M.Sc. Semester-I
Core Course-2 (CC-2)
Reaction Mechanism in Organic Chemistry

I. Nature of Bonding in Organic Molecules

L1. Benzene and Criteria for Aromaticity

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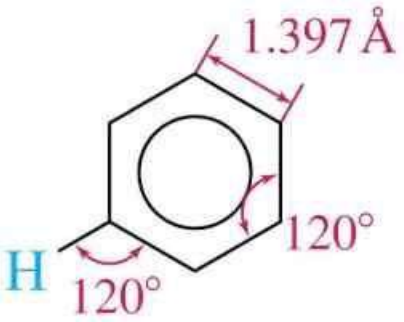
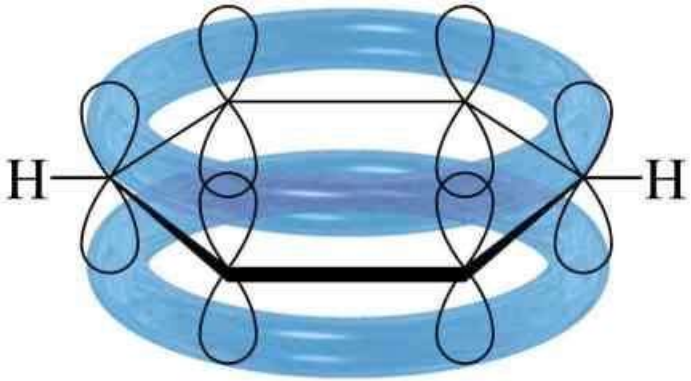
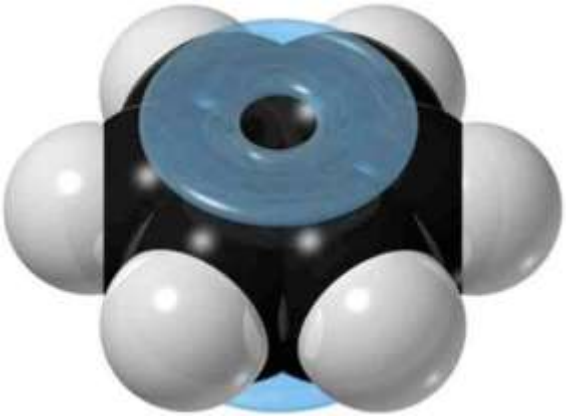
Benzene (C_6H_6) is not "Cyclohexatriene"!





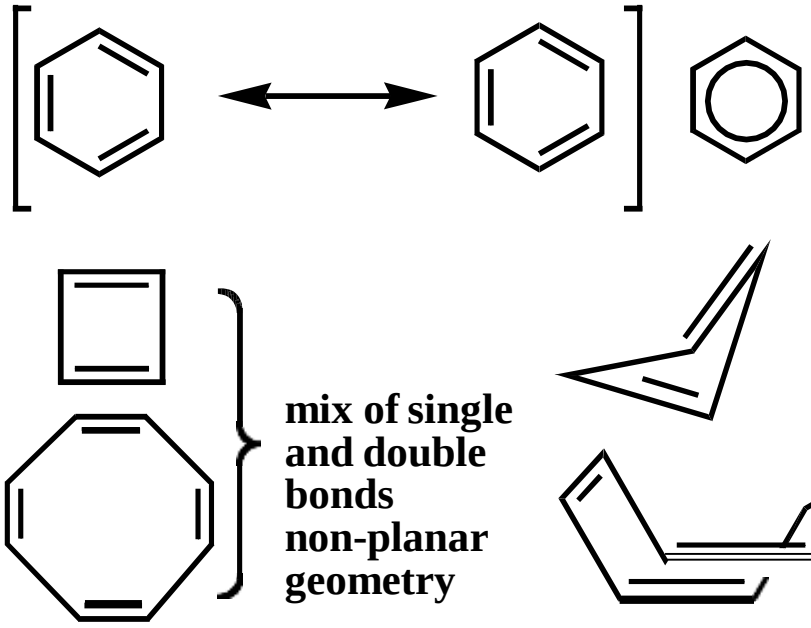


C=C 1.34Å
C-C 1.54Å

Each sp^2 hybridized C in the ring has an unhybridized *p*-orbital perpendicular to the ring which overlaps around the ring

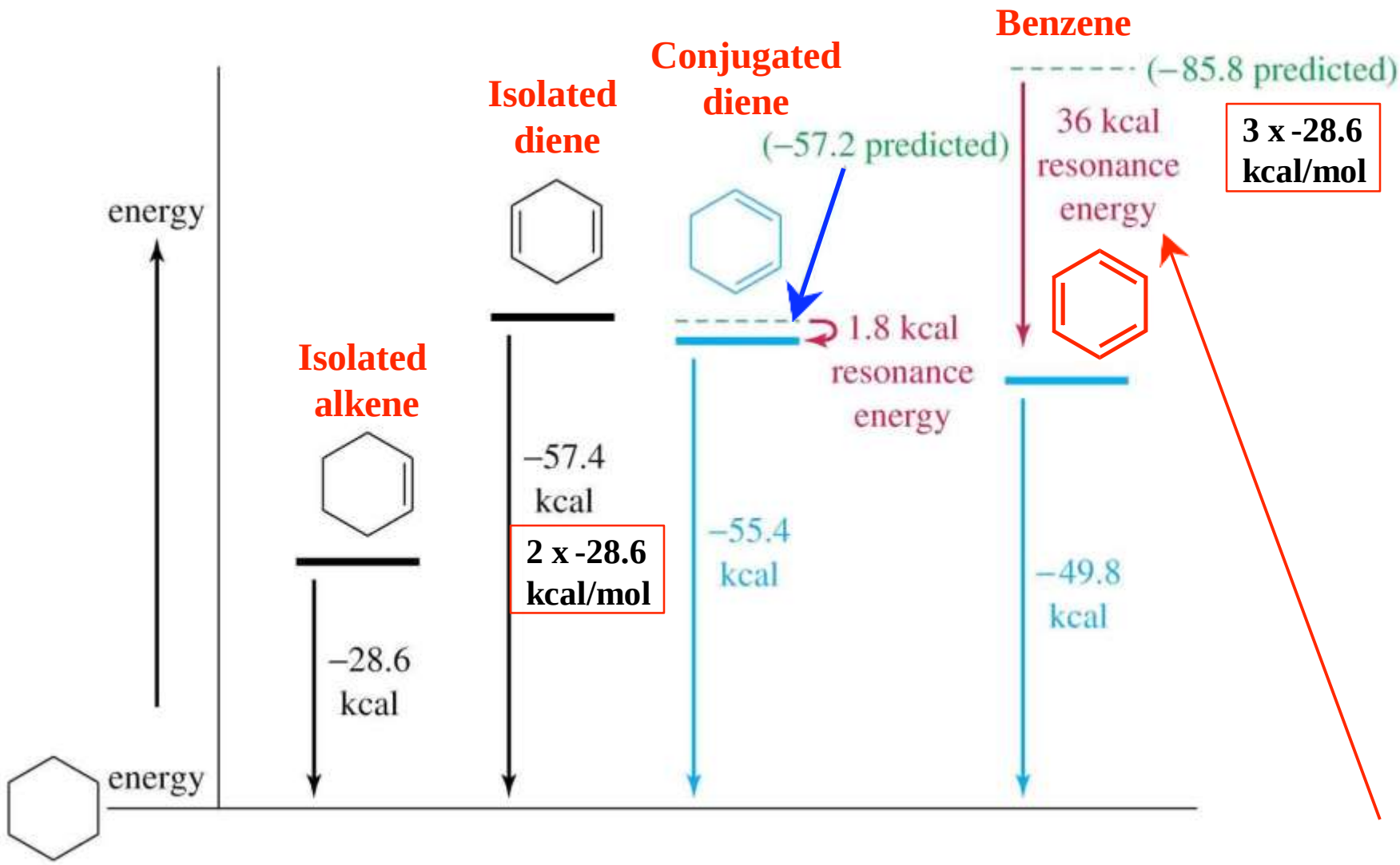
Criteria for Aromaticity

1. **Structure must be cyclic**
2. **Unhybridized p orbital in continuous cyclic system**
3. **Able to adopt a planar geometry**
4. **Fulfills Huckel's Rule and includes (4n + 2) electrons n = 0, 1, 2, 3, 4…….. (the 2, 6, 10, 14….electrons)**



- **Initially, all cyclic conjugated hydrocarbons were proposed to be aromatic**
- **However, cyclobutadiene is so reactive that it dimerizes before it can be isolated**
- **Cyclooctatetraene adds Br_2 readily.**
- **Look at Molecular Orbitals (MOs) to explain aromaticity in benzene-like molecules**

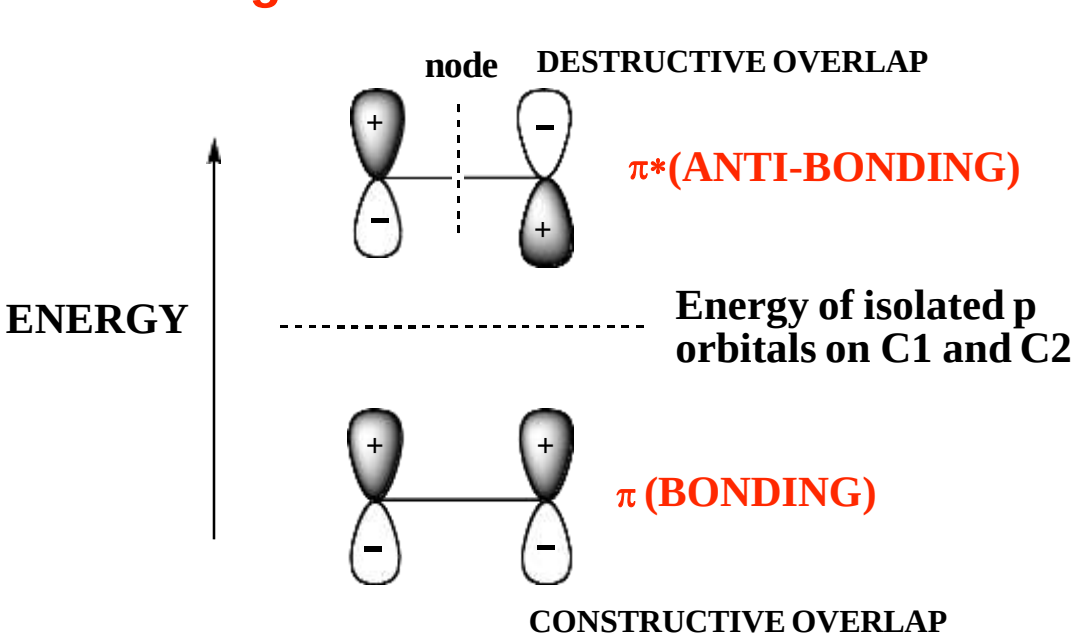
Catalytic hydrogenation of benzene and various cyclohexenes

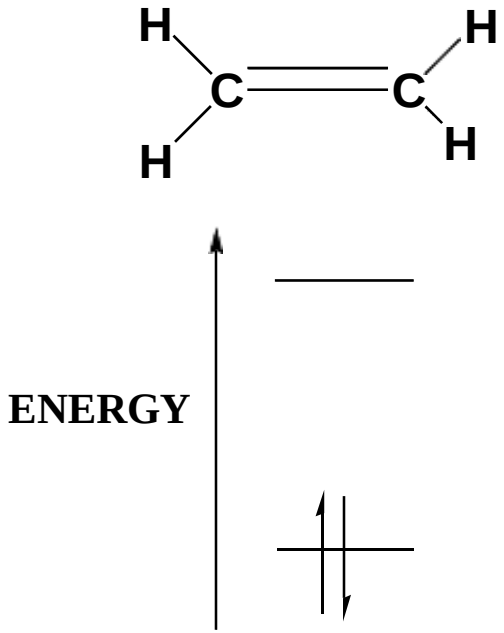


Magnitude of aromatic stabilization = 36 kcal/mol

Constructing π-Molecular Orbitals diagram

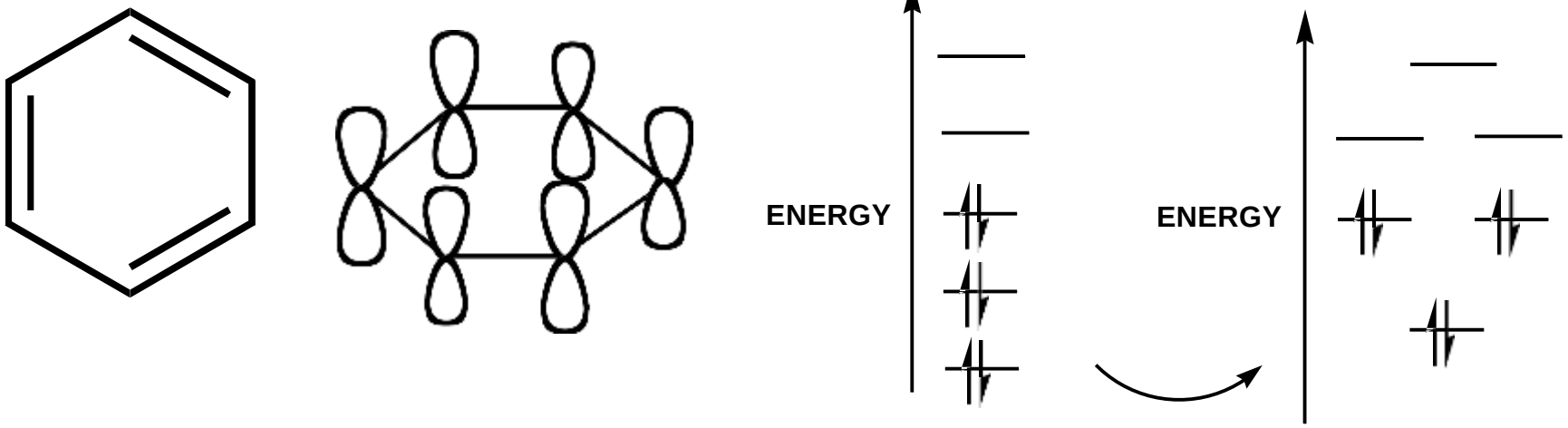
- π molecular orbitals are the sideways overlap of *p* orbitals
- *p* orbitals have 2 lobes. Plus (+) and minus (-) indicate the opposite phases of the wave function, not electrical charge
- When lobes overlap constructively, (+ and +, or - and -) a bonding MO is formed
- When + and - lobes overlap,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





π-Molecular Orbitals for Benzene

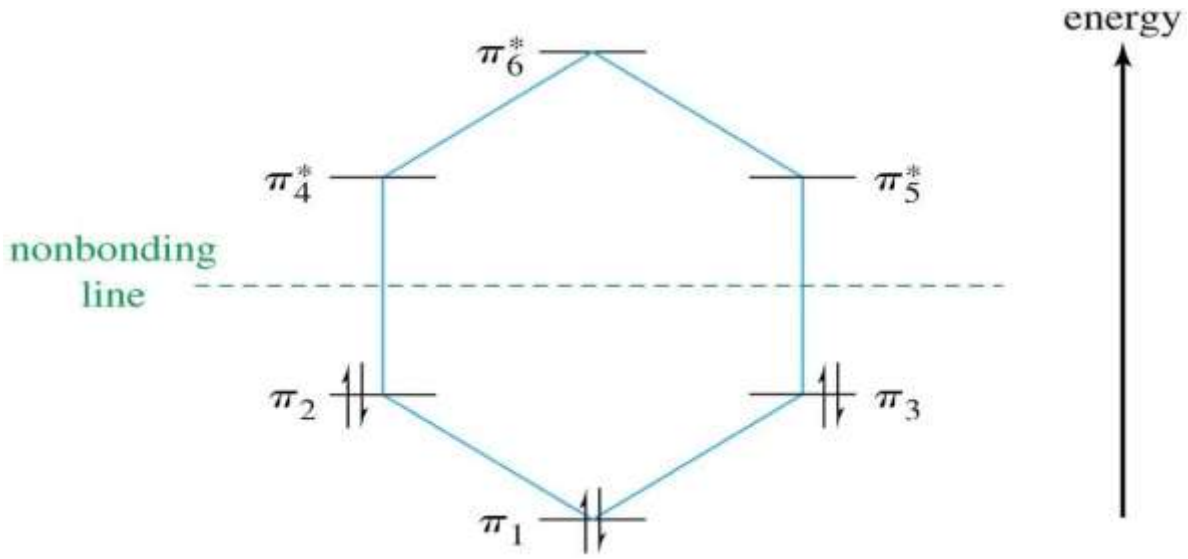
- Six overlapping *p*-orbitals must form six molecular orbitals
- Three will be three bonding, three antibonding orbitals
- Lowest energy MO will have all bonding interactions, no nodes
- As energy of MO increases, the number of nodes increases
- System symmetric so 2 pairs of degenerate orbitals



π - Molecular Orbital Energy Diagram for Benzene

6 atomic orbitals - 6 molecular orbitals

System symmetric so 2 pairs of degenerate orbitals



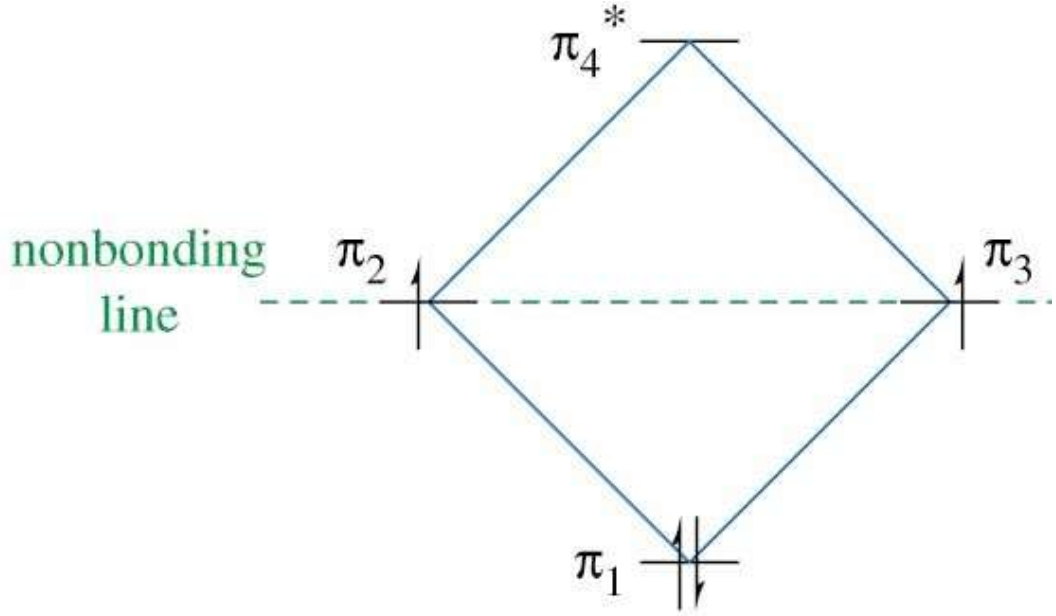
The six electrons fill three bonding pi orbitals.

All bonding orbitals are filled (“closed shell”), an extremely stable arrangement (Aromatic Stabilization).

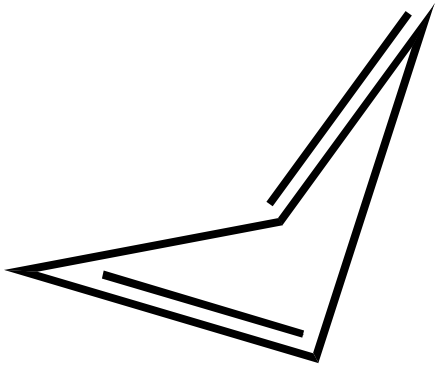
π - Molecular Orbital Energy Diagram for Cyclobutadiene

Following Hund's rule, two electrons are in separate orbitals because they are at same energy.

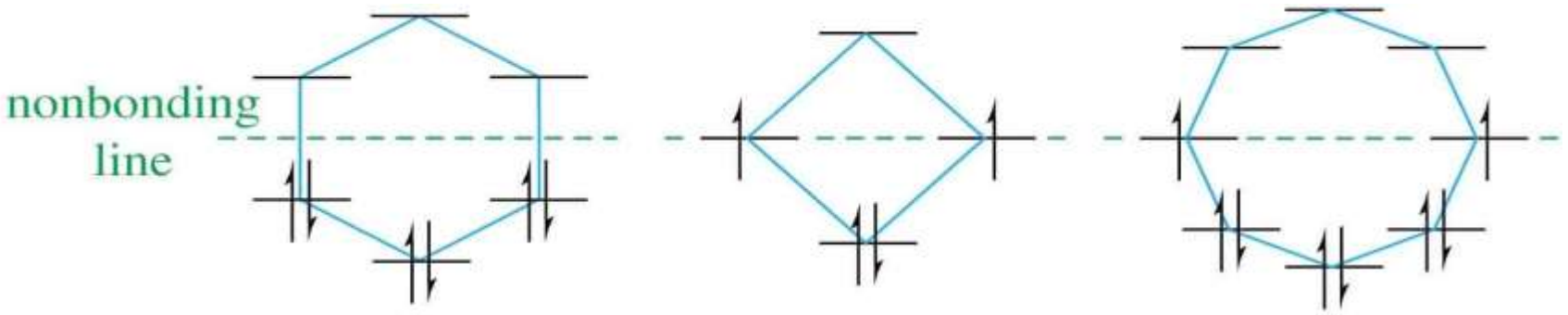
Most stable if filled with an electron pair (as with benzene)



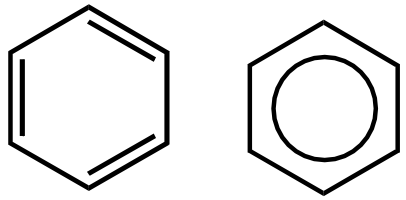
If cyclobutadiene adopted a planar geometry - two of the molecular orbitals would each have a single unpaired electron - very unstable. Applies to any (4 n) system Cyclobutadiene is ANTIAROMATIC



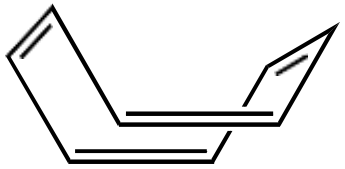
Aromatic Anti-aromatic Non-aromatic



(4n + 2)



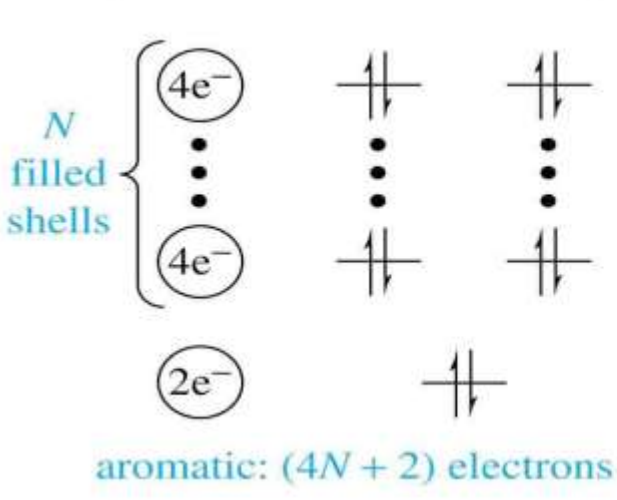
(4n)



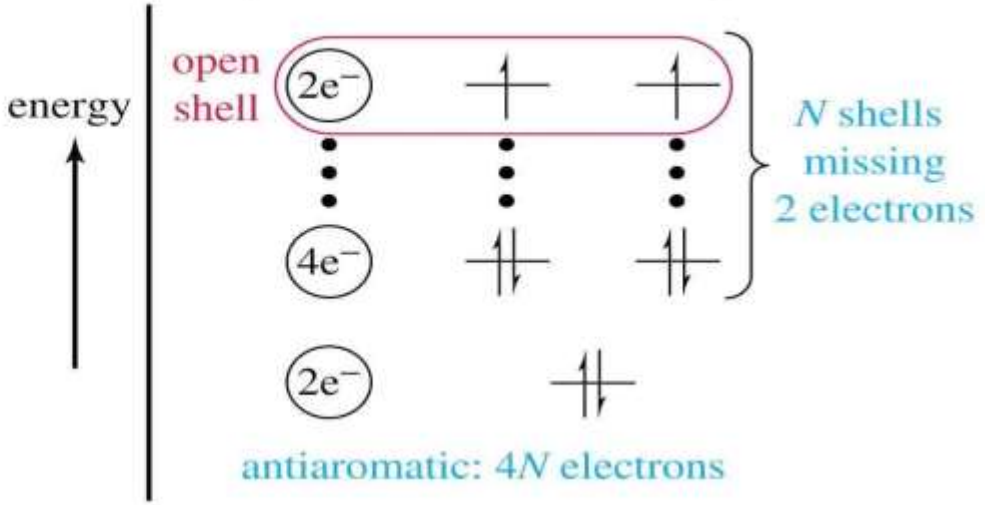
All bond lengths same

Combination of single and double bonds

(vacant orbitals not shown)



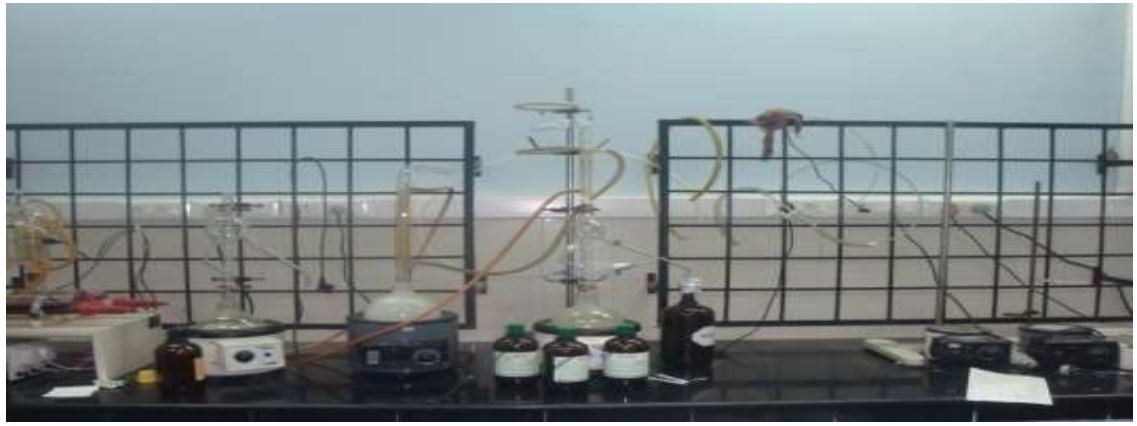
(vacant orbitals not shown)



Cyclobutadiene - Anti-aromatic

Cgclooctatetraene- Non-aromatic due to loss of planarity

Thank You



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