

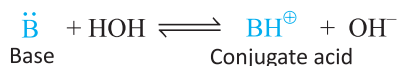
BASICITY

Section - 2

Organic Compound as Base :

Nitrogen containing organic compounds having upshared electron pair on nitrogen atom acts as organic base.

The strength of a base $\ddot{B}$, in water, may be determined by considering the equilibrium.



The equilibrium constant in water, K_b is given by $K_b = \frac{[\text{BH}^{\oplus}][\text{OH}^{\ominus}]}{[\ddot{B}]}$

Strength of base $\propto K_b$

$$\propto \frac{1}{\text{p}K_b}$$

The strength of base $\ddot{B}$ can also be described in terms of K_a and $\text{p}K_a$ of conjugate acid, $\text{BH}^{\oplus}$ of base.



Strength of conjugate acid $\text{BH}^{\oplus} \propto K_{a_{\text{conjugate acid}}}$
 $\propto \frac{1}{\text{p}K_{a_{\text{conjugate acid}}}}$

Strength of base $\ddot{B} \propto \frac{1}{\text{strength of conjugate acid } (\text{BH}^{\oplus})}$

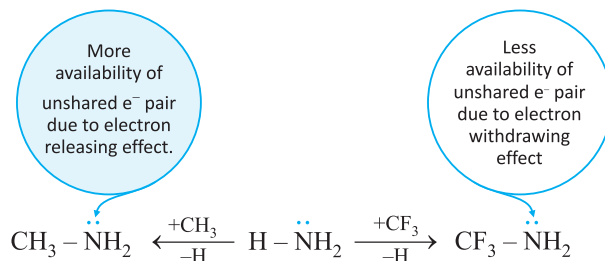
The “stronger” $\text{BH}^{\oplus}$ is as an acid, the “weaker” $\ddot{B}$ will be as a base.

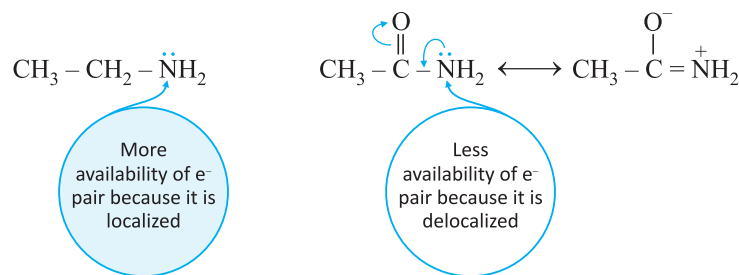
Thus the smaller the numerical value of $\text{p}K_a$ for $\text{BH}^{\oplus}$ the weaker $\ddot{B}$ is as a base.

Note : $K_a \times K_b = K_w$ or $\text{p}K_a + \text{p}K_b = 14$

Strength of base $\propto \text{p}K_{a_{\text{BH}^{\oplus}}}$

- $\Rightarrow$ Strength of organic base depends upon availability of unshared electron pair on basic site.
- $\Rightarrow$ Availability of unshared electron pair on basic site increases due to presence of electron releasing group and it decreases due to presence of electron withdrawing group.
- $\Rightarrow$ Availability of unshared electron pair decreases due to delocalization of unshared electron pair through resonance, as illustrated by following examples.





Further, strength of organic base also depends upon stability of its conjugate acid ($\text{BH}^{\oplus}$).

$$\begin{aligned} \text{Stability of conjugate acid} &\propto \frac{1}{\text{Positive charge density of conjugate acid}} \\ &\propto \text{Extent of solvation of conjugate acid} \\ &\propto \text{Extent of delocalization of positive charge of conjugate acid} \\ &\propto \text{Number of ERGs} \\ &\propto \text{Strength of ERG} \\ &\propto \frac{1}{\text{Number of EWGs}} \\ &\propto \frac{1}{\text{Strength of EWGs}} \end{aligned}$$

I. Aliphatic Base : [Aliphatic Amine]

The strength in nitrogenous bases is related to the availability of the unshared electron pair on nitrogen. This availability of electron pair increases due to the increasing **inductive effect** of alkyl groups in aliphatic amines.

	NH_3	$\text{Me}-\text{NH}_2$	$\text{Me}-\text{NH}-\text{Me}$
$\text{pK}_{\text{a}_{\text{BH}^+}}$	9.25	10.64	10.77
		$\text{Et}-\text{NH}_2$	$\text{Et}-\text{NH}-\text{Et}$
		10.67	10.93

The introduction of an **alkyl group** into ammonia **increases** the basic strength markedly as expected. The introduction of a second alkyl group further increases the basic strength, but the net effect of introducing the **second alkyl group** is very much **less marked** than with the first. It is due to crowding around nitrogen atom because crowding decreases readiness with which a basic site take up protons.

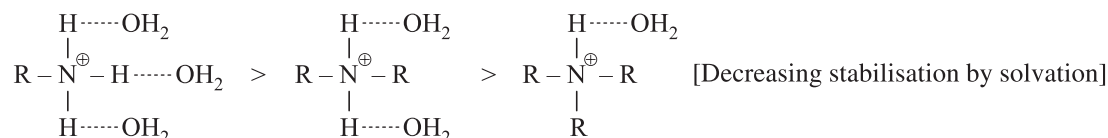
The introduction of a **third alkyl group** actually **decreases the basic strength**.

	$\text{Me}-\text{NH}-\text{Me}$	$\begin{array}{c} \text{Me} \\ \\ \text{Me}-\text{N}-\text{Me} \end{array}$	[Decrease in basic strength]
$\text{pK}_{\text{a}_{\text{BH}^+}}$	10.77	9.80	
	$\text{Et}-\text{NH}-\text{Et}$	$\begin{array}{c} \text{Et} \\ \\ \text{Et}-\text{N}-\text{Et} \end{array}$	[Decrease in basic strength]
$\text{pK}_{\text{a}_{\text{BH}^+}}$	10.93	10.80	

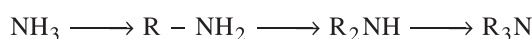
This is due to the fact that the basic strength of an amine in water is determined by

- (i) Electron availability on the nitrogen atom, also by
- (ii) The extent to which the cation (conjugate acid, $\text{BH}^{\oplus}$) can undergo solvation, and so become stabilized.

Note : The more hydrogen atoms attached to nitrogen in the cation, the greater the possibilities of powerful solvation via hydrogen bonding between these and water.



Thus on going along the series



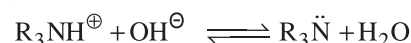
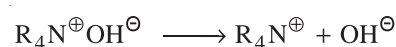
The inductive effect will tend to increase the basicity, but progressively less stabilisation of the cation (conjugate acid) by hydration will occur, which will tend to decrease the basicity. The net effect of introducing successive alkyl groups thus becomes progressively smaller, and a change takes place on going from a secondary to a tertiary amine.

Order of basic strength (in aqueous solutions)



Note : No such changeover is observed when measurement of basicity are made in a solvent in which hydrogen bonding cannot take place. For example in chlorobenzene the order of basicity of the butylamines is $\text{BuNH}_2 < \text{Bu}_2\text{NH} < \text{Bu}_3\text{N}$.

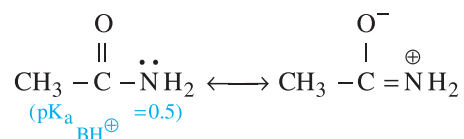
⇒ Tetraalkylammonium hydroxide ($\text{R}_4\text{N}^{\oplus} \text{OH}^{\ominus}$) yield basic solutions comparable in strength with the mineral alkalies. This is because it remain completely ionized and there is no possibility of converting to an unionised form, as with tertiary amines.



⇒ The effect of introducing EWG eg. Cl, NO_2 , close to a basic site is to decrease the basicity, due to their electron withdrawing inductive effect.

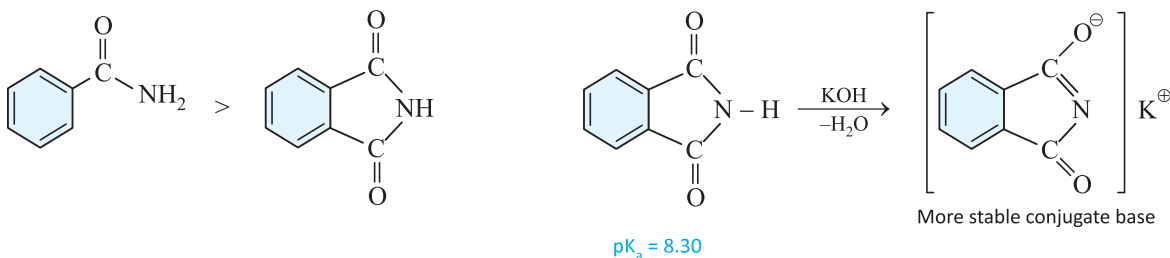
The amine $(\text{CF}_3)_3\ddot{\text{N}}$ is found to be virtually non-basic, due to the three powerfully electron withdrawing CF_3 groups.

⇒ Amides are weaker base than amines due to electron-withdrawing mesomeric effect of $-\text{C}=\text{O}$ group.

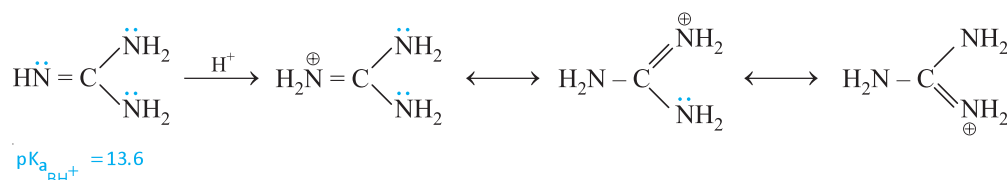


⇒ Imides, far from being basic, are often sufficiently acidic to form alkali metal salts.

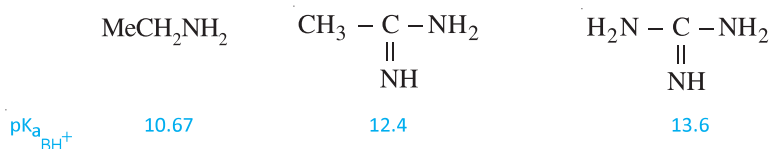
Order of basic strength



⇒ In some cases **delocalisation** of unshared electron pair **increase basic strength** of amines as seen in **guanidine**, $\text{HN}=\text{C}(\text{NH}_2)_2$. **Guanidine is one of the strongest organic nitrogenous bases known**. It is because its conjugate acid ($\text{BH}^\oplus$), $\text{H}_2\text{N}^+=\text{C}(\text{NH}_2)_2$ is stabilized by delocalization of positive charge symmetrically due to the formation of three exactly **equivalent** contributing structures.

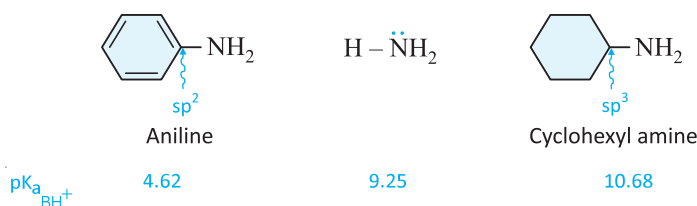


Note : A somewhat analogous situation occurs with the **amidines**, $\text{R}-\text{C}(\text{NH})=\text{NH}_2$

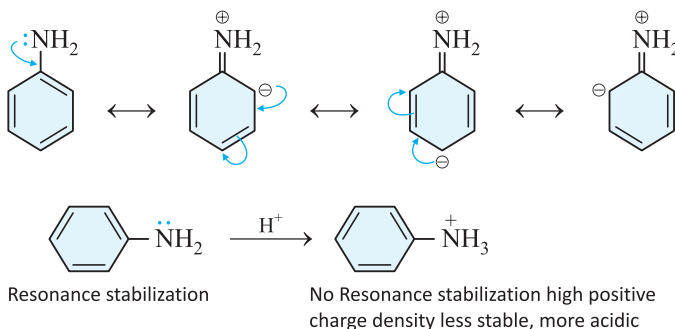


II. Aromatic Bases :

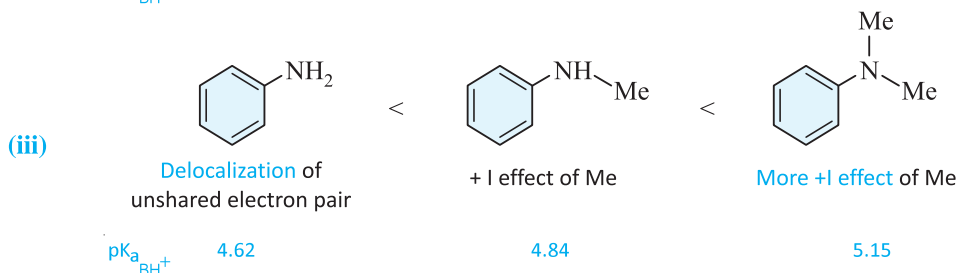
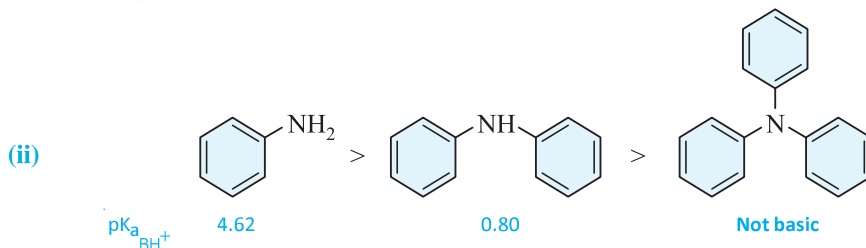
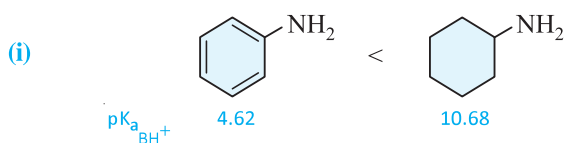
Generally aromatic bases are weaker than aliphatic bases or ammonia.



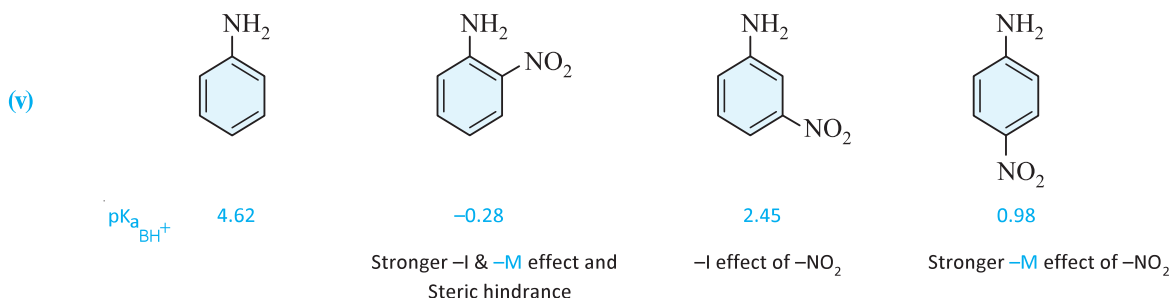
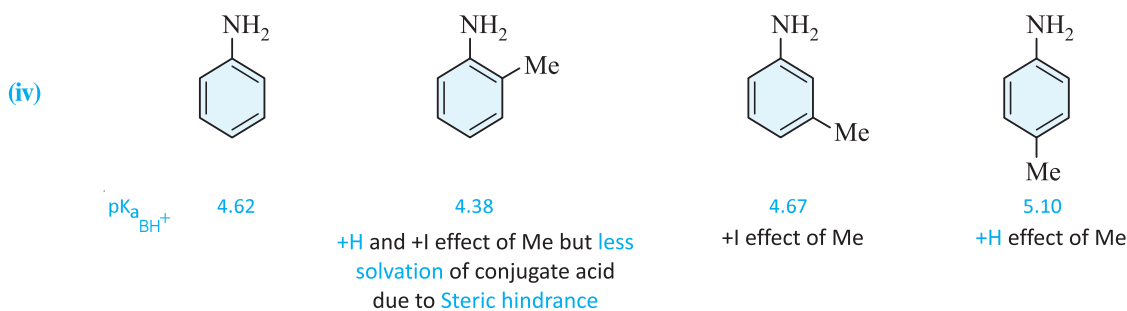
In aniline the nitrogen atom is bonded to an sp^2 hybridised carbon atom but, more significantly the unshared electron pair on nitrogen can participate in delocalization through resonance. Hence there is less availability of electron pair for protonation.



Order of Basic Strength :

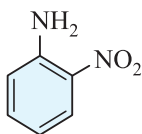


➤ This small increase in basic strength with introduction of alkyl eg. Me group on to the nitrogen atom of aniline, suggest that cation stabilisation through H-bonded solvation [responsible for the irregular behaviour of aliphatic amine] has less influence on the overall effect. The major determinant of basic strength in alkyl-substituted anilines remains mesomeric stabilisation of the aniline molecule [more stabilized by resonance] with respect to the cation.

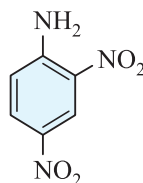


Note : The extra base weakening effect, when the substituent is in the *o*-position is due in part to the short distance over which its inductive effect is operating, and also to direct interaction, both steric and by hydrogen bonding, with the -NH₂ group.

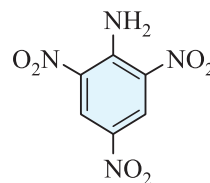
(vi)



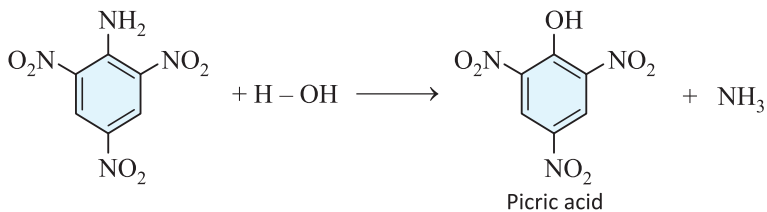
Such a weak base that its salts are largely hydrolysed in aqueous solution



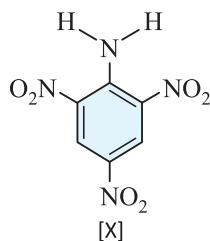
Very weak base insoluble in aqueous acid



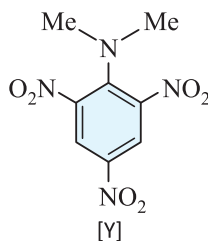
Extremely weak base, it resembles an amide, it is called **picramide** and readily undergoes hydrolysis to picric acid



(vii)



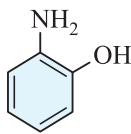
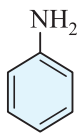
Powerful electron withdrawing **mesomeric effect** of NO_2 groups



No delocalization of lone pair electron in ring and no base weakening by **mesomeric electron withdrawing effect** of NO_2 because of **steric inhibition of resonance**.

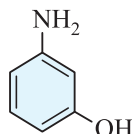
[Y] is about **40,000** times stronger a base than that [X]

(viii)



+R effect
-I effect

Less stabilization of conjugate acid by solvation



-I effect



+R effect

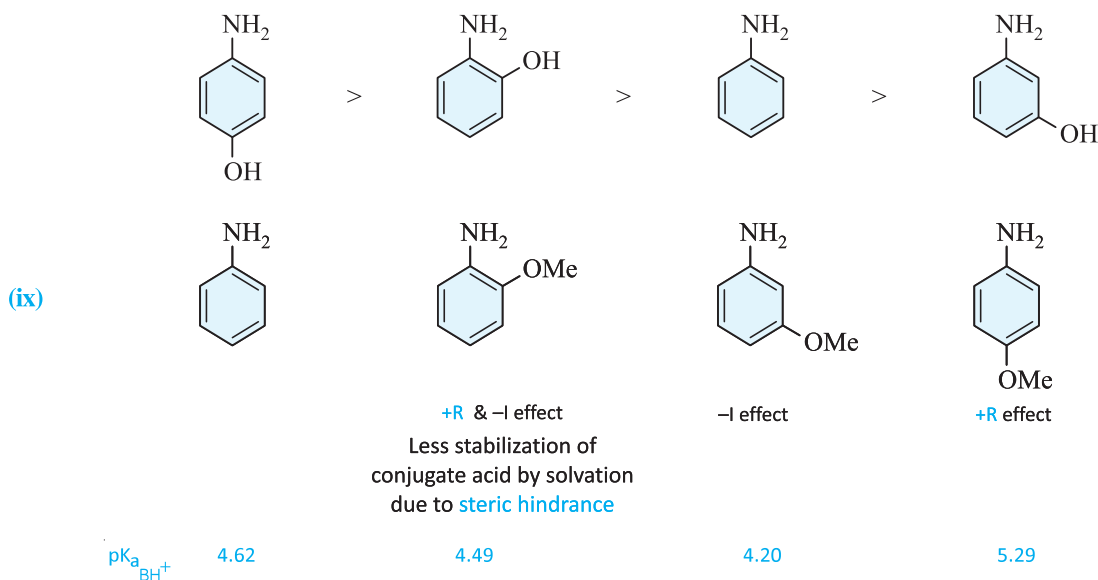
$\text{pK}_{\text{a}}_{\text{BH}^+}$ 4.62

4.72

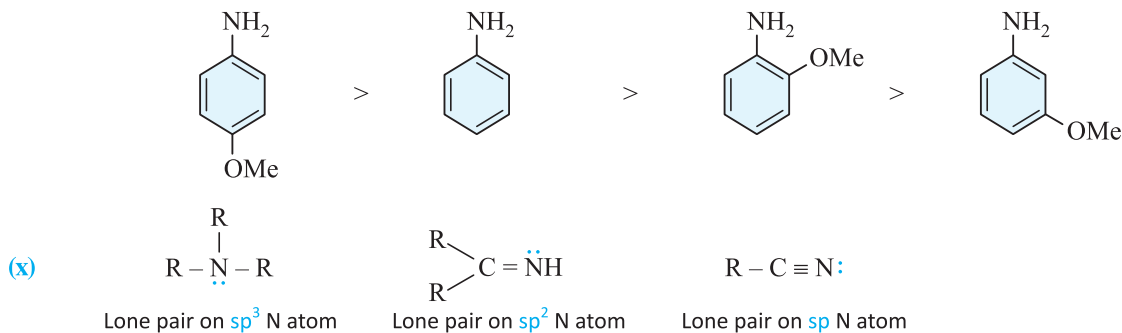
4.17

5.30

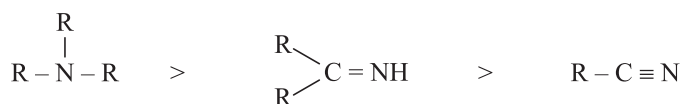
Order of Basic Strength :



Order of Basic Strength :

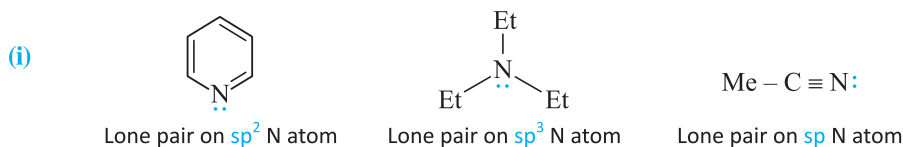


Order of basic strength observed is as follows.

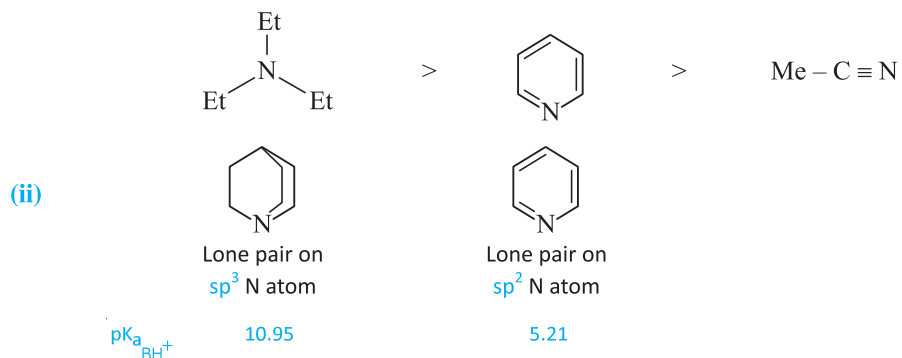


This is due to the fact that as the nitrogen atom becomes progressively more multiple bonded, its lone pair of electrons is accommodated in an orbital that has progressively **more s-character**. The electron pair is thus drawn closer to the **nitrogen nucleus**, and held more tightly by it. Thereby becoming less available for forming a bond with a proton, with decline in the basicity of the compound.

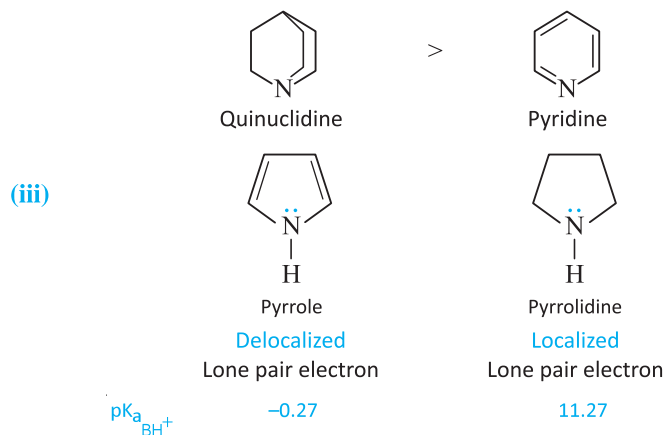
III. Heterocyclic Bases :



Order of Basic Strength :



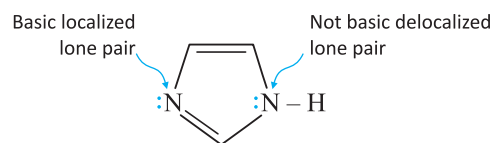
Order of Basic Strength :



Order of Basic Strength :



Most Non-basic (pyrrole - like) nitrogen have three single bonds, and most basic (pyridine-like) nitrogen have a double bond in the ring.



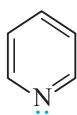
(v)



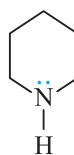
Delocalized lone pair

 $pK_{a_{BH^+}}$

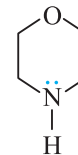
-0.27

Localized lone pair sp^2 N atom

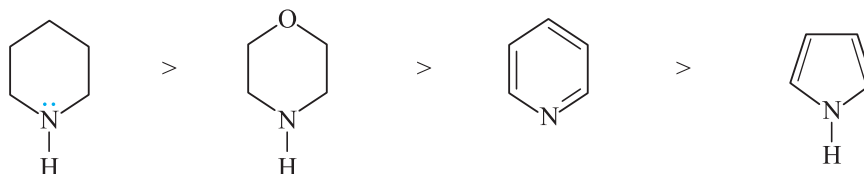
5.21

Localized lone pair sp^3 N atom

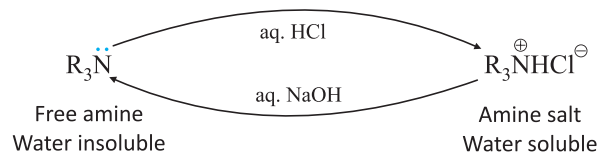
11.12

Localized lone pair sp^3 N atom
- I effect of 'O' atom

9.3

Order of Basic Strength :**Purification and Separation of Amines :**

Protonation of an amine gives an amine salt. These salt are ionic, high melting, non-volatile solids. They are much more soluble in water than the parent amines, and they are only slightly soluble in nonpolar organic solvents. Formation of amine salts can be used to isolate and characterize amines. Most amines containing more than six carbon atoms are relatively insoluble in water. In dilute aqueous acid, these amines form their corresponding ammonium salts, and they dissolve. Formation of a soluble salt is one of the characteristic **functional group tests** for amines.



The formation of amine salts can be used for purification of amine. The amine is initially more soluble in ether than in water. Addition of dilute HCl converts it to the water soluble hydrochloride salt. Neutralization with NaOH regenerate the free amine. The formation of amine salts is also used to separate amines from less basic compounds.

