CHEMISTRY CORE, SEM II
CHE CC203 ORGANIC CHEMISTRY

- **UNIT-1: AROMATIC HYDROCARBONS**
- **PART-1: AROMATICITY**

By
- Ms. Amita Prasad,
Department of Chemistry,
Patna Women's College

AROMATICITY

- The latest theory of aromaticity is given by Huckel.
- It successfully explains the aromatic character in:
    1. Benzenoid System &
    2. Non-Benzenoid System

POSTULATES OF HUCKEL THEORY OF AROMATICITY

- The compound should be cyclic, planar and conjugated.
- The ring carbon atoms should be sp^2 hybridised. This ensures maximum overlapping of p-orbitals for extended π bonding.
- There should be a cyclic cloud of delocalized π electrons above and below the plane of the molecule.
- The cyclic π cloud must contain (4n+2) π electron (n=0, 1, 2,..)
- Huckel numbers are 2, 6, 10, 14, 18, etc. (for n=0, 1, 2, 3 etc.)
- Cyclic compound with (4n) π electrons are called anti-aromatic compounds.
- Anti-aromatic compounds are less stable than their open chain analogues.

TYPES OF AROMATIC COMPOUND

Benzenoid (Contains benzene ring)		Non-Benzenoid (Do not contain benzene ring)
Carbocyclic The ring is made of C atoms only. E.g. Benzene, Naphthalene.	**Heterocyclic** The ring contains at least one hetero atom. E.g. Pyridine etc.	Aromatic ions like Cyclopropenyl cation, Cyclopentadienyl anion etc.

BENZENOID AROMATIC COMPOUND

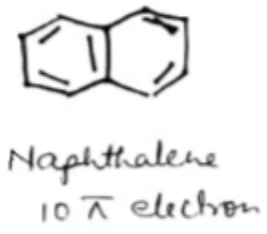
1. Benzene

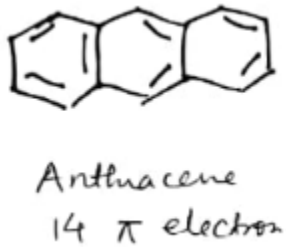
- It is planar, conjugated monocyclic compound.
- It has π cloud of 6 electrons.
- Obeys Huckel's rule(4n+2) = 6 π electrons.
- The 6 π electrons are known as aromatic sextet.
- All substituted benzene possess aromatic sextet and hence are aromatic in nature.

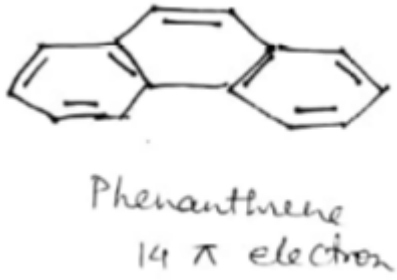
BENZENOID AROMATIC COMPOUND

2. Polycyclic compound:

Polycyclic conjugated system like naphthalene, anthracene, phenanthrene etc. are benzenoid aromatics







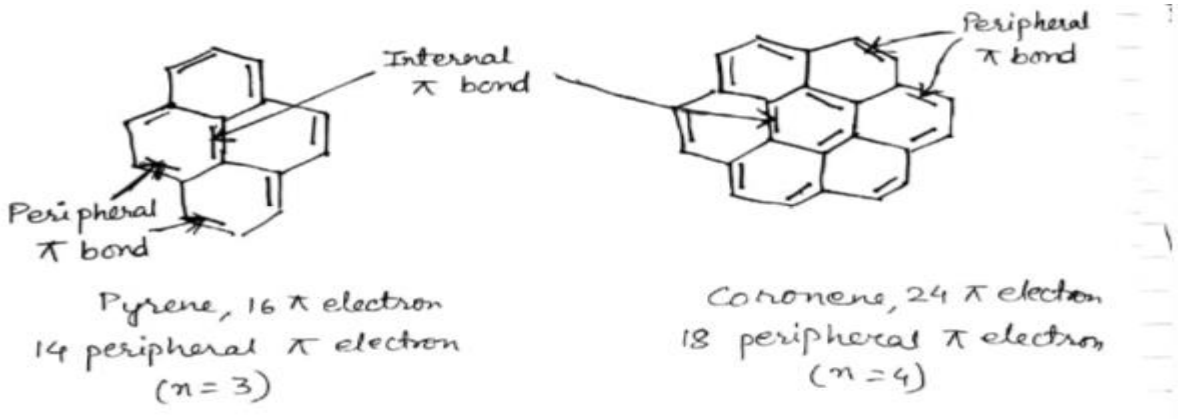
Napthalene	Anthracene	Phenanthrene
10 π electron	14 π electron	14 π electron

[Aromatic in nature]

BENZENOID AROMATIC COMPOUND

3. Pyrene and Coronene:

- These have 16 and 24 π electrons respectively and hence do not obey Huckel's rule yet these are typical benzenoid aromatic compound (as shown by experimental data).
- In these cases only the peripheral π electron contribute to the Huckel's magical number.



- Therefore, in such polycyclic system, Huckel's rule should be applied to peripheral (conjugated) π electrons only.

BENZENOID AROMATIC COMPOUND

4. Heterocyclic Compound:

- In 5 membered compound like Pyrrole and Furan, the ring carbon atom are sp^2 hybridised.

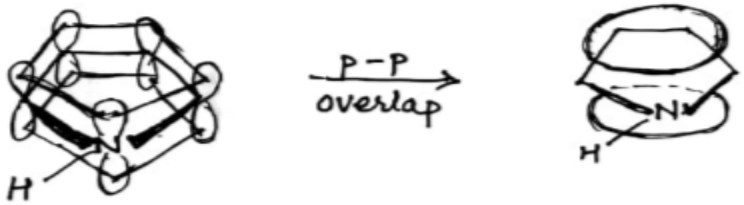
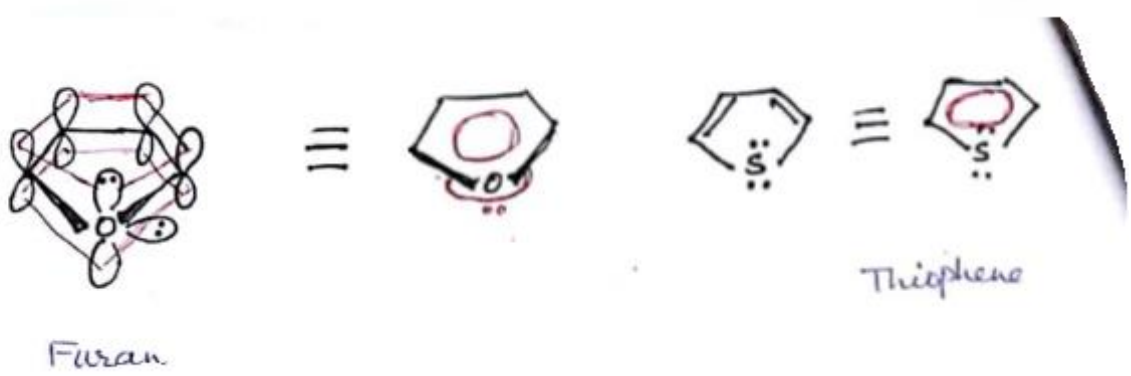


Fig: Pyrrol

- This sp^2 hybridised orbital is used for σ bond between C and C, and C and H.
- The unhybridised p orbital on C contain single electron while that on N contain 2 electrons.
- The lateral overlap of these p-orbitals result in delocalized π molecular orbital above and below the ring. This MO satisfies Huckel's Rule (n=1, 6π electrons). Hence it is aromatic.

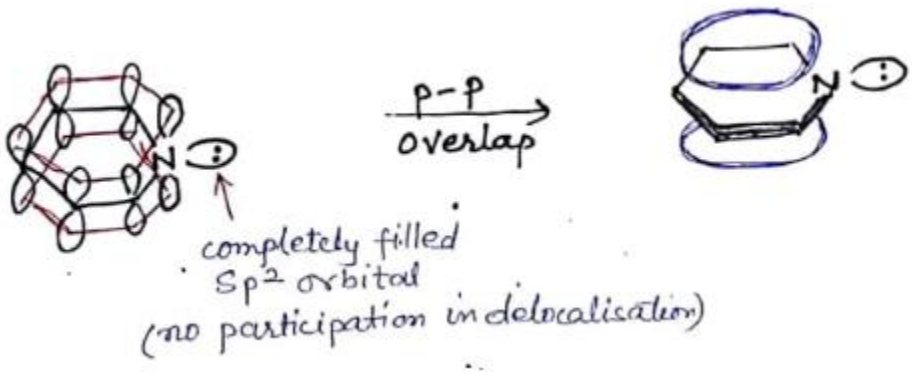
BENZENOID AROMATIC COMPOUND

- In case of Furan, the 4 C atoms and O atoms are sp^2 hybridized. The unhybridized p-orbitals on C (containing lone pair of electrons) overlap laterally to form a delocalized π MO containing 6 electrons, making it aromatic. Same is the case with thiophene.



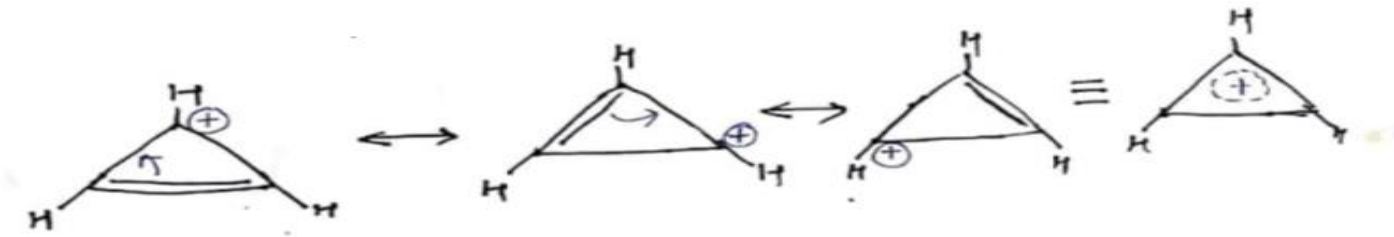
BENZENOID AROMATIC COMPOUND

- In 6-membered heterocyclic compound like pyridine C_5H_5N, all the ring C atom and N are sp^2 hybridized. The unhybridized p-orbital overlap laterally to form π MO above and below the ring making the molecule aromatic.

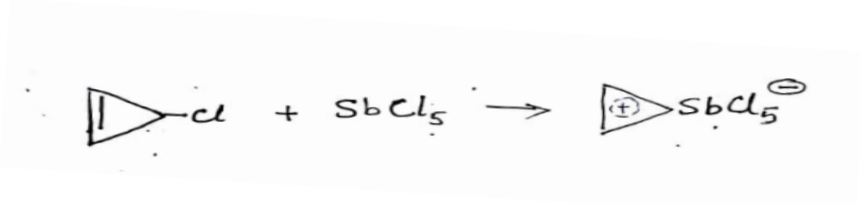


NON-BENZENOID AROMATIC COMPOUND

1. Cyclopropenyl cation: This cation is a closed shell of $(4n+2)\pi$ electrons (n=0). Hence, it is a stable aromatic system



- Several stable cyclopropenium salts are known.

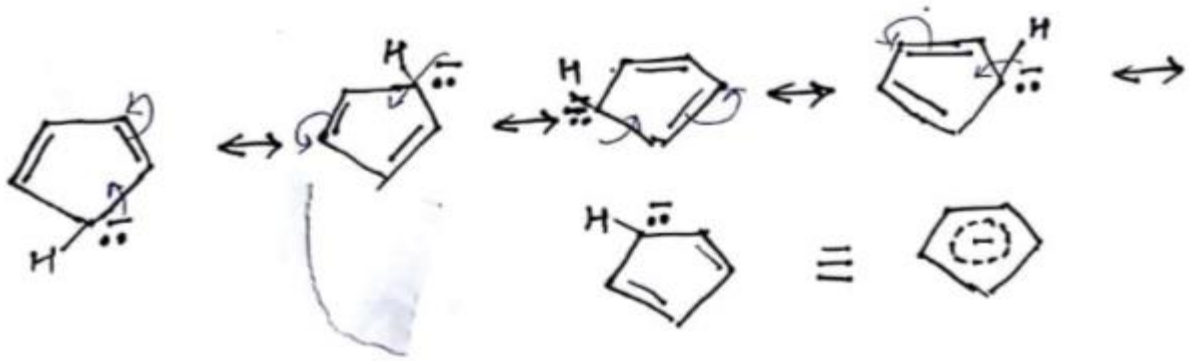


cyclopropenyl hexachloro -antimonate (stable)

NON-BENZENOID AROMATIC COMPOUND

2. Cyclopentadienyl anion:

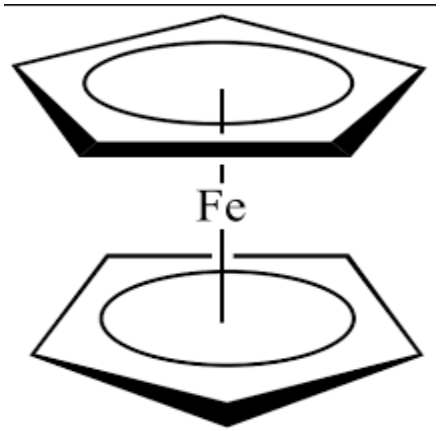
- This anion is a cyclic (4n+2)π electron system (n=1)



- Stable potassium cyclopentadienide and dicyclopentadienyl iron (ferrocene) have been prepared.

NON-BENZENOID AROMATIC COMPOUND

Cyclopentadienide Potassium



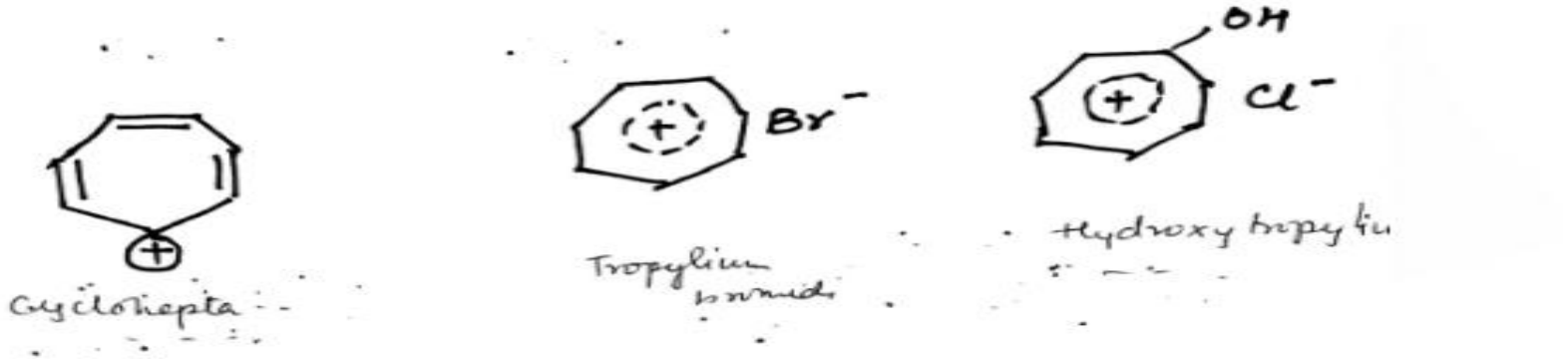
ferrocene (stable)

- Ferrocene, an orange solid (melting point 173 degree celcius) undergoes aromatic substitution reactions like Fridel Crafts acylation.

NON-BENZENOID AROMATIC COMPOUND

3. Cycloheptatrienyl Cation (Tropylium ion):

- This cation follows (4n+2)π electron system and is stable. Stable tropylium salts have been prepared which show aromatic character.



Cycloheptatrienyl cation (tropylium ion, 6π electron) 7 resonating structures.

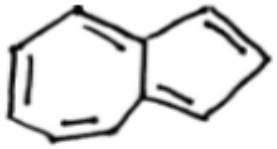
Tropylium bromide (stable)

Hdroxytropylium chloride (stable)

NON-BENZENOID AROMATIC COMPOUND

4. Azulene:

- It has 10 π electron and is non-benzenoid aromatic compound (4n+2 = 10- electron, n=2). It is an intense blue stable solid (melting point 99 degree celcius) and undergoes electrophilic substitution reaction like other aromatic compounds.



Azulene
10 π electron

NON-BENZENOID AROMATIC COMPOUND

5. Annulenes:

- Mono cyclic conjugated polyenes containing 10 or more carbon atoms in the ring are called annulenes. They are named by prefixing the no. of C atoms placed in square brackets. [14] and [18] Annulenes, obey Huckel's (4n+2) rule and show aromatic character.

[14] Annulene [18] Annulene

Annulene with large no (≥30) C atoms are non arromatic.