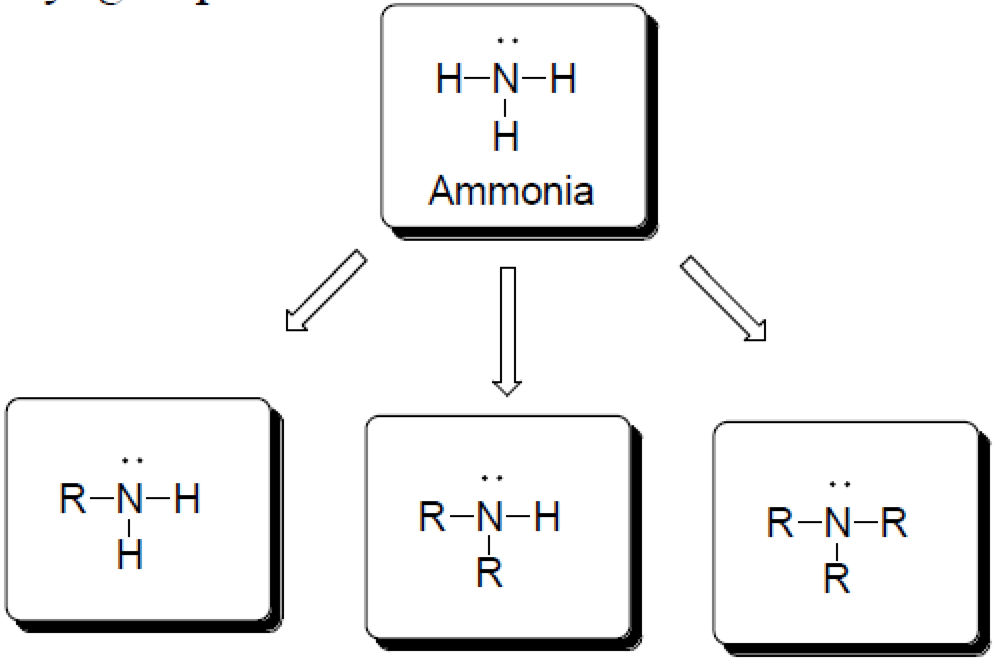
AMINES

Amines

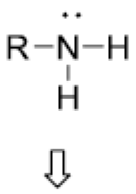
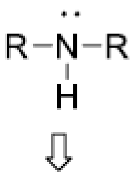
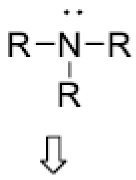
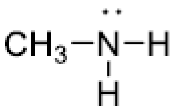
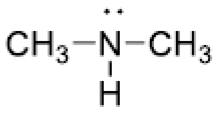
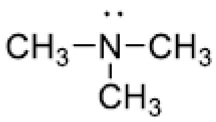
Amines are organic derivatives of ammonia in which one or more of the hydrogen atoms of ammonia have been replaced by alkyl or aryl groups .



Amines

Classification of Amines

Amines are classified as primary, secondary or tertiary based on the degree of substitution on nitrogen (number of alkyl or aryl residues attached to the nitrogen).

	 $\mathrm{R}-\overset{\cdot\cdot}{\underset{\substack{\vert \\ \mathrm{H}}}{\mathrm{N}}}-\mathrm{H}$	 $\mathrm{R}-\overset{\cdot\cdot}{\underset{\substack{\vert \\ \mathrm{H}}}{\mathrm{N}}}-\mathrm{R}$	 $\mathrm{R}-\overset{\cdot\cdot}{\underset{\substack{\vert \\ \mathrm{R}}}{\mathrm{N}}}-\mathrm{R}$
Example	 $\mathrm{CH_3}-\overset{\cdot\cdot}{\underset{\substack{\vert \\ \mathrm{H}}}{\mathrm{N}}}-\mathrm{H}$	 $\mathrm{CH_3}-\overset{\cdot\cdot}{\underset{\substack{\vert \\ \mathrm{H}}}{\mathrm{N}}}-\mathrm{CH_3}$	 $\mathrm{CH_3}-\overset{\cdot\cdot}{\underset{\substack{\vert \\ \mathrm{CH_3}}}{\mathrm{N}}}-\mathrm{CH_3}$
# of substituents	One	Two	Three
Classification	Primary amine	Secondary amine	Tertiary amine

Note the difference in classification of alcohols and amines: Alcohols are classified by the number of alkyl groups on the α-carbon, but amines (as is with amides) are classified by the number of alkyl or aryl groups attached to the nitrogen.

IUPAC Nomenclature of Amines

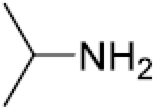
In the IUPAC nomenclature, aliphatic amines are named in two ways depending on the complexity of their structure:

(a) Simple primary amines are named by appending the suffix –**amine** to the name of the alkyl group (radical). Consequently, they are named as **alkylamines or arylamines**.

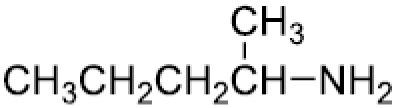
Under this nomenclature, the amino group is presumed to be connected to C-1.

$CH_3CH_2-NH_2$

Ethylamine

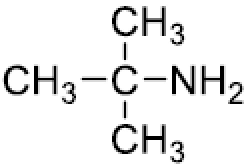


Isopropylamine



$CH_3CH_2CH_2\overset{\overset{\Large CH_3}{|}}{C}H-NH_2$

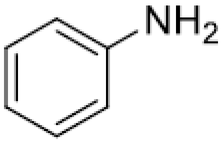
1-Methylbutylamine



$CH_3-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-NH_2$

tert-Butylamine

Cyclohexylamine

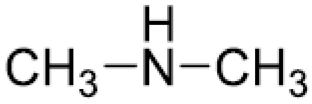


Phenylamine

IUPAC Nomenclature of Amines

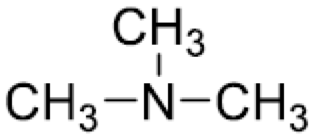
Symmetrical secondary and tertiary amines are named by adding to the name of the radical, a prefix “di-“ or “tri-”, respectively, and the suffix –amine.

Examples



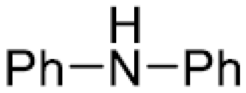
$CH_3-\overset{H}{N}-CH_3$

Dimethylamine



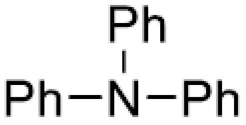
$CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$

Trimethylamine



$Ph-\overset{H}{N}-Ph$

Diphenylamine



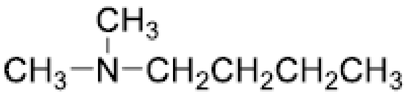
$Ph-\overset{Ph}{\overset{|}{N}}-Ph$

Triphenylamine

IUPAC Nomenclature of Amines

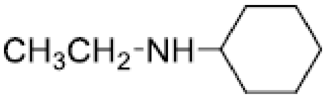
Unsymmetrically substituted secondary and tertiary amines are named as *N*-substituted derivatives of primary amines. The longest carbon chain provides the parent name and the others are considered *N*-substituents of the parent chain. The prefix *N*- (italicized) is added as a locant to identify substituents on the amino nitrogen as needed.

Examples

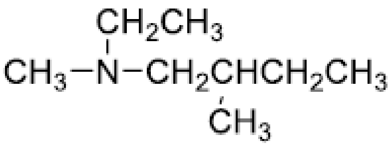


$$\mathrm{CH_3{-}\overset{CH_3}{\overset{|}{N}}{-}CH_2CH_2CH_2CH_3}$$

N,*N*-Dimethylbutylamine

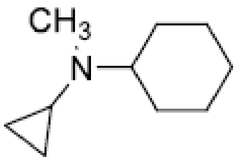


N-Ethylcyclohexylamine



$$\mathrm{CH_3{-}\overset{CH_2CH_3}{\overset{|}{N}}{-}CH_2\underset{\underset{CH_3}{|}}{CH}CH_2CH_3}$$

N-Ethyl-*N*,2-dimethylbutylamine

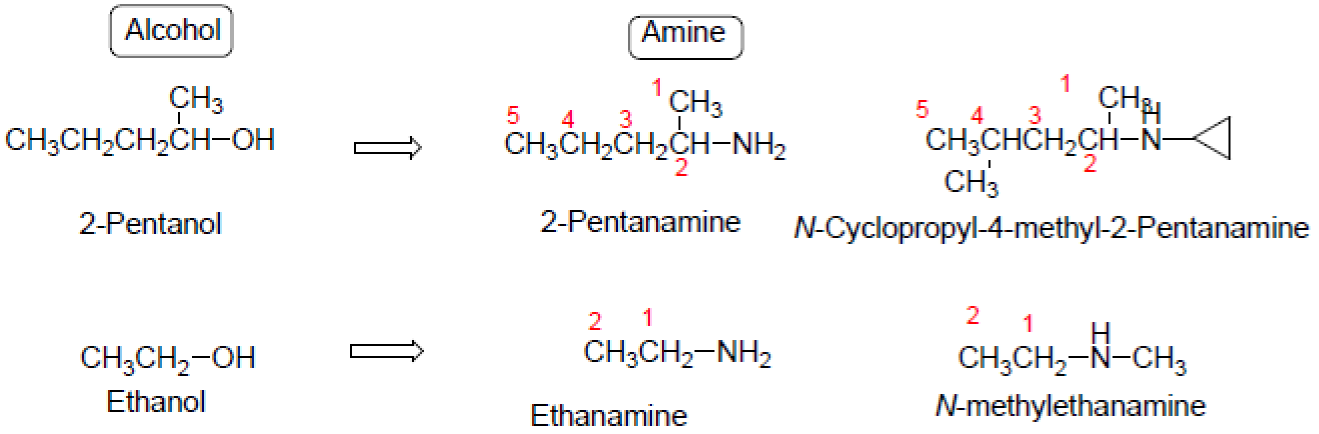


N-Cyclopropyl-*N*-methylcyclohexylamine

IUPAC Nomenclature of Amines

(b) The alternative system of naming aliphatic amines is analogous to that of alcohols. The names of amines are derived by adding the **-amine** suffix to the systematic name of the parent alkane. Consequently, amines are named as **alkanamines**.

The process begins by identifying the longest carbon chain that contains the amino group and then numbering from the end of the chain that gives the amino group the lowest locant.



2-Pentanol

2-Pentanamine

N-Cyclopropyl-4-methyl-2-Pentanamine

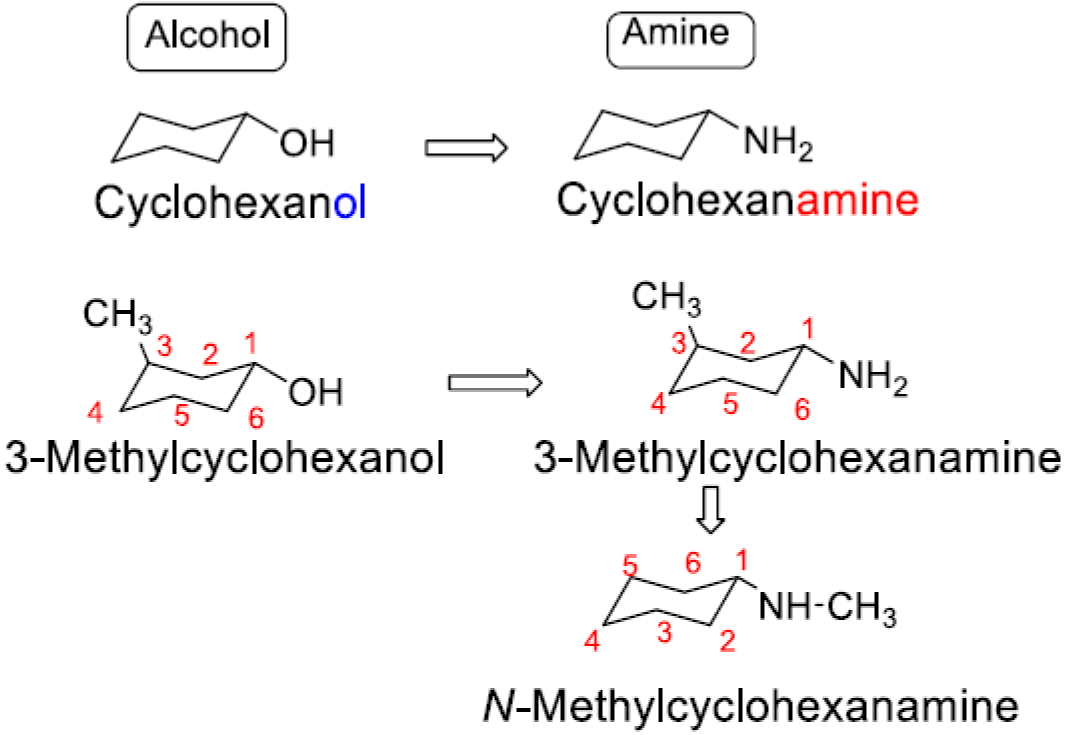
Ethanol

Ethanamine

N-methylethanamine

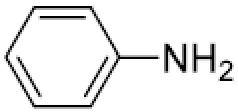
IUPAC Nomenclature of Amines

Aliphatic amines in which the amino group is attached directly to a ring are also named in the same way as **cycloalkanamine**s. The numbering in substituted system begins from the carbon attached to the amino group.

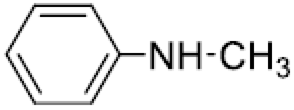


IUPAC Nomenclature of Aromatic Amines

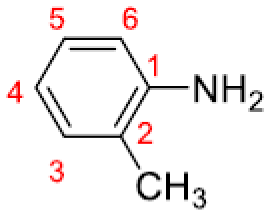
Aromatic amines are named as derivatives of aniline. Substituted anilines are numbered beginning at the carbon that bears the amino group and the direction of numbering is governed by the usual ‘first point of difference’.



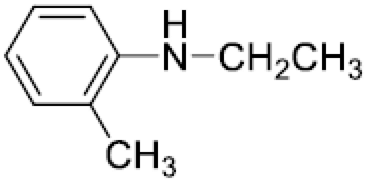
Aniline



N-Methylaniline



2-Methylaniline



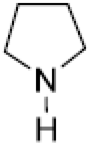
N-Ethyl-2-methylaniline

IUPAC Nomenclature of Heterocyclic Amines

Heterocyclic amines are cyclic compounds in which one or more of the atoms of the ring are nitrogen atoms.

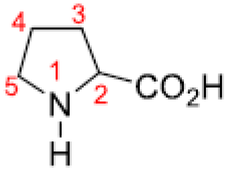
Parent Heterocycle

Derivative



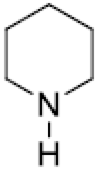
Pyrrolidine

Azacyclopentane



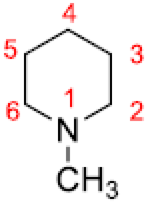
Pyrrolidine-2-carboxylic acid (Proline)

Azacyclopentane-3-carboxylic acid



Piperidine

Azacyclohexane



N-Methylpiperidine

or

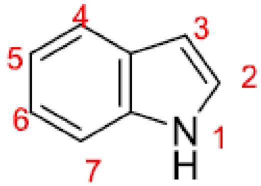
1-Methylpiperidine

IUPAC Nomenclature of Heterocyclic Amines

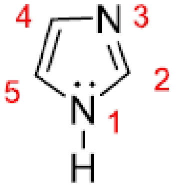
Aromatic heterocyclic amines also exist. The heterocyclic nitrogen is always numbered as position 1

Examples

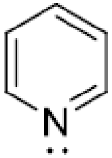
Pyrrole



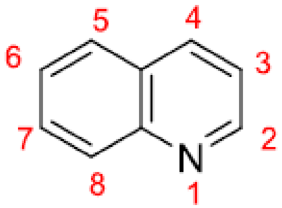
Indole



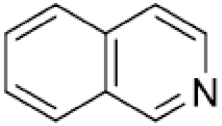
Imidazole



Pyridine



Quinoline



Isoquinoline

Properties of Amines

Physical Properties of Amines

Just like alcohols, amines are polar compounds. However, because nitrogen is less electronegative than oxygen, the N-H bond is less polar than the O-H bond and hydrogen bonds between amine molecules are weaker than those between alcohol molecules.

The polar nature of amines influences many of its physical properties such as boiling point. For similarly constituted compounds, alkylamines have boiling points which are higher than those of alkanes, but lower than those of alcohols.

Examples

	$CH_3CH_2CH_3$	$CH_3CH_2NH_2$	CH_3CH_2OH
	Propane	Ethylamine	Ethanol
Boiling Point	-42 °C	17 °C	78 °C

Physical Properties of Amines

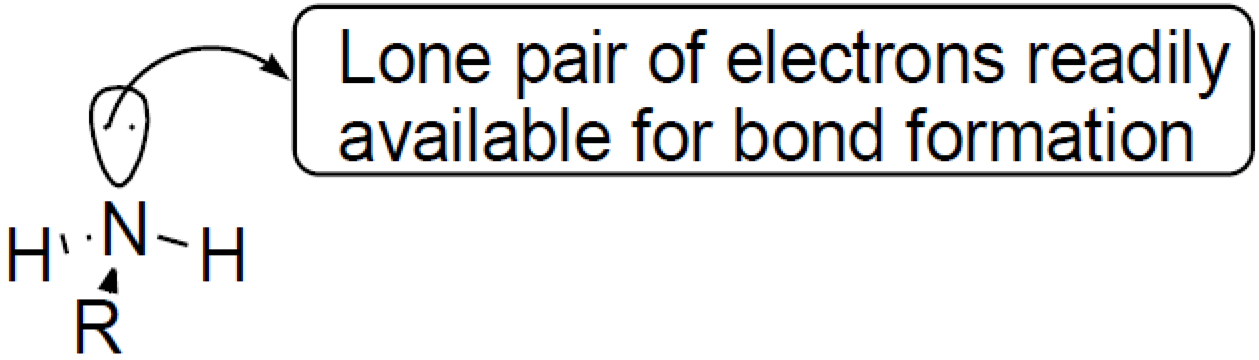
Primary and secondary amines have N-H bonds, allowing them to form intermolecular hydrogen bonds. Because primary amines have two N-H bonds, hydrogen bonding is more significant in primary amines than in secondary amines. Having no N-H bonds, pure tertiary amines cannot engage/participate in hydrogen bonding between their own molecules. Since hydrogen bonding significantly affects the boiling point of compounds, it is not surprising that among isomeric amines, primary amines have the highest boiling points and tertiary amines the lowest.

Examples

	$CH_3CH_2CH_2NH_2$	$CH_3CH_2NHCH_3$	$(CH_3)_3N$
	Propylamine (Primary amine)	*N*-Methylethylamine (Secondary amine)	Triethylamine (Tertiary amine)
Boiling Point	50 ^{o}C	34 ^{o}C	3 ^{o}C

Basicity of Amines

The unshared pair of electrons on the nitrogen atom of an amine dominates the chemistry of amines and is responsible for the basicity (sharing their lone pair of electrons with a proton) and nucleophilicity (sharing their lone pair with an electrophilic carbon) .

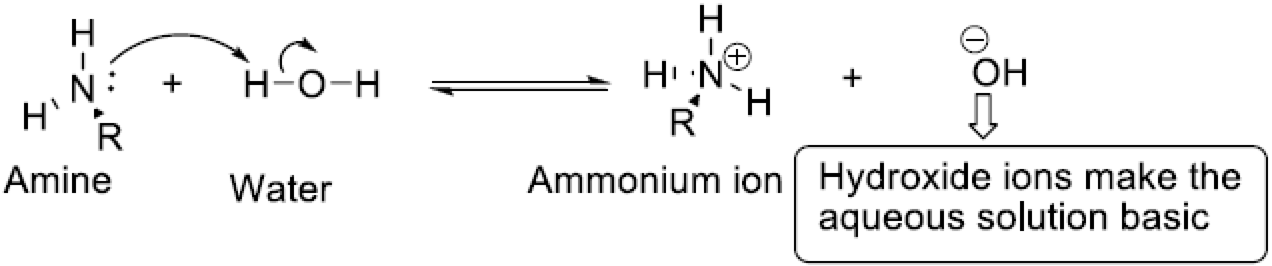


Lone pair of electrons readily available for bond formation

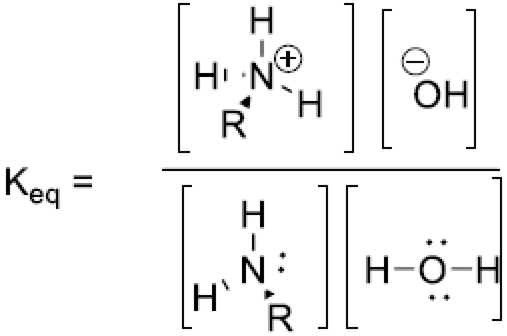
Although amines are weak bases, they are considerably more basic than alcohols, ethers, and water. Indeed as a class of organic compounds, amines are the strongest bases of all neutral molecules.

Basicity of Amines

When an amine is dissolved in water, an equilibrium is established in which the water acts as an acid and transfers a proton to the amine. Aqueous solutions of amines are basic because of the following equilibrium:



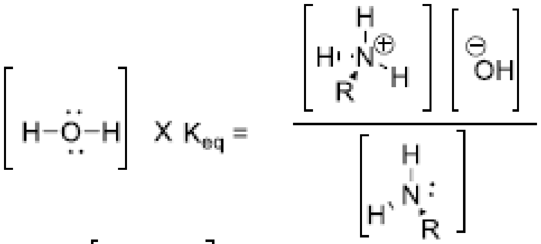
Hydroxide ions make the aqueous solution basic



Basicity of Amines

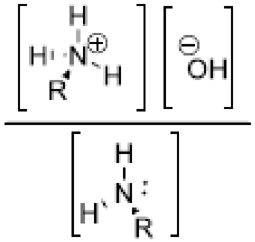
When the measurement is taken in water, the $[H_2O]$ remains fairly constant

Moving the constant $[H_2O]$ to combine it with the equilibrium constant generates the equation:



A new constant $\left[\mathrm{H{-}\ddot{O}{-}H}\right] \times K_{eq}$ called the base constant is obtained

Base constant $\equiv$ K_b =

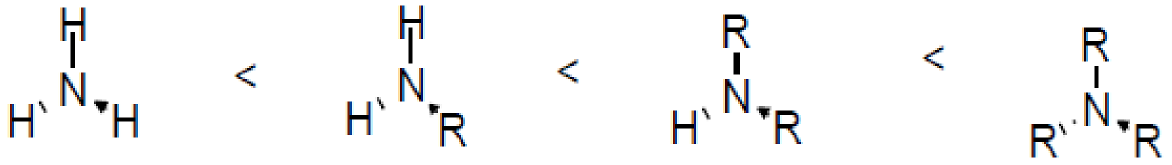


The base constant K_b or its pK_b ($-\log K_b$) can, therefore, be used to compare the relative basicities of the various amines. From the equation, it should be clear that groups (electron-donating) that stabilize the positive charge on nitrogen enhance the basicity of the amine.

Variation of Basicity Among Alkylamines

The basicity of alkylamines in the gas-phase increases in the order:

Order of basicity in gas-phase

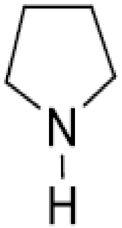


Ammonia (Least basic) < Primary amine < Secondary amine < Tertiary amine (Most basic)

The electron release from alkyl groups provides the principle mechanism by which the conjugate acid of the amine is stabilized in the gas-phase. The more alkyl groups attached to the positively charged nitrogen, the more stable the alkylammonium ion becomes.

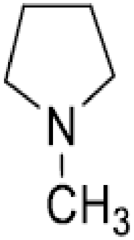
Basicity of Saturated Heterocyclic Amines

Saturated heterocyclic amines are just as basic as the typical acyclic amines that contain the same heteroatom. For example, pyrrolidine, piperidine and morpholine behave like typical secondary amines. *N*-Methylpyrrolidine behaves like a typical tertiary amine.



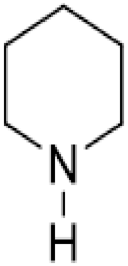
Pyrrolidine

$pK_b = 2.7$



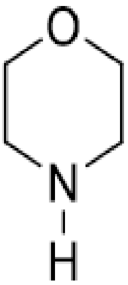
N-Methylpyrrolidine

$pK_b = 3.7$



Piperidine

$pK_b = 2.9$

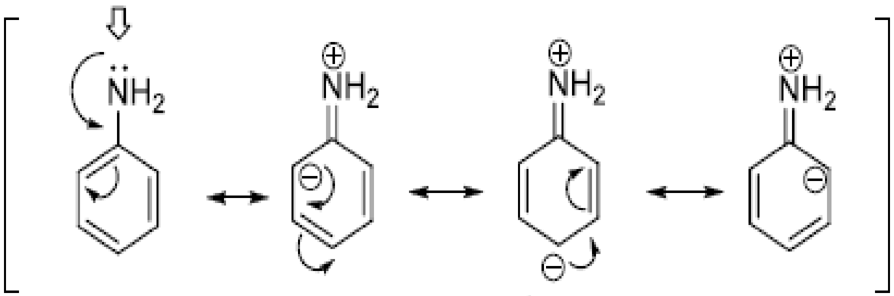


Morpholine

$pK_b = 4.7$

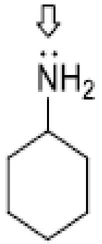
Basicity of Arylamines

Aniline is a weaker base than cyclohexylamine because the electron pair on nitrogen of aniline is delocalized by interaction with the π-system of the aromatic ring and is less readily available for bonding to a proton. The unshared electron pair in cyclohexylamine is localized on nitrogen, less strongly held, and therefore available in an acid-base reaction.



Electron pair in aniline is delocalized into aryl ring hence not readily available to act as a base

Resonance structures for Aniline

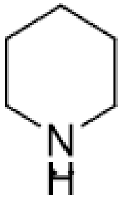


Electron pair localized on nitrogen and hence available to act as a base

Cyclohexylamine

Basicity of Aromatic Heterocyclic Amines

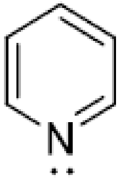
Although non-aromatic heterocyclic amines such as piperidine are similar in basicity to alkylamines, when nitrogen is part of an aromatic ring as in certain heteroaromatic amines such as pyridine, its basicity decreases markedly.



Piperidine

$pK_b = 2.8$

is more basic than



Pyridine

$pK_b = 8.8$

Pyridine is less basic than an alkylamine because the lone pair electrons on nitrogen are held in an sp^2 orbital (more s character thus a smaller orbital, electron more tightly held, less available for sharing), while those in the alkylamine are held in an sp^3 orbital (lesser s character, larger orbital, electron less tightly held and thus more readily available for sharing).

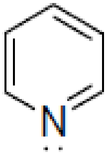
Basicity of Aromatic Heterocyclic Amines

Certain other heteroaromatic amines such as pyrrole in which the electron pair on nitrogen is part of the aromatic electron cloud are even less basic than pyridine.

Aromaticity achieved through participation of lone pair of electron on nitrogen

Pyrrole

$pK_b \sim 15$



Aromaticity achieved without participation of lone pair of electron on nitrogen

Pyridine

$pK_b = 8.8$

Pyridine is more basic than pyrrole since the lone pair of electrons on nitrogen is readily available to initiate bond formation, while that of pyrrole is held up in the aromatic cloud.