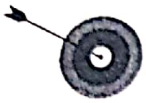
9A.4 HUCKEL'S RULE AND AROMATICITY

In 1931, Huckel gave a rule for monocyclic compounds, which states that *the cyclic compounds containing* $(4n + 2)$ *delocalized* π *electrons exhibit aromatic character.* Here, n can be zero or a whole number. For example, for $n = 0$ the value of $(4n + 2)$ is 2 and for $n = 1$, the $(4n + 2)$ is 6 and so on. This means that systems containing 2, 6, 10, 14, 18, 22, and so on, delocalized π electrons show aromatic behaviour.



A compound is said to exhibit **aromaticity** if it satisfies all of the following conditions simultaneously:

(i) It is cyclic.
(ii) It is *planar*. In general presence of sp^2 hybridized carbons in the system imparts planarity.
(iii) It exhibits *continuous delocalization* of π electrons (continuous delocalization is possible if p orbitals are available on each carbon for overlap).
(iv) It should follow *Huckel's rule*, also known as *Huckel magic number*, that is, it should have $(4n + 2)$ number of delocalized π electrons where n is zero or a whole number.

9A.5 AROMATICITY IN BENZENE AND OTHER CYCLIC SYSTEMS

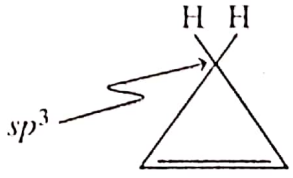
Aromaticity is not restricted to benzene and its derivatives but is also extended to other cyclic systems, cyclic ions, fused cyclic systems, and heterocyclic compounds. Following examples discuss the concept of aromaticity in different systems.

9A.5.1 Aromaticity and the Three Membered Ring Systems

Cyclopropene

Characteristics of cyclopropene molecule are as follows:

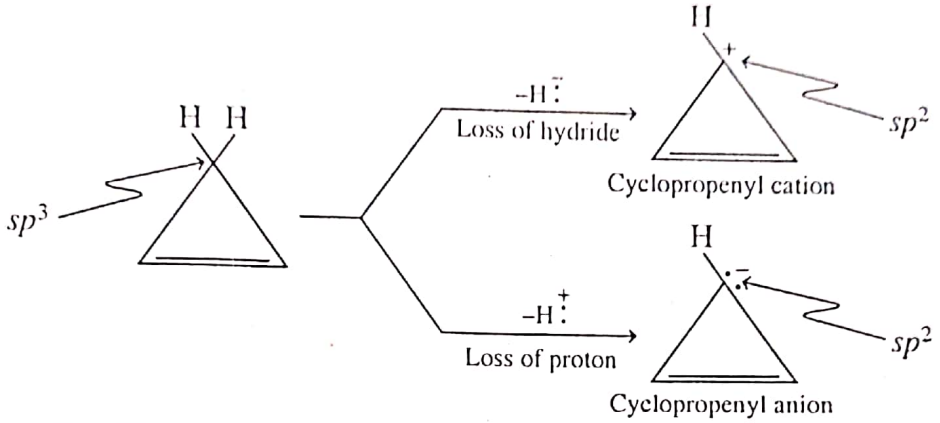
(i) It is cyclic
(ii) It is planar
(iii) It does not exhibit continuous delocalization. One of the carbon in cyclic system is sp^3 hybridized and thus, p orbital is not available on that carbon for delocalization.
(iv) Obeys Huckel's rule, as the number of delocalized π electrons is two.



Thus, cyclopropene is **not aromatic** as all the conditions are not simultaneously satisfied. The condition of continuous delocalization is not followed.

Cyclopropenyl Ions

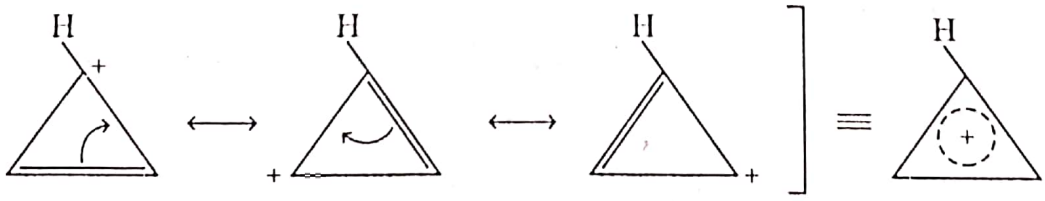
The sp^3 hybridized carbon in cyclopropene is not involved in delocalization. Removal of a hydrogen (either as a proton (H^+) or as a hydride (H^-)) from this carbon results in the formation of an anion or a cation where all the carbons are sp^2 hybridized and thus, continuous delocalization of π electrons takes place.



Cyclopropenyl cation

Characteristics of cyclopropenyl cation are as follows

(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization. All the carbons of cyclic system are sp^2 hybridized, and thus p orbitals are available for delocalization.



Resonance stabilization of cyclopropenyl cation

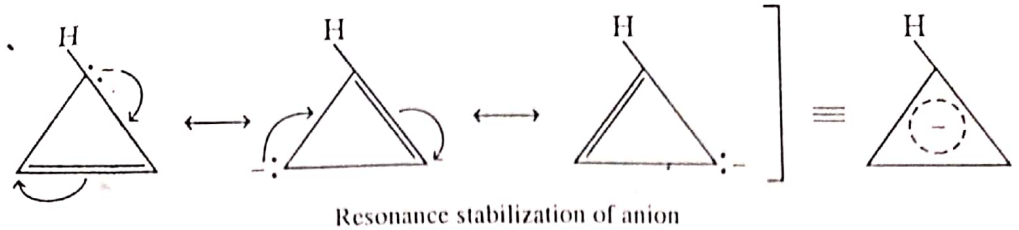
(iv) Obeys Huckel's rule, as the number of delocalized π electrons is two.

Thus, cyclopropenyl cation is **aromatic**, as all the conditions are simultaneously satisfied.

Cyclopropenyl anion

Characteristics of cyclopropenyl anion are as follows

(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization. All the carbons of cyclic system are sp^2 hybridized, and thus p orbitals are available for delocalization.



Resonance stabilization of anion

Lone pair of electron participates in delocalization with π electrons of the ring. The total number of **delocalized π electrons** is **thus four.**

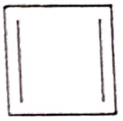
(iv) Does not obey Huckel's rule, as the number of delocalized π electrons is four.

Thus, cyclopropenyl anion is **not aromatic**, as all the conditions are not simultaneously satisfied.

9A.5.2 Aromaticity and Four Membered Ring Systems

Cyclobutadiene

Characteristics of cyclobutadiene are as follows



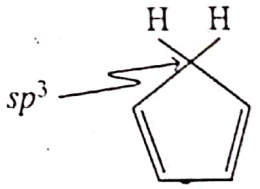
(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization. All the carbons of cyclic system are sp^2 hybridized, and thus p orbitals are available for delocalization.
(iv) Does not obey Huckel's rule, as the number of delocalized π electrons is four.

Thus, cyclobutadiene is **not aromatic** as all the conditions are not satisfied simultaneously. The condition of Huckel's rule is not followed.

9A.5.3 Aromaticity and Five Membered Ring Systems

Cyclopentadiene

Characteristics of cyclopentadiene are as follows

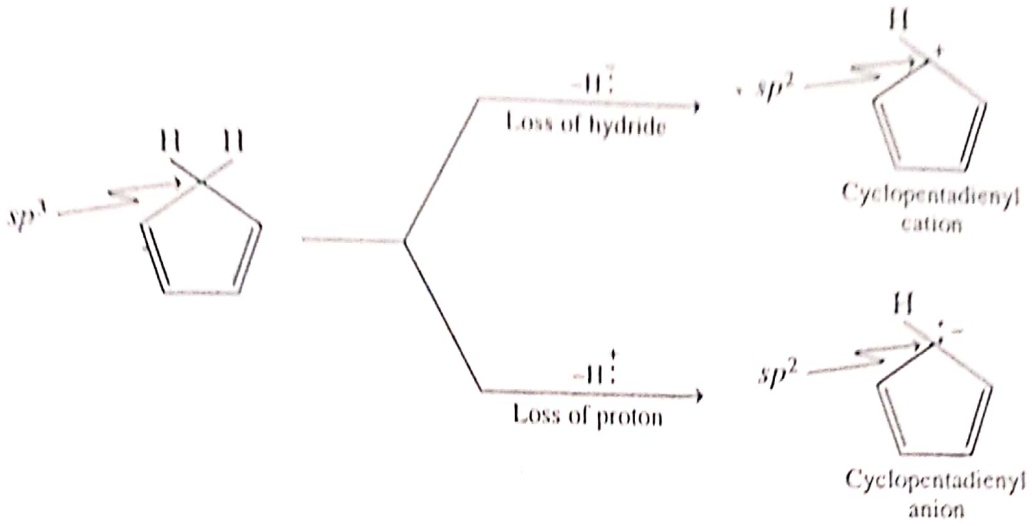


(i) It is cyclic
(ii) It is planar
(iii) It does not exhibit continuous delocalization. one of the carbon in cyclic system is sp^3 hybridized, and thus p orbital is not available on that carbon for delocalization.
(iv) Does not obey Huckel's rule, as the number of delocalized π electrons is four.

Thus, cyclopentadiene is **not aromatic** as all the conditions are not simultaneously satisfied. The conditions of continuous delocalization and that of Huckel's rule is not followed.

Cyclopentadienyl Ions

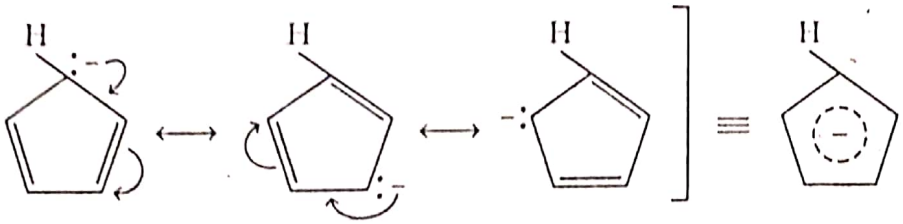
The sp^3 hybridized carbon in cyclopentadiene is not involved in delocalization. Removal of a hydrogen (either as a proton (H^+) or as a hydride (H^-)) from this carbon results in the formation of an anion or a cation where all the carbons are sp^2 hybridized and thus, continuous delocalization of π electrons takes place.



Cyclopentadienyl anion

Characteristics of cyclopentadienyl anion are as follows

(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization. All the carbons of cyclic system are sp^2 hybridized, and thus p orbitals are available for delocalization.



Resonance stabilization of anion

Lone pair of electrons participates in delocalization with π electrons of the ring. The total number of **delocalized π electrons** is thus **six**.

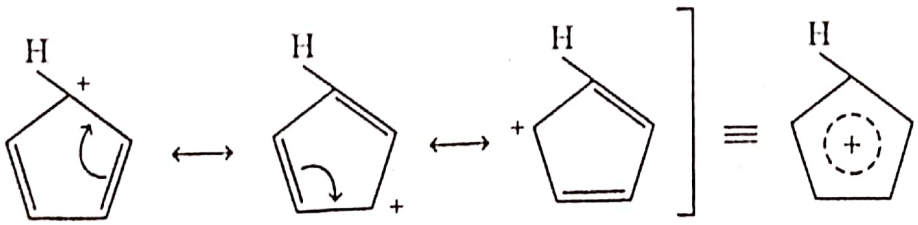
(iv) Obeys Huckel's rule, as number of delocalized π electrons is six.

Thus, cyclopentadienyl cation is **aromatic**, as all the conditions are satisfied simultaneously.

Cyclopentadienyl cation

Characteristics of cyclopentadienyl cation are as follows

(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization. All the corbons of cyclic system are sp^2 hybridized and thus p orbitals are available for delocalization.



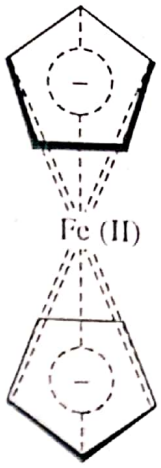
Resonance stabilization of cation

(iv) Does not obey Huckel's rule, as number of delocalized π electrons is four.

Thus, cyclopentadienyl cation is **not aromatic**, as all the conditions are not satisfied simultaneously. The condition of Huckel's rule is not followed.

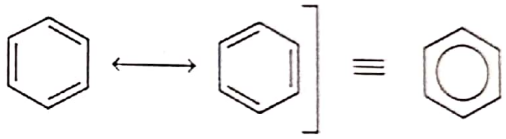
Aromaticity in Ferrocene

Ferrocene is an organometallic compound with the Fe (II) sandwiched between two cyclopentadienyl anion rings. It is a stable molecule that undergoes typical aromatic substitution reactions. The cyclopentadienyl anion is an aromatic system and aromatic character of ferrocene is attributed to the presence of two such cyclopentadienyl rings.



9A.5.4 Aromaticity and Six Membered Ring Systems

Benzene



Characteristics of benzene are as follows

(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization. All the carbons of cyclic system are sp^2 hybridized, and thus p orbitals are available for delocalization.
(iv) Obeys Huckel's rule, as the number of delocalized π electrons is six.

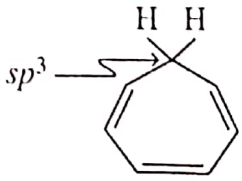
Thus, benzene is **aromatic** as all the conditions are satisfied simultaneously.

9A.5.5 Aromaticity and Seven Membered Ring Systems

Cycloheptatriene

Characteristics of cycloheptatriene are as follows

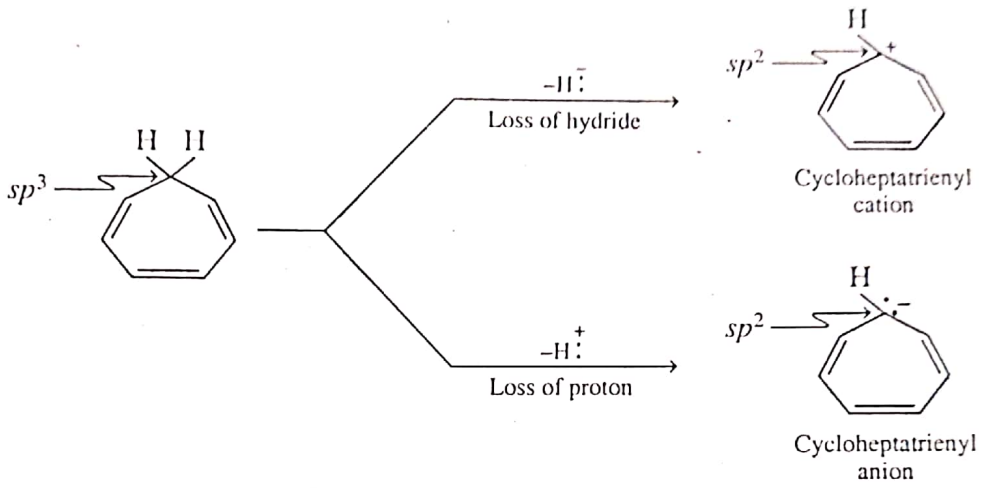
(i) It is cyclic
(ii) It is planar
(iii) It does not exhibit continuous delocalization. One of the carbon in cyclic system is sp^3 hybridized, and thus p orbital is not available on that carbon for delocalization.
(iv) It obeys Huckel's rule, as the number of delocalized π electrons is six.



Thus, cycloheptatriene is **not aromatic**, as all the conditions are not satisfied simultaneously. The condition of continuous delocalization is not followed.

Cycloheptatrienyl Ions

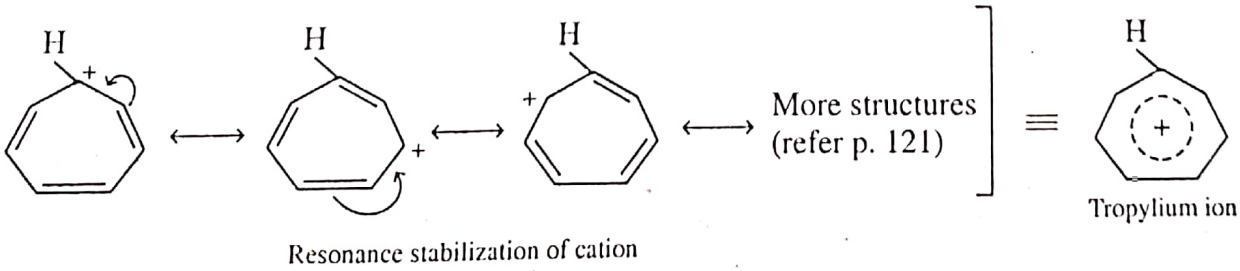
The sp^3 hybridized carbon in cycloheptatriene is not involved in delocalization. Removal of a hydrogen (either as a proton (H^+) or as a hydride (H^-)) from this carbon results in the formation of an anion or a cation, where all the carbons are sp^2 hybridized and thus, continuous delocalization of π electrons takes place.



Cycloheptatrienyl cation (Tropylium ion)

Characteristics of cycloheptatrienyl cation are as follows

(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization. All the carbons of cyclic system are sp^2 hybridized, and thus p orbitals are available for delocalization.



Resonance stabilization of cation

(iv) Obeys Huckel's rule, as the number of delocalized π electrons is six.

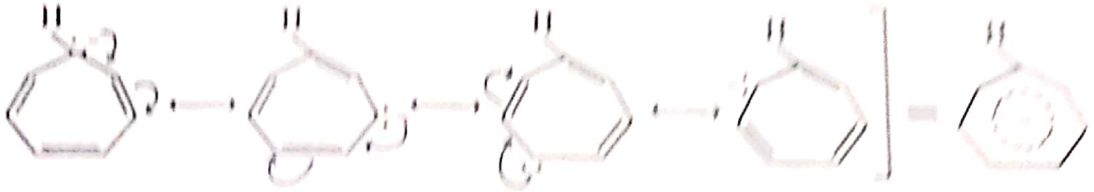
Thus, cycloheptatrienyl cation is **aromatic**, as all the conditions are satisfied simultaneously.

Cycloheptatrienyl anion

Characteristics of cycloheptatrienyl anion are as follows

(i) It is cyclic
(ii) It is planar

(iii) It exhibits continuous delocalization. All the carbons of cyclic system are sp^2 hybridized and thus p orbitals are available for delocalization.



Resonance stabilization of anion

Four pair of electron participates in delocalization with π electrons of the ring. The total number of delocalized π electrons is then eight

(iv) Does not obey Huckel's rule, as number of delocalized π electrons is eight.

Thus, cycloheptatrienyl anion is **not aromatic**, as all the conditions are not satisfied simultaneously. The condition of Huckel's rule is not followed.

9A.5.6 Aromaticity and Eight Membered Ring Systems

Cyclooctatetraene

Characteristics of cyclooctatetraene are as follows

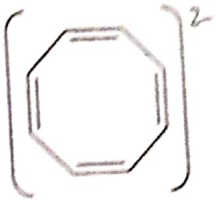
(i) It is cyclic
(ii) It is non-planar
(iii) All the carbons are sp^2 hybridized and p orbitals are available for delocalization. Due to non-planar structure overlap of all the p orbitals does not occur.
(iv) Does not obey Huckel's rule, as the number of delocalized π electrons is eight.

It exists as non-planar tub shaped structure.

Non-planar (tub shaped)

Thus, cyclooctatetraene is **not aromatic** as all the conditions are not satisfied simultaneously. The condition of planarity and that of Huckel's rule is not followed.

Cyclooctatetraenyl dianion



Characteristics of cyclooctatetraenyl dianion are as follows

(i) It is cyclic
(ii) It is planar
(iii) It exhibits continuous delocalization.
(iv) Obeys Huckel's rule, as the number of delocalized π electrons is ten.

Thus, cyclooctatetraenyl anion is **aromatic**, as all the conditions are satisfied simultaneously.

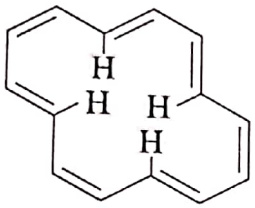
9A.5.7 Aromaticity and Annulenes

Monocyclic systems with conjugated double bonds are termed *annulenes*. Bracketting a number indicates the ring size. For example, cyclobutadiene is [4]annulene, benzene is [6]annulene, and cyclooctatetraene is [8]annulene. The term annulene is used frequently for large ring size monocyclic systems (C_{10} and more).

Similarly, in case of **[14]annulene** (structure-III) the large ring size somewhat compensates the steric hindrance due to inner hydrogens and molecule has nearly planar structure. The molecule shows aromaticity but is not very stable.

However aromaticity and stability in such molecule can be increased effectively by introducing a *triple bond in the system*. The introduction of triple bond replaces the hydrogens and prevents the steric hindrance thereby, providing sufficient overlap of orbitals. This increases the aromatic character in dehydro **[14]annulene** (structure-IV, *dehydro* means two hydrogen less than the parent molecule). The two sets of *p* orbitals in triple bonds are mutually perpendicular. One of them, which is in the same plane as the *p* orbitals of the ring system, participates in delocalization while the other being in perpendicular plane does not participates in delocalization. Thus the total number of electrons participating in delocalization in dehydroannulene (structure-IV) remains the same as in [14]annulene. Relieve in steric strain increases delocalization of electrons, which in turn increase the aromatic character of the system. Further as discussed earlier, the bridged [14]annulenes [structure-V] also exhibit more aromatic character and are stable systems.

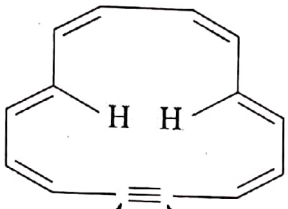
Structure-III



The four inner hydrogens cause steric hindrance. [14] annulene is aromatic but is less stable.

- 14 delocalized π electrons
- Aromatic

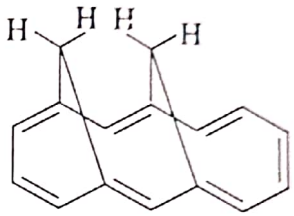
Structure-IV



Triple bond reduces the steric hindrance by replacing two hydrogens. Only one of the π bond participates in delocalization

- 14 delocalized π electrons
- Increased aromaticity

Structure-V



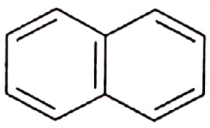
Bridging removes all the hydrogens and relieves the molecule from steric hindrance. This results in effective delocalization and increases the aromatic character.

- 14 delocalized π electrons
- Increased aromaticity

9A.5.8 Aromaticity and Other Ring Systems

Fused ring system

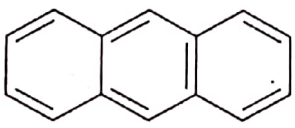
In the following examples of fused ring systems all the carbons are sp^2 hybridized and π electrons are delocalized among all the carbons of the rings.



Naphthalene

- Planar
- Obeys Huckel's rule (10 π electrons)

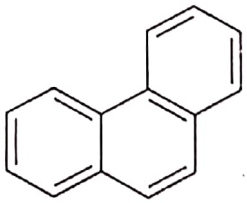
Aromatic



Anthracene

- Planar
- Obeys Huckel's rule (14 π electrons)

Aromatic



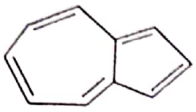
Phenanthrene

- Planar
- Obeys Huckel's rule (14 π electrons)

Aromatic

Azulene

Azulene is a nonbenzenoid fused ring system unlike naphthalene, anthracene and phenanthrene that are benzenoid systems (containing fused benzene rings). In azulene a seven and five membered ring systems are fused together. Azulene is an aromatic system and readily undergoes electrophilic substitution reactions.



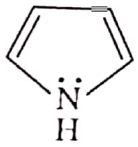
Azulene

- Cyclic, planar molecule
- Obeys Huckel's rule as it contains 10 delocalized π electrons.
- Exhibits Aromaticity

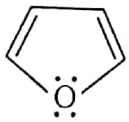
Delocalization in azulene

Due to this delocalization azulene is slightly **dipolar**. The five membered ring has higher electron density than seven membered ring. Thus, electrophilic substitution occurs in 5-membered ring.

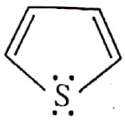
Aromatic heterocyclic compounds



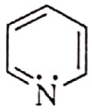
Pyrrole



Furan



Thiophene



Pyridine

All the above heterocyclic compounds are aromatic. The carbons as well as nitrogen, oxygen, and sulfur are sp^2 hybridized which give a planar structure. In each case, the total number of delocalized π electrons is *six*, that is, Huckel's rule is followed. In pyrrole, furan, and thiophene, a lone pair of electrons present in *p* orbital of nitrogen, oxygen, and sulfur respectively participates in delocalization with *p* orbital of sp^2 hybridized carbons. In pyridine, the lone pair of electrons on nitrogen does not participate in delocalization. (For further details on aromaticity, see Chapter 26 on Heterocyclic Compounds).

Anti-aromatic and Non-aromatic Compounds

The compounds that do not exhibit aromatic character may be classified as anti-aromatic and non-aromatic.

Anti-aromatic: The cyclic *planar* molecules with continuous delocalization but *having 4n number of delocalized π electrons* are said to *be anti-aromatic*. For example, cyclobutadiene (number of delocalized π electrons = 4; see section 9A.5.2).