



12086CH13

Unit 13 Amines

Objectives

After studying this Unit, you will be able to

- describe amines as derivatives of ammonia having a pyramidal structure;
- classify amines as primary, secondary and tertiary;
- name amines by common names and IUPAC system;
- describe some of the important methods of preparation of amines;
- explain the properties of amines;
- distinguish between primary, secondary and tertiary amines;
- describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.

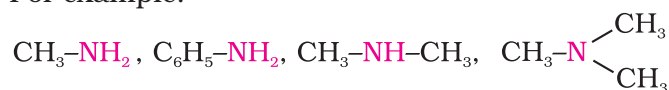
“The chief commercial use of amines is as intermediates in the synthesis of medicines and fibres”.

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dye stuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes. In this Unit, you will learn about amines and diazonium salts.

I. AMINES

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.

For example:



13.1 Structure of Amines

Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore, sp^3 hybridised and the geometry of amines is pyramidal. Each of the three sp^3 hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C-N-E, (where E is

C or H) is less than 109.5° ; for instance, it is 108° in case of trimethylamine as shown in Fig. 13.1.

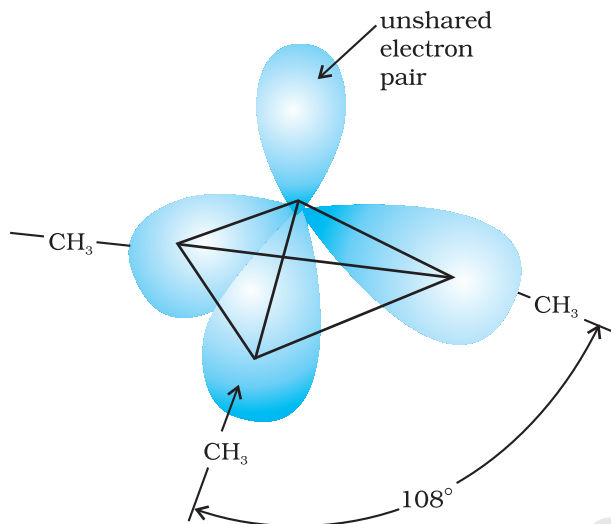
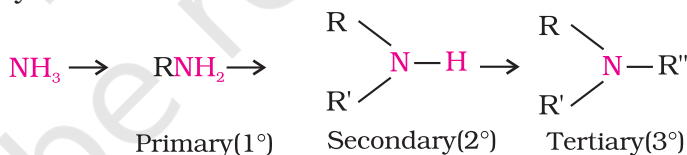


Fig. 13.1 Pyramidal shape of trimethylamine

13.2 Classification

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule. If one hydrogen atom of ammonia is replaced by R or Ar, we get RNH_2 or ArNH_2 , a primary amine (1°). If two hydrogen atoms of ammonia or one hydrogen atom of R-NH_2 are replaced by another alkyl/aryl(R') group, what would you get? You get $\text{R-NHR}'$, secondary amine. The second alkyl/aryl group may be same or different. Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine. Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.



13.3 Nomenclature

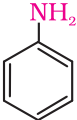
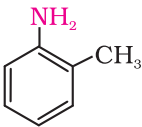
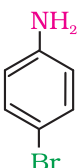
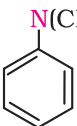
In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g., methylamine). In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In IUPAC system, primary amines are named as **alkanamines**. The name is derived by replacement of 'e' of alkane by the word amine. For example, CH_3NH_2 is named as methanamine. In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to the carbon atoms bearing $-\text{NH}_2$ groups and suitable prefix such as di, tri, etc. is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained. For example, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ is named as ethane-1, 2-diamine.

To name secondary and tertiary amines, we use locant N to designate substituent attached to a nitrogen atom. For example, $\text{CH}_3\text{NHCH}_2\text{CH}_3$ is

named as N-methylethanamine and $(\text{CH}_3\text{CH}_2)_3\text{N}$ is named as N, N-diethylethanamine. More examples are given in Table 13.1.

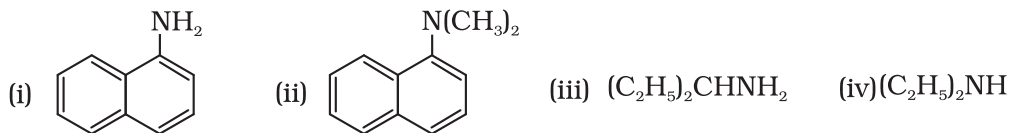
In arylamines, $-\text{NH}_2$ group is directly attached to the benzene ring. $\text{C}_6\text{H}_5\text{NH}_2$ is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name. While naming arylamines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'. Thus in IUPAC system, $\text{C}_6\text{H}_5-\text{NH}_2$ is named as benzenamine. Common and IUPAC names of some alkylamines and arylamines are given in Table 13.1.

Table 13.1: Nomenclature of Some Alkylamines and Arylamines

Amine	Common name	IUPAC name
$\text{CH}_3-\text{CH}_2-\text{NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$	<i>n</i> -Propylamine	Propan-1-amine
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{NH}_2 \end{array}$	Isopropylamine	Propan-2-amine
$\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_2-\text{CH}_3 \\ \\ \text{H} \end{array}$	Ethylmethanamine	N-Methylethanamine
$\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Trimethylamine	N,N-Dimethylmethanamine
$\begin{array}{c} \text{C}_2\text{H}_5-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ \\ \text{C}_2\text{H}_5 \end{array}$	<i>N,N</i> -Diethylbutylamine	<i>N,N</i> -Diethylbutan-1-amine
$\text{NH}_2-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}}=\overset{3}{\text{CH}_2}$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	<i>o</i> -Toluidine	2-Methylaniline
	<i>p</i> -Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	<i>N,N</i> -Dimethylaniline	<i>N,N</i> -Dimethylbenzenamine

Intext Questions

13.1 Classify the following amines as primary, secondary or tertiary:



13.2 (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

(ii) Write IUPAC names of all the isomers.

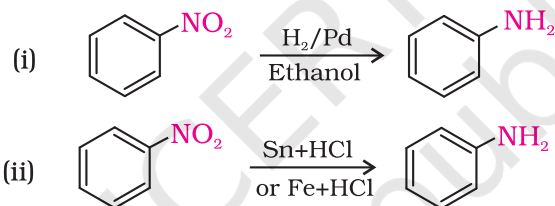
(iii) What type of isomerism is exhibited by different pairs of amines?

13.4 Preparation of Amines

Amines are prepared by the following methods:

1. Reduction of nitro compounds

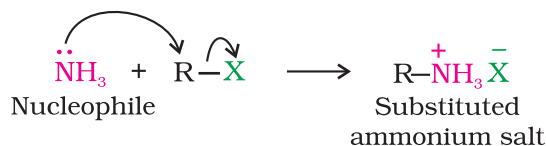
Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

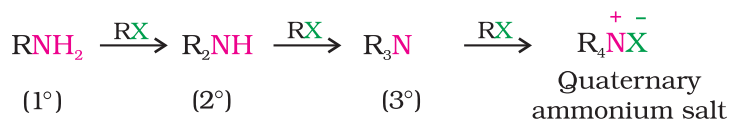


Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

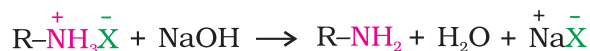
2. Ammonolysis of alkyl halides

You have read (Unit 10, Class XII) that the carbon - halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile. Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group. This process of cleavage of the C-X bond by ammonia molecule is known as **ammonolysis**. The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.





The free amine can be obtained from the ammonium salt by treatment with a strong base:



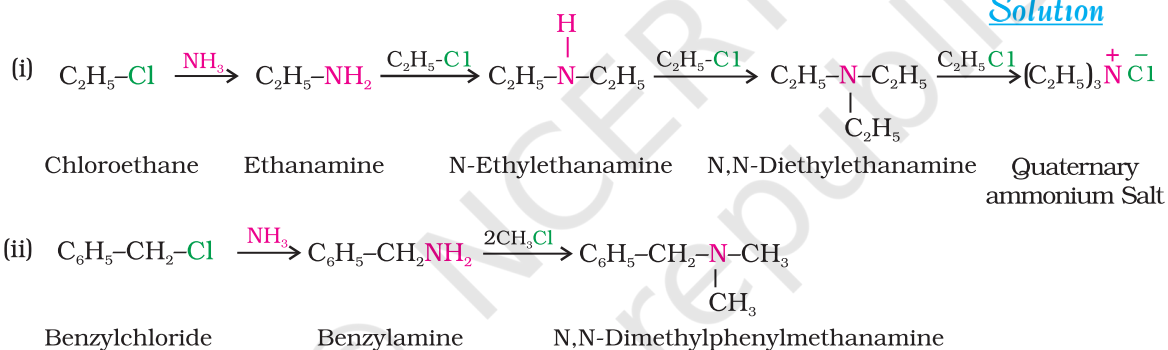
Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of ammonia.

The order of reactivity of halides with amines is $\text{RI} > \text{RBr} > \text{RCl}$.

Write chemical equations for the following reactions:

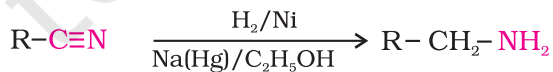
- (i) Reaction of ethanolic NH_3 with $\text{C}_2\text{H}_5\text{Cl}$.
 (ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl .

Example 13.1



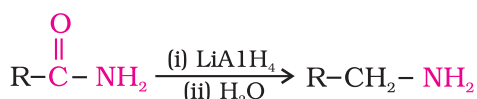
3. Reduction of nitriles

Nitriles on reduction with lithium aluminium hydride (LiAlH_4) or catalytic hydrogenation produce primary amines. This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.



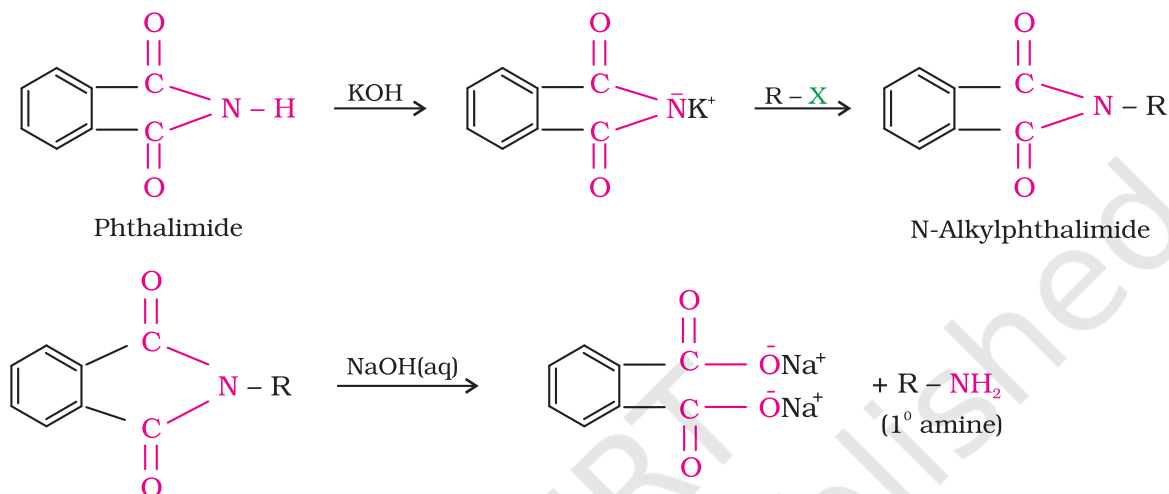
4. Reduction of amides

The amides on reduction with lithium aluminium hydride yield amines.



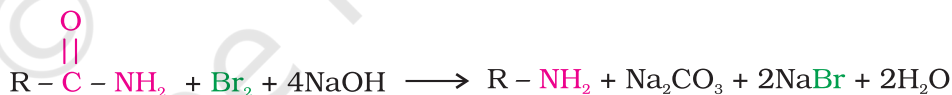
5. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



6. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.

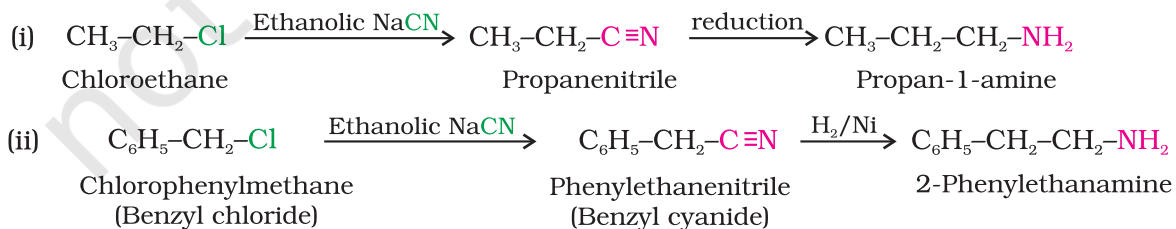


Example 13.2

Write chemical equations for the following conversions:

- (i) $\text{CH}_3-\text{CH}_2-\text{Cl}$ into $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$
- (ii) $\text{C}_6\text{H}_5-\text{CH}_2-\text{Cl}$ into $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{NH}_2$

Solution



Example 13.3

Write structures and IUPAC names of

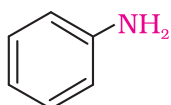
- the amide which gives propanamine by Hoffmann bromamide reaction.
- the amine produced by the Hoffmann degradation of benzamide.

Solution

- Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



- Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Aniline or benzenamine

Intext Question

13.3 How will you convert

- Benzene into aniline
- Benzene into N, N-dimethylaniline
- $\text{Cl-(CH}_2\text{)}_4\text{-Cl}$ into hexan-1,6-diamine?

13.5 Physical Properties

The lower aliphatic amines are gases with fishy odour. Primary amines with three or more carbon atoms are liquid and still higher ones are solid. Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. Considering the electronegativity of nitrogen of amine and oxygen of alcohol as 3.0 and 3.5 respectively, you can predict the pattern of solubility of amines and alcohols in water. Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why? Amines are soluble in organic solvents like alcohol, ether and benzene. You may remember that alcohols are more polar than amines and form stronger intermolecular hydrogen bonds than amines.

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

Intermolecular hydrogen bonding in primary amines is shown in Fig. 13.2.

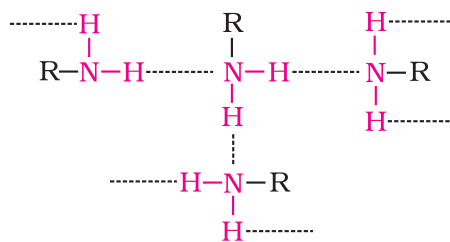


Fig. 13.2 Intermolecular hydrogen bonding in primary amines

Boiling points of amines, alcohols and alkanes of almost the same molar mass are shown in Table 13.2.

Table 13.2: Comparison of Boiling Points of Amines, Alcohols and Alkanes of Similar Molecular Masses

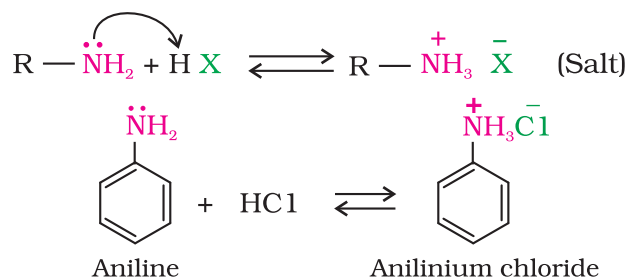
Sl. No.	Compound	Molar mass	b.p./K
1.	n-C ₄ H ₉ NH ₂	73	350.8
2.	(C ₂ H ₅) ₂ NH	73	329.3
3.	C ₂ H ₅ N(CH ₃) ₂	73	310.5
4.	C ₂ H ₅ CH(CH ₃) ₂	72	300.8
5.	n-C ₄ H ₉ OH	74	390.3

13.6 Chemical Reactions

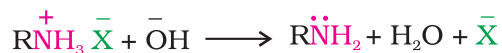
Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive. The number of hydrogen atoms attached to nitrogen atom also decides the course of reaction of amines; that is why primary (–NH₂), secondary (>N-H) and tertiary amines (>N-) differ in many reactions. Moreover, amines behave as nucleophiles due to the presence of unshared electron pair. Some of the reactions of amines are described below:

1. Basic character of amines

Amines, being basic in nature, react with acids to form salts.

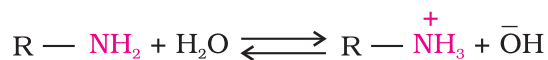


Amine salts on treatment with a base like NaOH, regenerate the parent amine.



Amine salts are soluble in water but insoluble in organic solvents like ether. This reaction is the basis for the separation of amines from the non basic organic compounds insoluble in water.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as **Lewis base**. Basic character of amines can be better understood in terms of their K_b and $\text{p}K_b$ values as explained below:



$$K = \frac{[\text{R} - \overset{+}{\text{N}}\text{H}_3][\text{OH}^-]}{[\text{R} - \text{NH}_2][\text{H}_2\text{O}]}$$

$$\text{or } K[\text{H}_2\text{O}] = \frac{[\text{R} - \overset{+}{\text{N}}\text{H}_3][\text{OH}^-]}{[\text{R} - \text{NH}_2]}$$

$$\text{or } K_b = \frac{[\text{R} - \overset{+}{\text{N}}\text{H}_3][\text{OH}^-]}{[\text{R} - \text{NH}_2]}$$

$$\text{p}K_b = -\log K_b$$

Larger the value of K_b or smaller the value of $\text{p}K_b$, stronger is the base. The $\text{p}K_b$ values of few amines are given in Table 13.3.

$\text{p}K_b$ value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom. Their $\text{p}K_b$ values lie in the range of 3 to 4.22. On the other hand, aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group.

Table 13.3: $\text{p}K_b$ Values of Amines in Aqueous Phase

Name of amine	$\text{p}K_b$
Methanamine	3.38
<i>N</i> -Methylmethanamine	3.27
<i>N,N</i> -Dimethylmethanamine	4.22
Ethanamine	3.29
<i>N</i> -Ethylethanamine	3.00
<i>N,N</i> -Diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
<i>N</i> -Methylaniline	9.30
<i>N,N</i> -Dimethylaniline	8.92

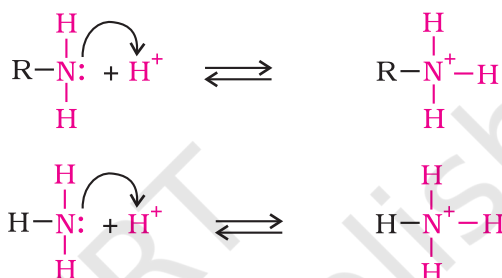
You may find some discrepancies while trying to interpret the K_b values of amines on the basis of +I or -I effect of the substituents present in amines. Besides inductive effect, there are other effects like solvation effect, steric hinderance, etc., which affect the basic strength of amines. Just ponder over. You may get the answer in the following paragraphs.

Structure-basicity relationship of amines

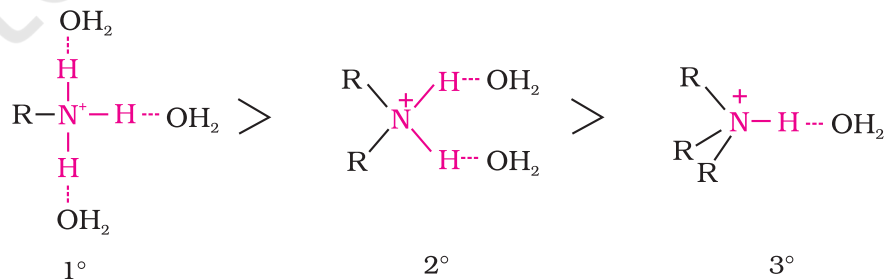
Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

(a) Alkanamines versus ammonia

Let us consider the reaction of an alkanamine and ammonia with a proton to compare their basicity.

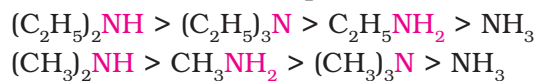


Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups. This trend is followed in the gaseous phase. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3 . The trend is not regular in the aqueous state as evident by their $\text{p}K_b$ values given in Table 13.3. In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. The order of stability of ions are as follows:



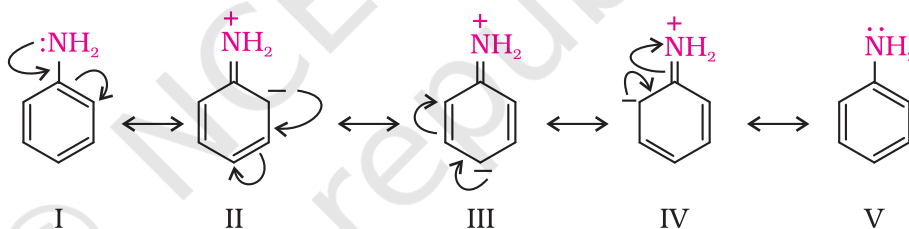
Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.

Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order. Secondly, when the alkyl group is small, like $-\text{CH}_3$ group, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH_3 group, there will be steric hindrance to H-bonding. Therefore, the change of nature of the alkyl group, e.g., from $-\text{CH}_3$ to $-\text{C}_2\text{H}_5$ results in change of the order of basic strength. Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hindrance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

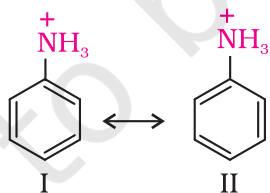


(b) Arylamines versus ammonia

$\text{p}K_b$ value of aniline is quite high. Why is it so? It is because in aniline or other arylamines, the $-\text{NH}_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. If you write different resonating structures of aniline, you will find that aniline is a resonance hybrid of the following five structures.



On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).



We know that greater the number of resonating structures, greater is the stability. Thus you can infer that aniline (five resonating structures) is more stable than anilinium ion. Hence, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like $-\text{OCH}_3$, $-\text{CH}_3$ increase basic strength whereas electron withdrawing groups like $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{X}$ decrease it.