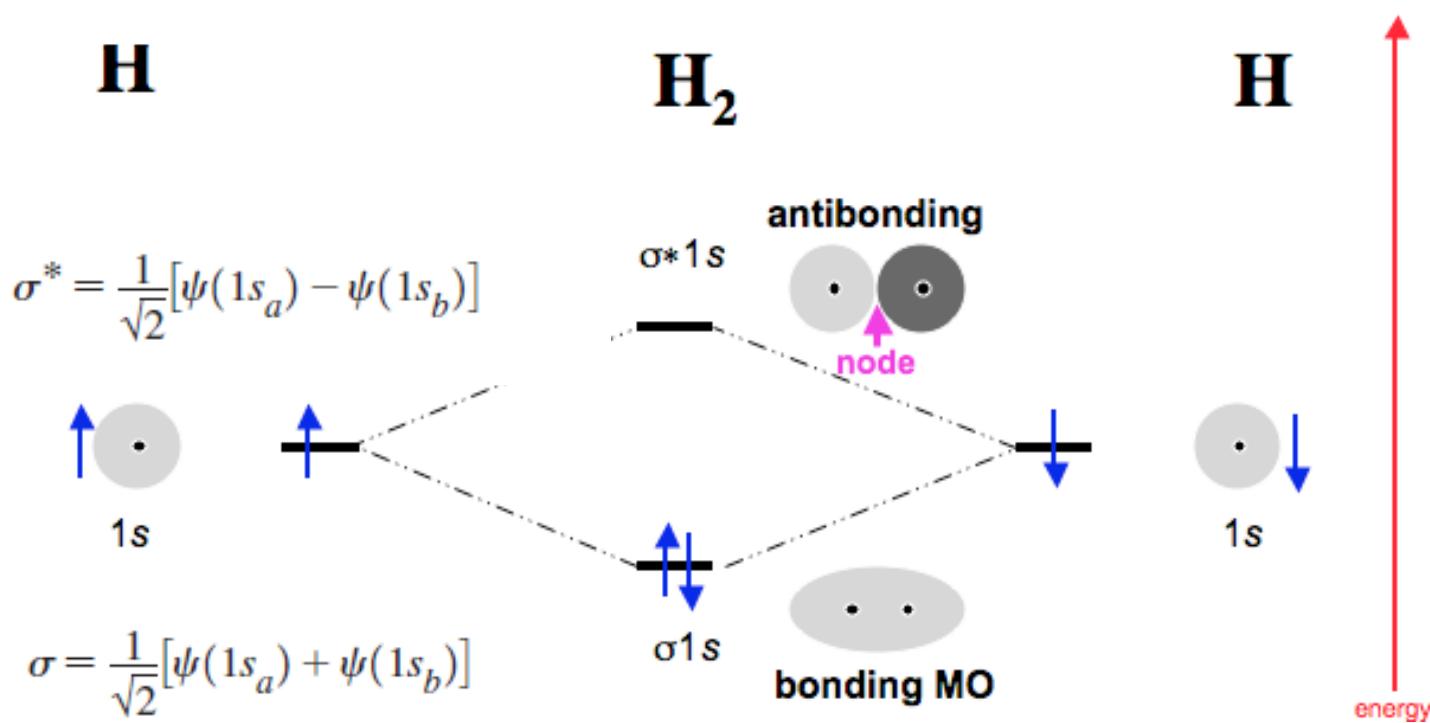
A **Linear Combination of Atomic Orbitals (LCAO)** is a quantum superposition of atomic orbitals and a technique for calculating molecular orbitals in quantum chemistry. The expression (linear expansion) for the j^{th} molecular orbital would be:

$$\Psi_j = c_{1j}\Phi_1 + c_{2j}\Phi_2 + \dots c_{nj}\Phi_n$$

or

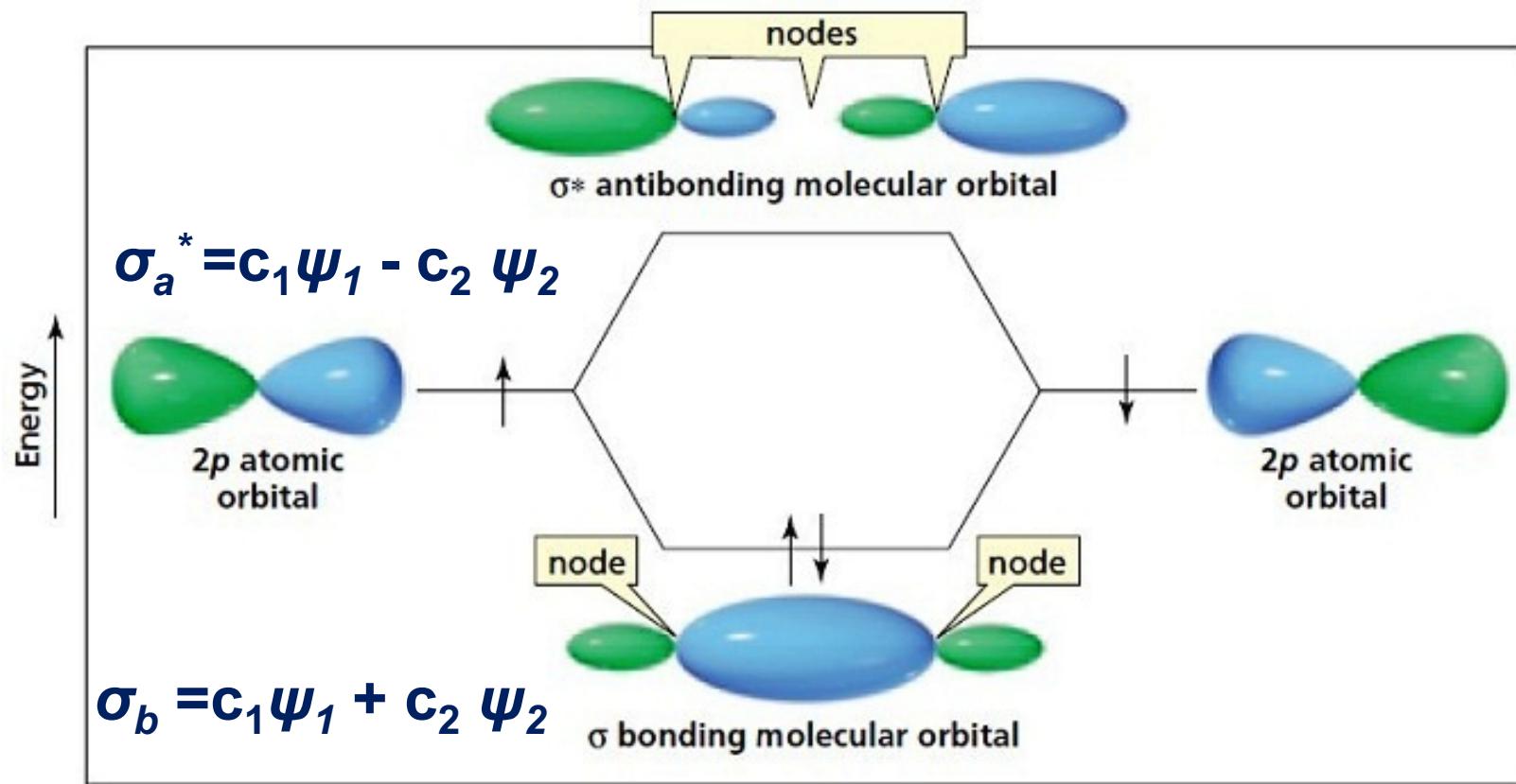
$$\Psi_j = \sum c_{rj}\Phi_r \quad r = 1, 2, \dots n$$

Overlap of s-Orbitals



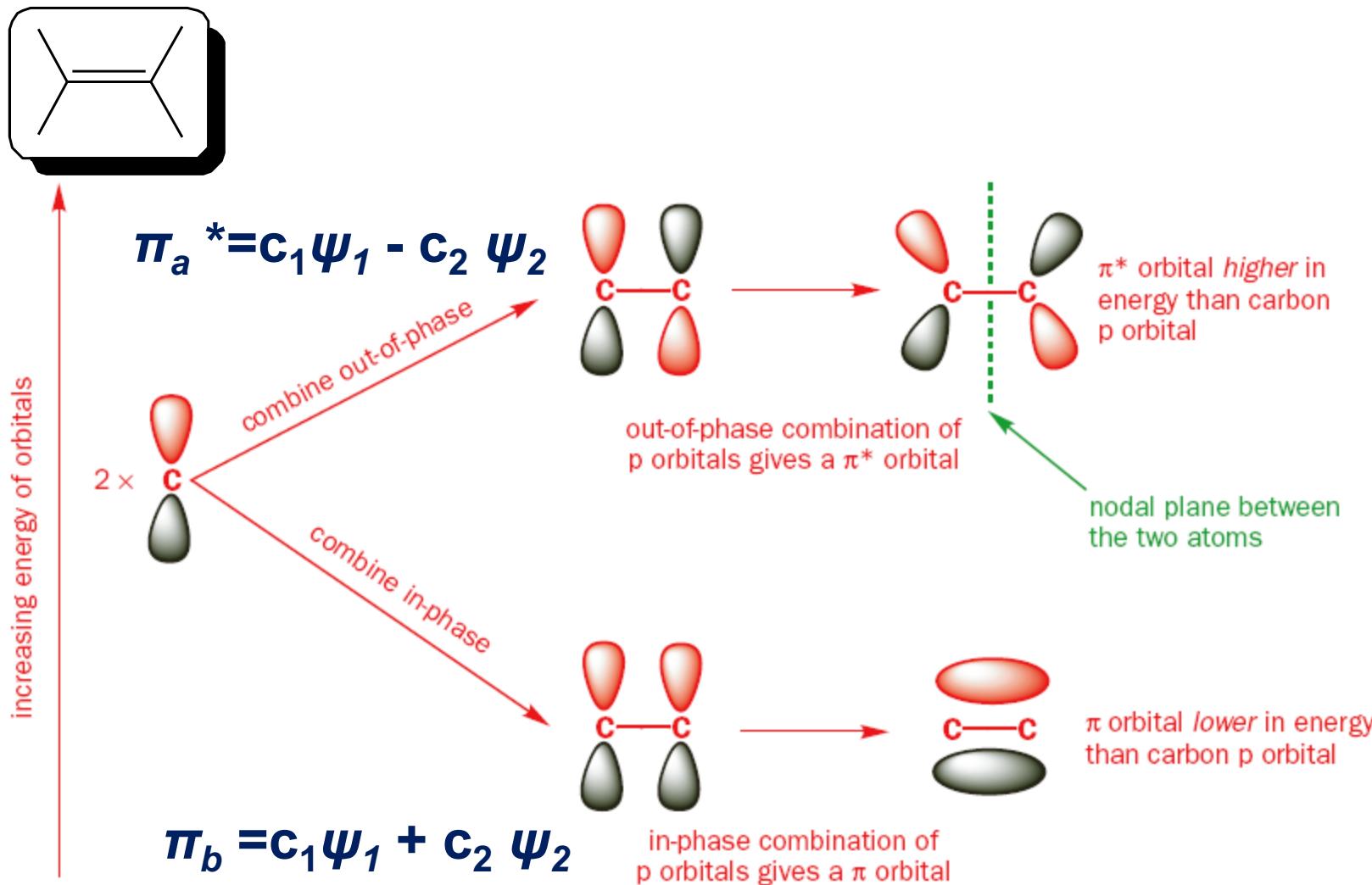
For any bonding molecular orbital (BMO) there should be a corresponding antibonding molecular orbital (ABMO)

Overlap of p-orbitals: Head-on overlap

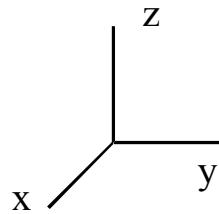


These orbitals are symmetrical even in presence of nodes
Symmetric along the axis

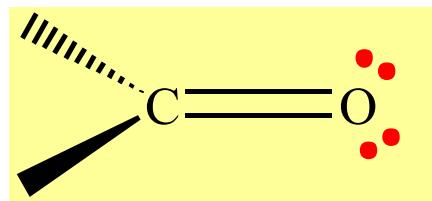
Types of Orbitals: Lateral Overlap



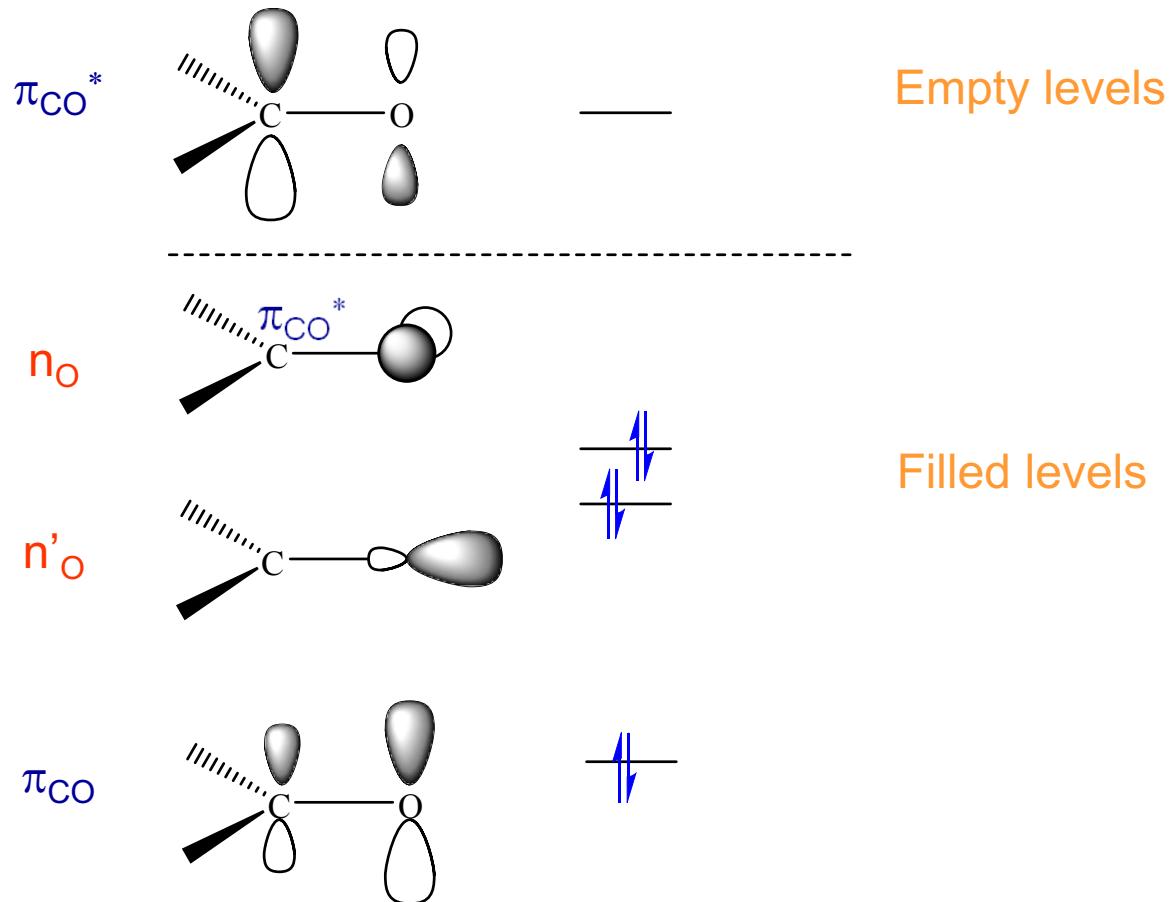
Types of Orbitals: Formaldehyde



In xy-plane



Frontier MOs



Nonbonding molecular orbital (NBO) Not involved in bonding! 27

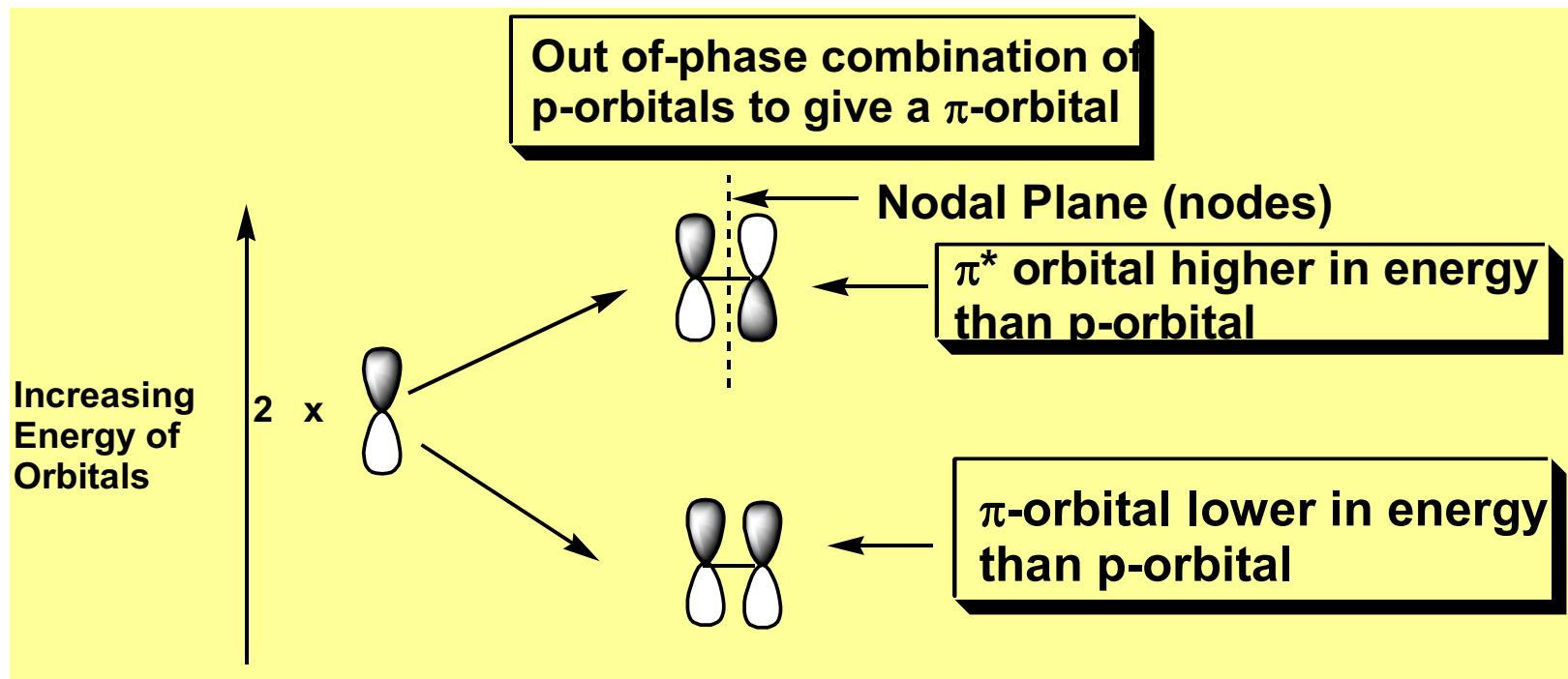
So How Do We Draw Molecular Orbitals ??

Ethylene MOs

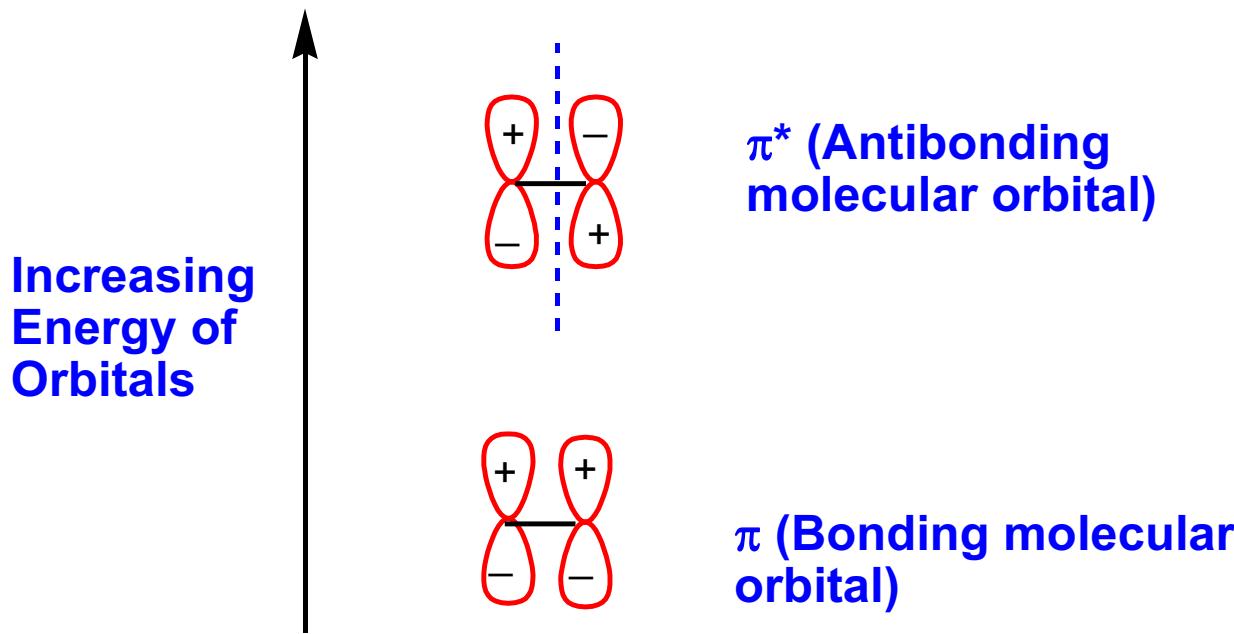
Ethylene shows interesting properties due to the presence of a π -bond

The C-C p-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,



Ethylene MOs



Total Number of π -electrons = 2

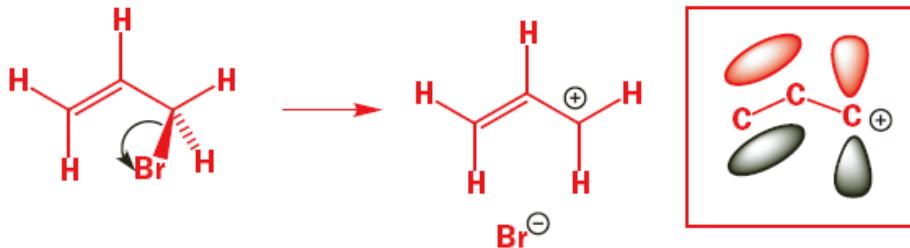
Total Number of π -orbitals = 2

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

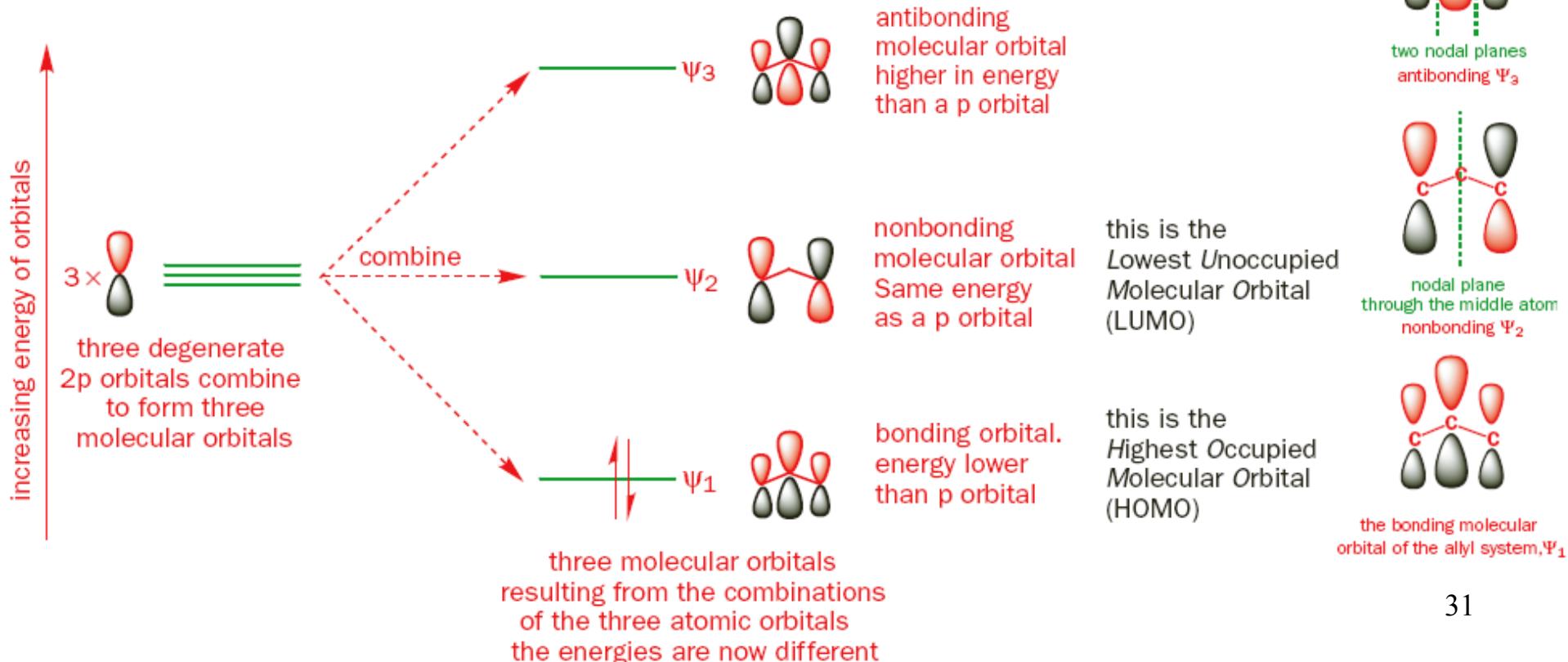
Note: Number of nodes in n^{th} MO is $n-1$

How about MOs for allyl system?

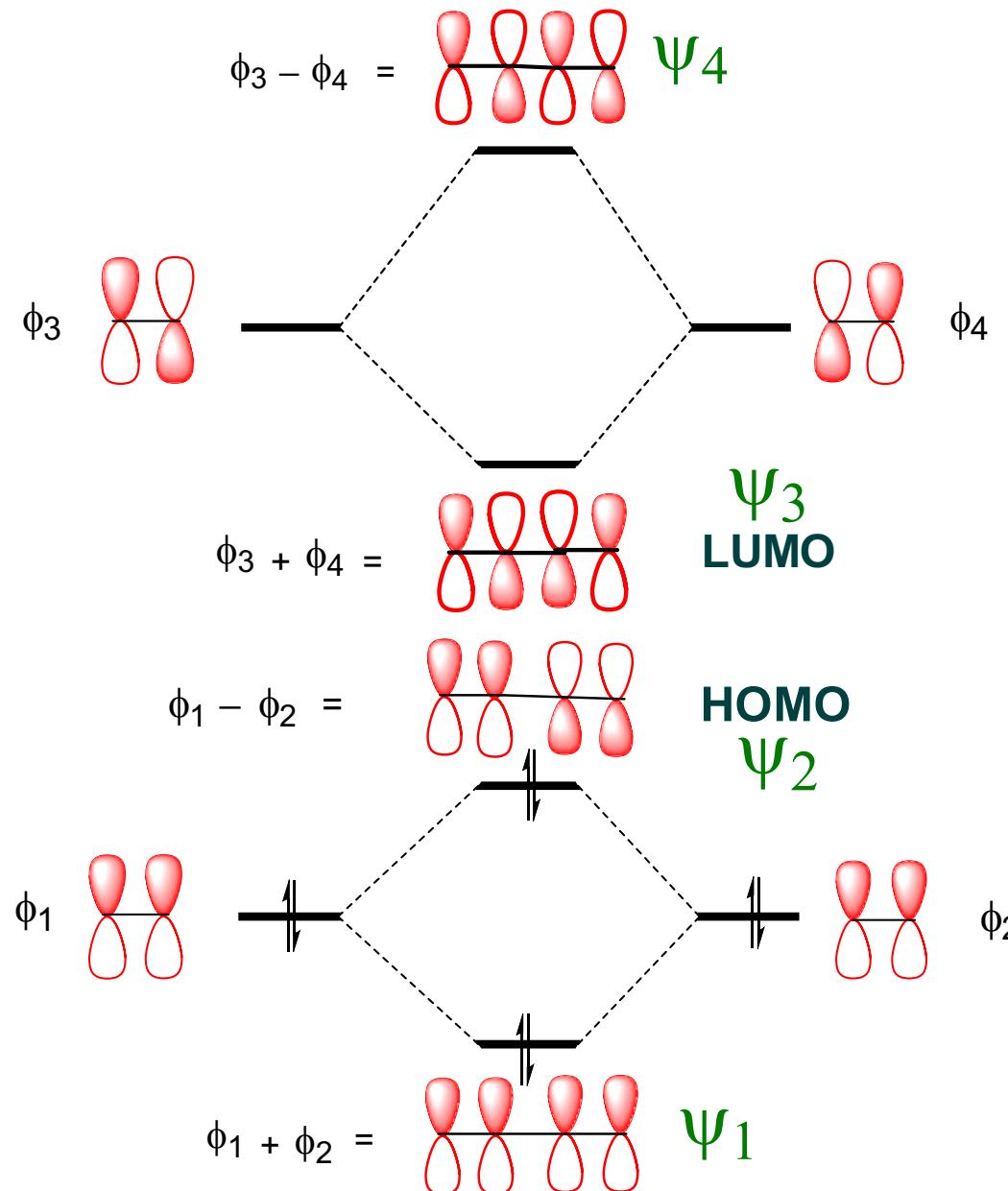
the p orbital has the correct symmetry to combine with the π bond to form a new molecular orbital for the allyl system



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



Can we construct butadiene MOs?



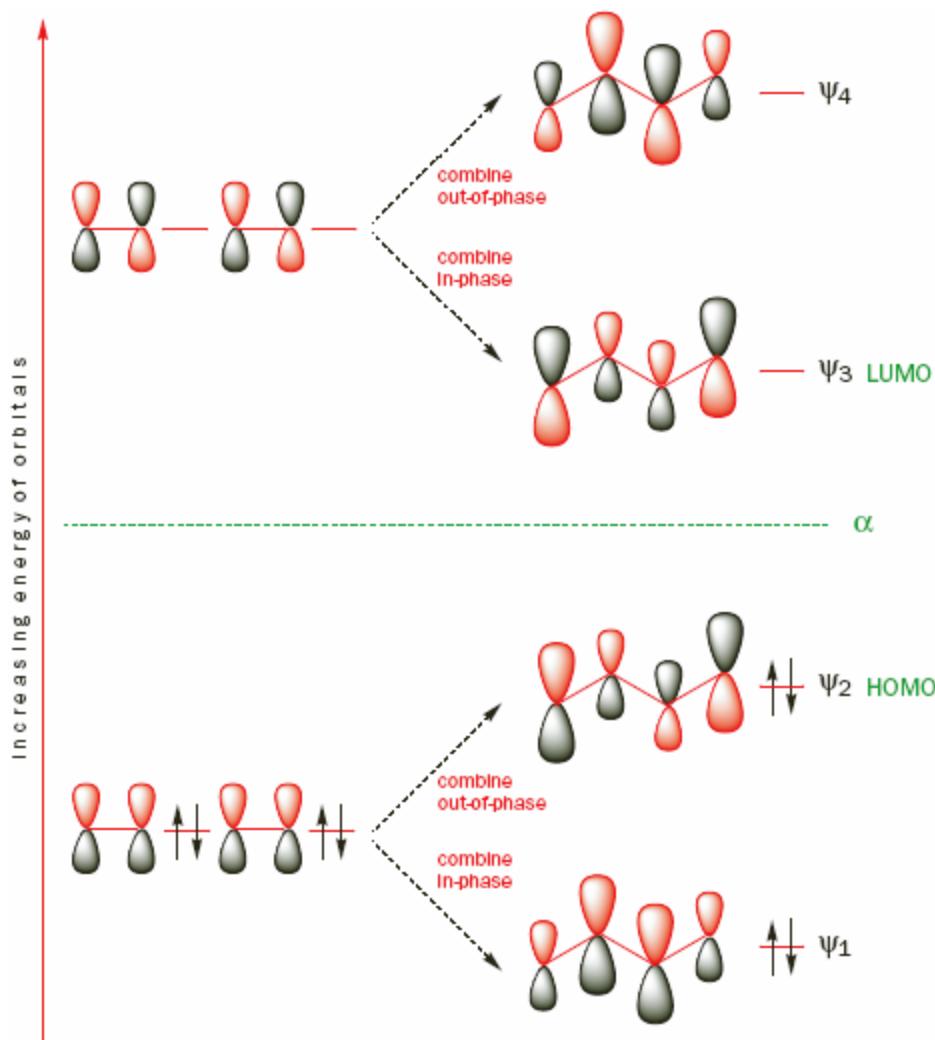
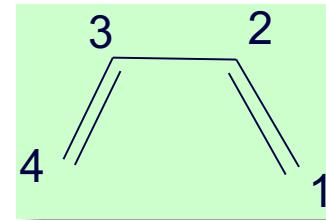
LUMO is lower in energy than the LUMO of ethylene

HOMO is higher in energy than the HOMO of ethylene

Butadiene MOs

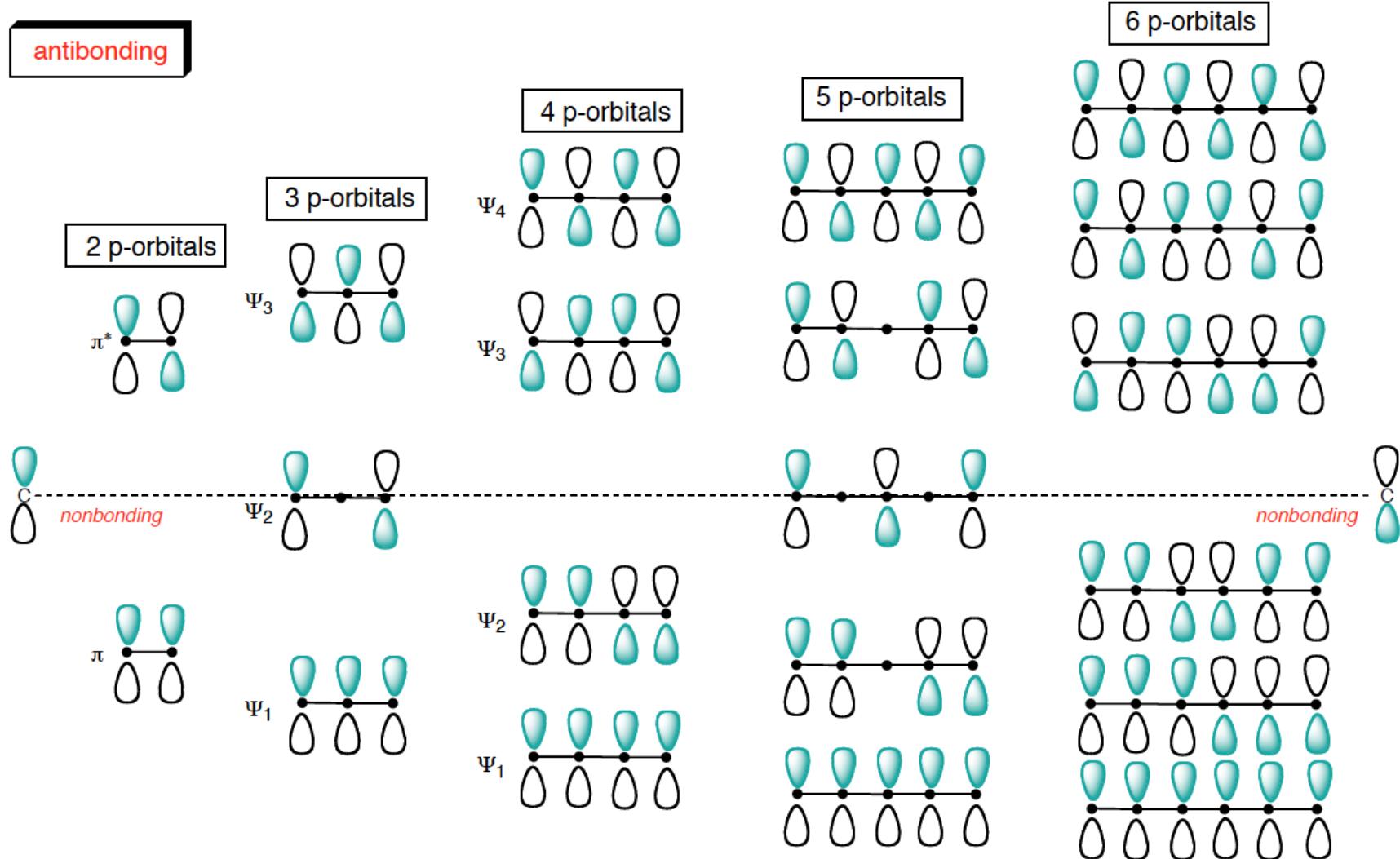
Total number of $p\pi$ -orbitals = 4

Total number of π -electrons = 4



Butadiene is more reactive than ethylene

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.

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?

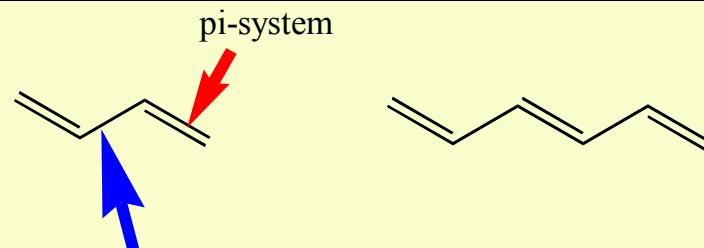
π -Molecular Orbitals Using Huckel MO Theory

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 $p\pi$ 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



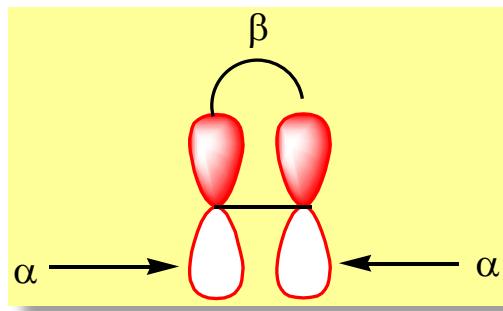
Energies of MOs in terms of Integrals

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

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

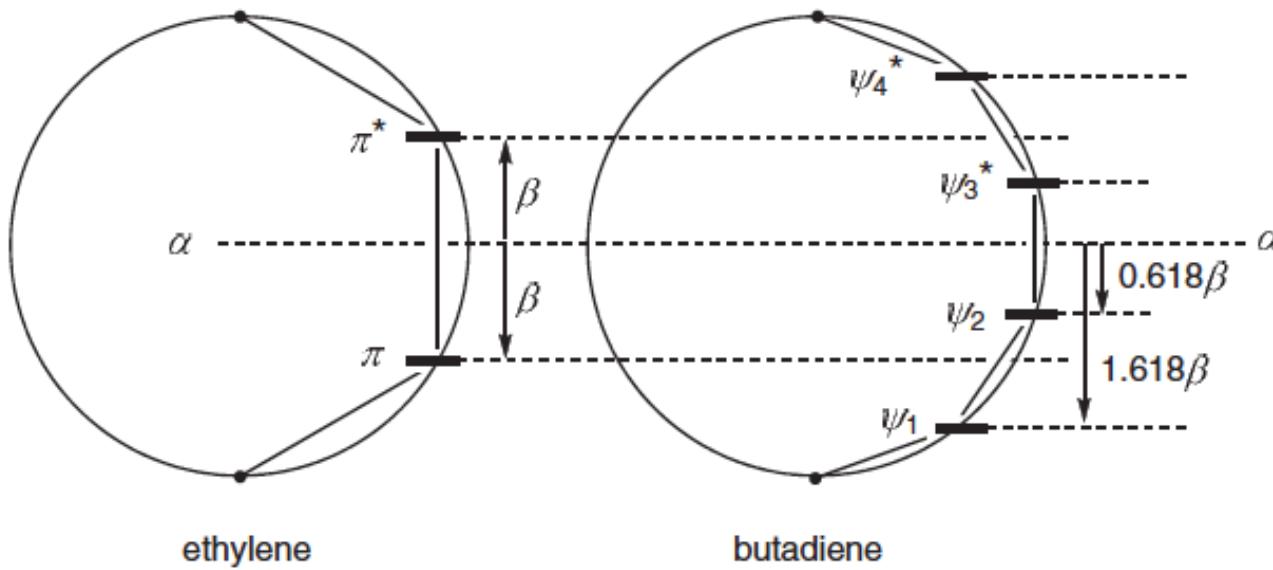
- The energy of the j^{th} MO for a cyclic polyene with $N \text{ p}\pi$ orbitals is given by

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

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 the π molecular orbitals of ethylene and butadiene by geometry



Dummy atoms at top and bottom of circle

Divide semicircle into ' $n+1$ ' equal arcs (parts)

Energy of the electron is given by the expression:

$$E = 2\beta \cos \frac{k\pi}{n+1}$$

k is the number of the atom along
the sequence of n atoms

Energies of MOs

For ethylene

Energy of LUMO = $\alpha - \beta$

Energy of HOMO = $\alpha + \beta$

For Butadiene

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

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

Linear polyenes

When the number of orbitals in the chain increases, the energies will be as,

For

Highest energy MO = $\alpha - 2\beta$

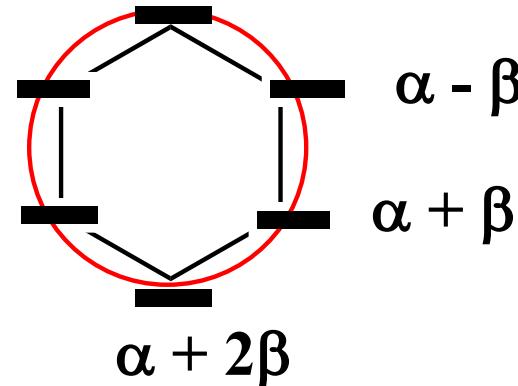
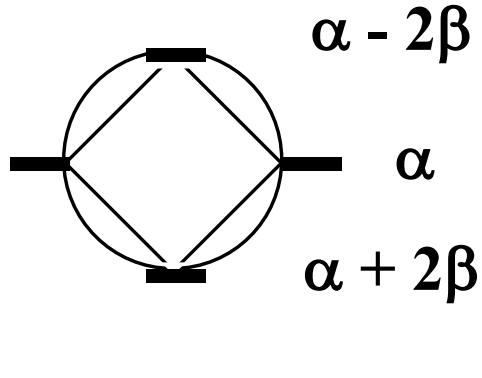
Lowest energy MO = $\alpha + 2\beta$

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

(Note: no dummy atoms in the cyclic system!)

Energies of MOs

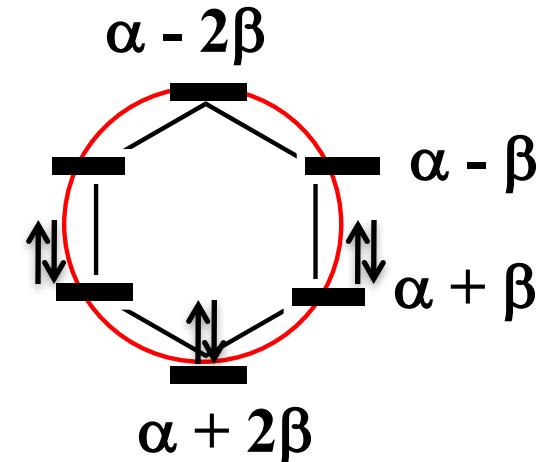
Calculate the total energy of π -electrons in benzene?

Total number of π -electrons = 6

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

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

$$6\alpha + 8\beta$$



If the double bonds were localized (not conjugated)!

Equivalent to three ethylenes

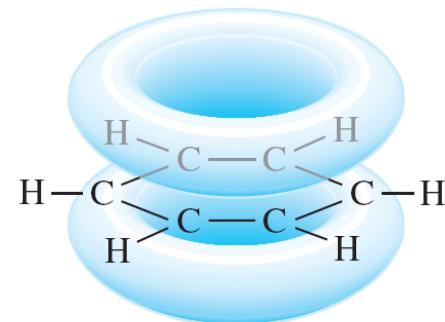
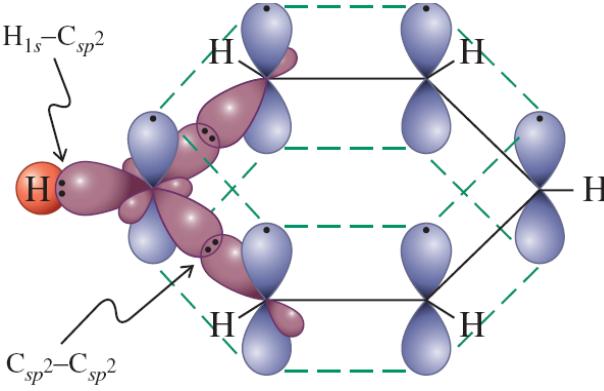
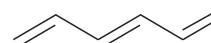
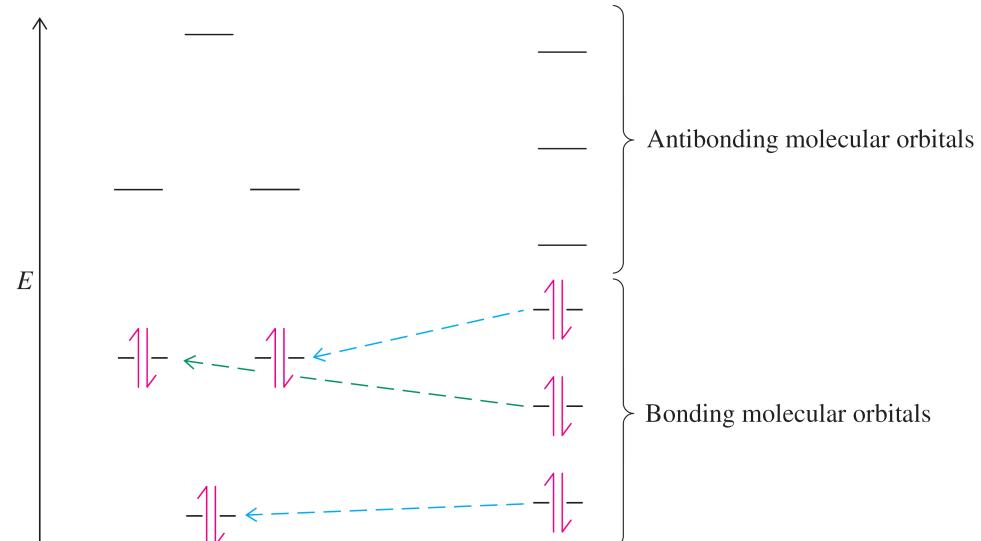
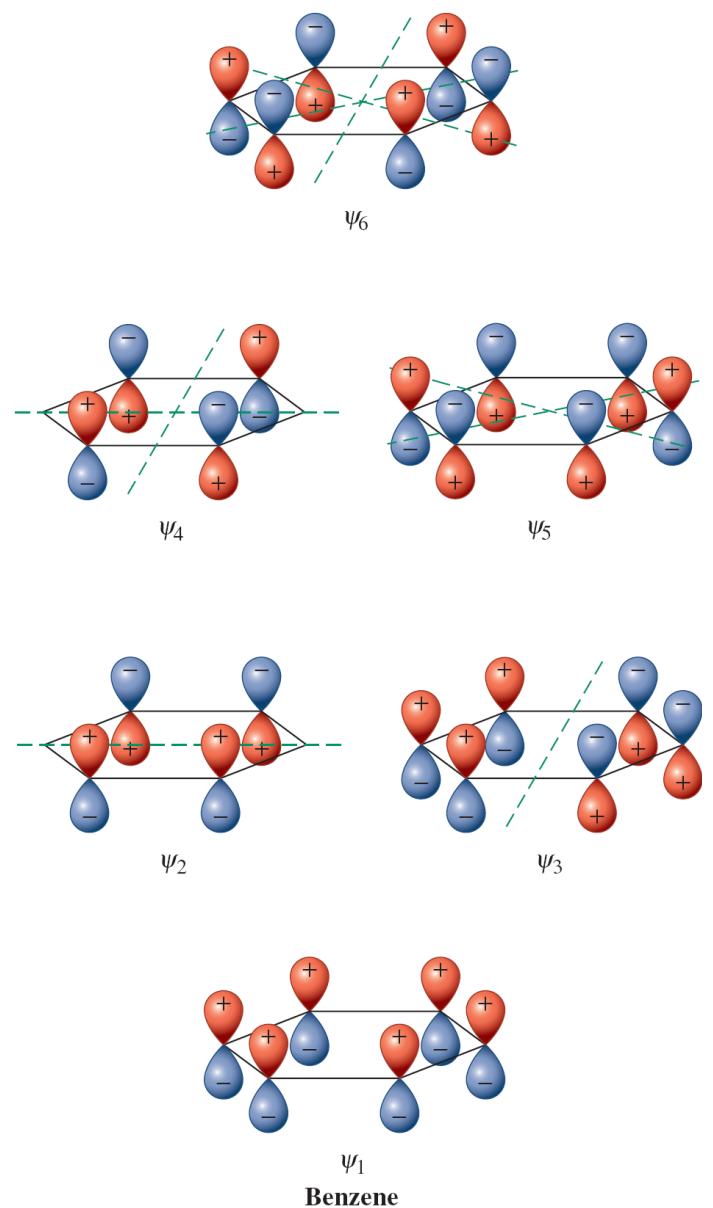
Total energy = $6 * (\alpha + \beta)$

Additional Stabilization in Benzene (fully delocalized) = 2β

What is the resonance stabilization energy in benzene?

Can we calculate to energy of electrons in cyclobutadiene?

π Molecular Orbitals of Benzene



Huckel's Rule of Aromaticity

- To be aromatic, a compound must
 - Be cyclic.
 - Have one p orbital on each atom of the ring.
 - Be planar or nearly planar so that there is continuous or nearly continuous overlap of all p orbitals of the ring.
 - Have a closed loop of $(4n + 2)$ π electrons in the cyclic arrangement of p orbitals.
- Analogous systems with $4n \pi$ electrons are described as **anti-aromatic**

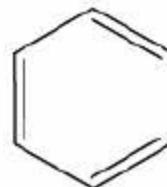
Modern definition of aromaticity:

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

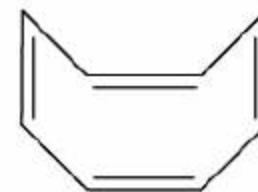
Aromatic, Antiaromatic and Nonaromatic



cyclobutadiene
[4]-annulene
antiaromatic



benzene
[6]-annulene
aromatic



cyclooctatetraene
[8]-annulene
nonaromatic

Benzene (aromatic) \Rightarrow (1) cyclic & planar (2) uninterrupted π e
(3) odd e-pairs; 3 pairs; 6e ($= 4 \times 1 + 2$)

Cyclobutadiene (antiaromatic) \Rightarrow (1) cyclic & planar
(2) uninterrupted π e (3) even e-pairs; 2 pairs; 4e ($= 4 \times 1$)

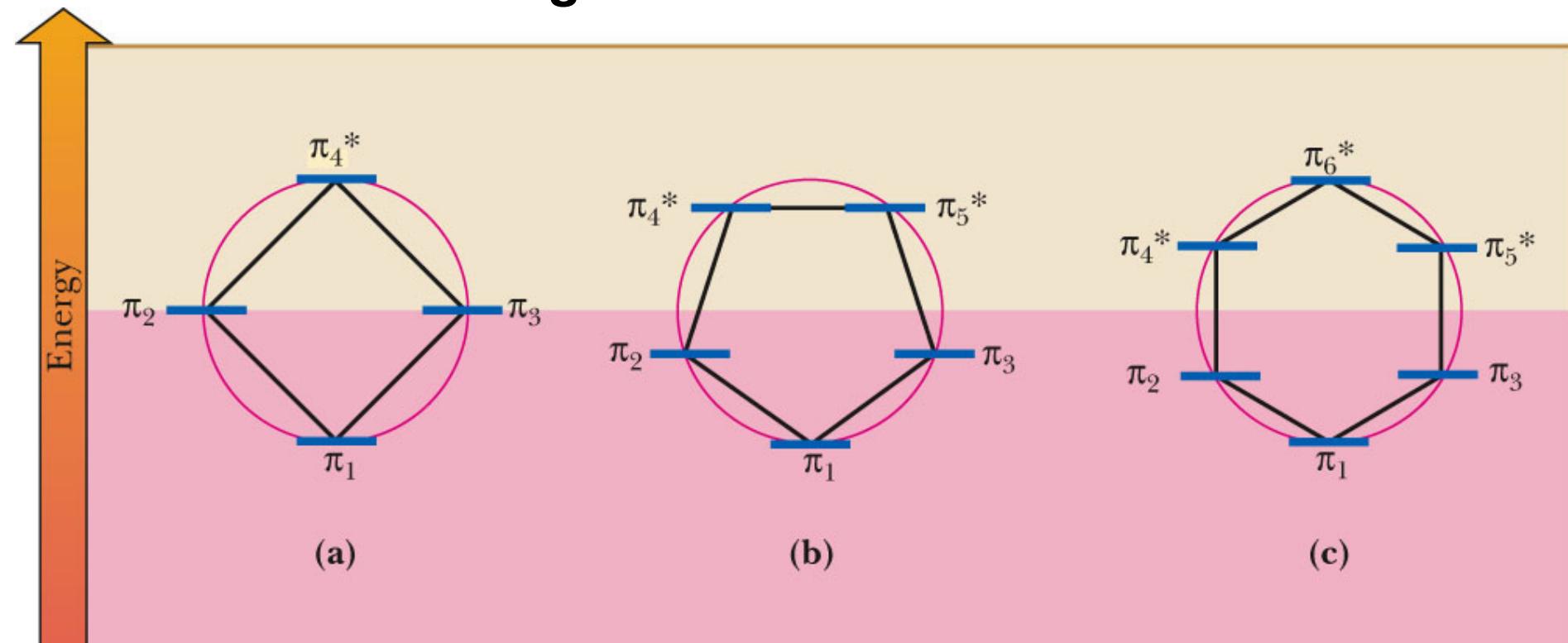
Cyclooctatetraene (nonaromatic) \Rightarrow (1) nonplanar
(2) even e-pairs (8e = 4×2) (no incentive to be planar)

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.

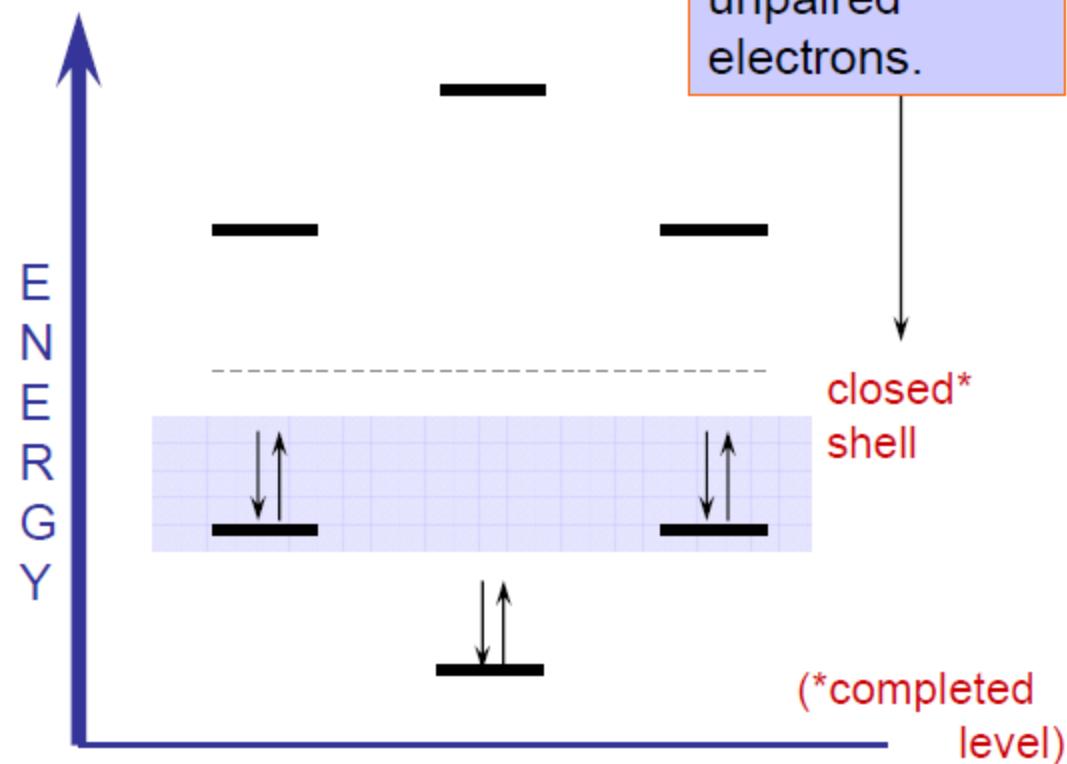
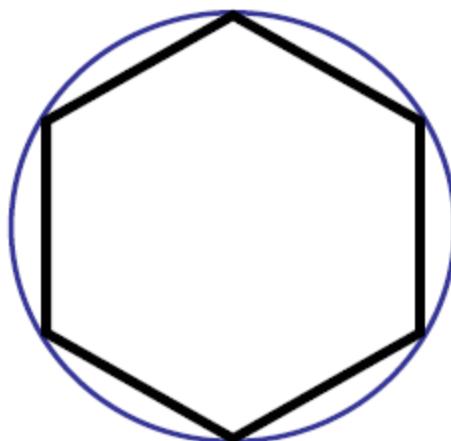


BENZENE



6π electrons

AROMATIC

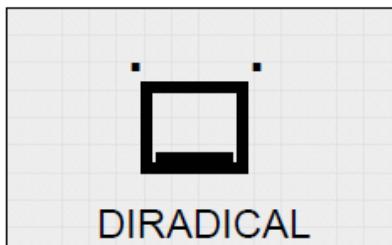
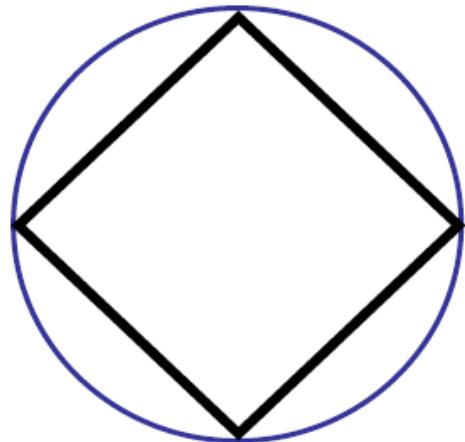


Aromatic compounds will have all of the occupied π M.O. levels completely Filled, with **no** unpaired electrons.

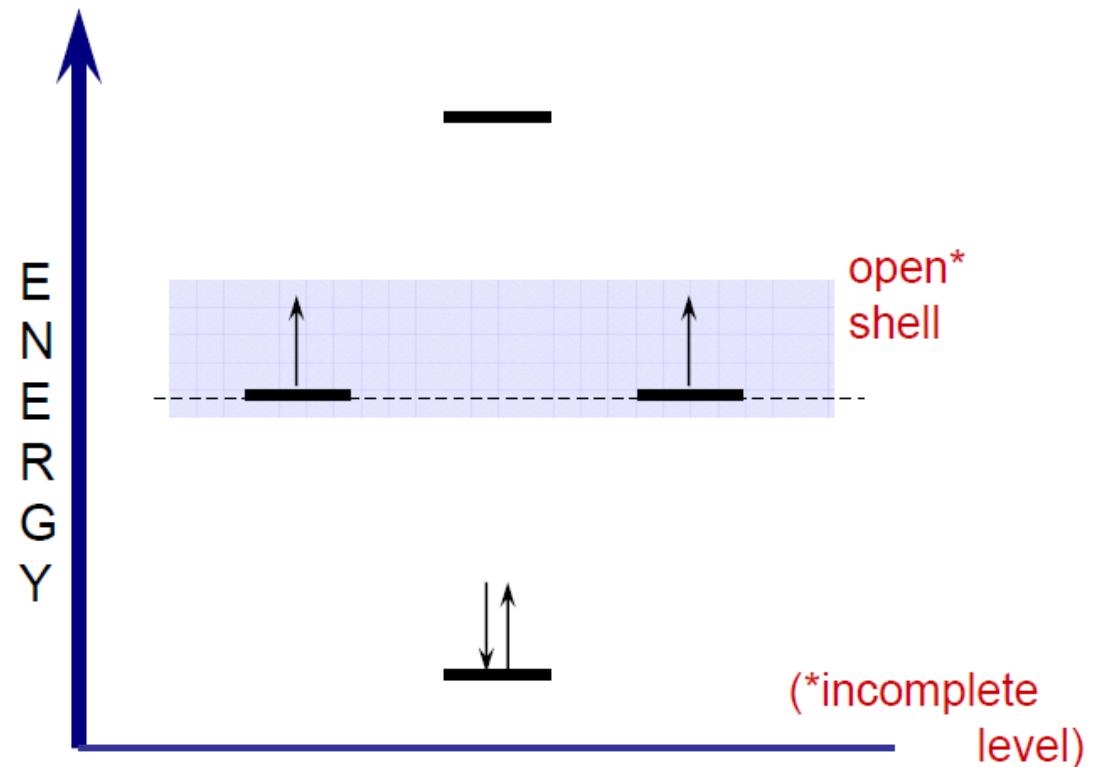
CYCLOBUTADIENE



4π electrons



DIRADICAL



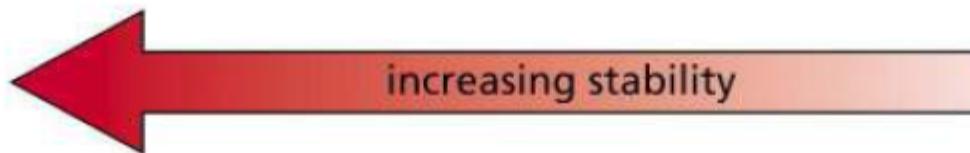
Antiaromaticity

A compound is anti-aromatic if it :

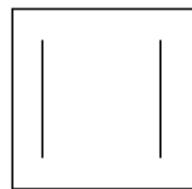
- (1) is Planar and cyclic
- (2) Has Uninterrupted ring of π cloud
- (3) Contains even number of pairs of π electrons ($4n$)

relative stabilities

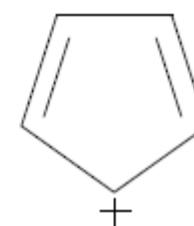
aromatic compound > cyclic compound with localized electrons > antiaromatic compound



Examples

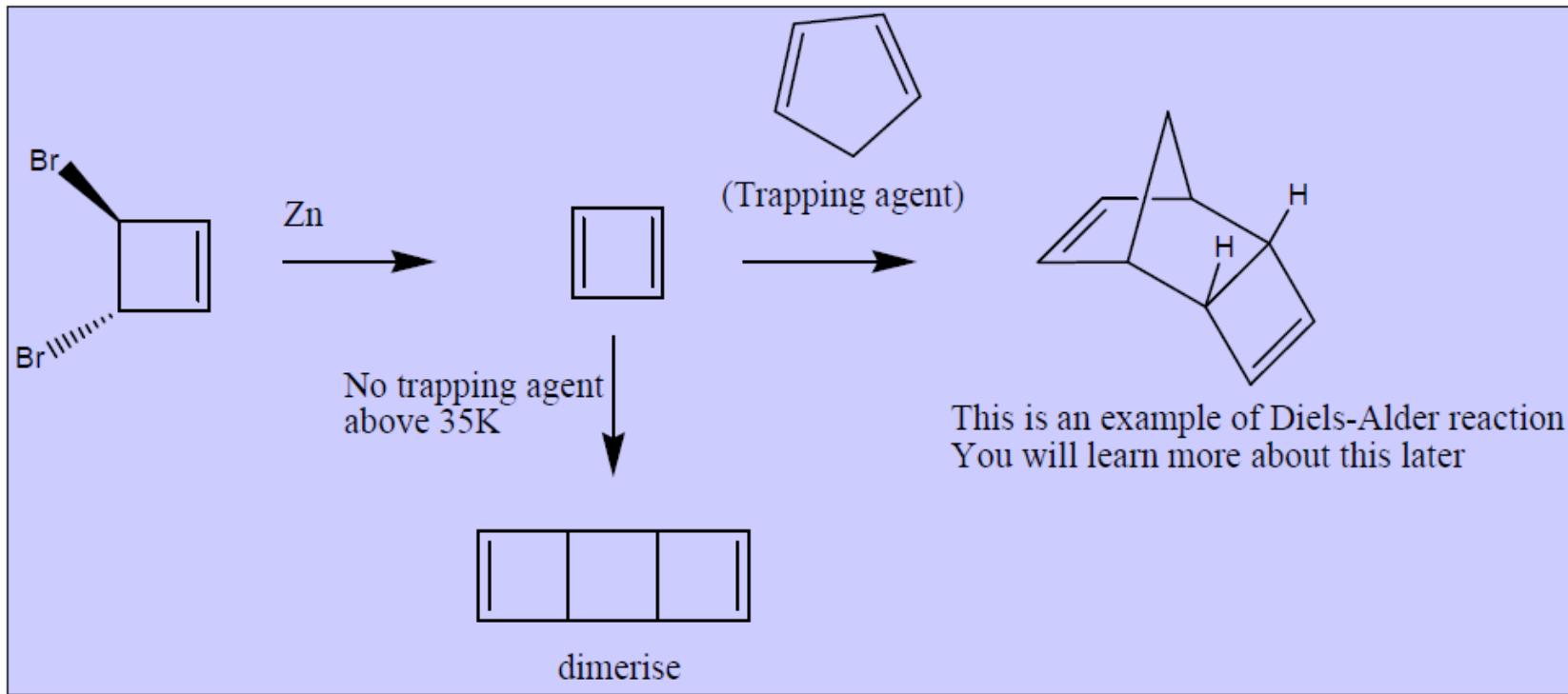


Cyclobutadiene

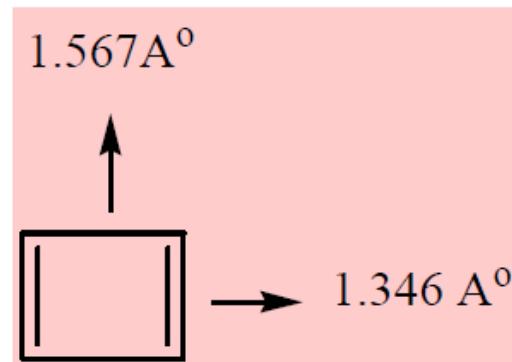


Cyclopentadienyl cation

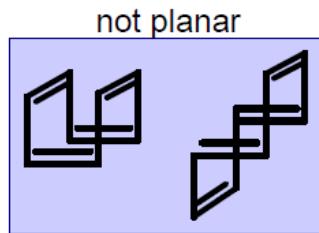
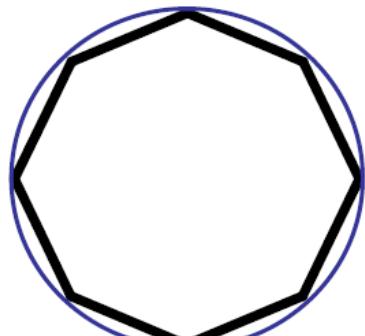
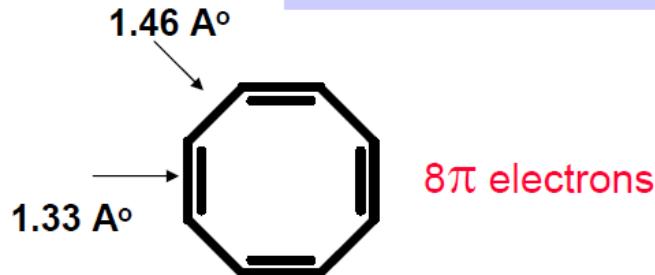
Both are antiaromatic (4 pi-electrons)



Cyclobutadiene 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.



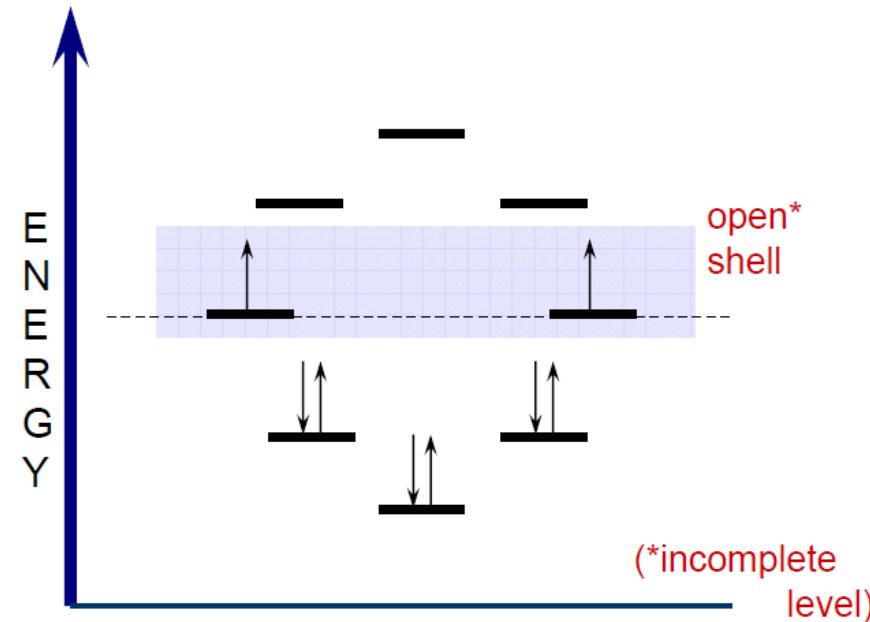
CYCLOOCTATETRAENE



ANTI-AROMATIC

Does not have a completed shell and has unpaired electrons.

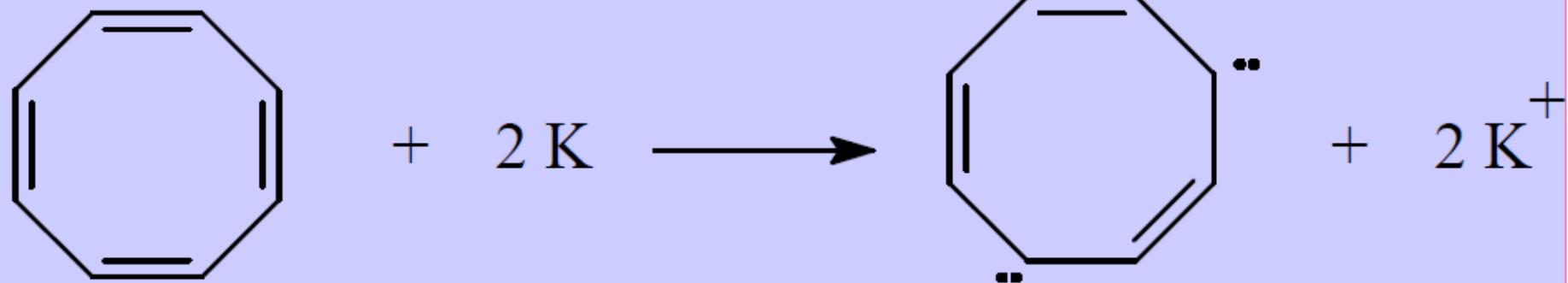
Does not have $4n+2 \pi$ electrons.



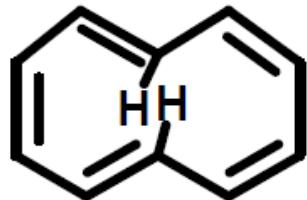
Planar cyclooctatetraene would be antiaromatic. To avoid it, the ring goes out of plane - possible as it is a larger ring.
It is Non-aromatic.

Dianion of [8]Annulene

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

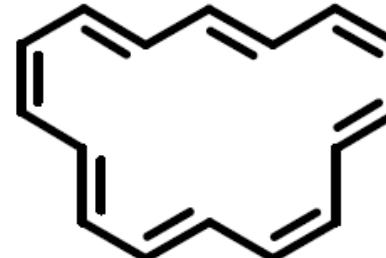


Some examples of Annulenes



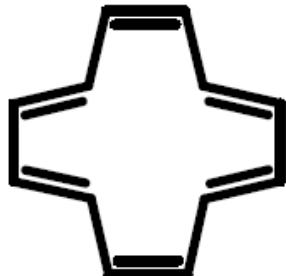
$10\pi = 4(2) + 2$
BUT CANNOT BE PLANAR
(see the hydrogens)

[10]-annulene



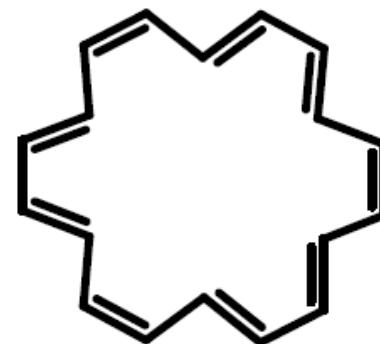
16π

[16]-annulene



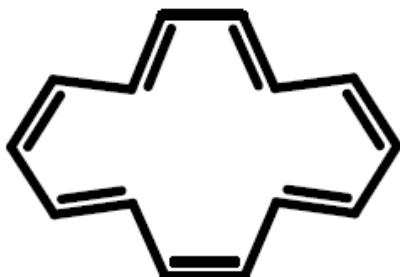
12π

[12]-annulene



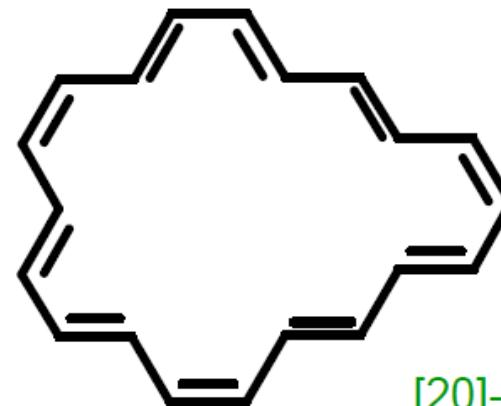
$18\pi = 4(4) + 2$
AROMATIC

[18]-annulene



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

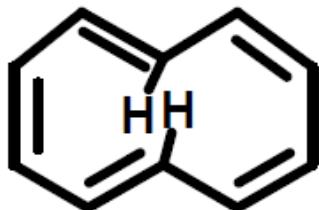
[14]-annulene



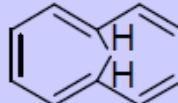
20π

[20]-annulene

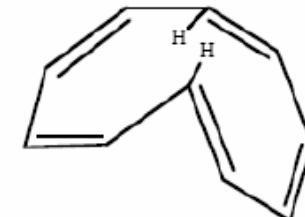
[10] Annulene



all cis
non-aromatic
(too strained
being planar)

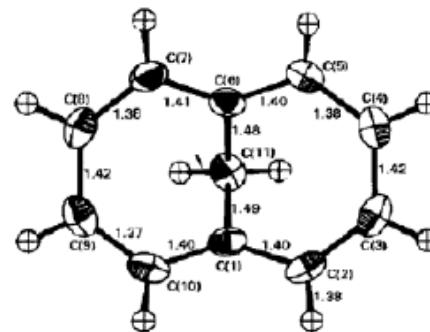
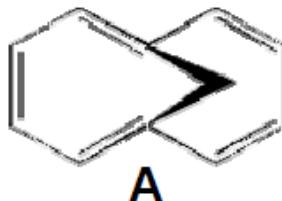


two trans
non-aromatic
(too sterically
crowded to be planar)



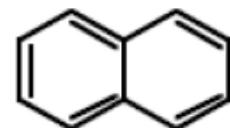
Becomes
nonplanar

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

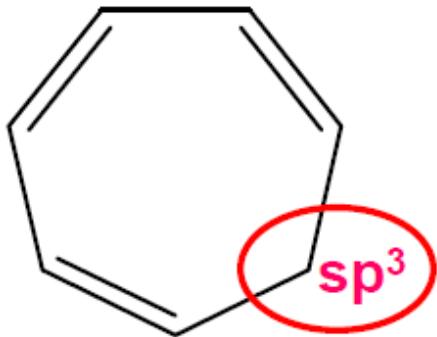


naphthalene

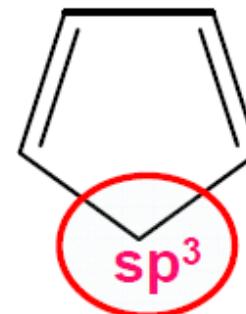
Directly connecting two Carbons in [10]annulene gives naphthalene
.....Again aromatic!

How about odd numbered rings?

Non-aromatics (with interrupted π cloud)



cycloheptatriene



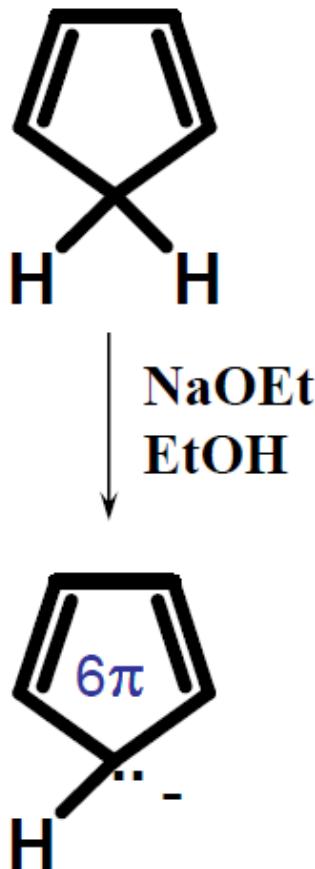
cyclopentadiene

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

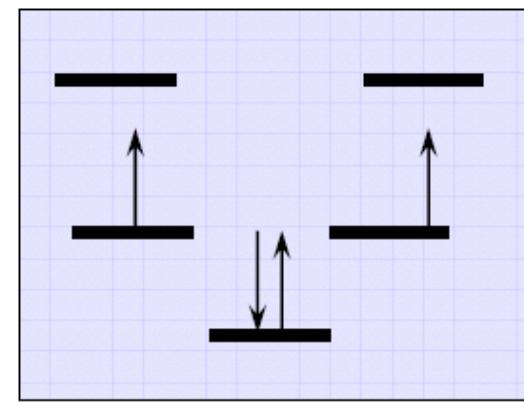
The methylene hydrogens are acidic.



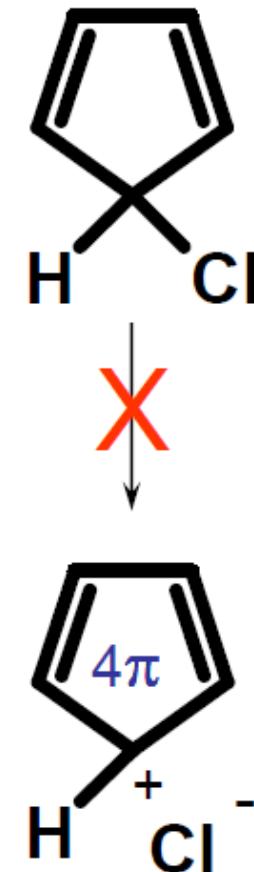
AROMATIC

The anion forms readily.

This compound does not dissolve in water.



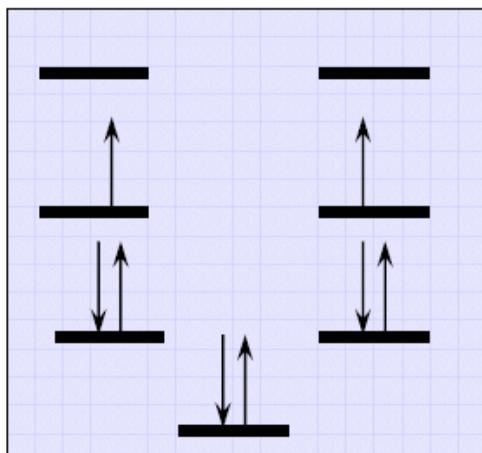
ANTI-AROMATIC



The cation does not form at all.

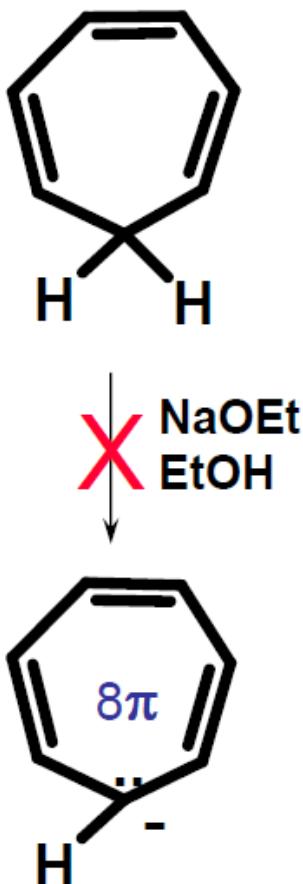
CYCLOHEPTATRIENYL ANION AND CATION

The methylene hydrogens are not acidic.

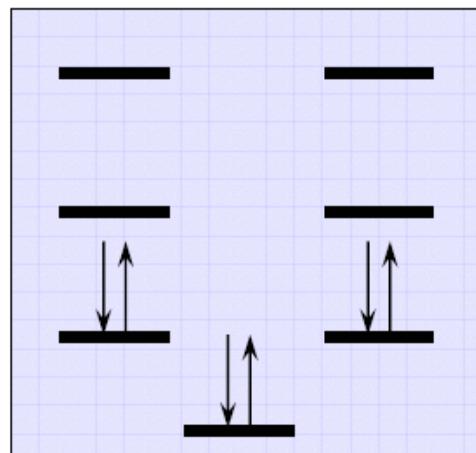


ANTI-AROMATIC

Doesn't form easily

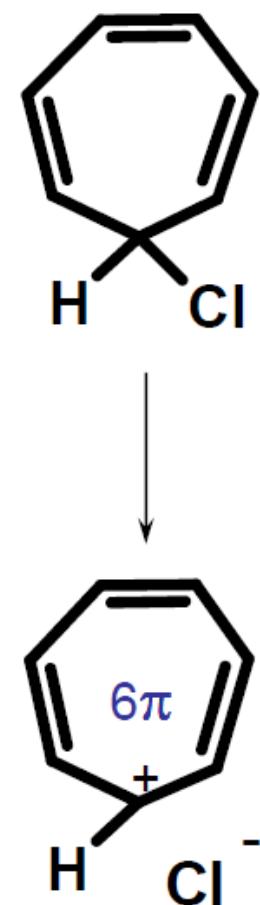


This compound ionizes easily in water.



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.

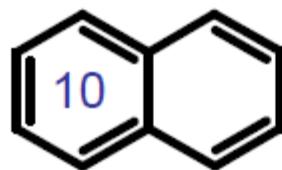
$4n+2$ series = 2, 6, 10, 14, 18, 22, 26, 30 etc.

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

5 pairs
 $(4x2+2)$

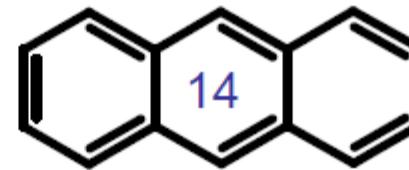


benzene



10

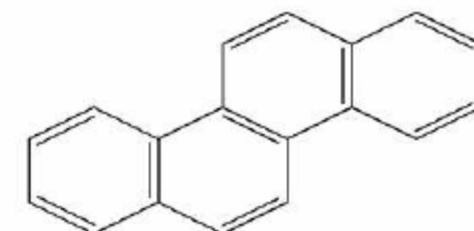
naphthalene



14

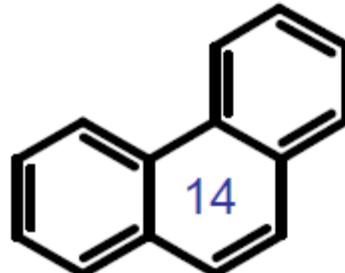
anthracene

9 pairs
 $(4x4+2)$



chrysene

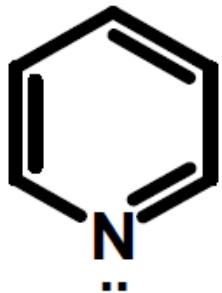
7 pairs
 $(4x3+2)$



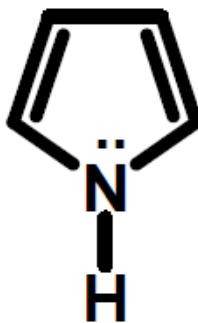
14

Phenanthrene

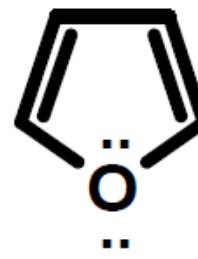
HETEROCYCLIC COMPOUNDS



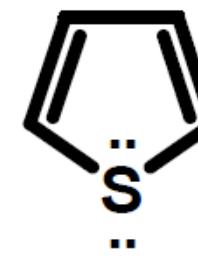
pyridine



pyrrole

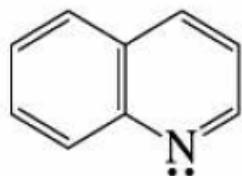


furan

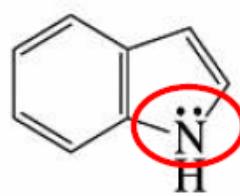


thiophene

Other Heterocyclic Aromatic Compounds



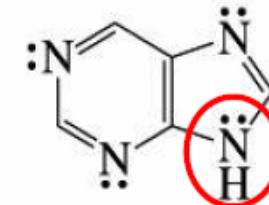
quinoline



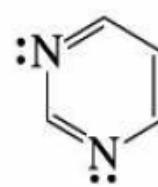
indole



imidazole



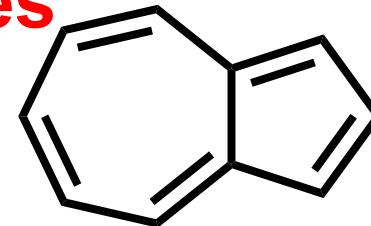
purine

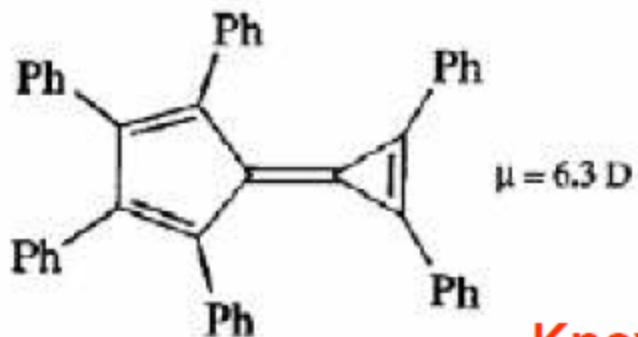


pyrimidine

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.

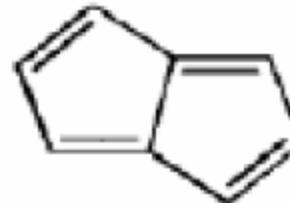
Effect of aromaticity on properties

- Cyclopentadiene pKa is 15 whereas that of cycloheptatriene is 46.
- Azulene has dipole moment of 1.8D.  azulene
- Tropylium bromide is actually ioninc 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.)



Known

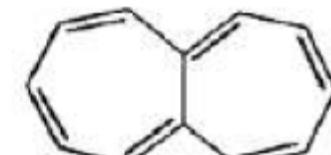
What could be the reason for
Its high dipole moment?



pentalene

Pentalene

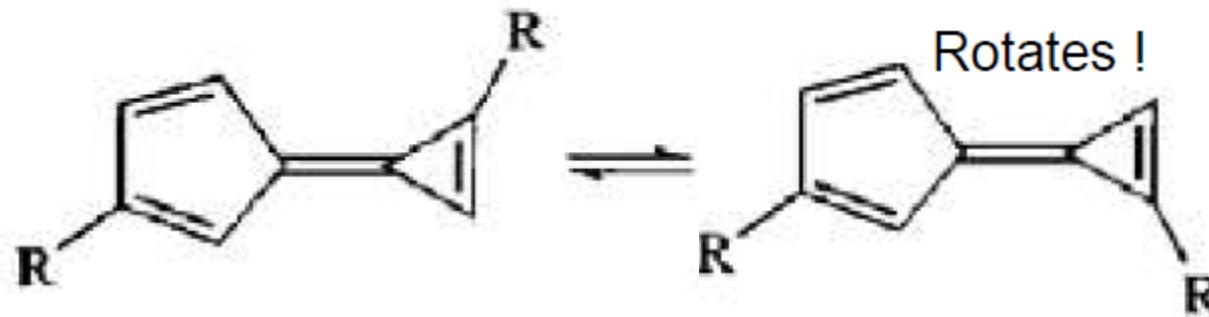
Unstable!



Heptalene

heptalene

But conjugate acid of heptalene is stable!!



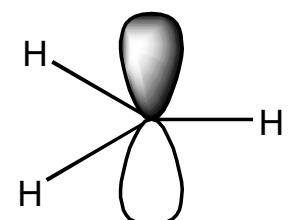
Significance of Orbital Energies

**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^+



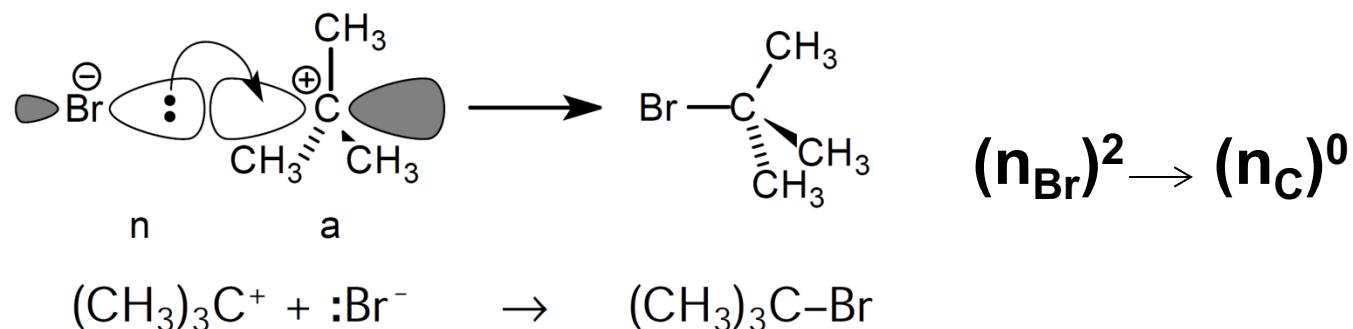
Electron Rich to Electron poor

Possible HOMO-LUMO Combinations

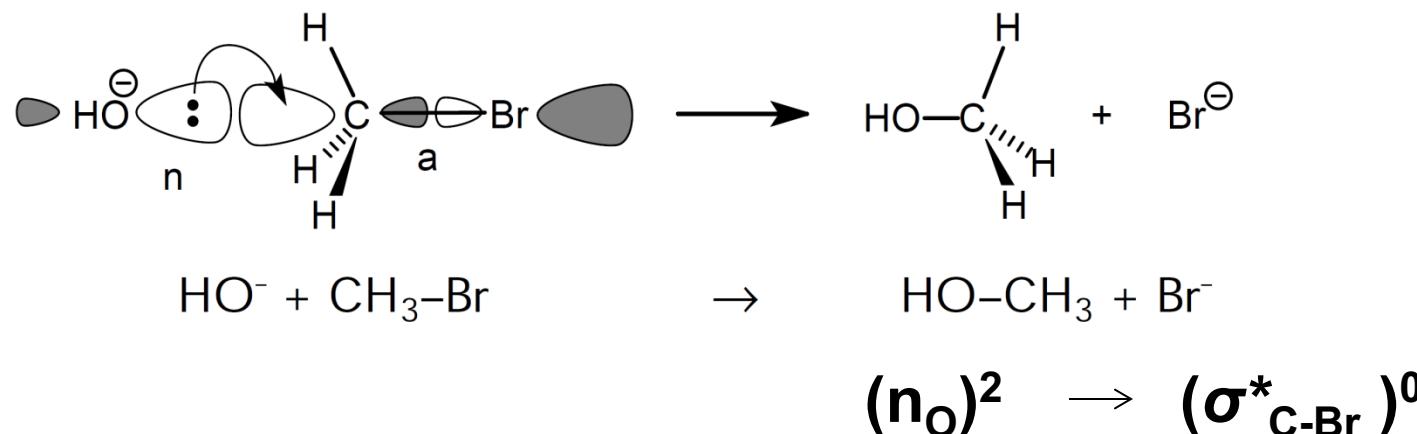
HOMO	LUMO	Result
an occupied n orbital	an empty a orbital	bond formation only
an occupied n orbital	a σ^* orbital	bond formation and bond rupture
an occupied n orbital	a π^* orbital	bond formation and bond rupture
a π orbital	an empty a orbital	bond formation and bond rupture
a π orbital	a σ^* orbital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

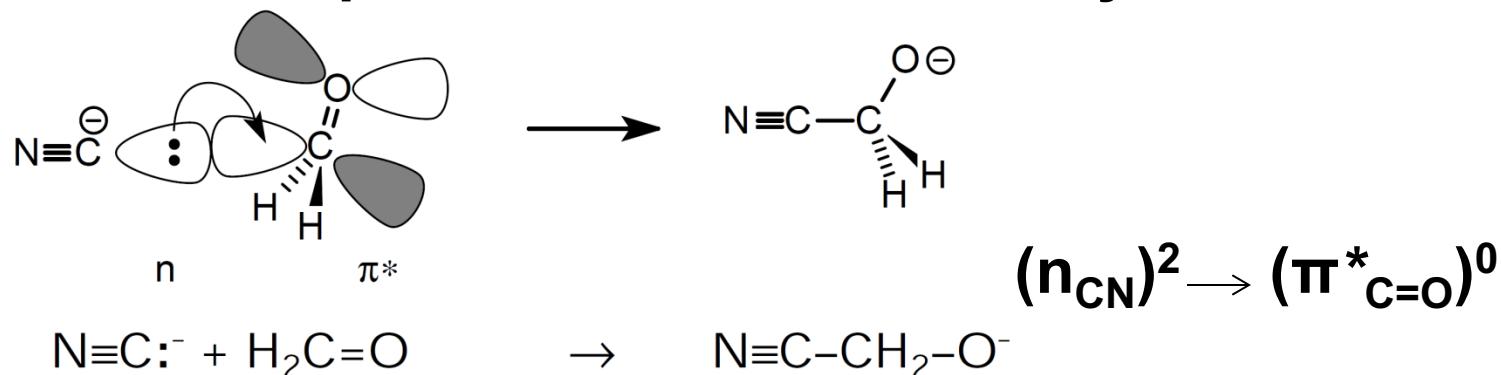


2. non bonding orbital + antibonding orbital (σ^*): S_N2

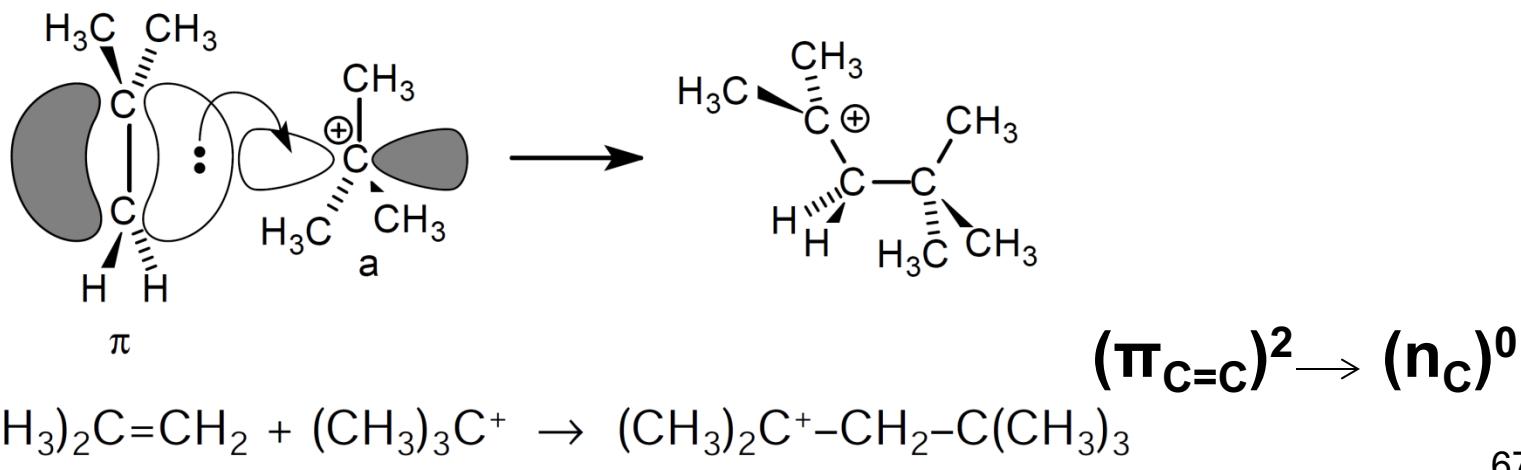


Explanation of Reactions Through Molecular Orbitals

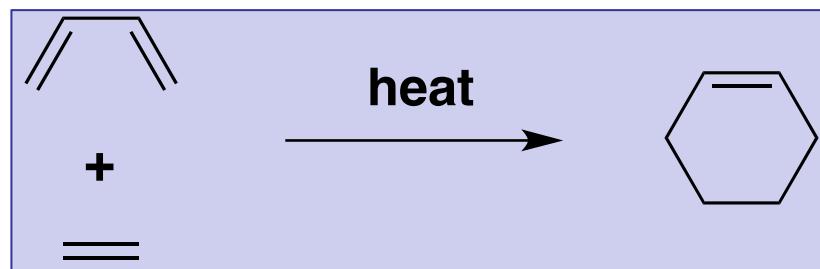
3. $n + \pi^*$: Nucleophilic addition on carbonyls



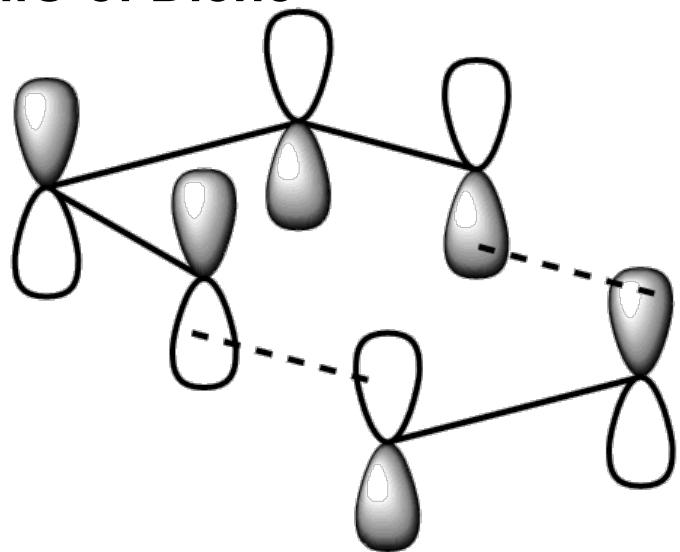
4. $\pi + a$: addition on olefins



FMO Treatment of [4+2] Cycloaddition reaction

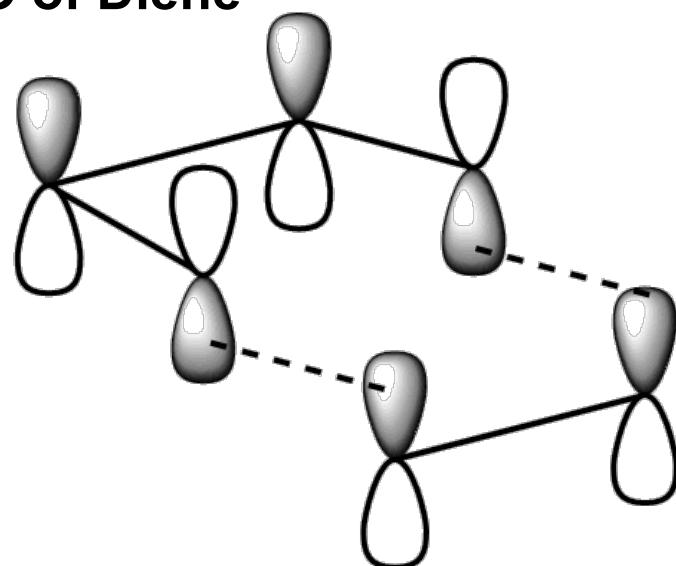


HOMO of Diene



LUMO of Dienophile

LUMO of Diene

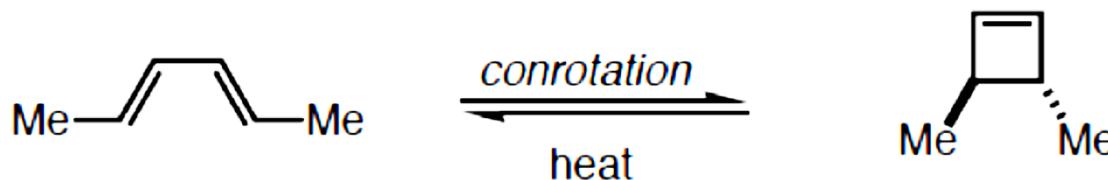


HOMO of Dienophile

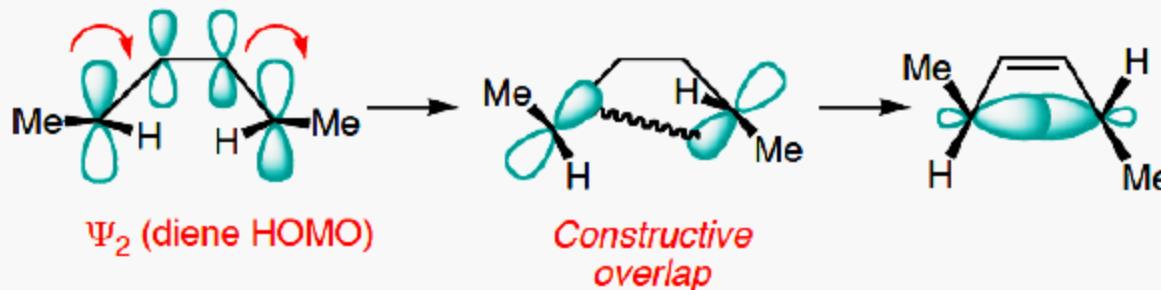
Phases match – leads to bond formation

What will be outcome with light as source of energy?!⁶⁸

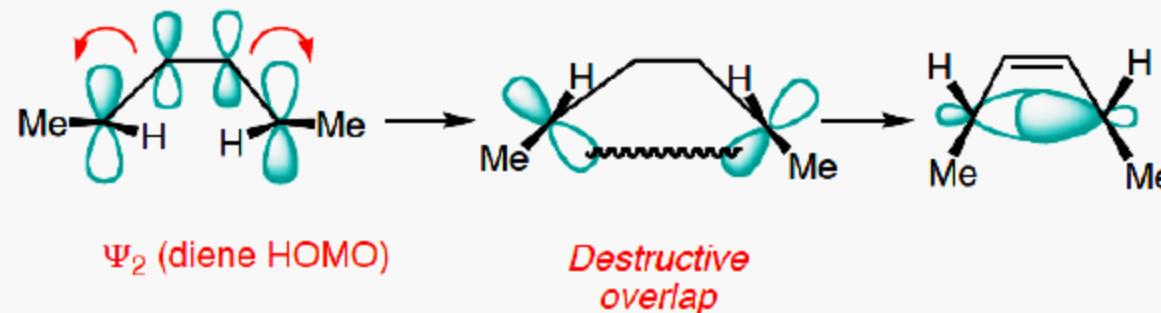
Electrocyclic Reactions Through Molecular Orbitals



- Conrotatory Closure: (Allowed and observed)



- Disrotatory Closure: (Forbidden and not observed)



What will be outcome with light as source of energy?!⁶⁹

THANK YOU

Generalizations for Acyclic Polyenes

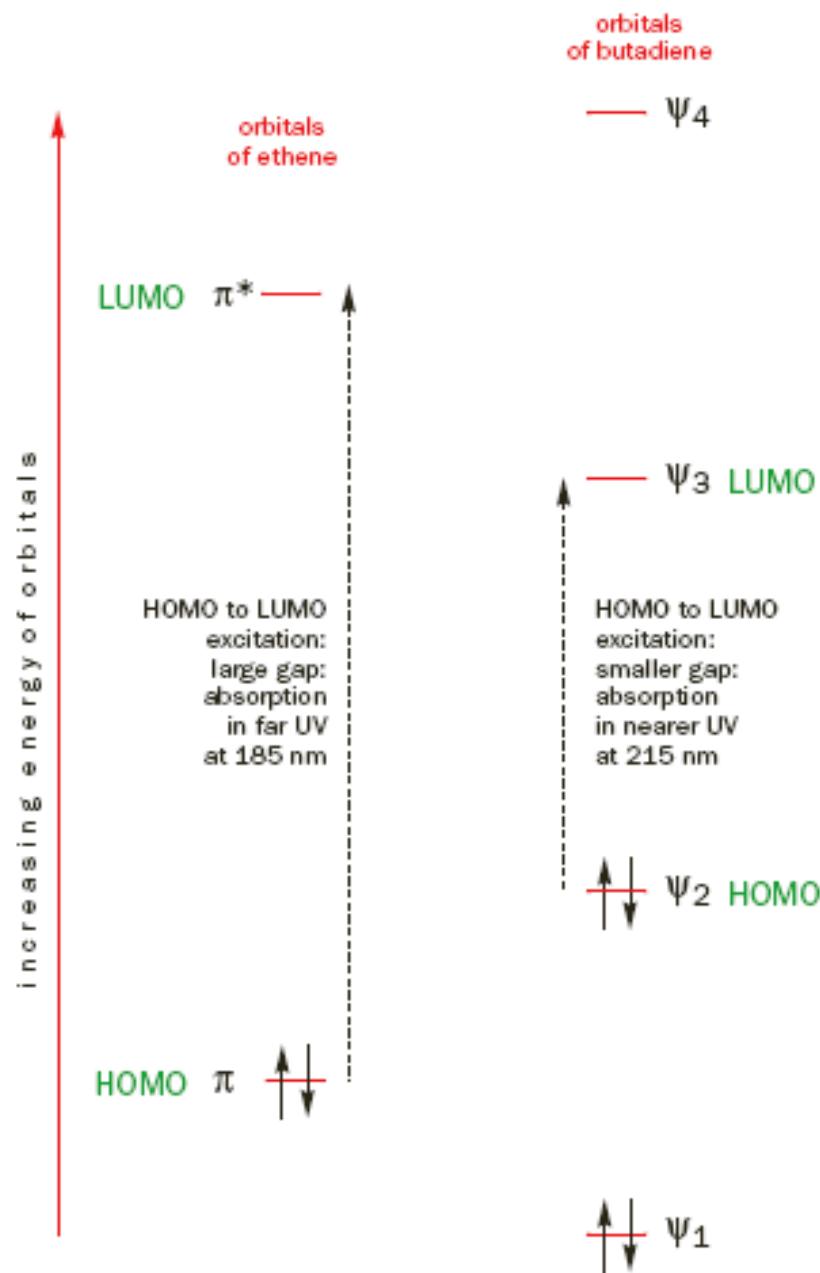
The lowest energy orbital is always symmetric with respect to the principal mirror plane

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

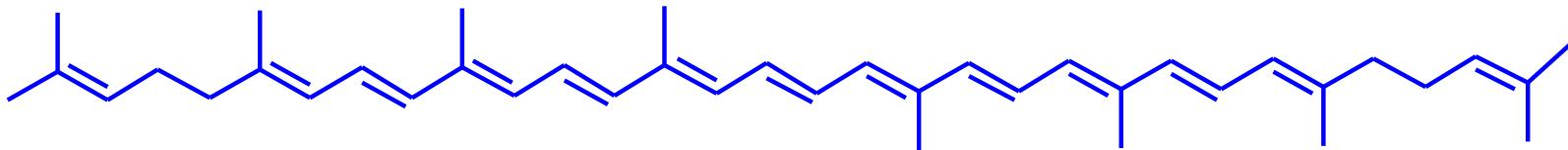
In systems with an odd number of atoms, the antisymmetric levels always have a node at the central carbon atom.

HOMO-LUMO Gap



Extended Conjugation and Colour

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.



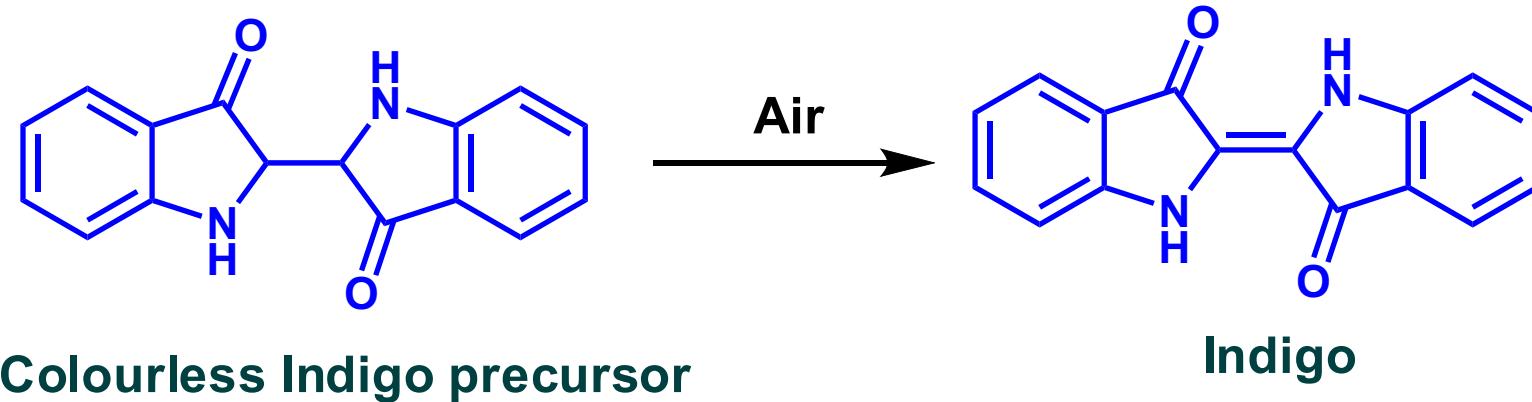
Lycopene, the red pigment present in tomatoes and other berries



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

Extended Conjugation and Color

The colour of the blue jeans come from the pigment indigo

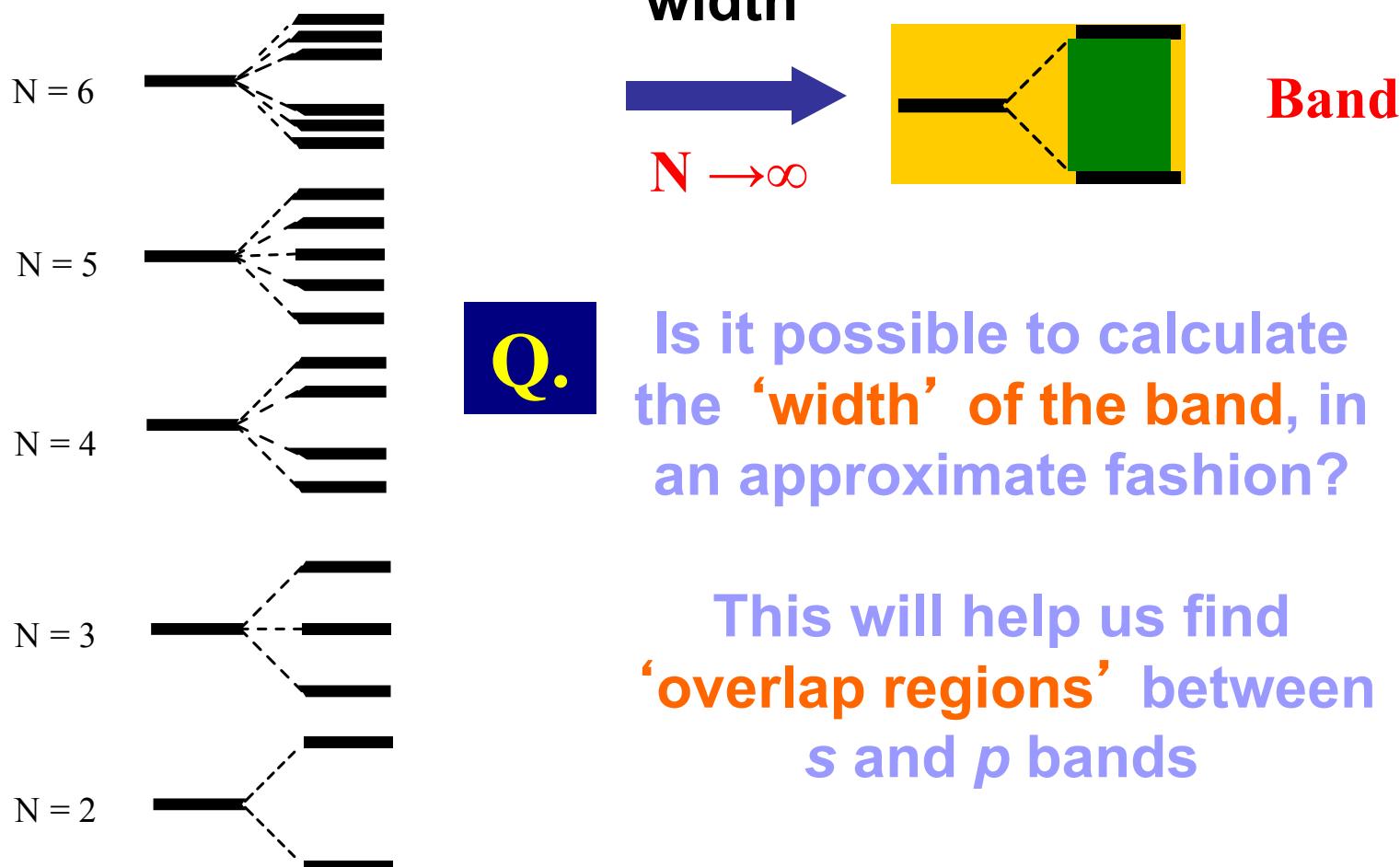


Jeans are generally dyed by immersion in a vat of reduced indigo, which is colourless since there is no conjugation.

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

Polyenes to Solids

When Number of atoms (N) in a polyene become infinitely large, the difference between neighboring energy levels (MO-levels) is infinitely small. But the band has a finite width



Polyenes-to-Solids Analogies

Approximate Analogs Between Molecular and Solid-State Terminologies

Molecular Orbital

HOMO

LUMO

HOMO-LUMO gap

Band Orbital

Valence Band

Conduction Band

Band gap

Refer: Moore's law
(processor speed of cpus)

Advanced and Related Topics: Organic Semiconductors,
Organic LEDs, Conducting Polymers

Hückel's Rule and Aromaticity

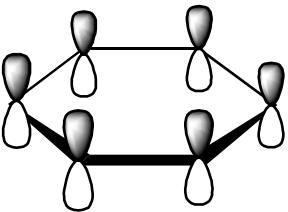
The compound must have an uninterrupted cyclic π -cloud of electrons

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

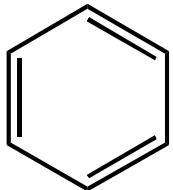
For the π -cloud to be uninterrupted, every atom in the ring must have a p-orbital

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 of Aromaticity



Number of π electrons = 6

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

Aromatic

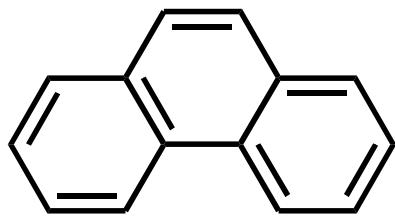


Number of π electrons = 4

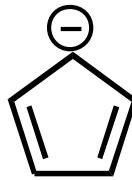
Where $n = 1$

Anti-aromatic

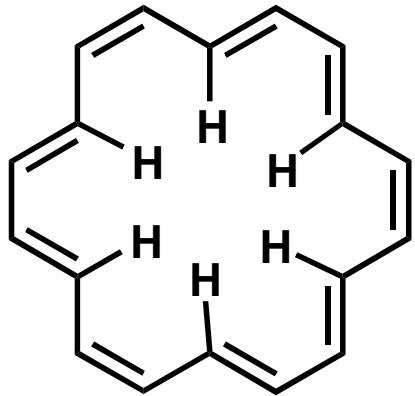
Examples for Aromatic Compounds



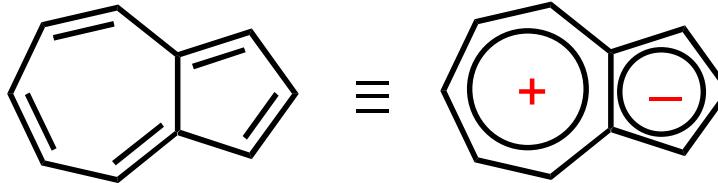
Phenathrene



cyclopentadienyl anion



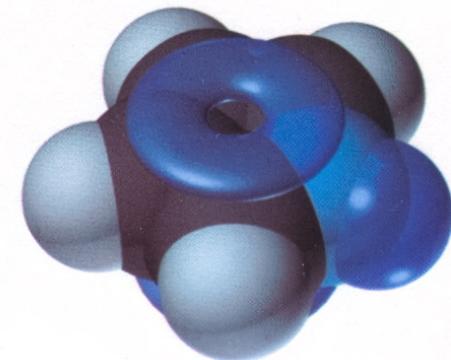
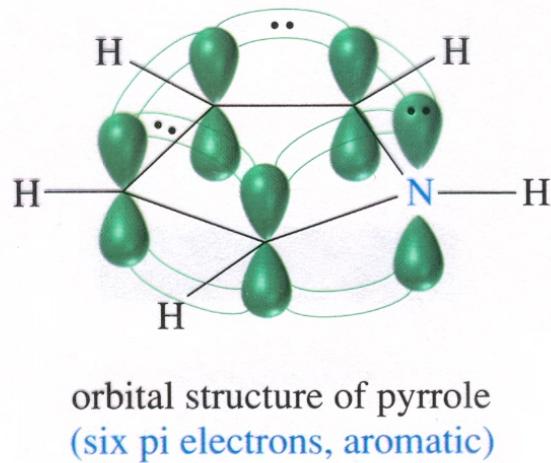
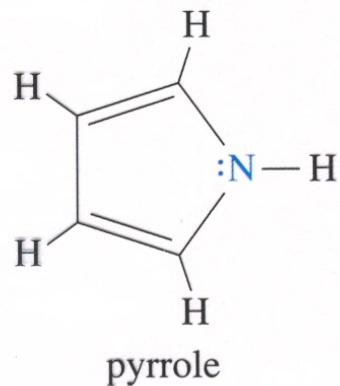
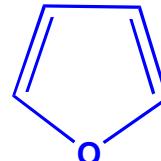
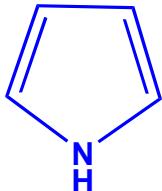
[18]-annulene



Azulene

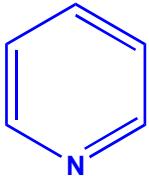
Aromatic Heterocyclic Compounds

Lone pair is part of the aromatic system



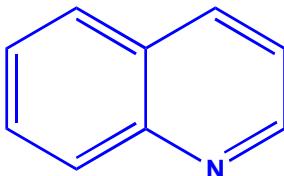
Aromatic Heterocyclic Compounds

Lone pair not involved in aromatic system



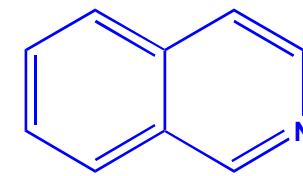
6 π electrons

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



10 π electrons

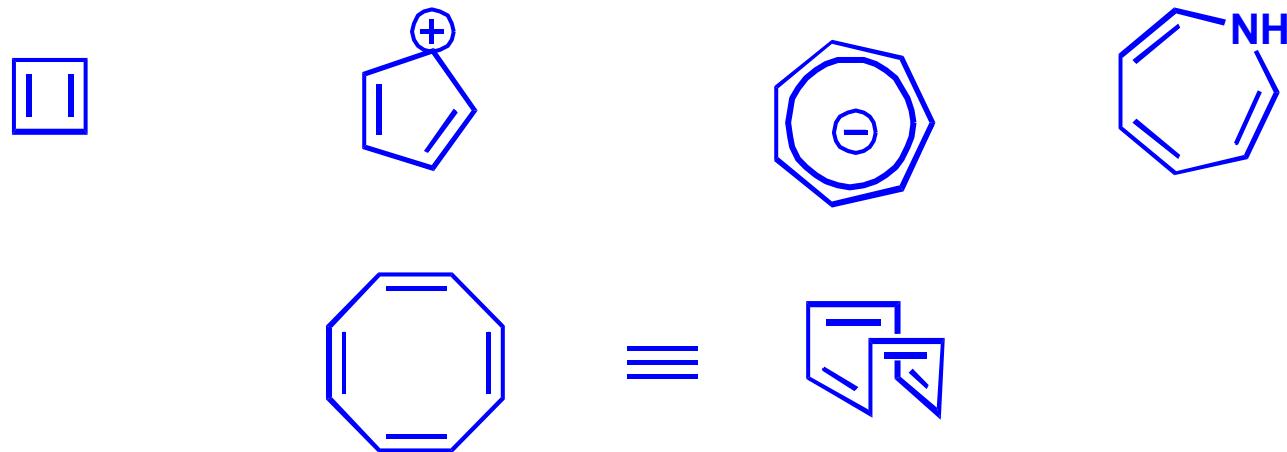
$$4n + 2 = 10, \text{ with } n=2$$



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



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

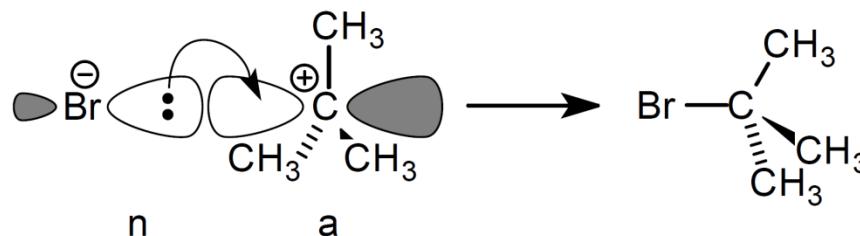
e.g., 1,2-cyclohexadiene or 1,3-cyclohexadiene

Possible HOMO-LUMO Combinations

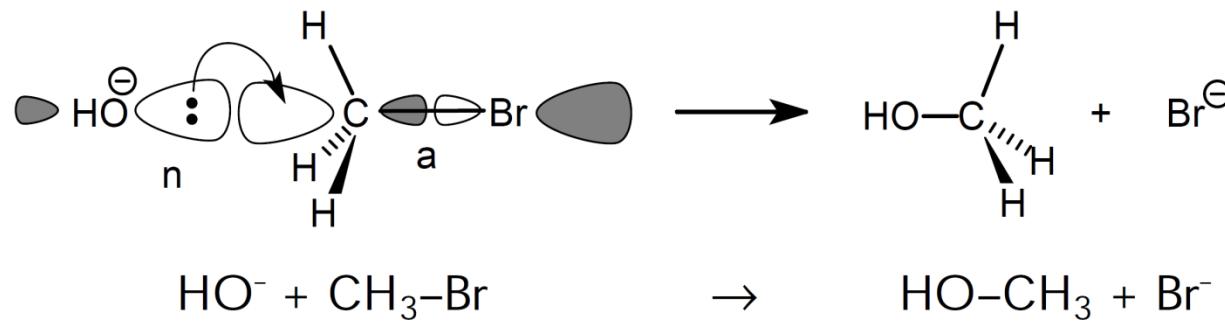
HOMO	LUMO	Result
an occupied n orbital	an empty a orbital	bond formation only
an occupied n orbital	a σ^* orbital	bond formation and bond rupture
an occupied n orbital	a π^* orbital	bond formation and bond rupture
a π orbital	an empty a orbital	bond formation and bond rupture
a π orbital	a σ^* orbital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

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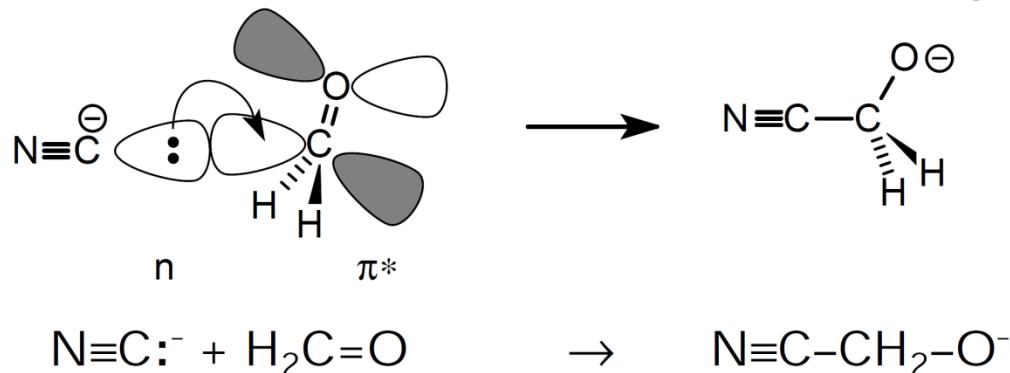


2. non bonding orbital + antibonding orbital (σ^*): S_N2

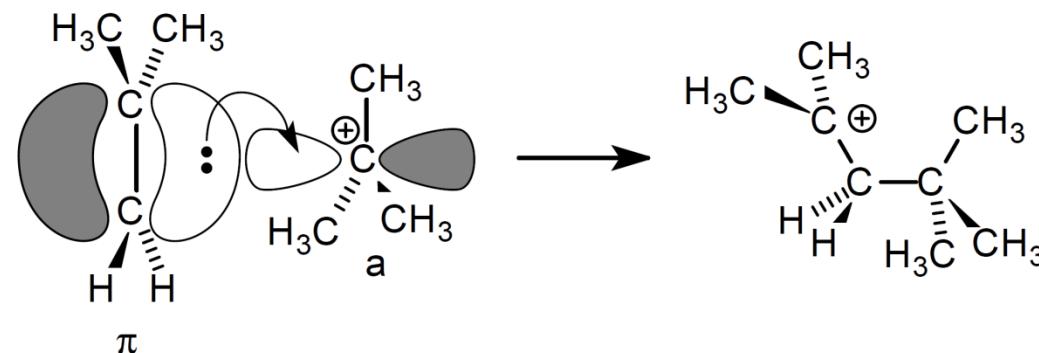


Explanation of Reactions Through Molecular Orbitals

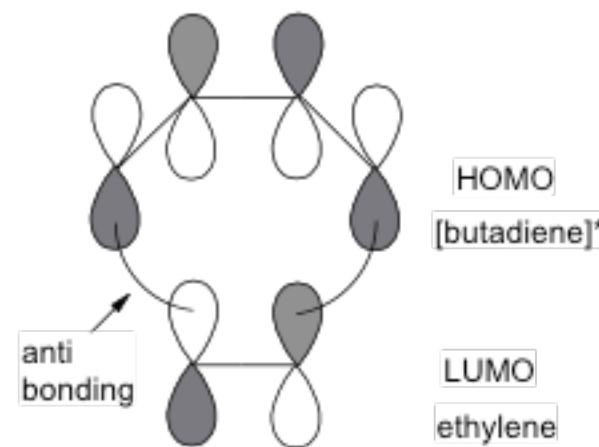
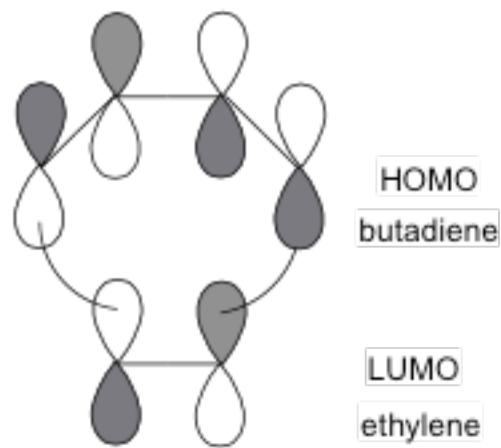
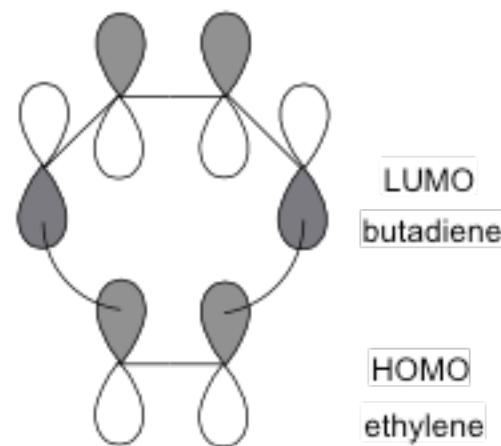
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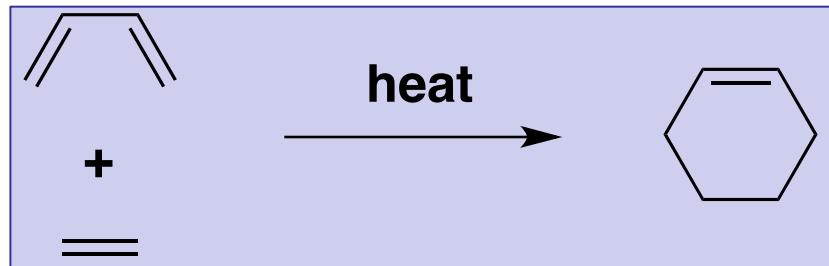
4. $\pi + a$: addition on olefins



FMO Treatment of [4+2] Cycloaddition reaction



$[4\pi_s + 2\pi_s]$
photochemically forbidden



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