

M.Sc. Semester-I
Core Course-II (CC-II)
Reaction Mechanism in Organic Chemistry



I. Nature of Bonding in Organic Molecules

L3. Stability of Aromatic Cations and Anions

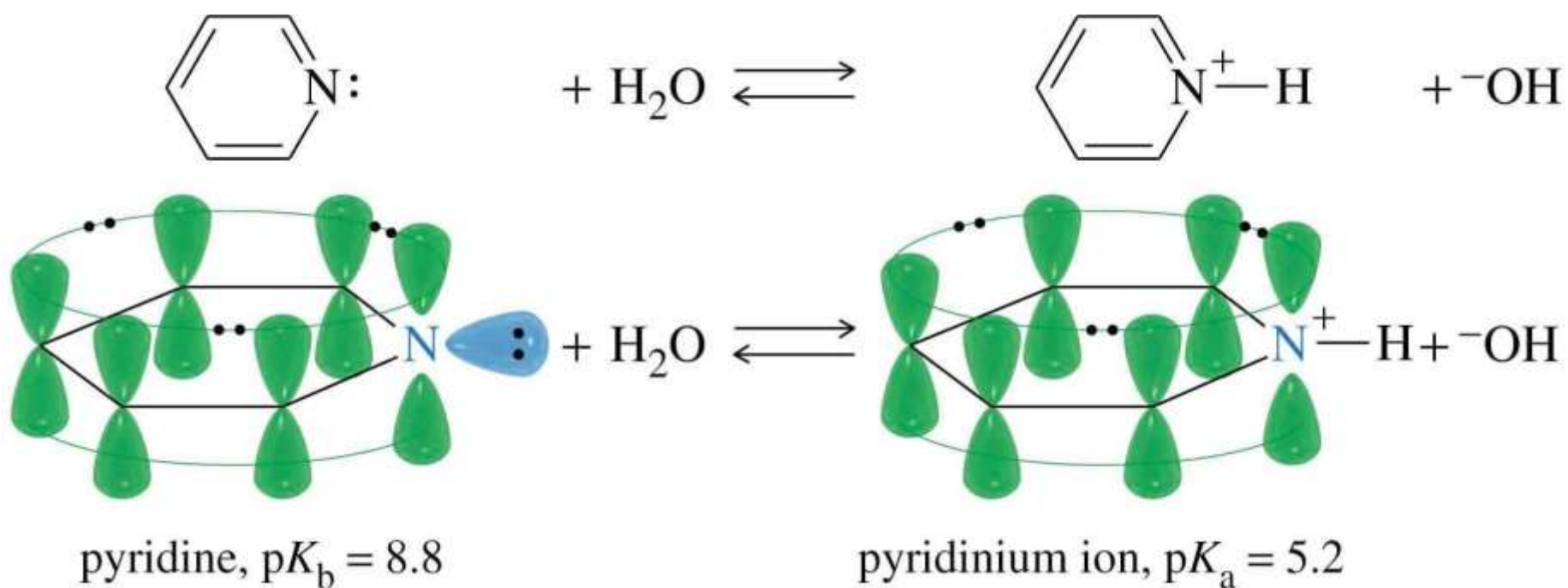


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Stability of Aromatic Cations and Anions:

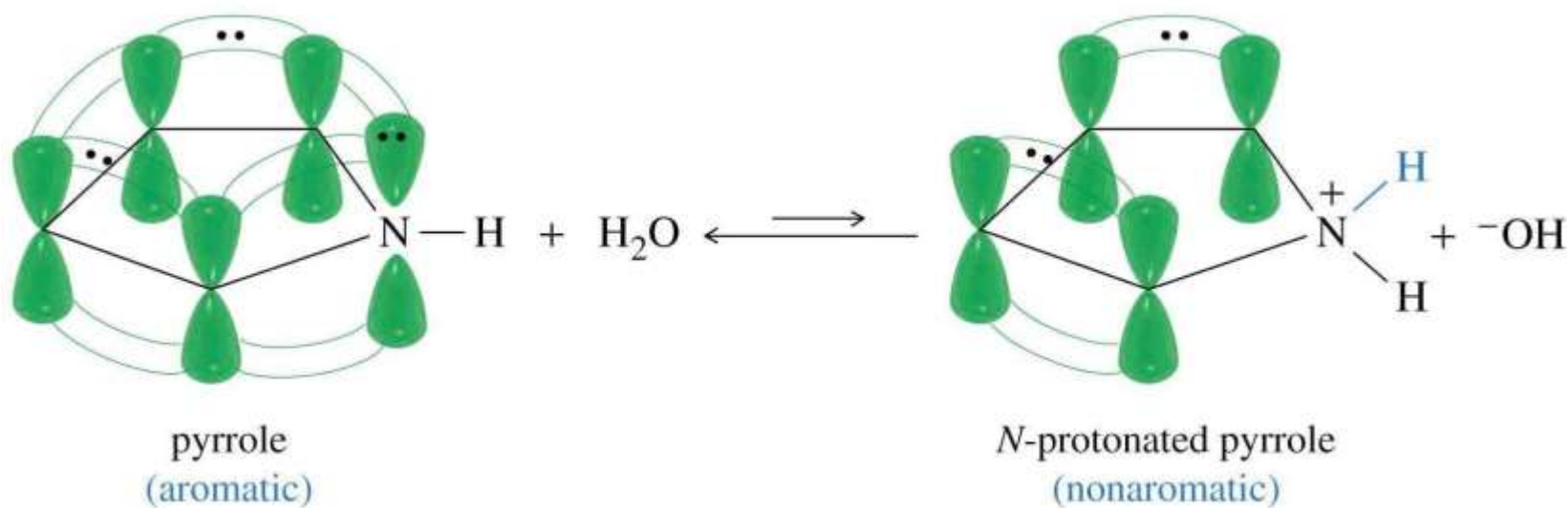
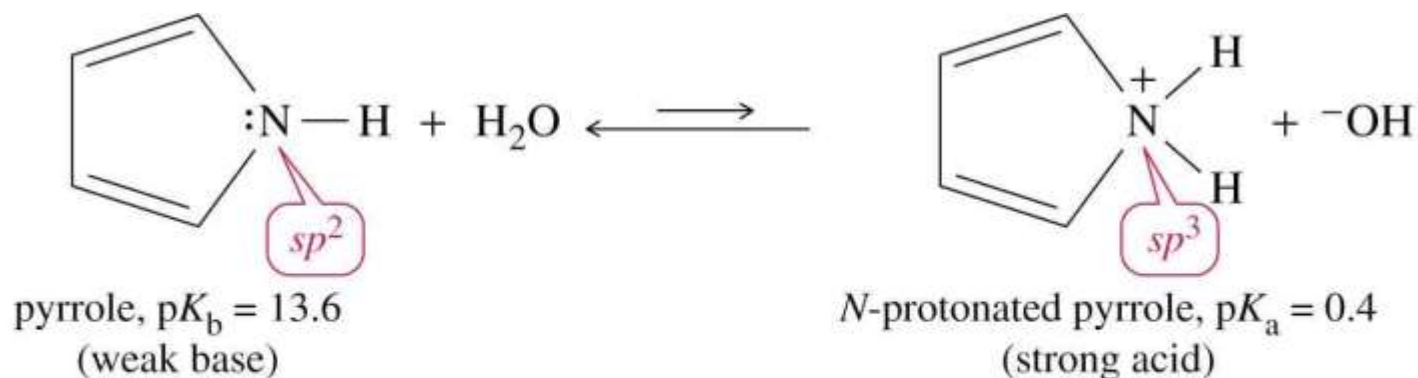
The Acidity of the Pyridinium Ion

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

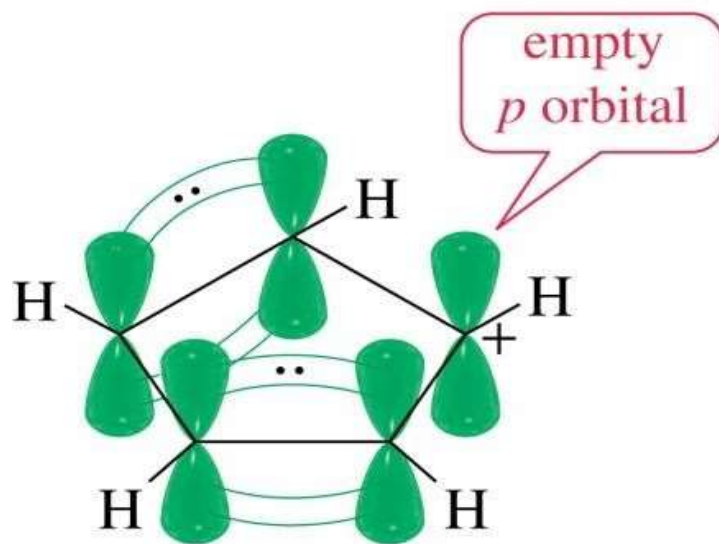
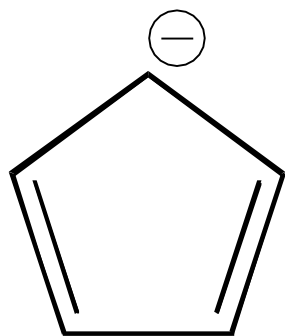


The Acidity of Protonated Pyrrole

Also aromatic, but lone pair of electrons is delocalized:
much weaker base.

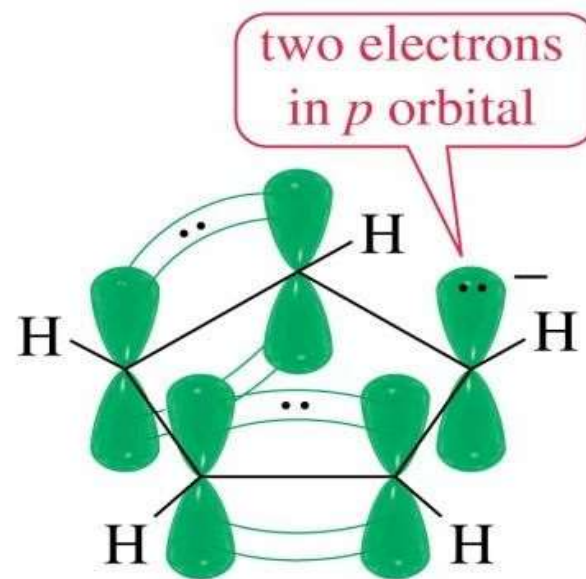
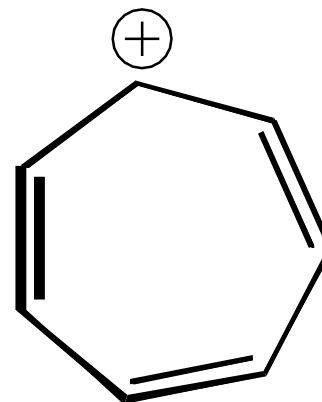


Cyclopentadienyl Anion



four electrons
cyclopentadienyl cation

Cycloheptatrienyl cation



six electrons
cycloheptatrienyl anion

Cyclopentadienyl Anion :

If 5 sp^2 carbons are joined in a planar ring, then the 5 unhybridized p orbitals could be lined up to form a continuous ring.

The 5π -electrons would make this system a neutral free radical species.

If we removed an electron to form a cation (4π -electrons), then Hückel's rule implies that it would be antiaromatic.

If we added an electron to the radical to produce an anion (6π -electrons), then Hückel's rule implies this would be aromatic.

Indeed, the cyclopentadienyl anion (cyclopentadienide) is found to be aromatic, and is therefore unusually stable relative to other anions.

Cycloheptatrienyl Cation:

Now if we consider seven sp^2 carbons aligned in a planar ring, this gives us 7π -electrons.

So the cycloheptatrienyl anion has 8 electrons, and the cycloheptatrienyl cation has 6 electrons.

Therefore the cycloheptatrienyl anion ($4N$, $N=2$) is antiaromatic (if it were to stay planar), and the cycloheptatrienyl cation ($4N+2$, $N=1$) is aromatic.

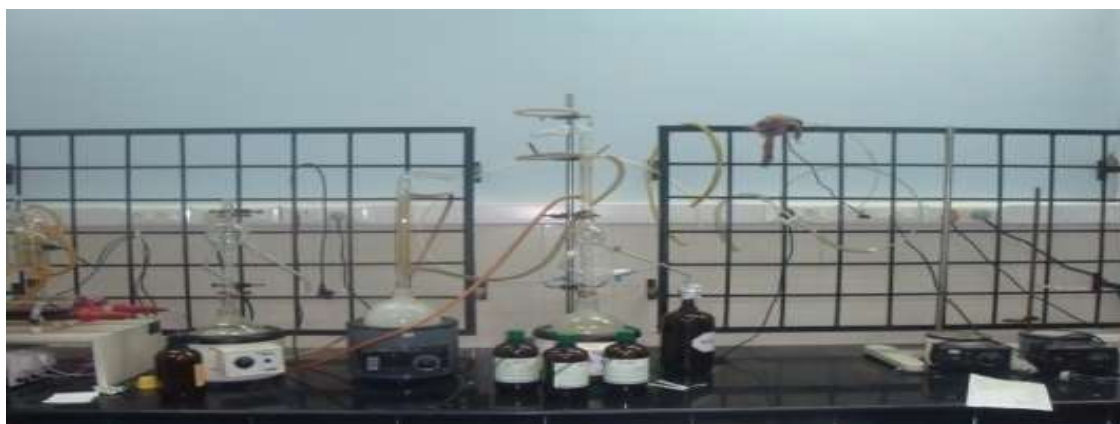
Again, it is MO theory that predicts the stability of the cation, and the instability of the anion, whereas resonance structures would lead us to believe that both were very stable.

The cycloheptatrienyl cation is easily formed, and is often called the *tropylium* ion.

It is an *aromatic* carbocation, and therefore less reactive than normal carbocations.

It is, of course, more stable than its open chain analogue.

Thank You



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