

## Aromatic Systems and their molecular structure.

Aromaticity - Derived from the word aroma, the earliest compounds studied had a pleasant smell, hence the name aromatic. However some aromatic compounds are odourless. Aromatic compounds are very stable due to resonance stability of the conjugated electrons and overlapping pi bonds. eg - Benzene.

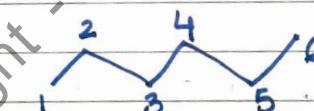
Criteria for determining Aromaticity

- ① Cyclic
- ② Planar
- ③ Conjugated
- ④ Hückel's Rule.

Cyclic implies a ring. A cyclic molecule is one in which the first and last carbon in the chain are bound to each other.



cyclohexane

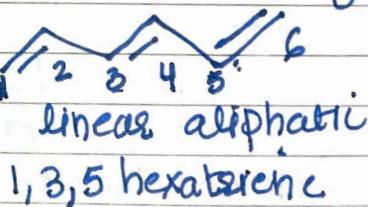
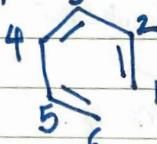


heptane.

carbon -1 is attached to carbon 2 but is also attached to C-6. In heptane C-1 and C-6 are not attached to each other making it a linear compound.



cyclic



linear aliphatic  
1,3,5 hexatriene

Planar - Since aromaticity depends on the ability of orbitals to overlap, the ring must have its

atoms in the same plane. i.e. flat

[ Hybridization - mixing of orbitals  
 -  $sp^3$  carbons are tetrahedral or 3-D  
 -  $sp^2$  carbons are trigonal planar or simply flat. (has available one empty P-orbital)  
 -  $sp$  - has carbons are linear  
 (has available two empty P-orbitals)]  
 (hybridization and geometry are related.)



Benzene

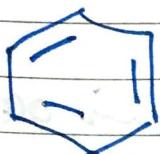


cyclohexadiene is

all carbon are  $sp^2$ -hybridized. not planar because two carbon are  $sp^3$  hybridize.

### Conjugation (dc. delocalization / Resonance)

We know that Bond order and Bond length are inversely proportional. i.e if the Bond order is 2 (double bond), so Bond length should be shorter, similarly if the Bond order is 1 (single bond) Bond length will be longer compared to the double bond.



In case of Benzene it was found from spectroscopy that all the bonds were equal

i.  $1.38 \text{ \AA}$  (between single and double bond). so. the

idea of delocalization came into existence. If more space is given to the electrons

- it will become delocalize and impart some kind of symmetry and stability to the molecule.

A conjugated molecule has its electrons distributed over the entire molecule, in this case over the entire ring. If there is an atom in the ring not capable of resonance it destroys the cyclic flow of electrons making it not fully conjugated.

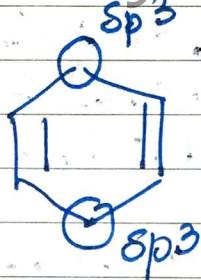


conjugation present and is capable of resonating at  $\pi$  bond through the entire ring

### Benzene (Aromatic)

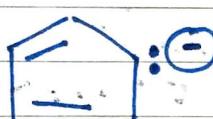


$sp^3$  conjugation present, it has resonance but cannot resonate over the entire ring because two carbons have  $sp^3$  type hybridization. ( $sp^3$  - already form bond cannot take electrons)



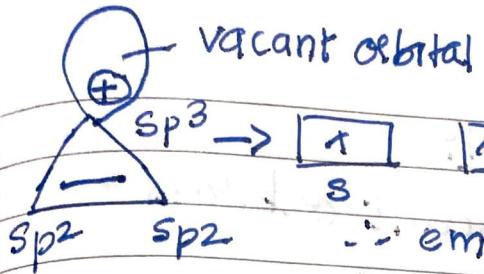
cannot resonate with each other.

(NOT Aromatic)

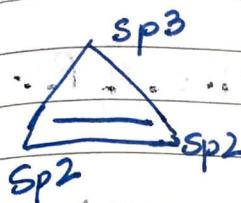


lone electron pair occupies the p-orbital and is able to resonate (Aromatic).

(carbon has to hybridize to  $sp^2$ )



$\rightarrow$  removed  $\therefore$   
 $\text{C}_6\text{T}_6$  is  $\text{sp}^2$   
 $\therefore$  empty p-orbital  $\boxed{1}$   $\boxed{1}$   $\boxed{1}$   
 hence electrons can delocalize  
 $\therefore$  aromatic

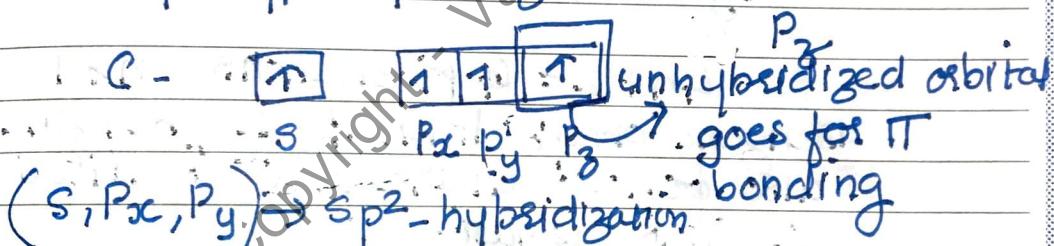


NO empty p-orbital  $\therefore$  no resonance  $\therefore$  not aromatic

### Condition for Resonance.

The orbitals must be parallel to cause resonance.

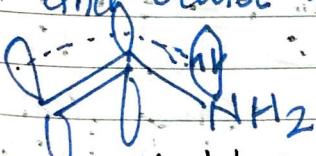
### $\text{sp}^2$ type hybridization.



- The unhybridized  $\text{P}$  orbitals are parallel to hybrid orbitals, hence can delocalize ( $\text{Pi}$  bond orbitals).



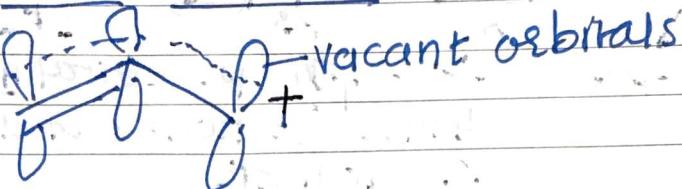
- Non bonding electron orbitals (i.e lone pair) becomes parallel to  $\text{Pi}$  bonding orbitals and cause resonance.



$\therefore \text{N}$  becomes  $\text{sp}^2$

Though N is  $\text{sp}^3$  hybridized the lone pair adjust itself parallel to the  $\text{Pi}$ -orbitals hence cause resonance

### (3) Vacant orbitals



### (4) Huckel's Rule $4n+2 = \text{Number of Resonating electrons}$

$$4n+2 = e^-$$

- \* Resonating electrons include both pi electrons and lone pairs.
- \* When solving for n, n must be equal to a whole number. If we get a fraction then the molecule does not obey Hückel's rule.

eg Benzene

$$4n+2 = 6 \text{ pi electrons } n=1$$

Benzene obeys Hückel's rule, benzene also follows all the previous criteria  
 $\therefore$  it is aromatic

- \* (Odd electron pairs follow Hückel's Rule  
even electron pairs - do not)

Number of electrons

2 4 6 8 10 12 14 16 18 20

○ - whole Num others - fraction

Number of electrons  $\div 2 = \text{Num of pairs}$

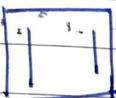
1 2 3 4 5 6 7 8 9 10

○ - odd electron pair other even e- pair  
 (Aromatic) (Antiaromatic)

Anti Aromatic: Aromatic and Anti Aromatic compound are nearly same. They follow all the three criteria (cyclic, planar, resonance) but disobey Hückel's rule.

Non aromatic - Missing at least one of the first 3 criteria. (cyclic, planar, resonance.)

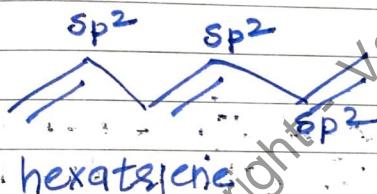
eg



- ① Cyclic
- ② Conjugated
- ③ Planar
- ④ Does not obey Hückel's Rule

i, 3 = cyclobutadiene

Anti Aromatic (even pairs of e<sup>-</sup>s)



hexatriene

- ① cyclic X
- ② planar ✓
- ③ conjugated ✓

∴ Non aromatic



sp<sup>3</sup>

- ① cyclic ✓
- ② planar X
- ③ conjugated X

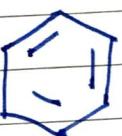
∴ non-aromatic

## Aromatic Hydrocarbons

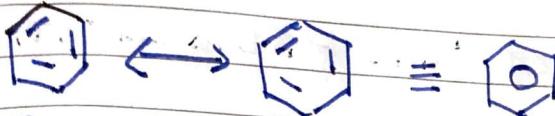
The hydrocarbons which exhibit aromaticity are called aromatic hydrocarbons. These compounds are classified into two types namely benzeneoid and non benzeneoid hydrocarbons.

Benzeneoid hydrocarbons : Benzene is the simplest benzeneoid hydrocarbon.

- Cyclic structure of benzene was proposed by Kekulé (1872)



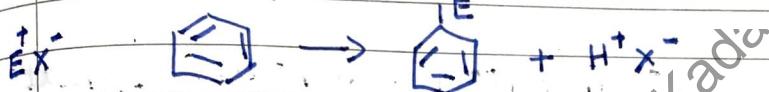
- The Lewis representation of benzene suggests that we deal with a six membered ring of carbon atoms that are held together by alternating single and double bonds.
- This implies that we should observe alternating short ( $1.33 \text{ \AA}$ ) and long ( $1.54 \text{ \AA}$ ) bond lengths.
- But experiments show that Kekulé structure is not correct. All C-C bonds are identical and benzene does not undergo addition reactions typical of double bonds.
- A correct description is given by resonance theory or by orbital models - Valence bond or molecular orbital.



Resonance structure      Resonance Hybrid.

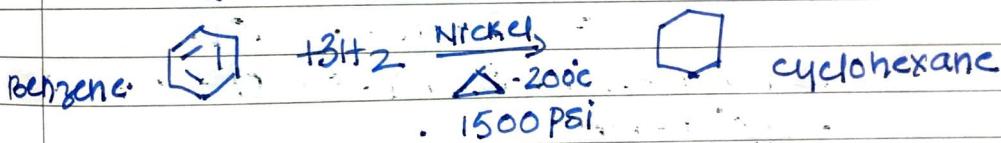
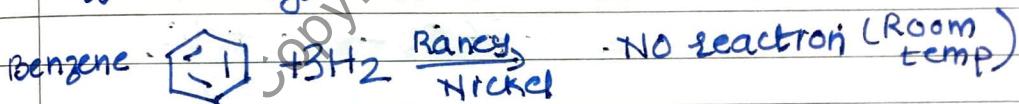
Benzene has 6 pi electrons and obeys Hückel's rule and so, benzene is very stable. This means benzene wants to retain its aromatic ring during all its reactions.

- ① One such reaction of benzene is electrophilic aromatic substitution reaction.

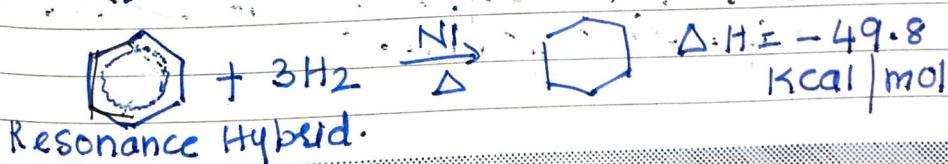
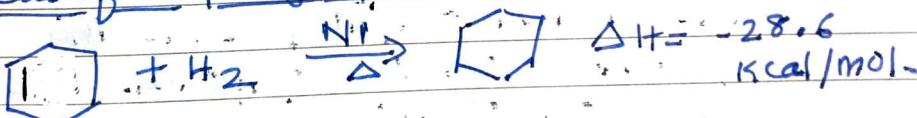


As the aromaticity of benzene is not distributed this reaction occurs spontaneously.

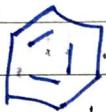
- ② In addition reaction of benzene this aromaticity is destroyed and hence benzene resists these reaction unlike other unsaturated hydrocarbons. But under special condition of high pressure and temperature it undergoes addition reaction.



- ③ Resonance Hybrid is more stable than any resonance structure (hypothetical structure).  
Heat of hydrogenation



The calculated value for the resonance structure



$$\text{three bonds} \quad \Delta H = -28.6 \times 3 \\ = -85.8 \text{ kcal/mol.}$$

Resonance Energy = Observed - calculated

$$= -49.8 - (-85.8) \\ = 36 \text{ kcal/mol.}$$

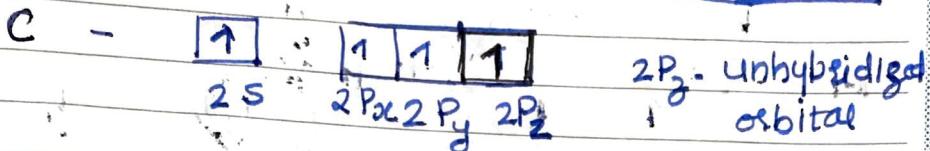
Heat of combustion - amount of heat evolved when one mole of organic compound is completely burnt in excess of oxygen or air.

$$\begin{aligned} \text{Resonance Energy} &= \frac{\text{observed heat} - \text{calculated}}{\text{heat of combustion}} \\ &= \frac{-760 - (-790)}{36 \text{ kcal/mol.}} \\ &= 36 \text{ kcal/mol.} \end{aligned}$$

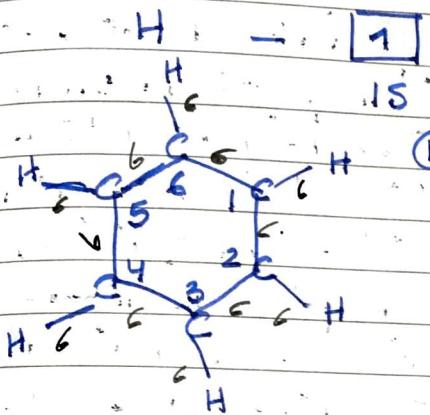
Hence Benzene is more stable because of resonance.

- Benzene is not easily oxidised by KMnO<sub>4</sub> and other oxidising agents indicating the marked stability of the ring thus aromatic compounds greatly differ from corresponding unsaturated aliphatic compounds.

# Molecular orbital structure of Benzene

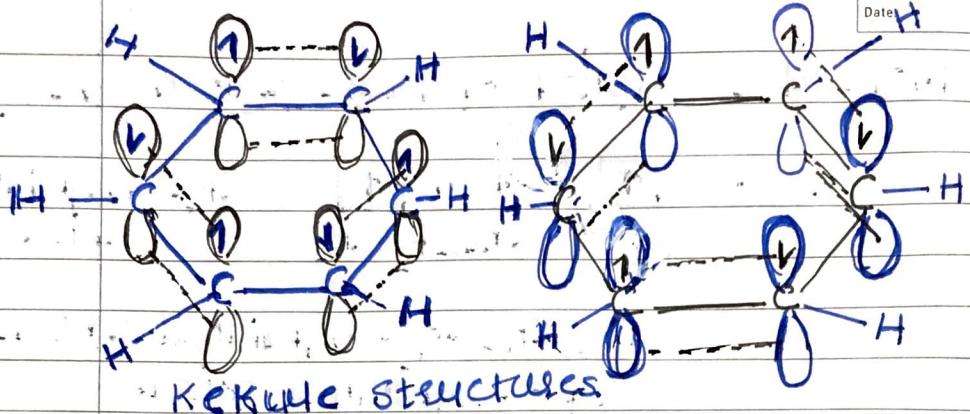


2S, 2P<sub>0x</sub>, 2P<sub>y</sub> - hybridized orbitals  
 sp<sup>2</sup> - hybridized orbitals



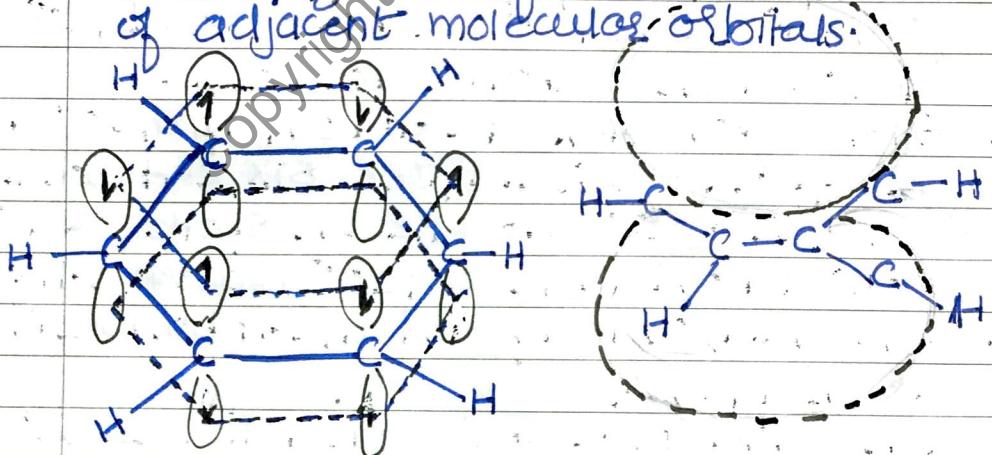
① Each carbon forms a sigma bond with adjacent carbons and Hydrogen.  
 $\text{carbon}(\text{C}_1) \rightarrow \text{C}_1 - \text{C}_2 \text{ sp}^2 - \text{sp}^2$   
 $\text{C}_1 - \text{C}_6 \text{ sp}^2 - \text{sp}^2$   
 $\text{C}_1 - \text{H} \text{ sp}^2 - \text{s}$

- ②  $\therefore$  SIX C-C sigma bonds are formed by the overlap of sp<sup>2</sup>-sp<sup>2</sup> orbitals. Thus a hexagonal ring is formed with a bond angle of 120° between the carbon-carbon bonds.
  - ③ Each carbon forms a C-H bond by the overlap of sp<sup>2</sup>-s orbitals. The SIX C-H bonds radiate outwards like the spokes of a wheel with a bond angle of 120° between C-H bonds.
  - ④ The hexagonal ring and all C-H bond are in the same plane.
  - ⑤ The unhybridized (P<sub>z</sub>) orbital is perpendicular to the plane of the ring, having one electron each. The adjacent P<sub>z</sub> orbital overlaps laterally to form three  $\pi$  bonds.
- The formation of Kekulé structures can be explained as follows.



Kekulé structures

However, the unhybridised  $2p_z$  (P) orbitals may overlap simultaneously with both the adjacent p-orbitals. This results in two circular cloudshut shaped bonds above and below the ring. This participation of p-orbitals electrons in several bonds is called delocalization. Thus, in terms of molecular orbital theory, resonance is actually delocalization of P-electrons in number of adjacent molecular orbitals.



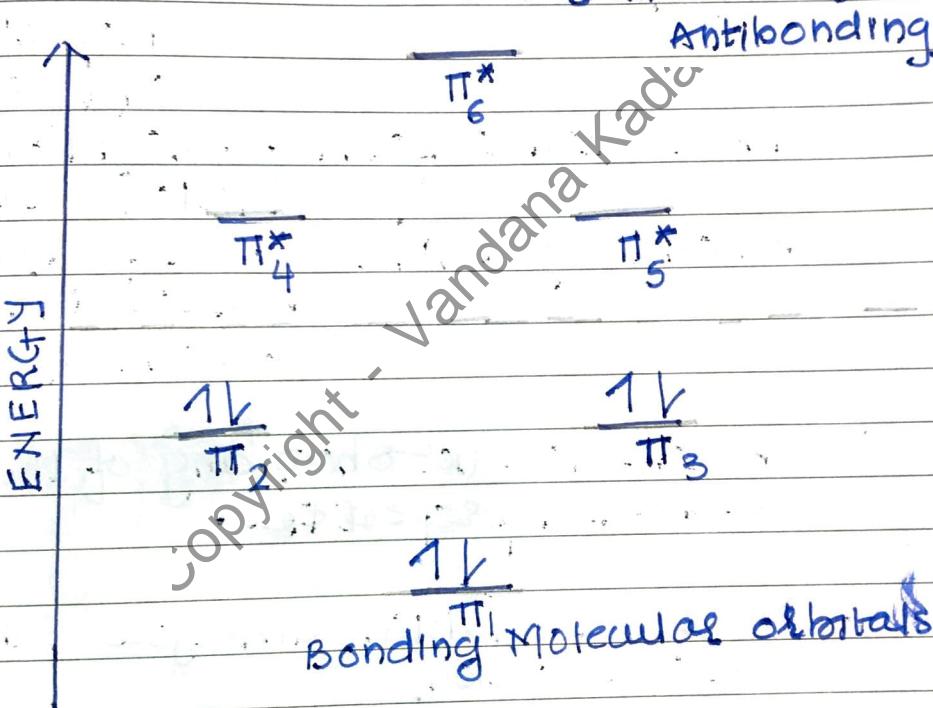
The circular cloud of  $\pi$  electrons is responsible for enhanced stability of the aromatic ring. Hückel's Rule modified in terms of molecular orbital theory.

The cyclic unsaturated compound will be aromatic if they contain  $(4n+2)$  delocalized  $\pi$  electrons in the form of a circular cloud above and below the plane of the ring.

### Molecular orbital diagram of Benzene.

$6\pi e^-$  Present in 6 carbon atoms.

$\therefore$  6 atomic orbitals, hence will form  
6 molecular orbitals  $< \begin{matrix} 3 \text{ bonding} \\ 3 \text{ antibonding} \end{matrix}$ .

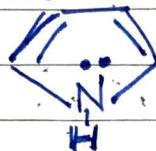


6 atomic orbitals of 6 carbon containing one electron each is  $2p_z^1$  orbital. Hence there are  $6\pi e^-$ . All the electrons are filled up in Bonding molecular orbital hence benzene molecule is more stable.

## Structure and Bonding in Pyrrole

Heterocyclic compounds are cyclic compounds containing hetero atoms such as nitrogen, sulphur, oxygen as a part of the ring structure.

Pyrrole is a five member ring made up of four carbon atoms and the hetero atom nitrogen.



Pyrrole is a nonconjugated double bond - should exhibit

properties of  
conjugated diene

Unsaturated compound - should show addition reaction

Secondary amine - expected to behave like a secondary amine

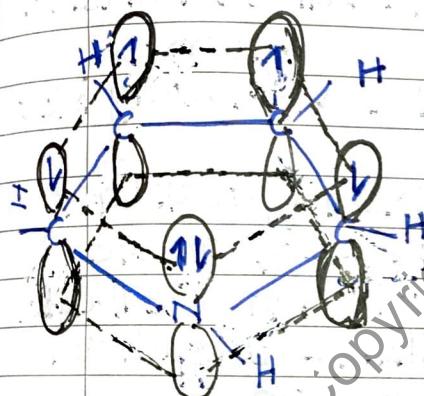
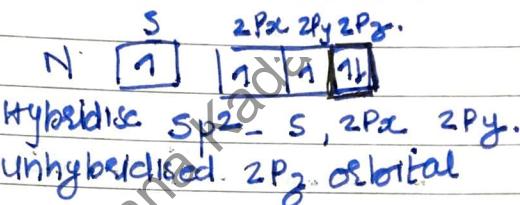
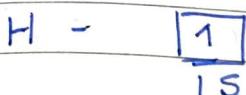
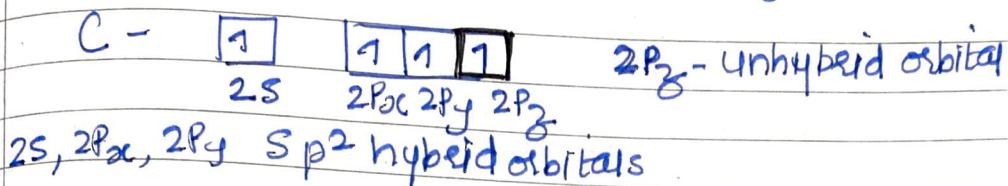
Pyrrole does not show any of the above expected properties.

1. Instead of addition undergoes substitution (few exception)
2. It is an extremely weak base.
3. lower heats of hydrogenation and combustion than expected.  
Hence it is more stable than expected.

Pyrrole is planar ring structure. The 4πe's and lone pair are in conjugation.

As it has 6 electrons, it obeys Hückel's Rule. hence it is aromatic in nature.

### Molecular orbital structure of pyrrole



- ① Each C and N have three Sp<sup>2</sup> hybrid orbitals
- ② Each C and N have one unhybridised orbitals. (2p<sub>z</sub>)

- ① All the atoms of pyrrole heterocyclic ring are in the same plane.
- ② The four carbon atoms and one Nitrogen atom are Sp<sup>2</sup> hybridized.
- ③ Two sp<sup>2</sup> orbitals of each atom are utilized to form 6 bond between the carbon atoms and also nitrogen.
- ④ The third sp<sup>2</sup> orbital forms 6 bond between carbon - Hydrogen and Nitrogen - Hydrogen.
- ⑤ The bond angles between the bonds is 120°

⑥ Each carbon atom in the ring contains a p-orbital ( $2p_z$ ) with one electron and nitrogen atom contains a p-orbital ( $2p_z$ ) with lone pair of electrons. These p-orbitals overlap with adjacent p-orbitals on either side to produce circular cloud of  $\pi$  electrons. This delocalized circular cloud of six  $\pi$ -electrons is above and below the plane. Hückel's Rule is fully satisfied, hence pyrrole ring shows aromaticity.

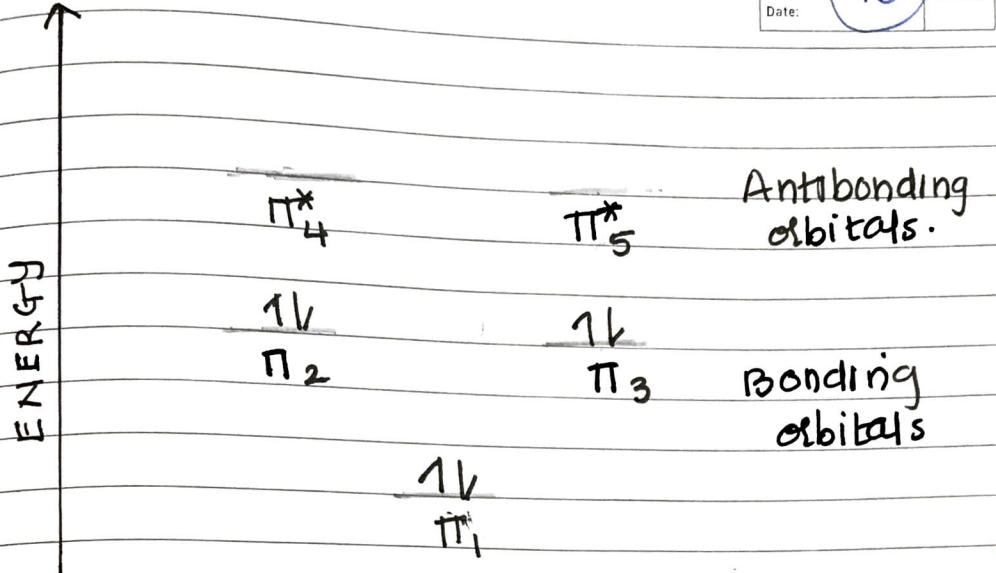
Because of  $\pi$  electron cloud - substitution reaction occurs.

$\pi$  electron cloud disturbed - Aromaticity is lost

Q. Why Pyrrole is an extremely weak base.  
Since the lone pair of electron on the nitrogen atom is involved in the  $\pi$ -electron cloud, it is not available to be shared with a proton. Hence pyrrole is an extremely weak base.

Molecular orbital diagram of Pyrrole.  
4 carbons and one Nitrogen

- ① 5 atomic orbitals combine to form 5 molecular orbitals. Three bonding orbitals and two anti bonding orbitals.
- ② There are 6 electrons -  $4\pi e^-$  of carbon and  $2\pi e^-$  of Nitrogen



All the electrons fill up the bonding molecular orbital, hence the molecule is highly stable.