

# AROMATIC SYSTEM & THEIR MOLECULAR STRUCTURE

- Define Aromaticity , Huckle's rule
- Structure & bonding of
- Benzene
- Pyrrole

# Aromaticity

- Organic compounds which resemble benzene in their chemical behavior are called aromatic compounds. They exhibit certain characteristic properties which are different from those of aliphatic and alicyclic compounds. These characteristic properties are collectively referred to as aromaticity or aromatic character.

- Aromaticity may be therefore defined as
- The ability of many cyclic compounds containing conjugation in their rings to undergo substitution reactions rather than the addition reactions, to resist oxidation & to exhibit a marked stability of their rings.

# Comparison of properties of benzene with alkenes

Reagent	Reaction with alkenes	Reaction with benzene
KMNO4	Rapid Oxidation	No reaction
Br2 in CCl4	Rapid Addition	No reaction
HBr	Rapid Addition	No reaction
H2 in presence of Ni	Rapid hydrogenation at 25°C & 1 atm pres	Slow hydrogenation at 100-200°C, 100 atm press

# Characteristics of aromatic compounds

- 1) They are highly unsaturated compounds.
- 2) They are cyclic compounds with five, six or seven membered rings.
- 3) Their molecules are flat as shown by physical methods such as X ray diffraction & electron diffraction methods.

- 4) They undergo electrophilic substitution reactions such as nitration, halogenation, sulphonation , Friedel-Crafts alkylation etc.
- 5) They show high thermodynamic stability as indicated by their low heats of combustion & hydrogenation.

- **HUCKLE'S RULE**
- In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have **aromatic** properties.  
His rule states that if a cyclic, planar molecule has  $4n+2 \pi$  electrons, it is considered **aromatic**.
- This rule is called as **Huckle's rule**.

What does  $4n+2$  mean?

In order for a molecule to be aromatic, it has to have the following characteristics:

- 1) follow Huckel's rule, having  $4n+2$  electrons in the delocalized, and conjugated p-orbital cloud;
- 2) the molecule must be able to be planar
- 3) the molecule must be cyclic
- 4) every atom in the ring must be able to participate in delocalizing the electrons by having a p-orbital or an unshared pair of electrons.

We can express this with the formula  $(4n + 2)$ , where n is a natural number (0, 1, 2, 3...)

For  $n = 0$ , we get  $(4 \times 0 + 2) = 2$

For  $n = 1$ , we get  $(4 \times 1 + 2) = 6$

For  $n = 2$ , we get  $(4 \times 2 + 2) = 10$

For  $n = 3$ , we get  $(4 \times 3 + 2) = 14$



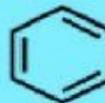
**$2\pi$  electrons**

**Aromatic**



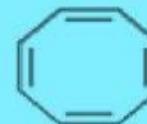
**$4\pi$  electrons**

**Not Aromatic**



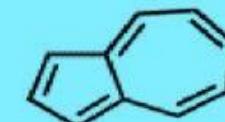
**$6\pi$  electrons**

**Aromatic**



**$8\pi$  electrons**

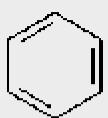
**Not Aromatic**



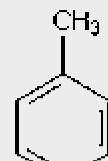
**$10\pi$  electrons**

**Aromatic**

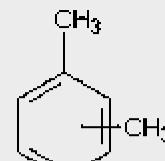
# Examples of aromatic compounds



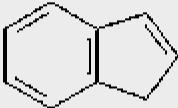
benzene



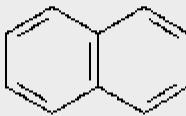
toluene



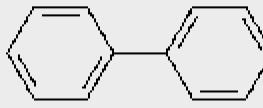
*o*-, *m*-, *p*-xylene



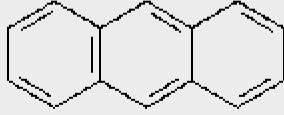
indene



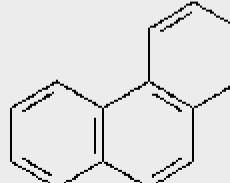
naphthalene



biphenyl



anthracene

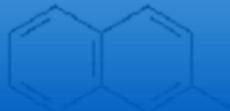


phenanthrene

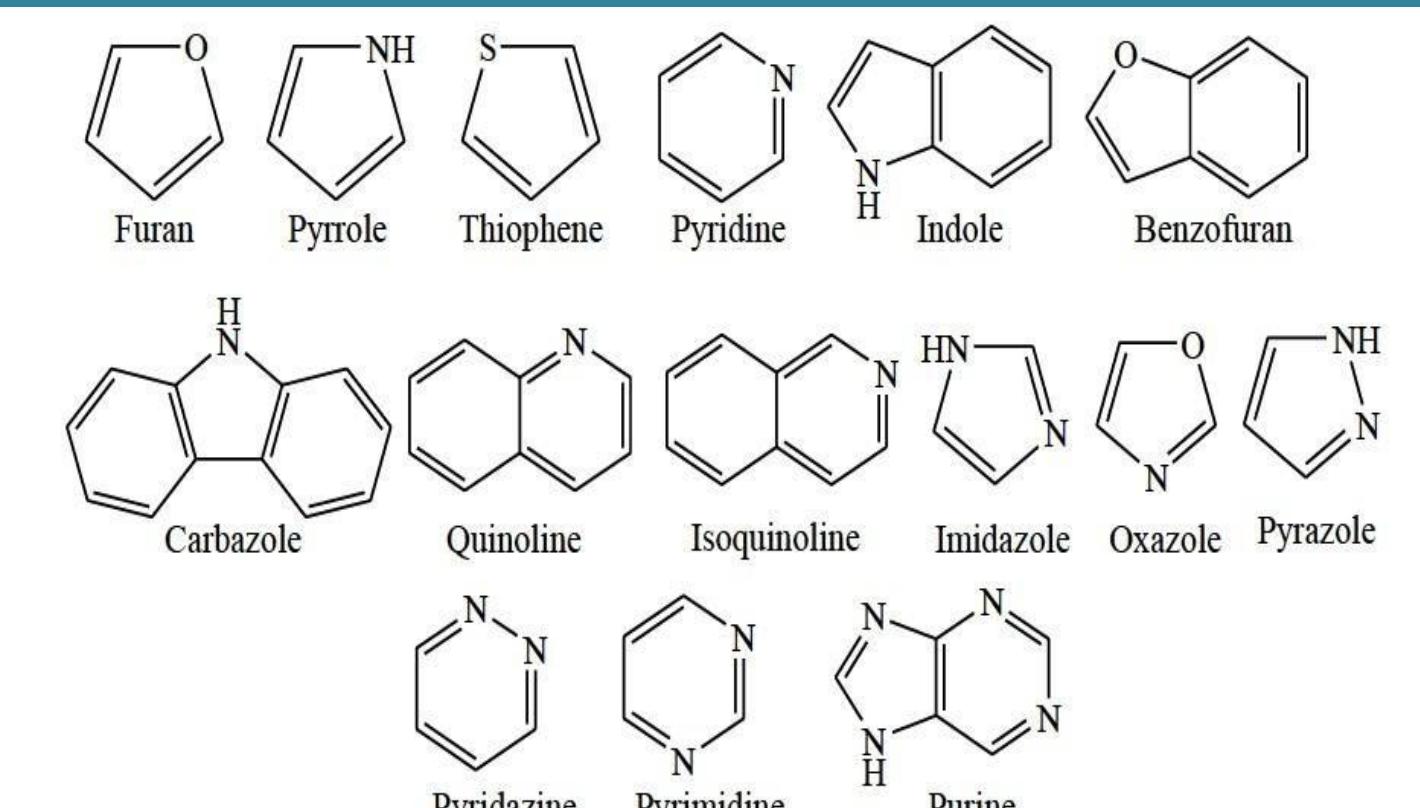
substances



products

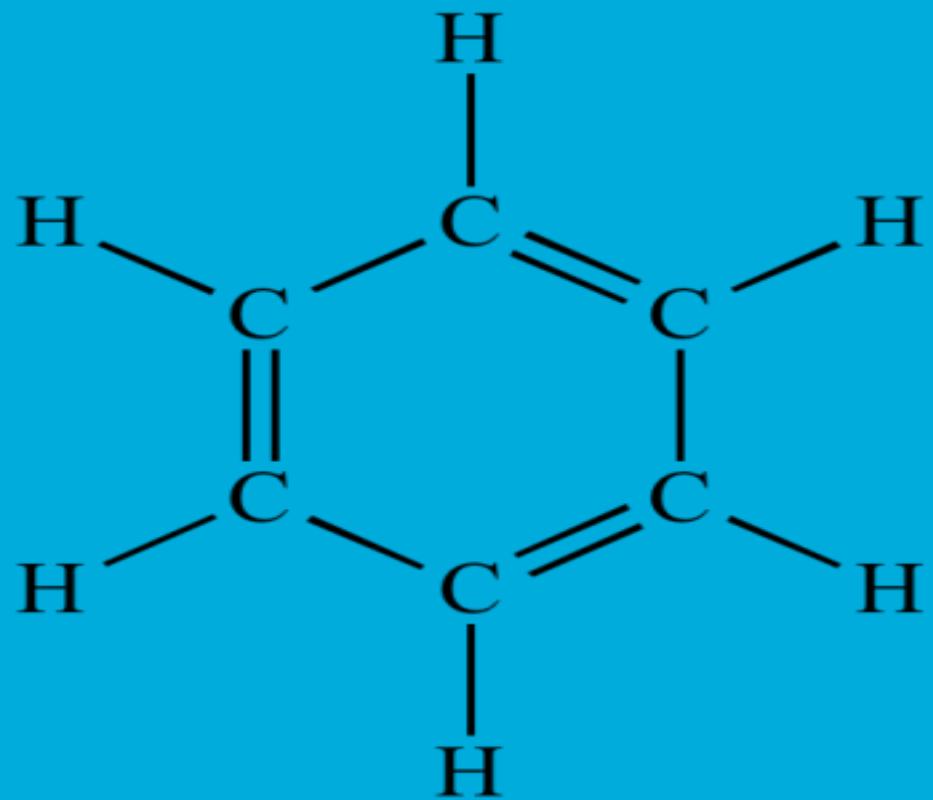


# Examples of aromatic heterocyclic compounds



**Figure 2.** Examples of aromatic heterocyclic compounds

# Kekule Structure of benzene



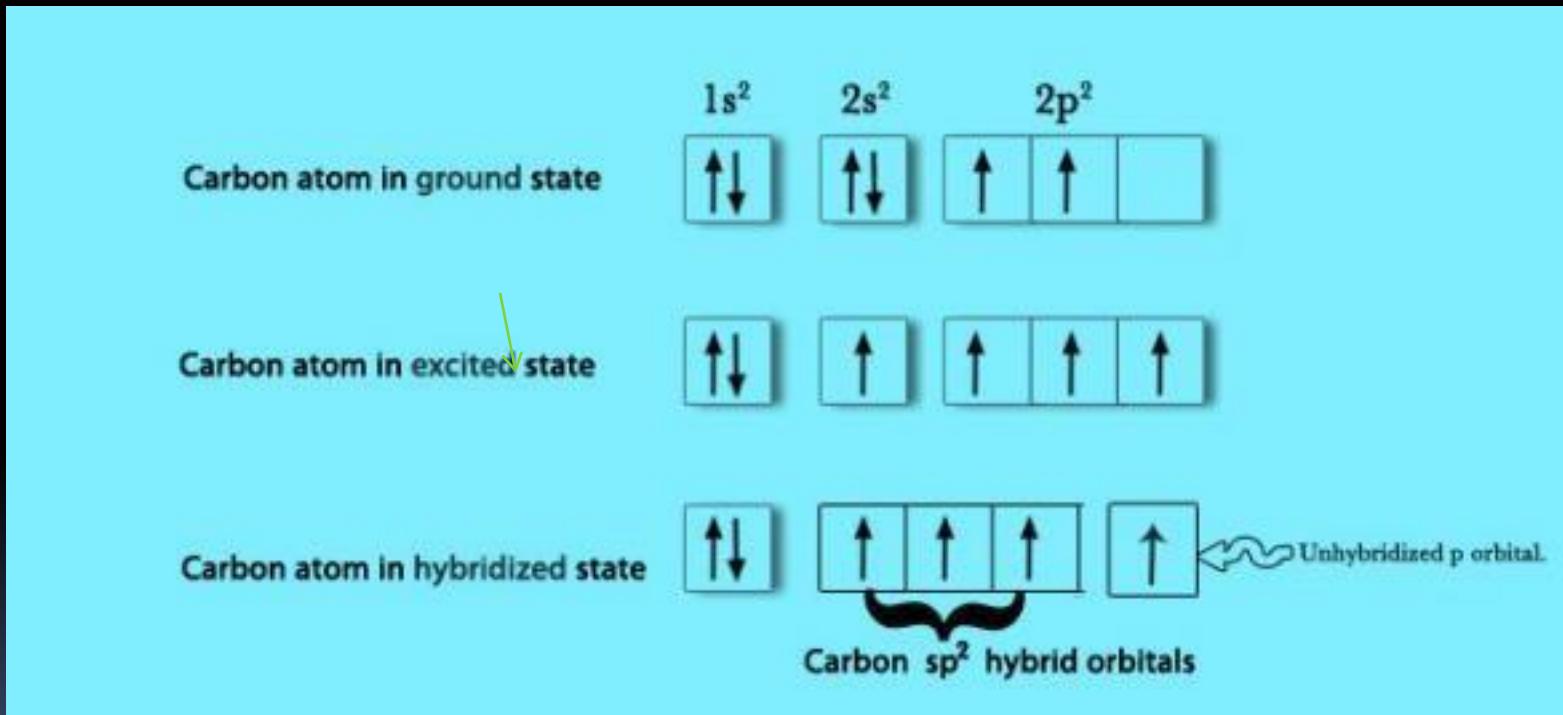
# Drawbacks of Kekul e Structure

- Benzene does not give addition reactions & fails to decolorize Baeyer's reagent (alkaline  $KMNO_4$ ).
- On the basis of Kekule structure , heat of combustion is expected to be 3449Kj/mole but the experimental value is 3298 KJ/mole.
- X ray diffraction studies shows that all the carbon-carbon bond lengths are identical & lie in between single & double bonds This is not accordance to Kekule structure.

# Drawbacks of Kekule Structure (Contd.)

- On the basis of Kekule structure, the heat of hydrogenation of benzene is expected to be 358 KJ/mol, however the experimental value is 208.5 KJ/mol. This shows that benzene is more stable than expected from Kekule structure.

# Molecular Orbitals of benzene



- Molecular formula of benzene is C<sub>6</sub>H<sub>6</sub>.
- In Benzene all carbon atoms are SP<sup>2</sup>hybridized. Out of three hybrid orbitals two SP<sup>2</sup> hybrid orbitals overlap with two SP<sup>2</sup> hybrid orbitals of two carbon atoms on either side to form C-C sigma bond. Third SP<sup>2</sup>hybrid orbitals overlap with 1s orbital of hydrogen atom to form C-H sigma bond.
- Each SP<sup>2</sup>hybridized carbon atom contains one un hybridized p orbital.
- Each un hybridized p orbital contains one electron. These six un hybridized p orbital overlap to form 3  $\pi$  bonds.

- There are six un hybridized 2p orbitals in benzene . These combine to form 6  $\pi$  molecular orbitals. Out of these three  $\pi$  molecular orbitals are bonding molecular orbitals ( $\pi_1$ ,  $\pi_2$  &  $\pi_3$ ) & three are anti bonding molecular orbitals ( $\pi^*_4$ ,  $\pi^*_5$  &  $\pi^*_6$  ).
- Benzene is planar & has alternate double bonds. The alternate double bonds in benzene are in continuous delocalization i.e Benzene exhibits resonance.

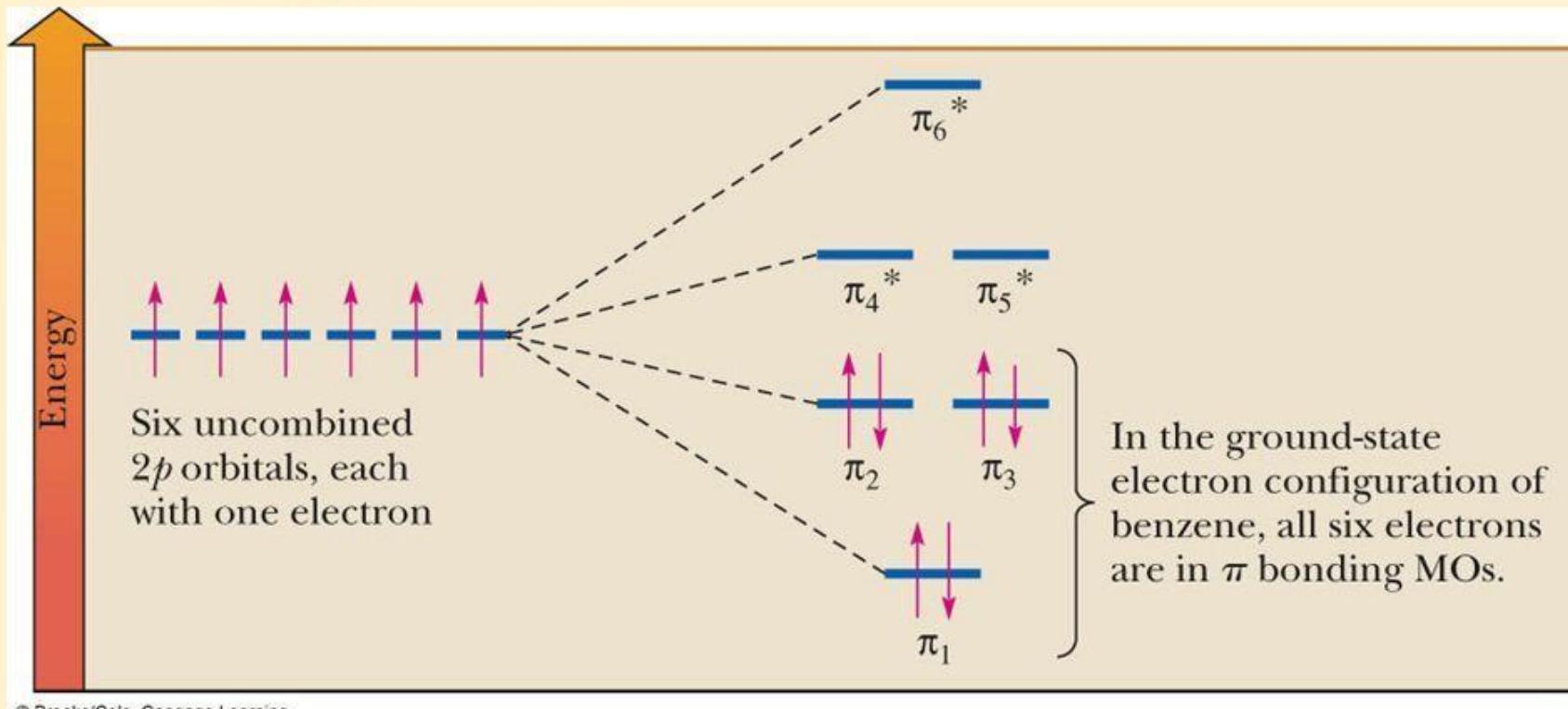
- The lowest energy molecular orbital is the  $\Pi_1$  bonding molecular orbital . It has no nodal planes & all six 2p orbitals are in the same phase & overlap.
- The next higher energy bonding molecular orbitals are  $\Pi_2$  &  $\Pi_3$ . These two are degenerate & have one nodal plane. These two constitutes Highest Occupied Molecular Orbital (HOMO) of benzene.

All the six  $\Pi$  electrons occupy in these three bonding molecular orbitals  $\Pi_1$ ,  $\Pi_2$  &  $\Pi_3$ .

- The next higher energy molecular orbitals are  $\Pi^*4$ ,  $\Pi^*5$  &  $\Pi^*6$  anti bonding molecular orbitals. These  $\Pi^*4$ ,  $\Pi^*5$  are degenerate & have two nodal planes. These are the Lowest Unoccupied Molecular Orbital (LUMO).
- The anti bonding molecular orbital with highest energy is  $\Pi^*6$ . It has three nodal planes. All the three anti bonding molecular orbitals  $\Pi^*4$ ,  $\Pi^*5$  &  $\Pi^*6$  do not contain any electrons.

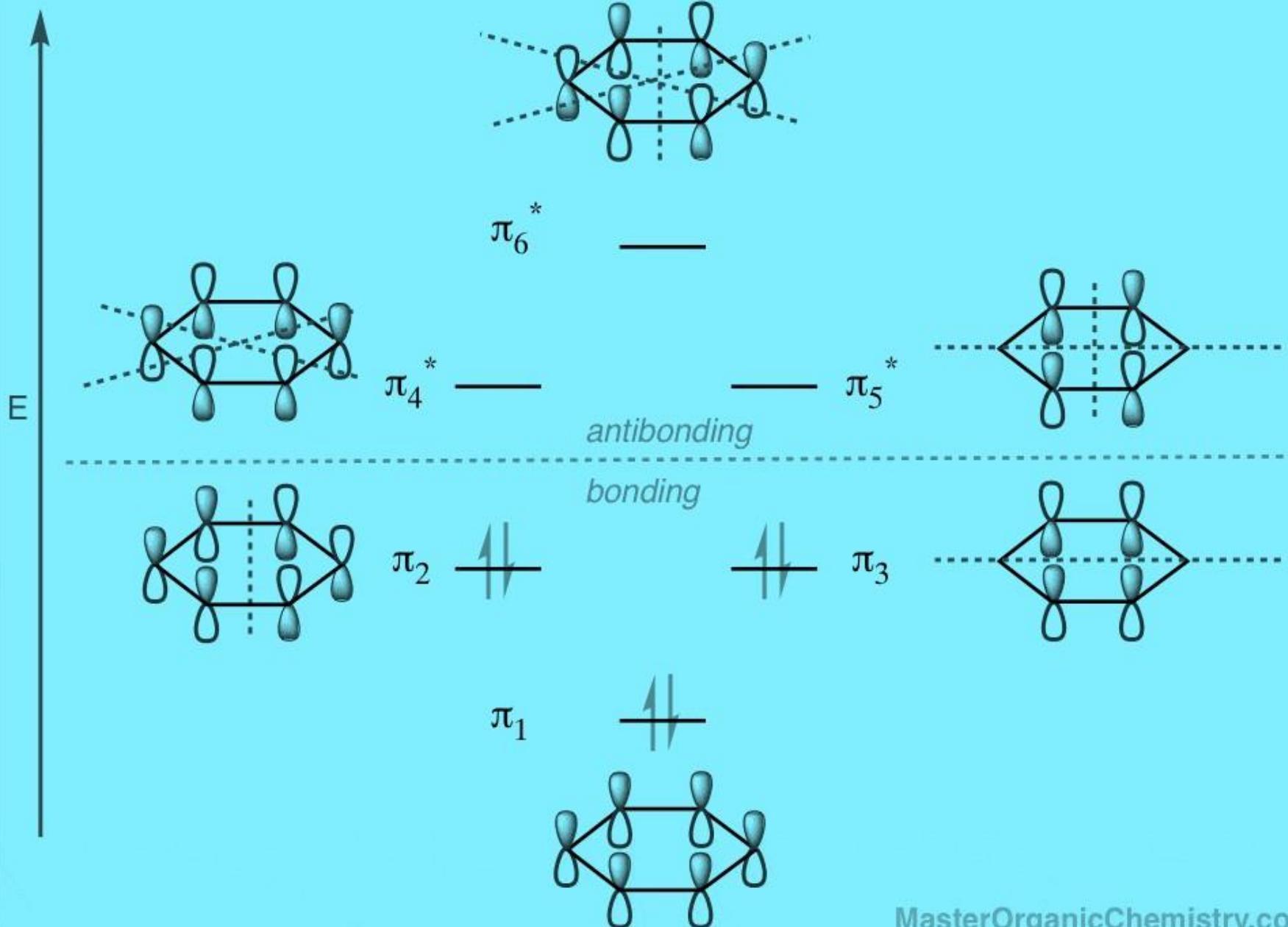
# Benzene-Molecular Orbital Model

- The molecular orbital representation of the pi bonding in benzene.

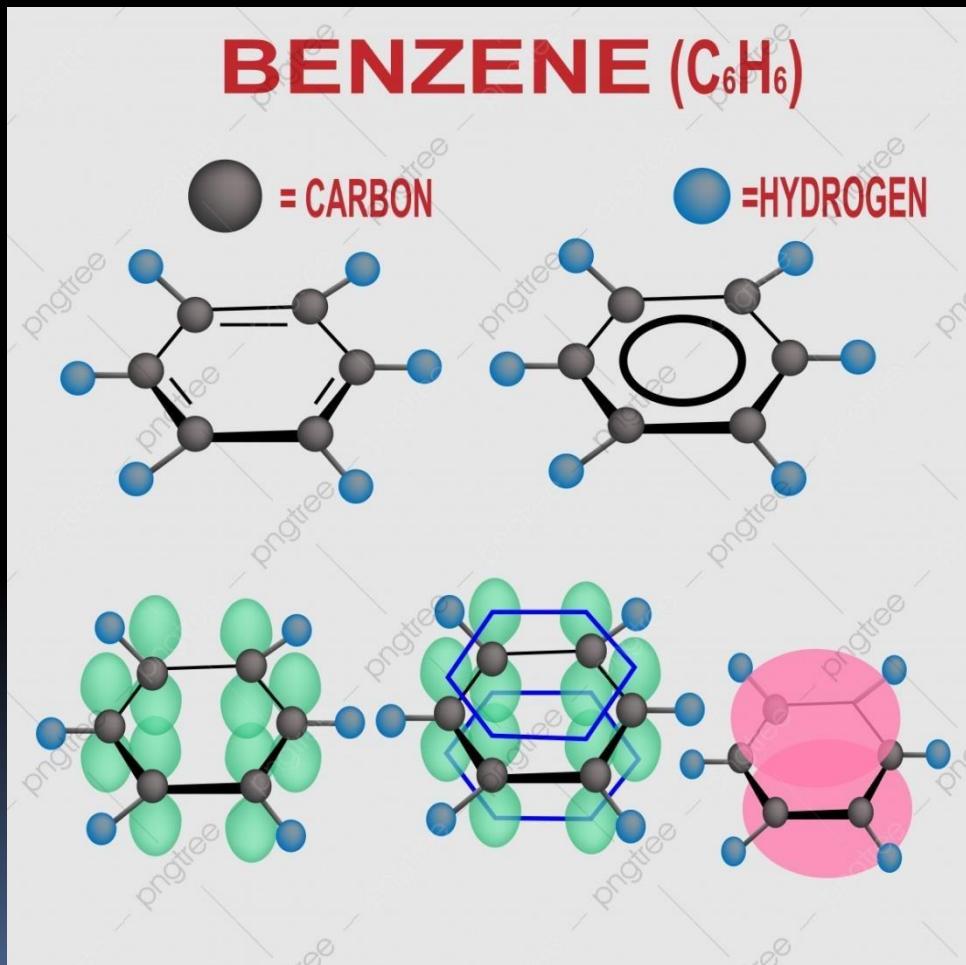


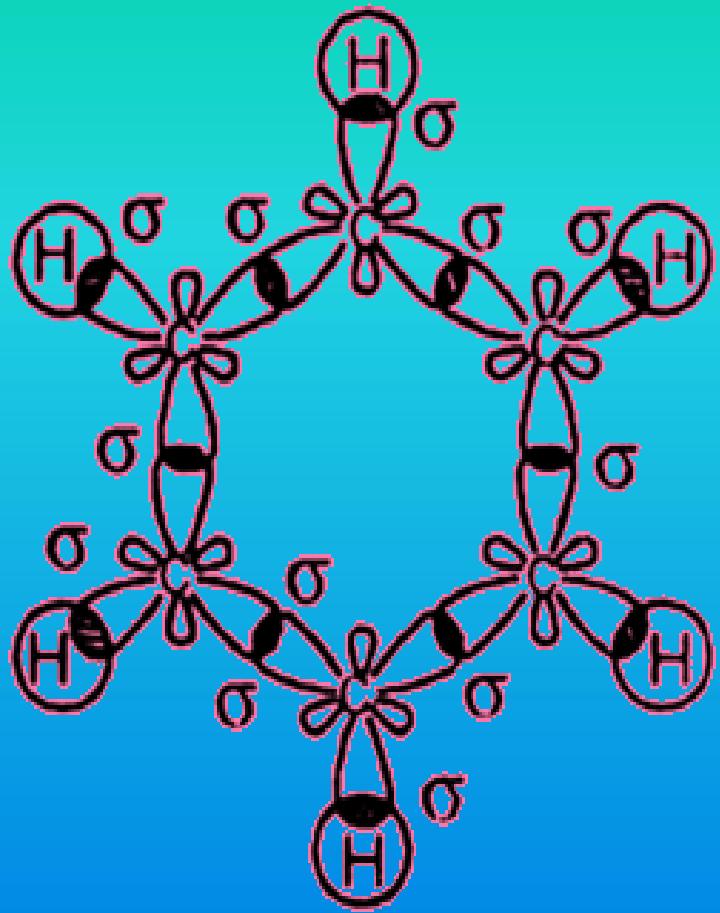
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## The Pi Molecular Orbitals of Benzene

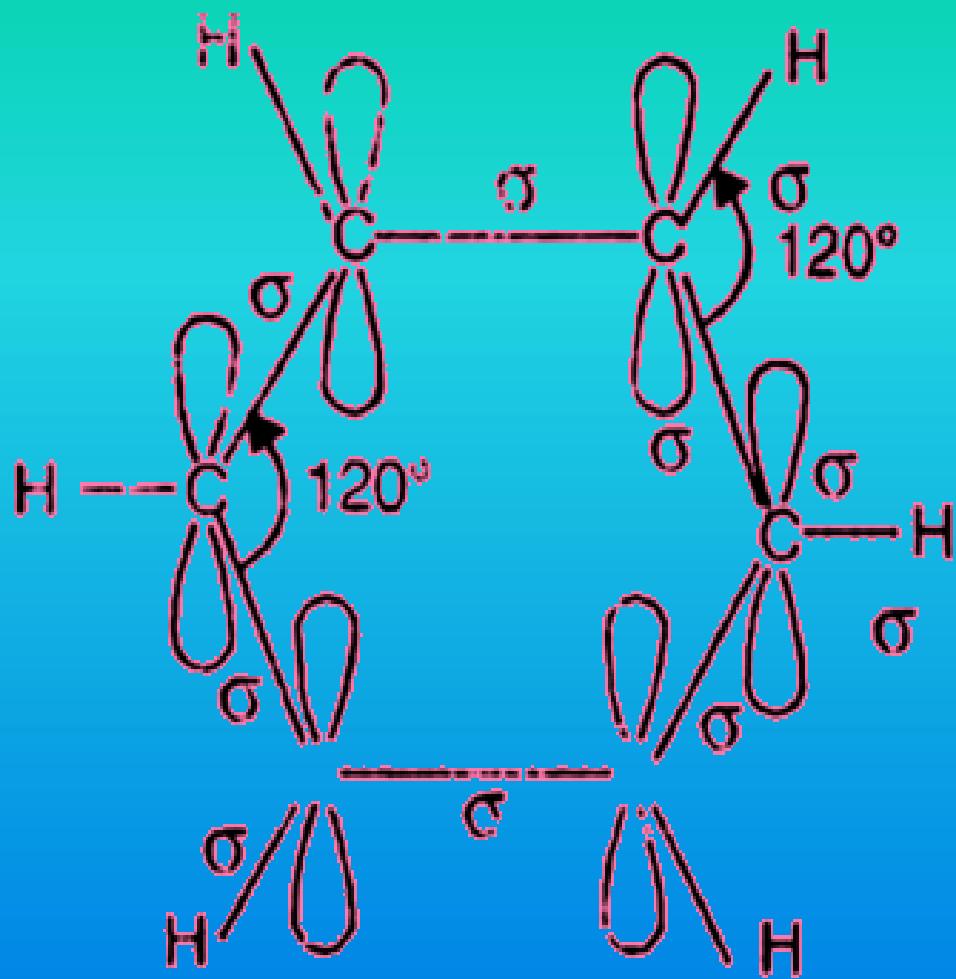


# Molecular Structure of Benzene



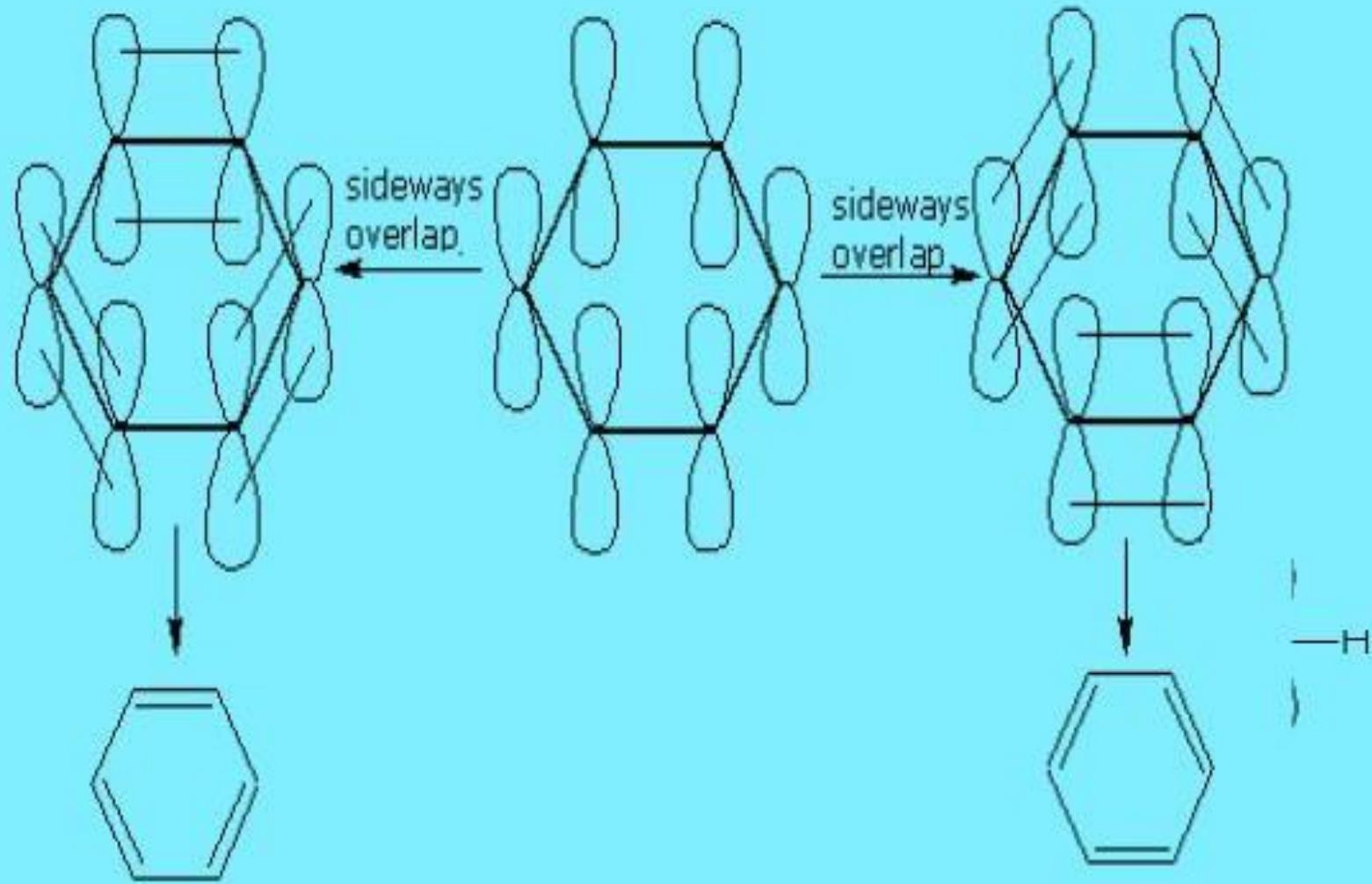


Formation of C-C  
and C-H  
sigma bonds



Sigma skeleton of  
benzene molecule

## Molecular Structure of BENZENE:



# Aromaticity of Pyrrole

- Pyrrole is cyclic and conjugated (that lone pair on nitrogen can contribute to the pi-system). There are two pi bonds and one lone pair of electrons that contribute to the pi system. This gives us 6 total pi electrons, which is a Huckel number (i.e. satisfies  $4n+2$ ). Therefore it's aromatic.

# Structure of pyrrole

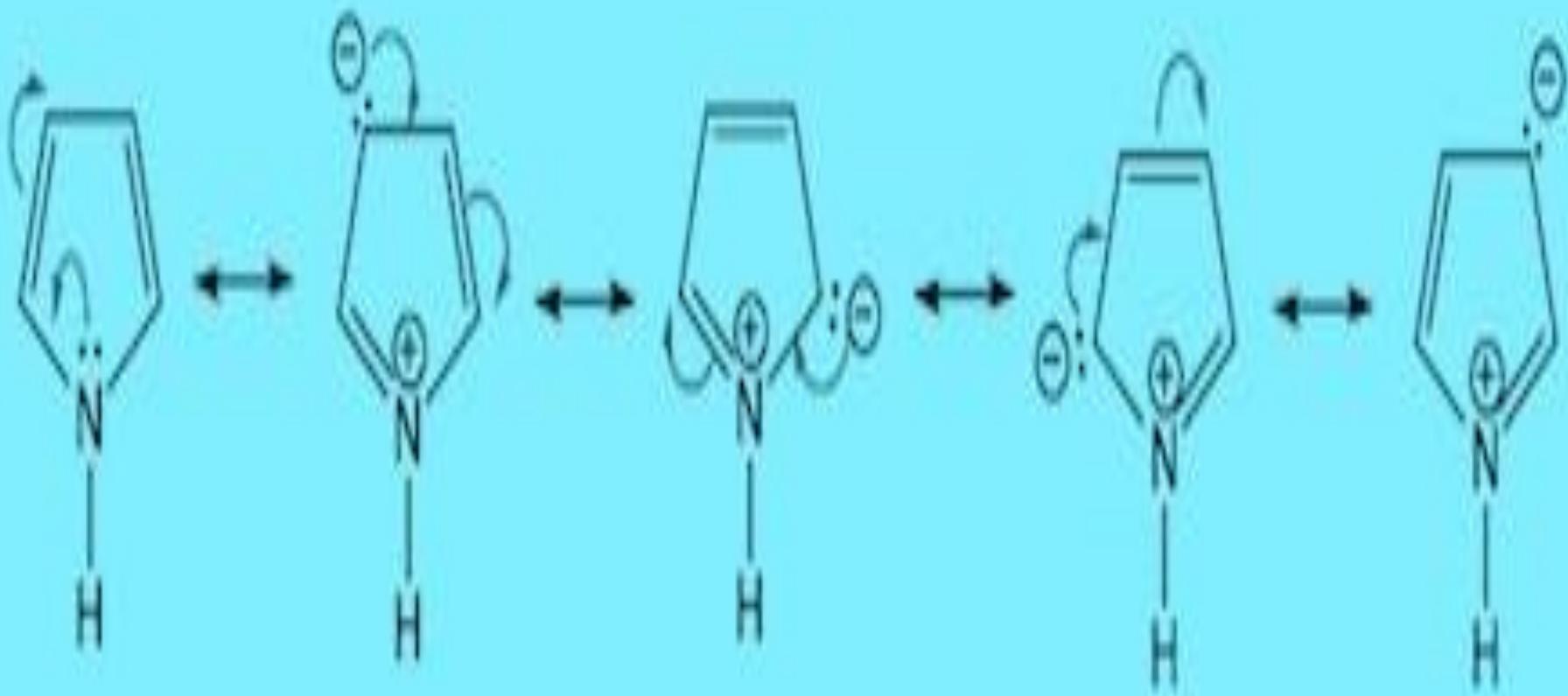


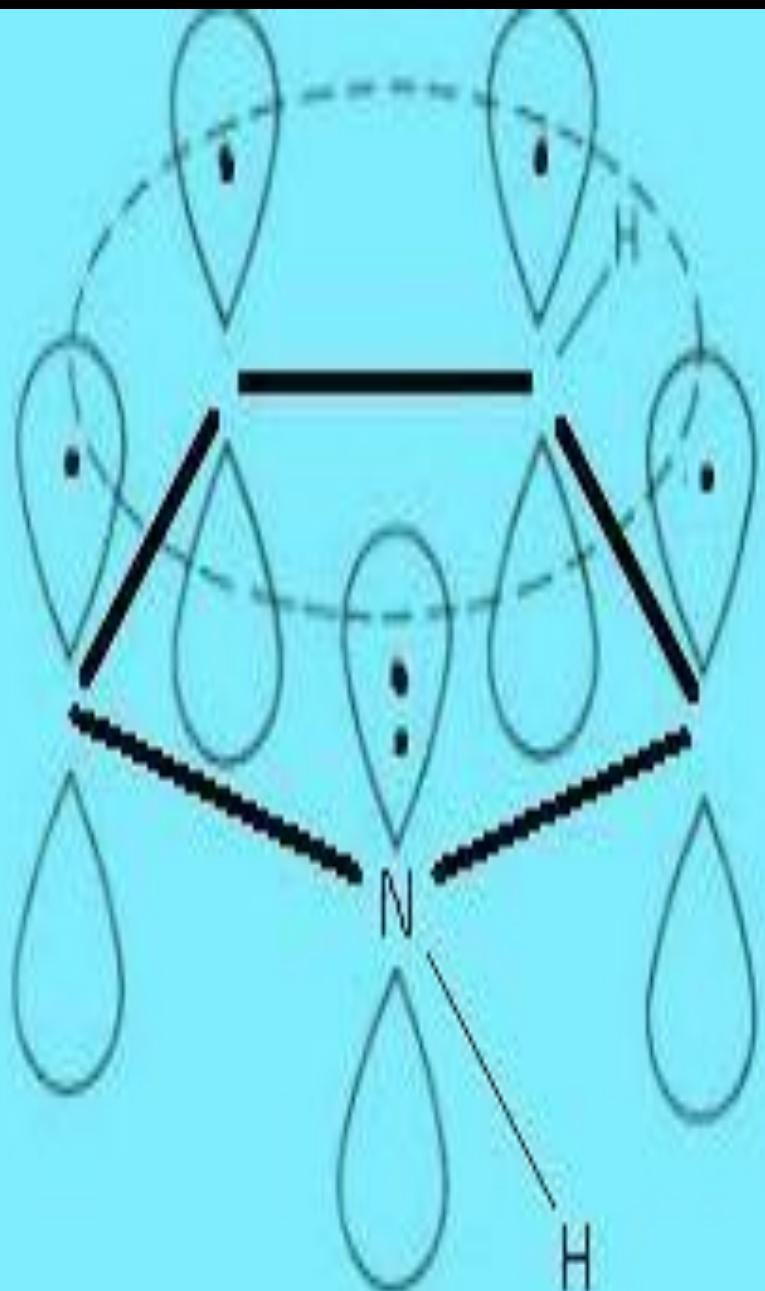
N

H

Pyrrole

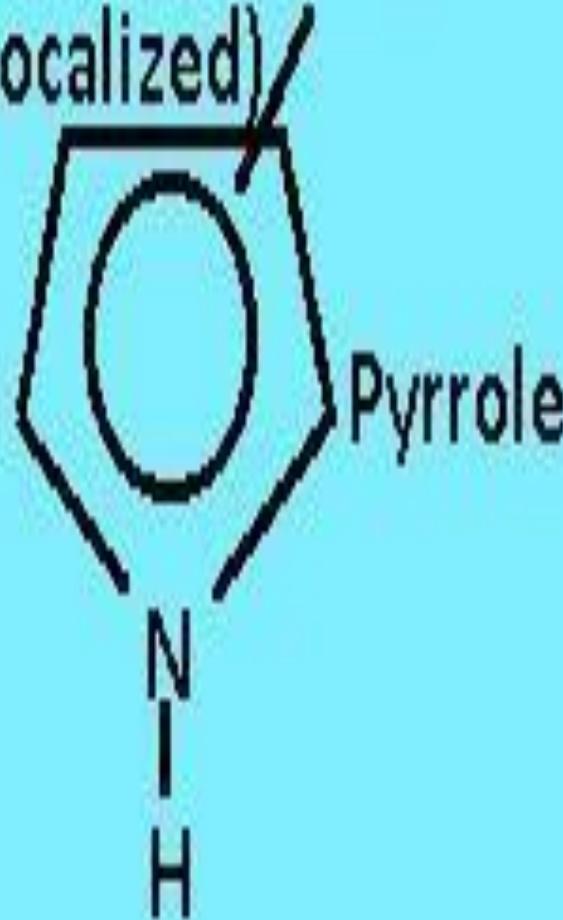
# Aromatic Structures of pyrrole





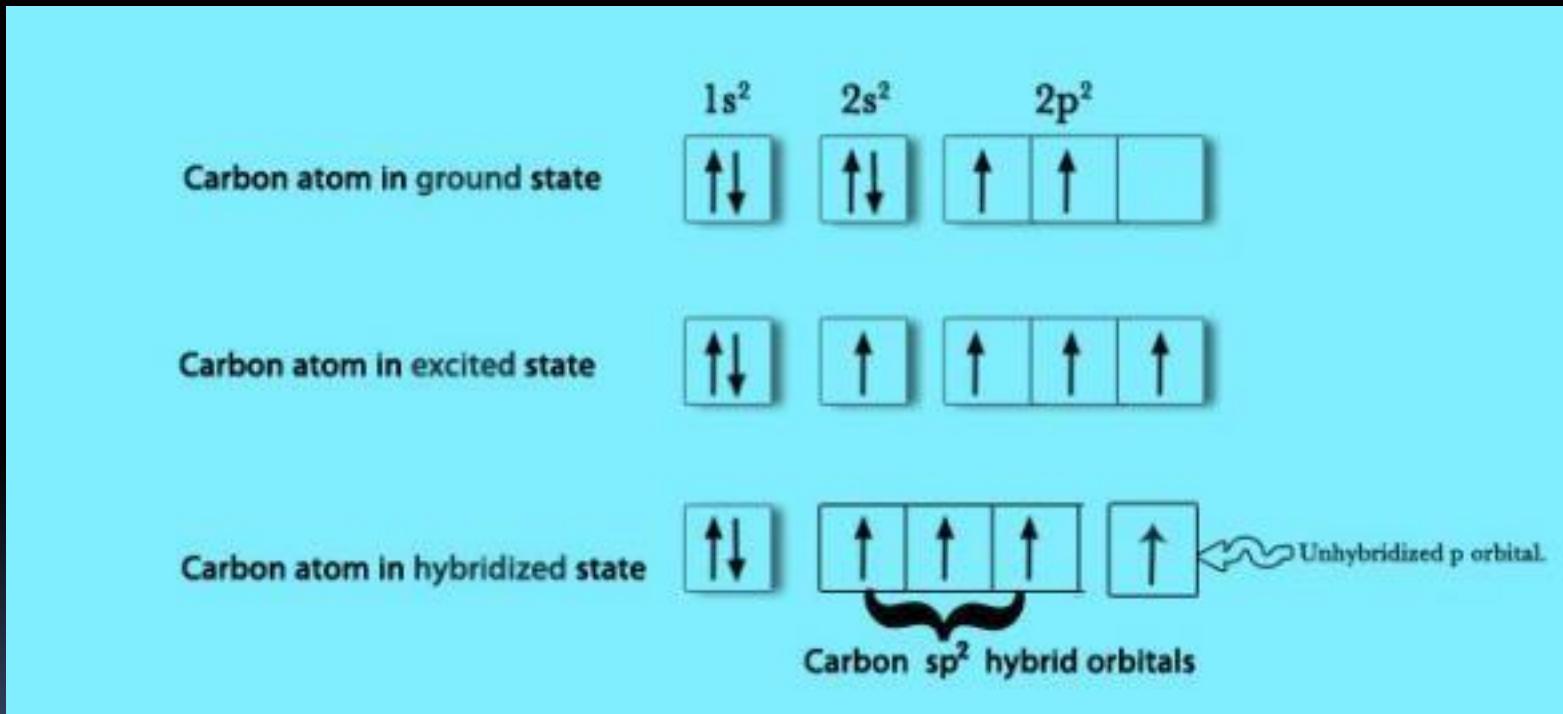
$\pi$  molecular orbital  
(delocalized)

$\equiv$

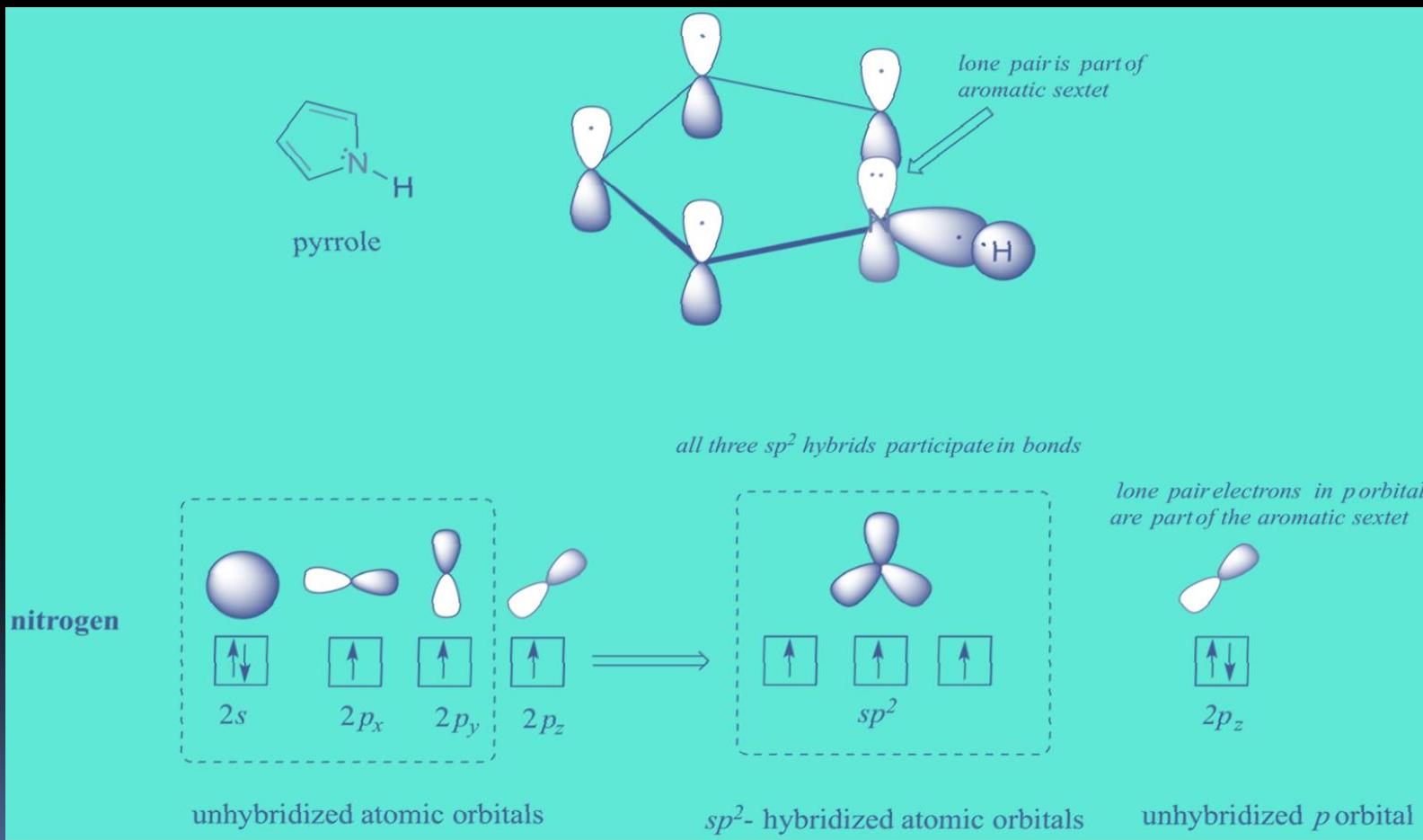


Pyrrole

# Hybridization of carbon in pyrrole



# Hybridization of Nitrogen in pyrrole

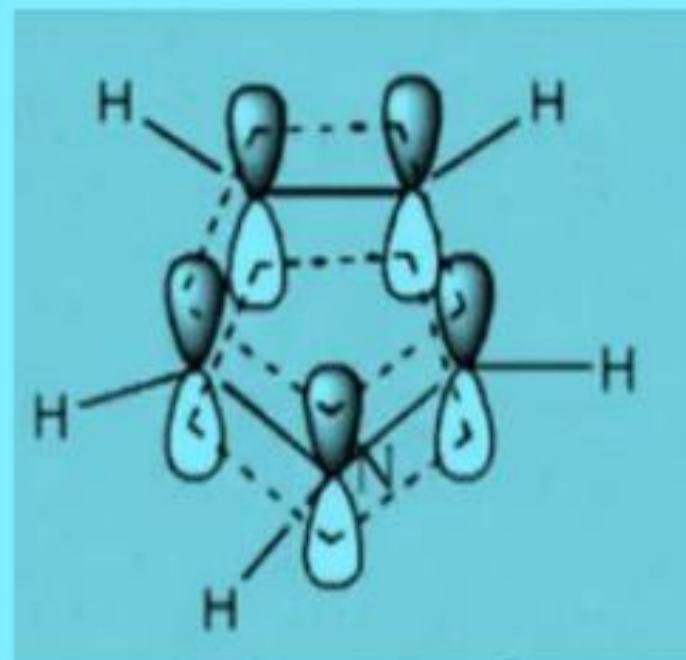


- Molecular Orbital Structure of Pyrrole
- All the atoms of pyrrole are in the same plane & the angle between the bonds in the ring are  $120^\circ$
- Further , all the atoms including the nitrogen atom are  $sp^2$ hybridized.
- Two  $SP^2$ hybrid orbitals of each carbon atom are utilized to form  $\sigma$  bond between the carbon-carbon atom & also carbon-nitrogen atom (depending on position of carbon atom in the pyrrole ring)

- The third  $SP^2$  hybrid orbital of carbon atom forms  $\sigma$  bond between carbon & hydrogen atom.
- Then each of the carbon atom contains an unhybridized p orbital with one electron & nitrogen contains an unhybridized p orbital with a pair of electrons.
- These p orbitals overlap with adjacent p orbitals on either side to produce  $\pi$  bond which result into circular cloud of  $\pi$  electrons above & below the plane of the ring.

# AROMATIC CHARACTER

- The hybridized orbitals of C and N atom are involved in axial overlap forming sigma bonds.
- Each unhybridized orbital of C atom has one electron while N atom has a pair of electrons.
- The sidewise overlap of the unhybridized orbitals results in a delocalised  $\pi$  electron cloud which accounts for the aromatic character of pyrrole.



- ★ Cyclic and planar structure
- ★ Delocalised  $\pi$ -electrons
- ★ Obeys HUCKLE's Rule,  $(4n+2)\pi$  electron rule