B.Sc. Semester-IV

Core Course-IX (CC-IX)

Organic Chemistry-III

III. Heterocyclic Compounds

15. Aromaticity in 5- and 6- Membered Heterocyclic Compounds

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Heterocyclic Compounds **22 Lectures**

Classification and nomenclature, Structure, aromaticity in 5-numbered and 6-membered rings containing one heteroatom; Synthesis, reactions and mechanism of substitution reactions of: Furan, Pyrrole (Paal-Knorr synthesis, Knorr pyrrole synthesis, Hantzsch synthesis), Thiophene, Pyridine (Hantzsch synthesis), Pyrimidine, Structure elucidation of indole, Fischer indole synthesis and Madelung synthesis), Structure elucidation of quinoline and isoquinoline, Skraup synthesis, Friedlander's synthesis, Knorr quinoline synthesis, Doebner- Miller synthesis, Bischler-Napieralski reaction, Pictet-Spengler reaction, Pomeranz-Fritsch reaction

Derivatives of furan: Furfural and furoic acid.

Coverage:

1. Aromaticity in 5- and 6- Membered Heterocyclic Compounds

Aromaticity in 5- and 6- Membered Heterocyclic Rings

To be classified as aromatic, a compound must have:

1. Cyclic structure
2. Coplanar structure.
3. Each atom of the ring must have a p orbital to form a delocalized π system i.e. no atoms in the ring can be sp^3 hybridized instead all atoms must be sp^2 hybridized.

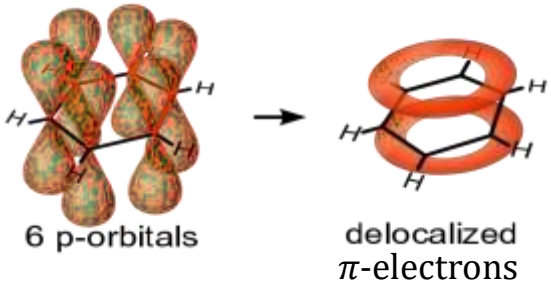
Conjugated C=C bonds (C=C-C=C-C=C)

4. Fulfill Huckel rule i.e. the system must have

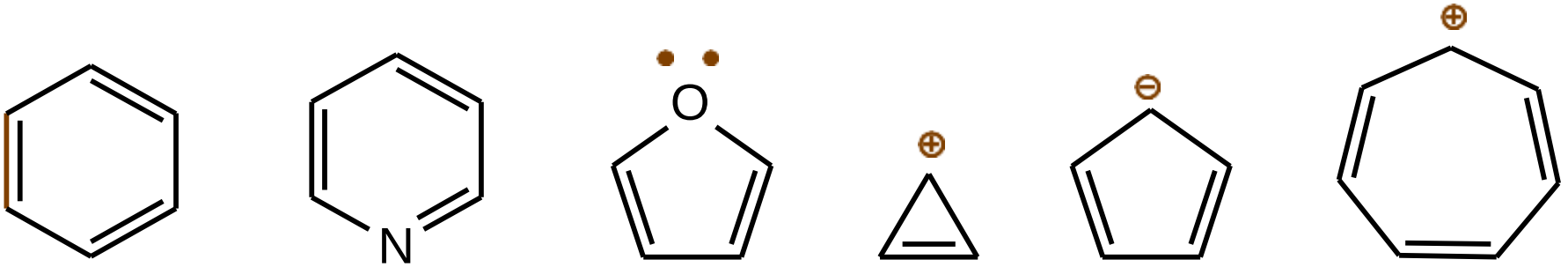
$4n + 2 = \pi$ lectrons :

thus by calculating n value it will be an integral number i.e. n=0, 1, 2, 3,

Erich Hückel

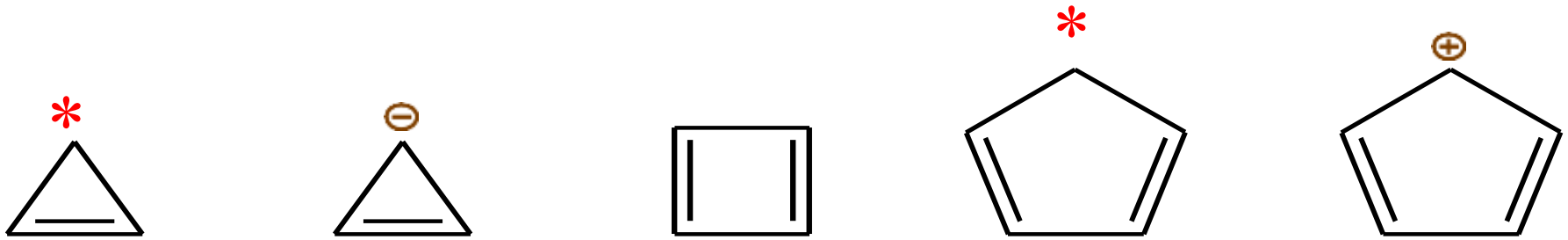


Examples of aromatic compounds:



n=1 n=1 n=1 n=0 n=1 n=1

Examples of non-aromatic compounds:



sp^3 C* n = 1/2 n = 1/2 sp^3 C* n = 1/2

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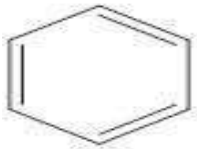
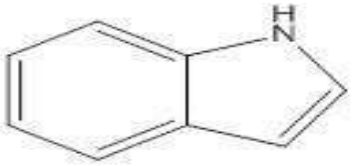
Aromatic Compounds

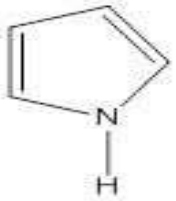


$4n + 2 = 6$
$n = 1$

$4n + 2 = 10$
$n = 2$



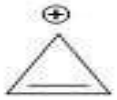
$4n + 2 = 6$
$n = 1$



$n = 1$

$n = 1$

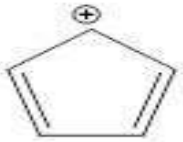
$4n + 2 = 4$
$n = 1$



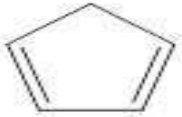
$4n + 2 = 2$
$n = 0$

Aromatic

But

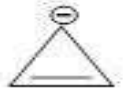


$4n + 2 = 4$
$n \neq 1$



$4n + 2 = 4$
$n \neq 1$

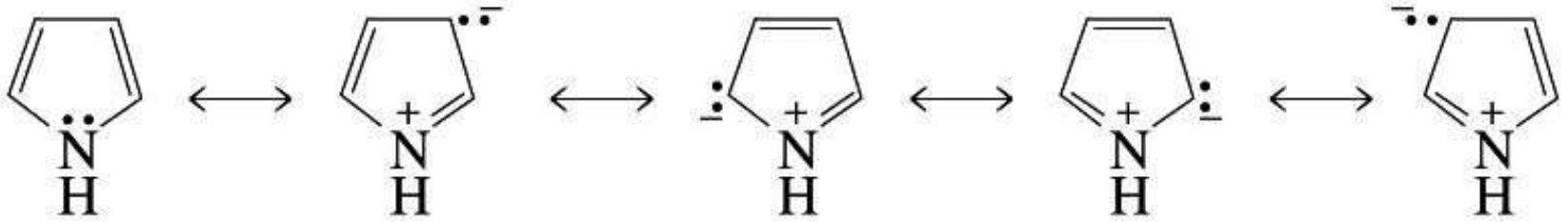
$4n + 2 = 8$
is not an integer



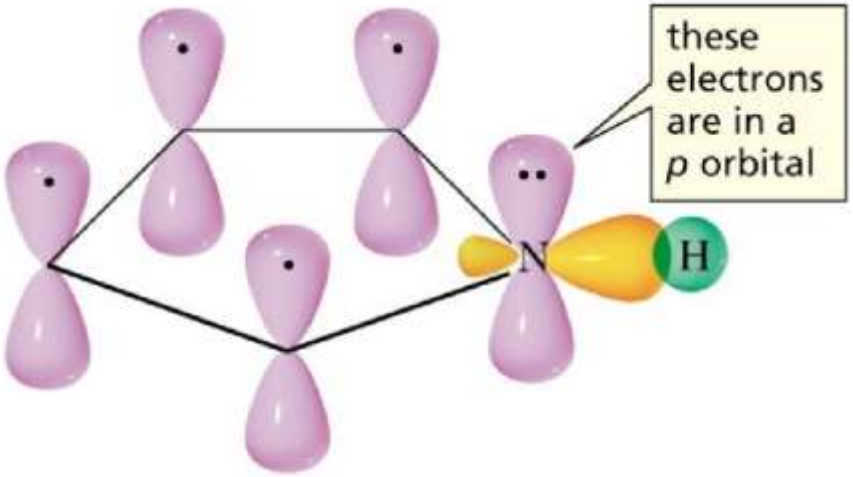
$4n + 2 = 4$
$n \neq 0$

not aromatic

Pyrrole is Aromatic

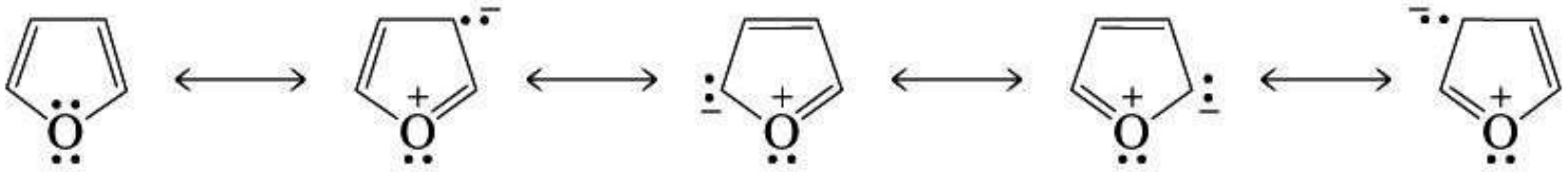


resonance contributors of pyrrole

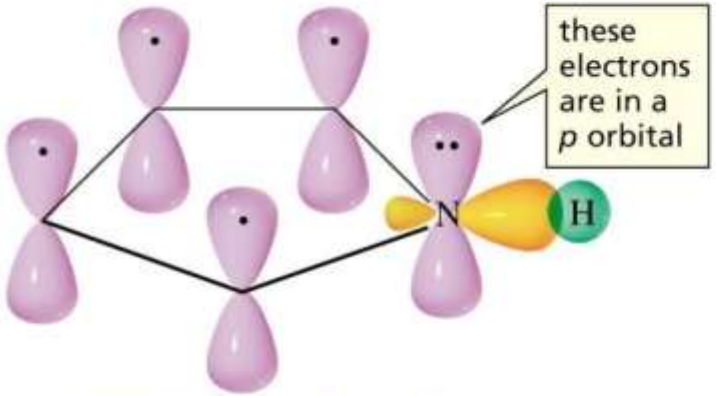


orbital structure of pyrrole

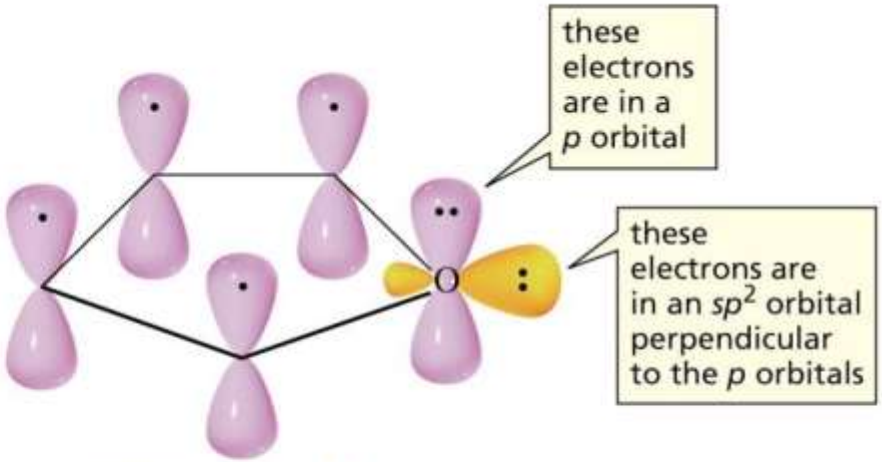
Furan is Aromatic



resonance contributors of furan



orbital structure of pyrrole

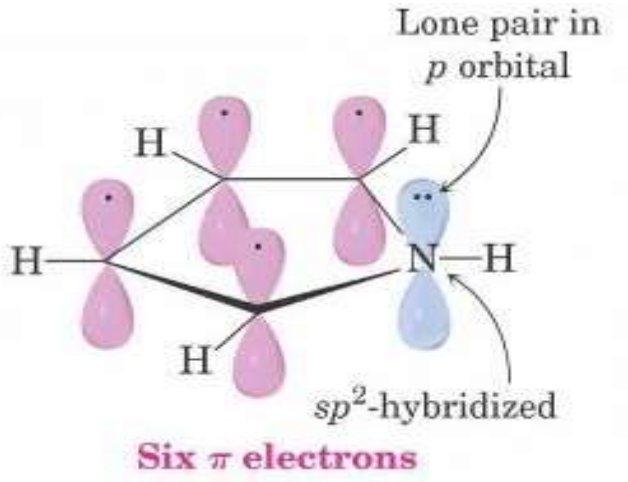


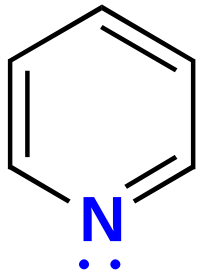
orbital structure of furan

Heterocyclic Compounds

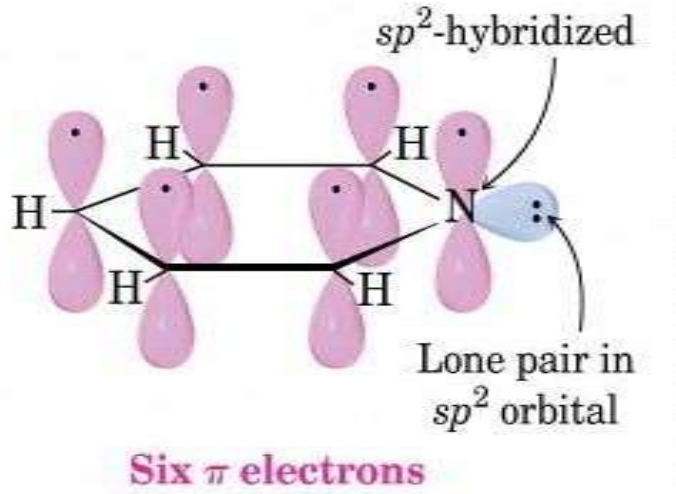
Heterocyclic Aromatic Compounds and Hückel's Rule:
Pyridine: π-electron structure resembles benzene (6 π-electrons) The nitrogen lone pair electrons are <u>not</u> part of the aromatic system.

But in pyrrole, lone pair of electrons is delocalized in the ring.



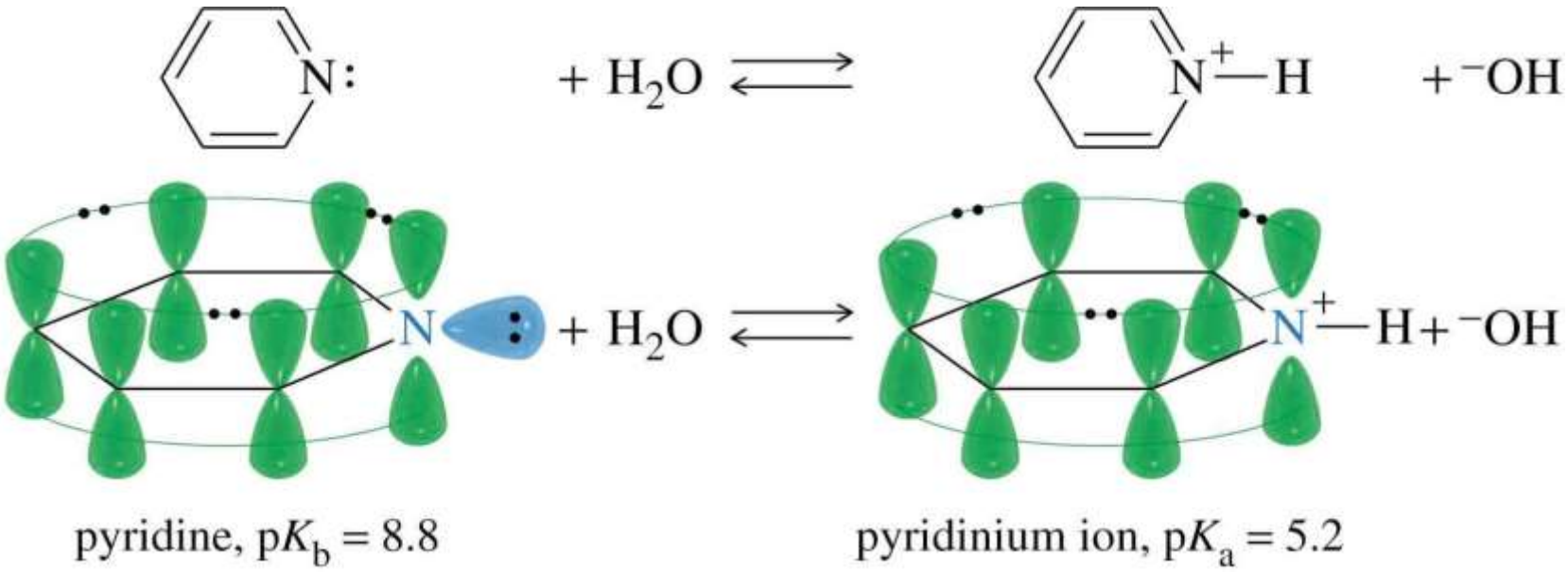


pyridine



The Acidity of the Pyridinium ion

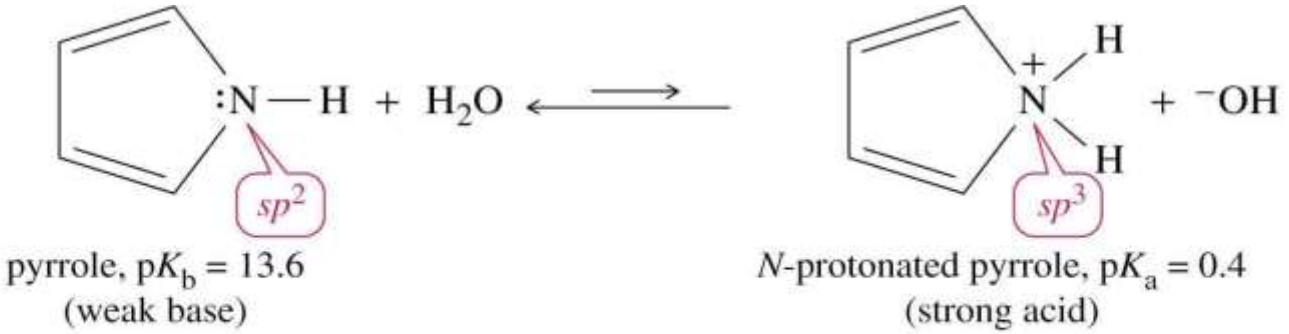
- **Heterocyclic aromatic compound.**
- **Nonbonding pair of electrons in sp^2 orbital, so weak base, $pK_b = 8.8$.**



The Acidity of Protonated Pyrrole

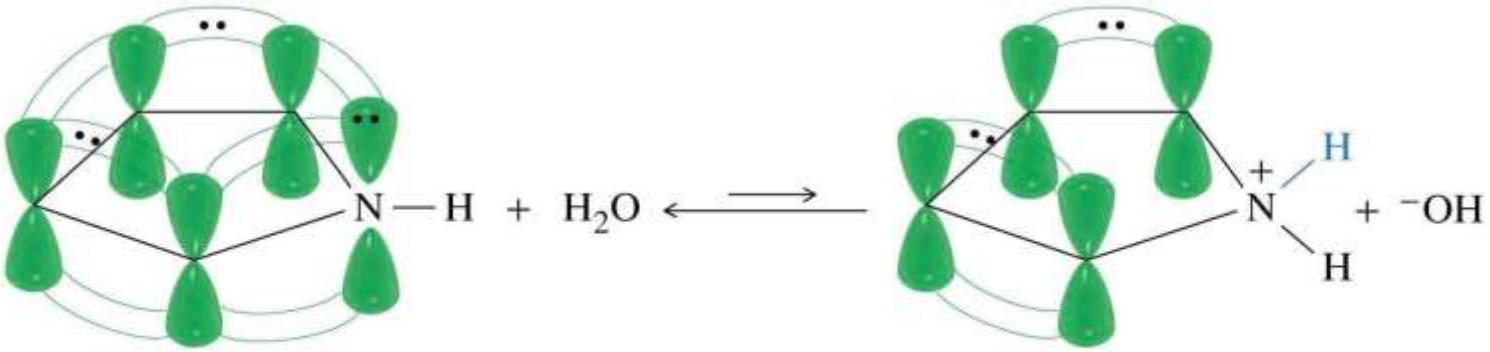
Also aromatic, but lone pair of electrons are delocalized:

Much weaker base.



pyrrole, $pK_b = 13.6$
(weak base)

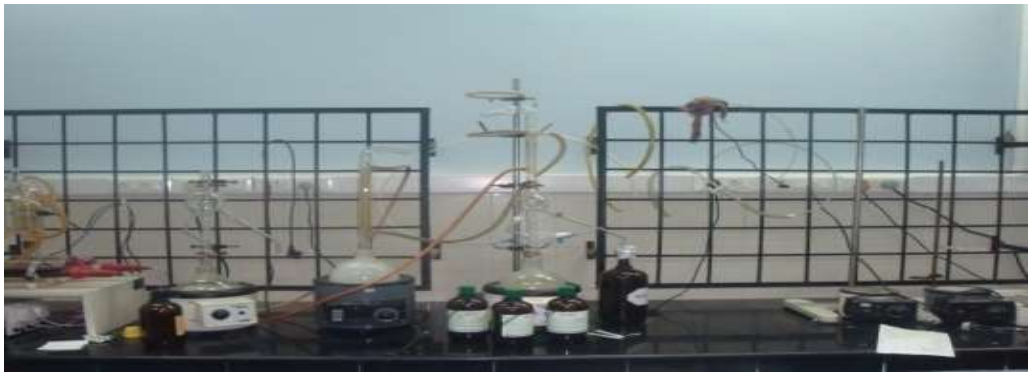
N-protonated pyrrole, $pK_a = 0.4$
(strong acid)



pyrrole
(aromatic)

N-protonated pyrrole
(nonaromatic)

Thank You



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