

# UNIT I

# Benzene and its derivatives



**RAFFLES**  
**UNIVERSITY**

Presented by

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## **UNIT I 10 Hours**

### **• Benzene and its derivatives**

**A.** Analytical, synthetic and other evidences in the derivation of structure of benzene, Orbital picture, resonance in benzene, aromatic characters, Huckel's rule

**B.** Reactions of benzene - nitration, sulphonation, halogenation reactivity, Friedelcrafts alkylation- reactivity, limitations, Friedelcrafts acylation.

**C.** Substituents, effect of substituents on reactivity and orientation of mono substituted benzene compounds towards electrophilic substitution reaction

**D.** Structure and uses of DDT, Saccharin, BHC and Chloramine

## **UNIT II 10 Hours**

- **Phenols\*** - Acidity of phenols, effect of substituents on acidity, qualitative tests, Structure and uses of phenol, cresols, resorcinol, naphthols
- **Aromatic Amines\*** - Basicity of amines, effect of substituents on basicity, and synthetic uses of aryl diazonium salts
- **Aromatic Acids\*** –Acidity, effect of substituents on acidity and important reactions of benzoic acid.

## **UNIT III 10 Hours**

### **• Fats and Oils**

- a. Fatty acids – reactions.
- b. Hydrolysis, Hydrogenation, Saponification and Rancidity of oils, Drying oils.
- c. Analytical constants – Acid value, Saponification value, Ester value, Iodine value, Acetyl value, Reichert Meissl (RM) value – significance and principle involved in their determination.

## **UNIT IV 08 Hours**

### **• Polynuclear hydrocarbons:**

a. Synthesis, reactions

b. Structure and medicinal uses of Naphthalene, Phenanthrene, Anthracene, Diphenylmethane, Triphenylmethane and their derivatives

## **UNIT V 07 Hours**

### **• Cyclo alkanes\***

Stabilities – Baeyer's strain theory, limitation of Baeyer's strain theory, Coulson and Moffitt's modification, Sachse Mohr's theory (Theory of strainless rings), reactions of cyclopropane and cyclobutane only

# Classification of organic molecules

Organic Compounds

Acyelic/Aliphatic

No rings / open chain

- Alkane,  $C_nH_{2n+2}$
- Alkene  $C_nH_{2n}$
- Alkyne:  $C_nH_{2n-2}$

Cyclic [Ring Compounds]

Carbocyclic [Ring structures  
contains only carbon]

Heterocyclic  
Ring structures

Contains ~~only~~ carbon along with  
(N, O, S)

↓                      ↓                      ↓  
Amino                  oxo                  thio

Alicyclic

cyclo Alkanes

Aromatic

[Benzene and derivatives]

## HISTORY

- ▶ The hydrocarbon that we now call benzene was first isolated in 1825 by Michael Faraday from an oily film that deposited from the gas used for lighting. Faraday did some experiments, and discovered that the new compound had equal numbers of carbons and hydrogens, and so named it 'carbureted hydrogen'


- ▶ Nine years after its discovery, another chemist, Mitscherlich, found he could produce the same substance by heating a chemical that had been isolated from gum **benzoin** – so he decided to call the compound **benzin**. Another suggestion was the German name, **benzol**, from the German öl, meaning oil. But in France and England the name **benzene** was used instead, to avoid the -ol ending confusing it with an alcohol.

# Introduction

- ▶ **Benzene** is an important organic chemical compound with the chemical formula  $C_6H_6$ . The benzene molecule is composed of **six** carbon atoms joined in a ring with **one** hydrogen atom attached to each carbon.
- ▶ benzene is classed as a hydrocarbon, Because it contains only carbon and hydrogen atoms.



# Description

- ▶ **Molecular formula** =  $C_6H_6$
- ▶ **Empirical formula** = C,H
- ▶ **Molecular mass** = 78
- ▶ **Percentage of carbon** = 93.6%
- ▶ **Percentage of hydrogen** = 6.4%
- ▶ **Structural formula** = 
- ▶ It is an aromatic hydrocarbon.
- ▶ **Physical state** = liquid at room temperature.
- ▶ **Melting point** =  $5.5^{\circ}C$
- ▶ **Boiling point** =  $80^{\circ}C$
- ▶ It is highly inflammable.
- ▶

- ▶ Benzene burns with smoke due to high percentage of carbon.
- ▶ It is insoluble in water.
- ▶ It is soluble in organic solvents.
- ▶ **Nature of reactions:**
  - (a) Substitution reactions
  - (b) Addition reactions (under special conditions)
- ▶ Benzene is a natural constituent of crude oil and is one of the elementary petrochemicals . Because of the cyclic continuous pi bond between the carbon atoms, benzene is classed as an aromatic hydrocarbon, the second  $[n]$ -annulene ( $[6]$ -annulene).
- ▶ Benzene is a colorless and highly flammable liquid with a sweet smell, and is responsible for the aroma around petrol stations.

# Structure

- ▶ All possible structures of Benzene



Clause  
Structure



Dewar  
Structure



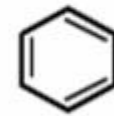
Ladenburg  
Structure



Armstrong  
Structure



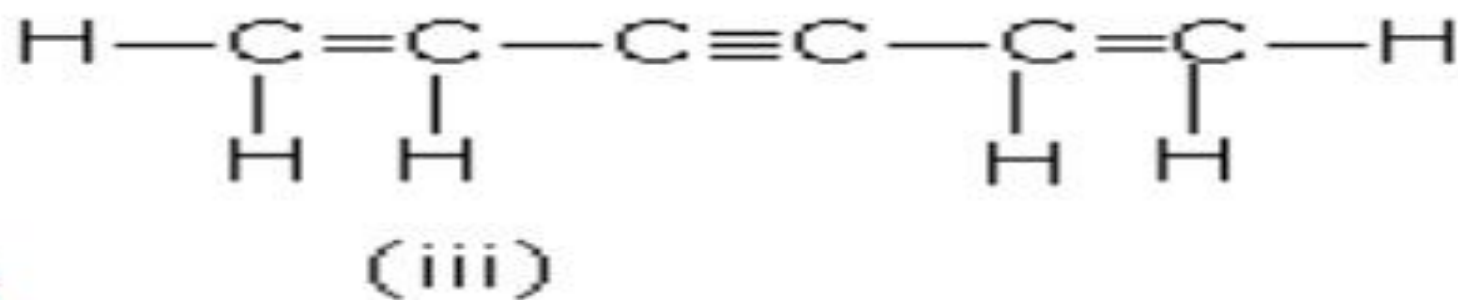
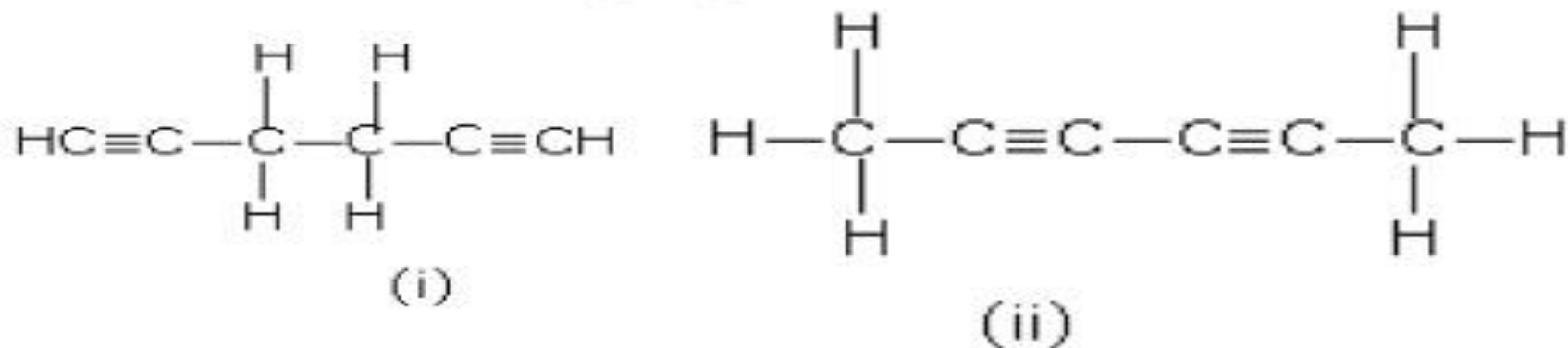
Thiele  
Structure



Kekule  
Structure

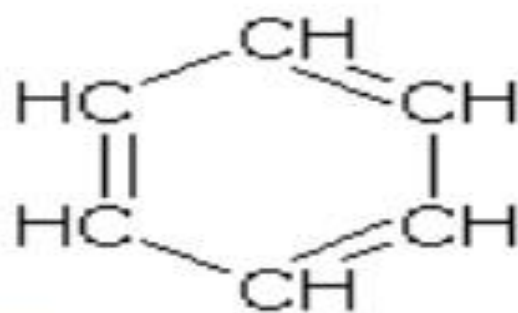
## Open chain structure

- ▶ Based upon observable facts given above and the tetravalency of carbon, the following open chain structures were proposed for benzene.

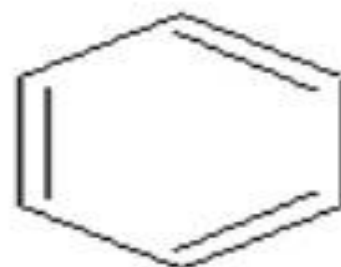


# Ring structure of Benzene

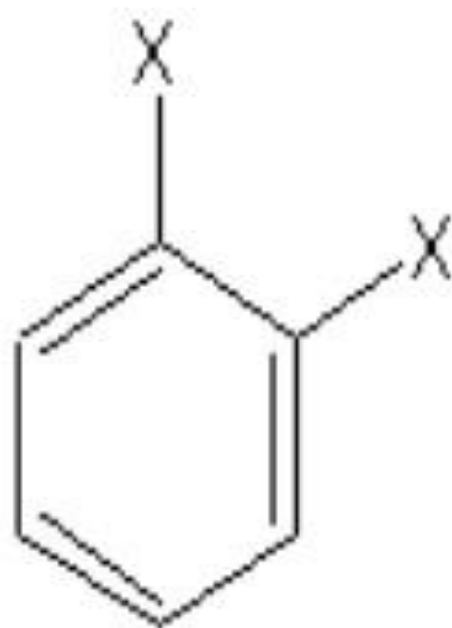
- ▶ After taking into account the above observed facts, Kekule (1865) suggested a ring structure for benzene. According to him, six carbon atoms occupied six corners of a regular hexagon in benzene and each carbon carried one hydrogen atom. To satisfy the tetravalency of carbon, the system consisted of alternate single and double bonds. Kekule's formula is shown below.



or

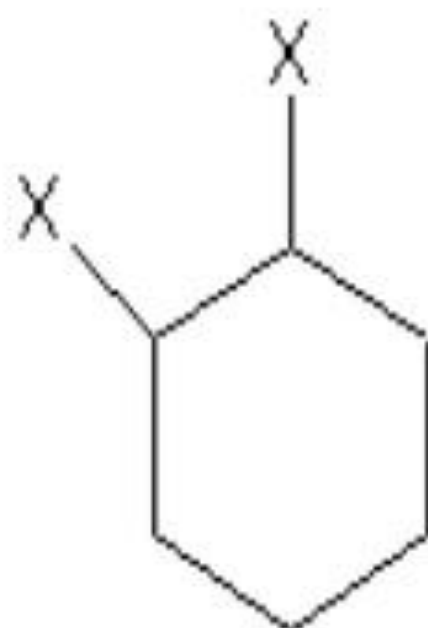


# Defects of kekule structure



Here, two ortho positions are characterised by single bonded carbon atoms

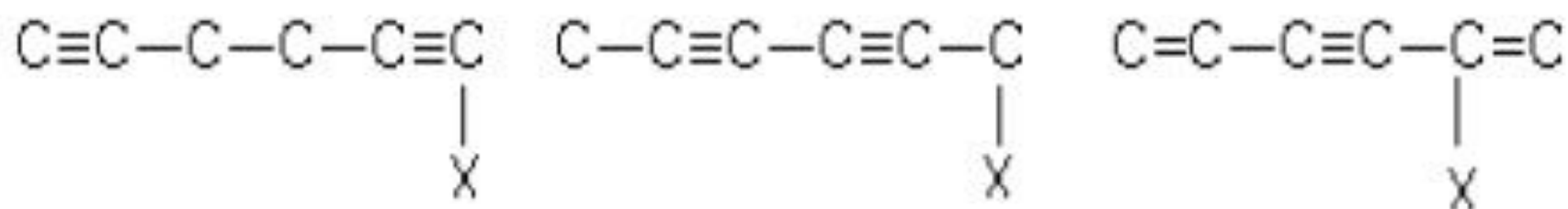
or



Here, two ortho positions are characterised by double bonded carbon atoms

## Drawbacks of open chain structure

- ▶ The open chain structure for benzene was rejected due to the following reasons:
- ▶ Addition reactions usually given by alkenes and alkynes are not given by benzene.
- ▶ Benzene forms only one kind of mono- substituted product. An open chain structure however, can form more than one kind of monosubstituted product as shown below:



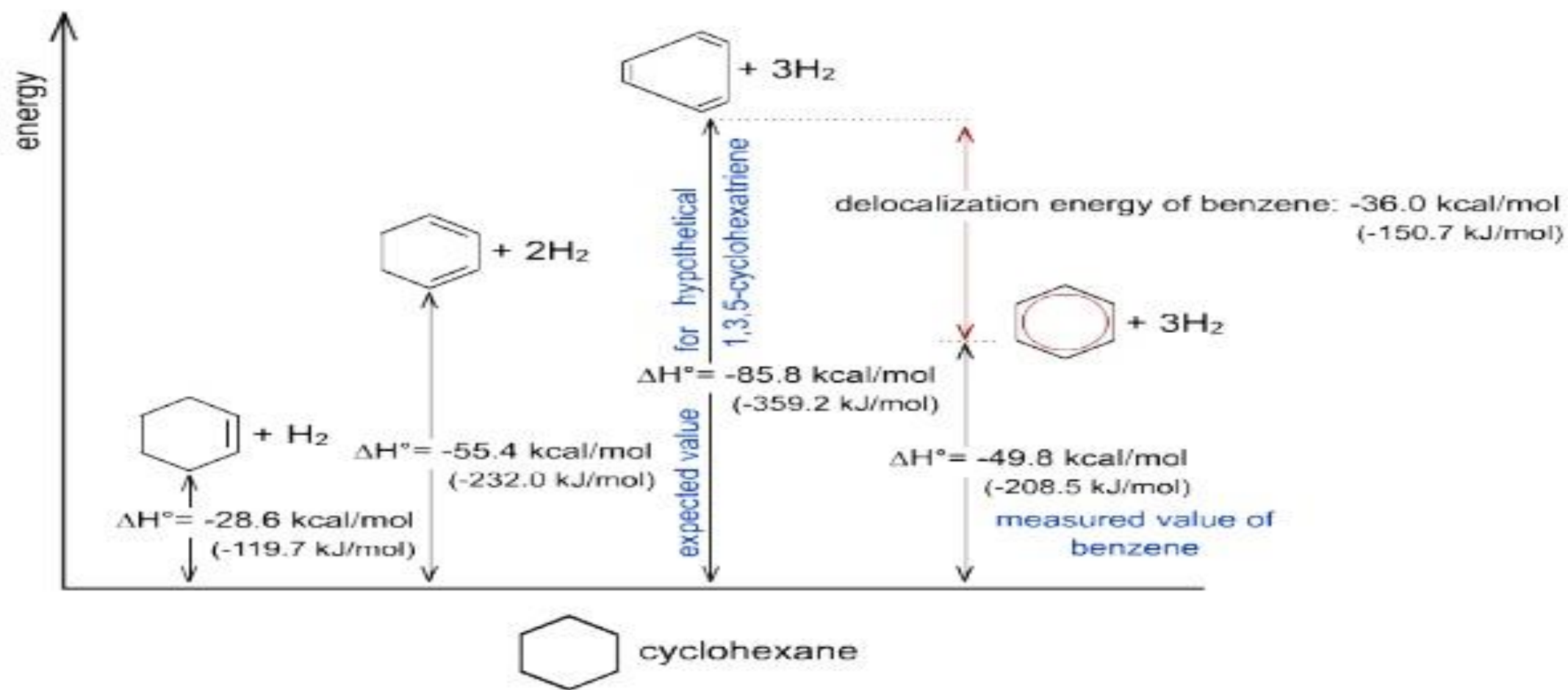
(hydrogens are not shown in these formulae for the sake of clarity)

# Kekule structure

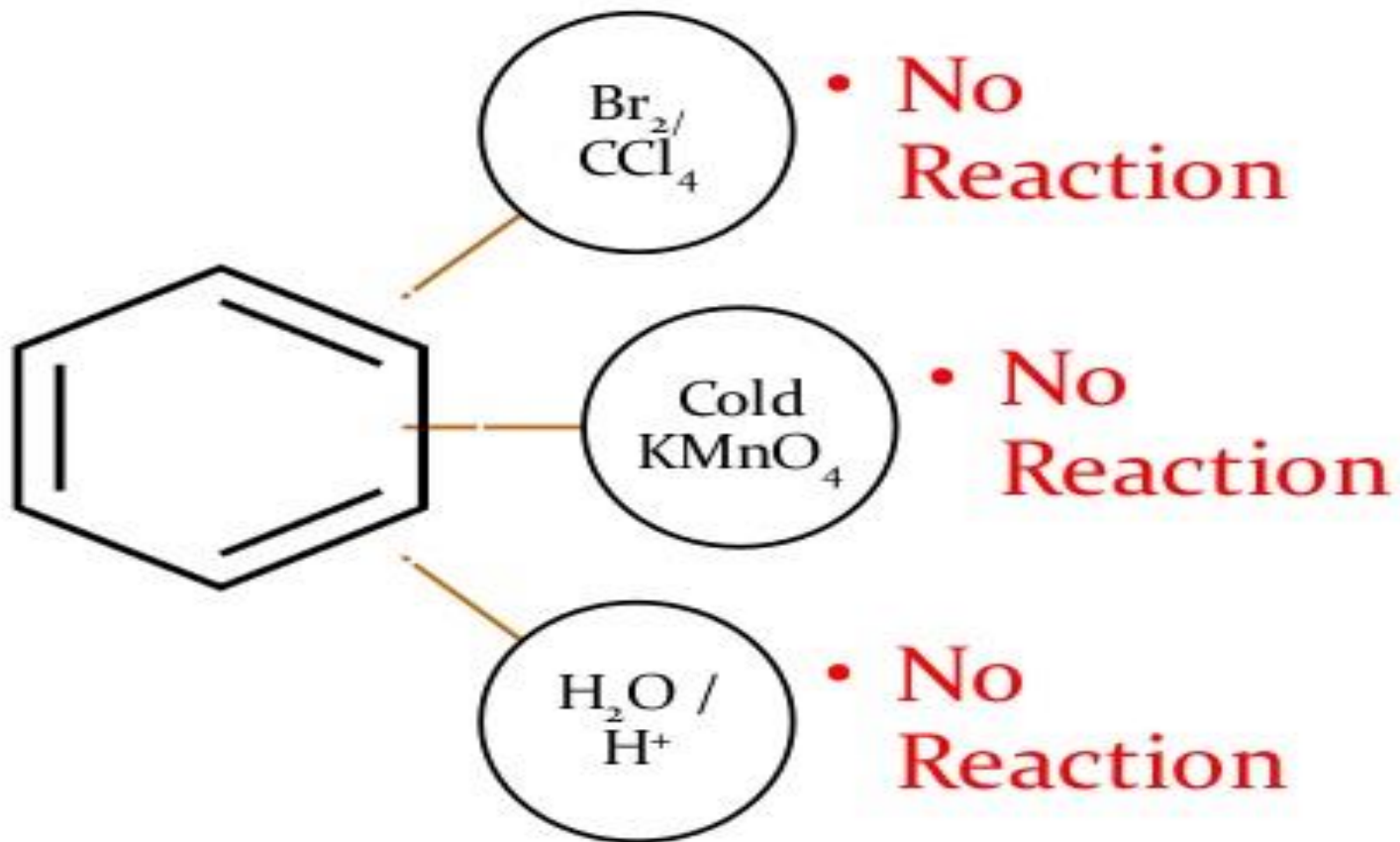
- ▶ **The Kekulé structure for benzene,  $C_6H_6$**
- ▶ **What is the Kekulé structure?**
- ▶ Kekulé was the first to suggest a sensible structure for benzene. The carbons are arranged in a hexagon, and he suggested alternating double and single bonds between them. Each carbon atom has a hydrogen attached to it.



# Resonance Energy of BENZENE:



**BENZENE** does not behave like Alkenes or Alkynes:



## Aromaticity

Aromaticity is a property of the **sp<sup>2</sup>** hybridized planar rings in which the p-orbital, one on each atom, allow cyclic delocalization of  $\pi$  electrons.

### CRITERIA:

RULE 1: An aromatic compound is **cyclic** and **planar**

RULE 2: Each atom in an aromatic ring has a **p-orbital** which is parallel so that a continuous overlap is possible around the ring

RULE 3: The cyclic pi-molecular orbital formed by overlap of p-orbital must contain  $(4n+2)$  pi electrons.

# Aromaticity (Hückel's Rules)

- Huckel's rules define the classification of aromatic and non-aromatic molecule.
- The criteria of aromatic molecule:
  - All the atoms are  $sp^2$  hybridised and in planar cyclic arrangement.



→ All atoms are  $sp^2$  but not a cyclic.  
→ Hence, non-aromatic



→ There is non- $sp^2$  atom.  
→ Hence, non-aromatic



→ All atoms are  $sp^2$  and a cyclic.  
→ Hence, could be aromatic

# Huckel's rules

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- Huckel's rule
  - Number of  $\pi$ -electrons is  $(4n+2)$ ,
  - How to calculate  $\pi$ -electrons?  $\rightarrow$ 
    - based on the structure, p-orbitals in  $sp^2$  arrangement has 1 electron



$\rightarrow$ Has 6  $\pi$ -electrons ( $4n+2$ ,  $n=1$ )  
 $\rightarrow$ Hence, aromatic



$\rightarrow$ Has 4  $\pi$ -electrons ( $4n$ ,  $n=1$ )  
 $\rightarrow$ Hence, anti-aromatic

# Huckel's Rule (summary)

