B.Sc. Semester-II
Core Course-III (CC-III)
Organic Chemistry-I

IV. Aromatic Hydrocarbons

11. Effects of Aromatic Stabilisation

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IV Aromatic Hydrocarbons **10 Lectures**

Aromaticity: Hückel's rule, aromatic/anti-aromatic/non-aromatic character of arenes, cyclic carbocations/carbanions and heterocyclic compounds with suitable examples.

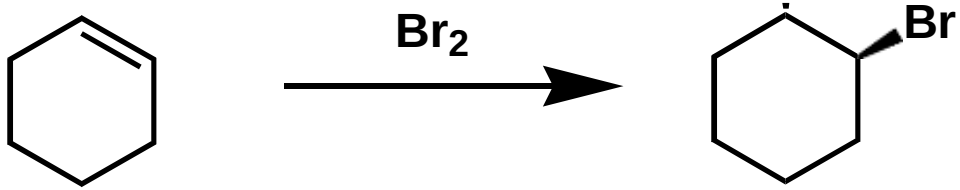
Electrophilic aromatic substitution: Halogenation, Nitration, Sulphonation and Friedel-Craft's alkylation/acylation with their mechanism. Directing effects of mono-functional groups.

Coverage:

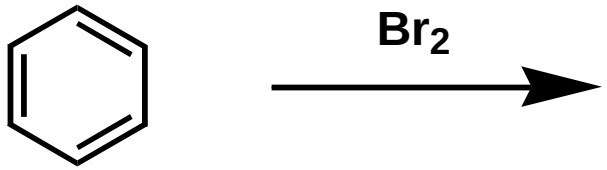
1. Effects of Aromatic Stabilisation

Effects of Aromatic Stabilisation

ADDITION



Bonds broken	Bonds made
π bond Br-Br bond	2 C-Br



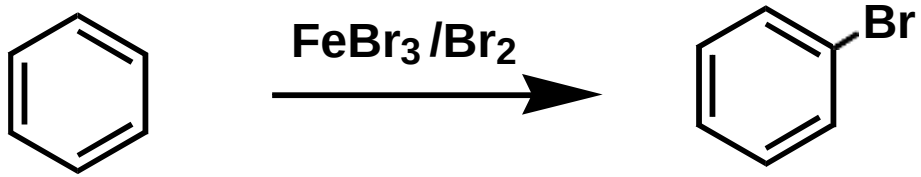
No reaction

If reaction occurred

Bonds broken	Bonds made
π bond Br-Br bond	2 C-Br

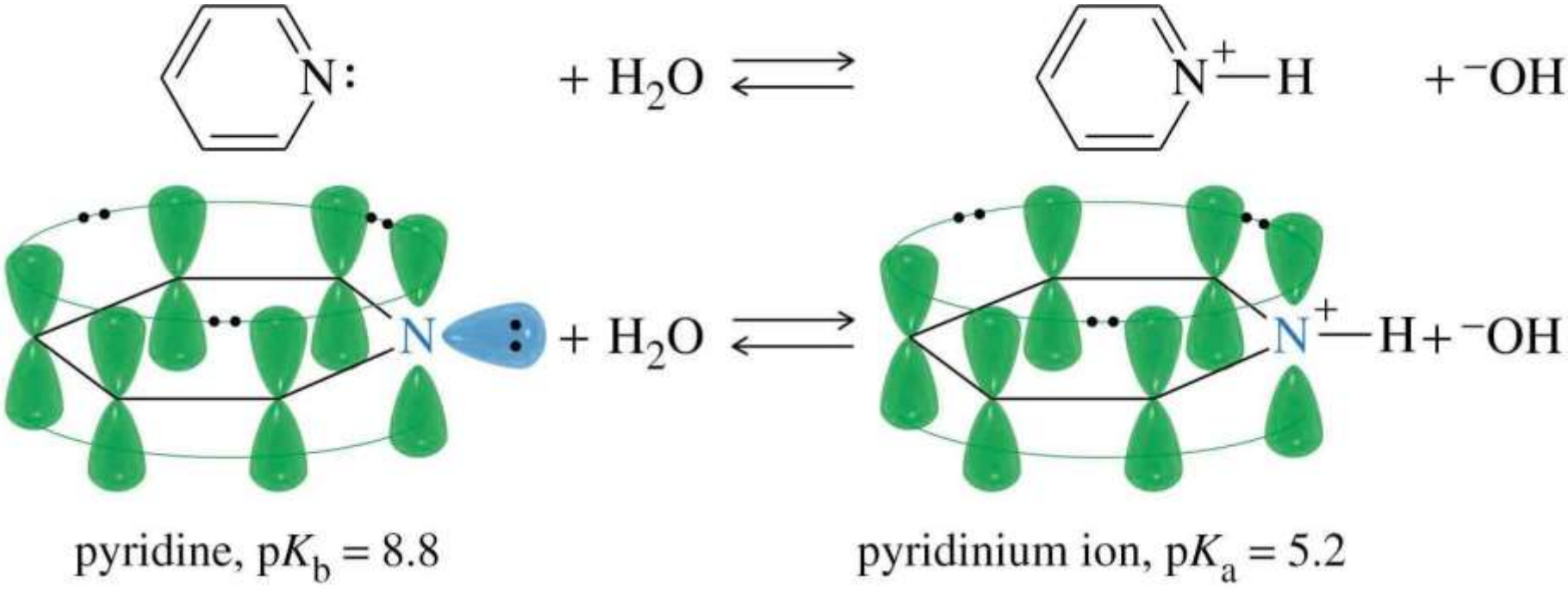
BUT would lose AROMATIC STABILISATION

INSTEAD - SUBSTITUTION



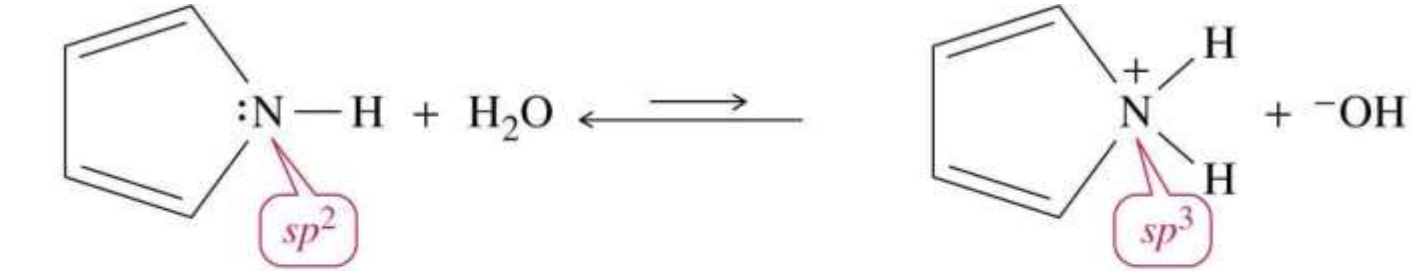
The Acidity of the Pyridinium Ion

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



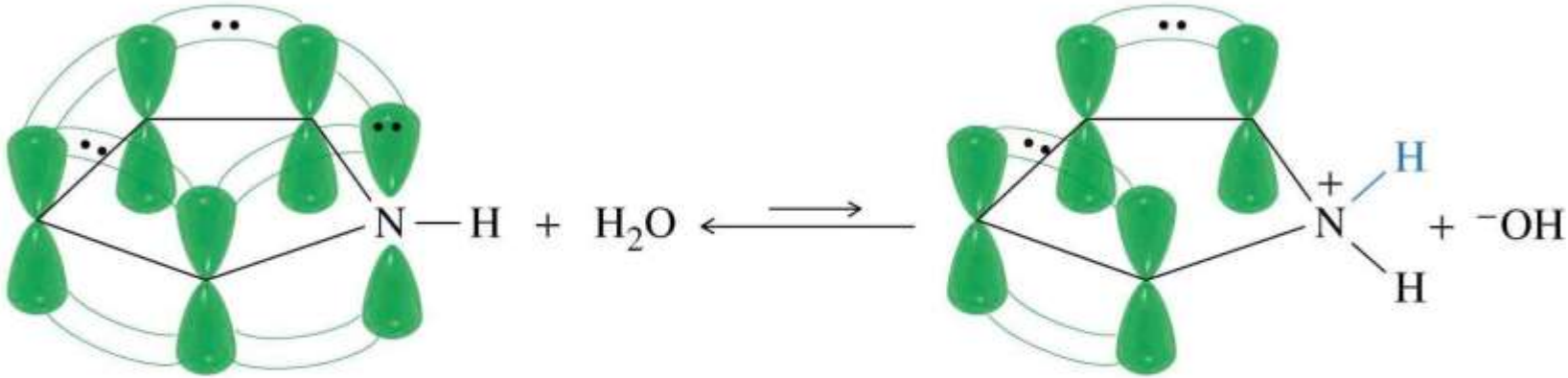
The Acidity of Protonated Pyrrole

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



pyrrole, $pK_b = 13.6$
(weak base)

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

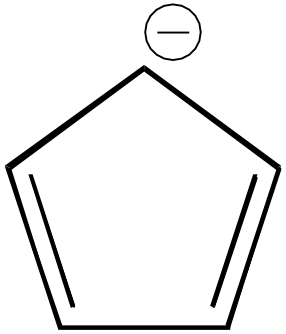


pyrrole
(aromatic)

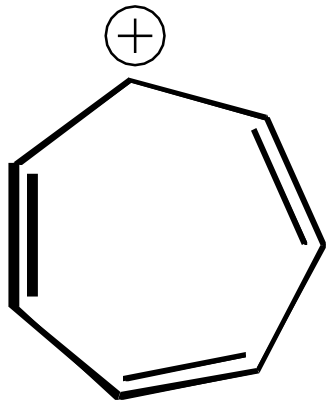
N-protonated pyrrole
(nonaromatic)

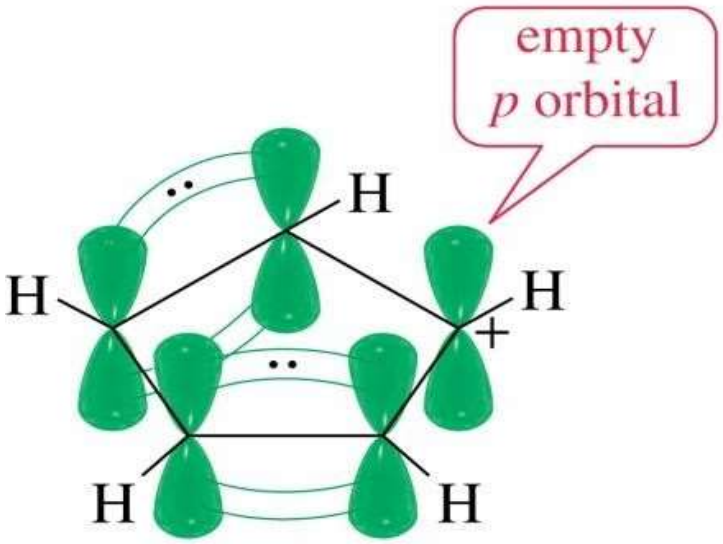
Stability of Aromatic Cations and Anions:

Cyclopentadienyl Anion

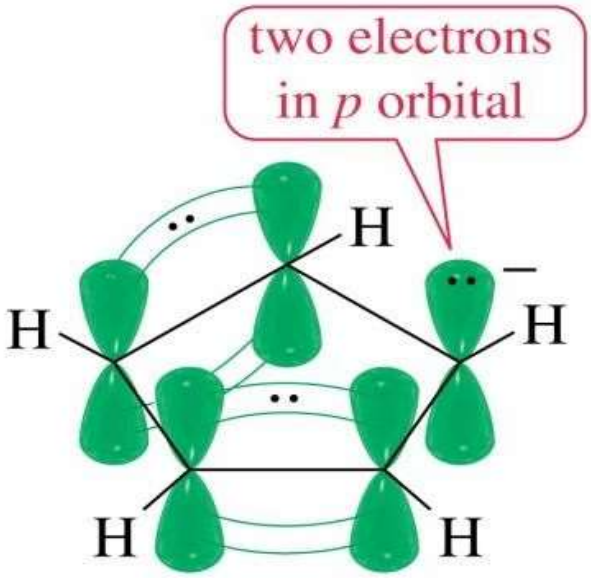


Cycloheptatrienyl cation





four electrons
cyclopentadienyl cation



six electrons
cyclopentadienyl 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.

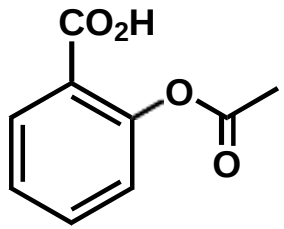
Again, it is MO theory that predicts the stability of the cation, and the instability of the anion, whereas resonance structures would lead us to believe that both were very stable.

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

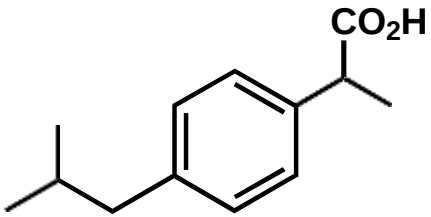
It is an *aromatic* carbocation, and therefore less reactive than normal carbocations.

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

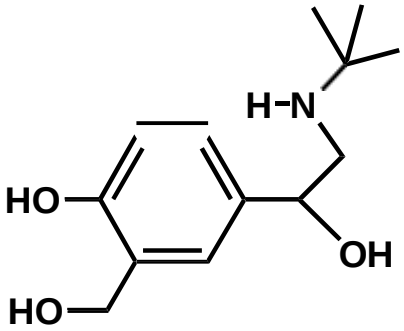
Benzene Derivatives : As Useful Drugs



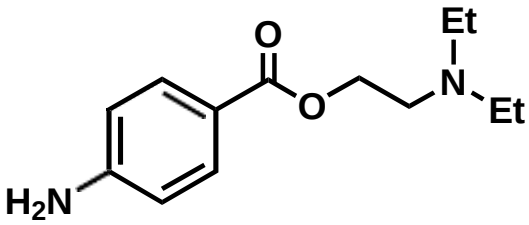
acetyl salicylic acid
ASPIRIN



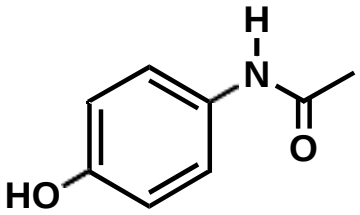
ibuprofen
ADVIL



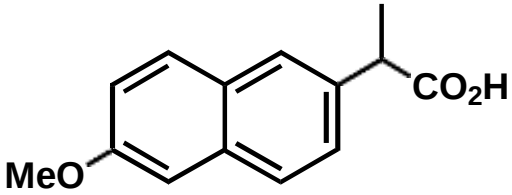
bronchodilator
ALBUTEROL



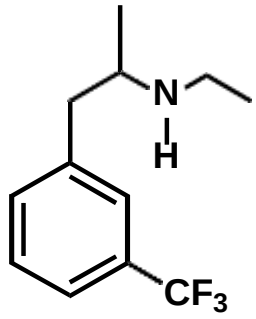
procaine
NOVOCAINE



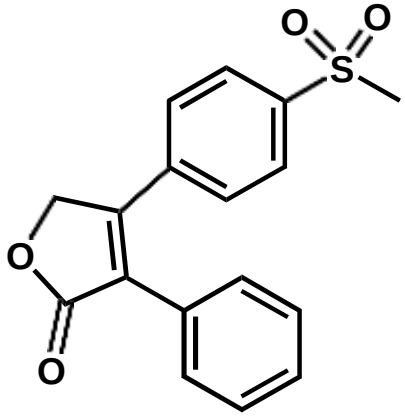
acetaminophen
TYLENOL



naproxen
ALEVE

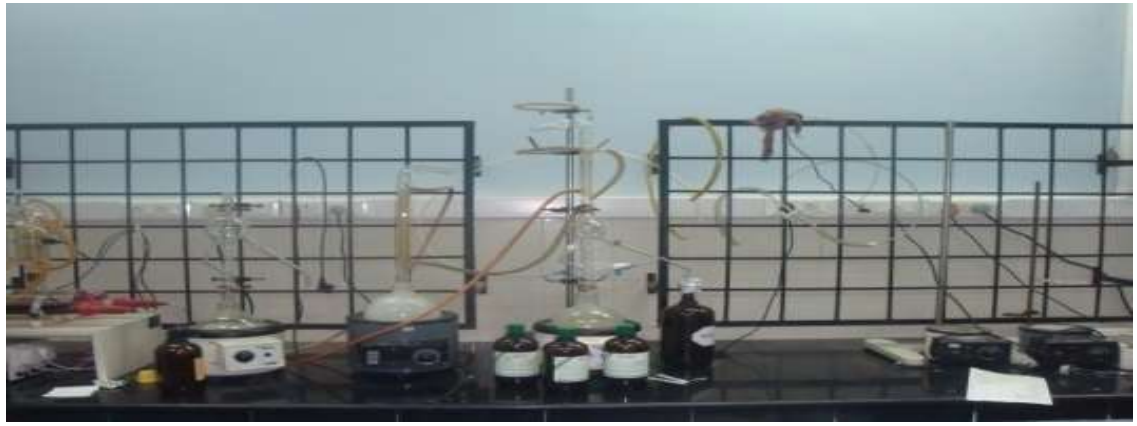


appetite suppresant
FENFLURAMINE



rocecoxib
VIOXX

Thank You



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