SRI AKILANDESWARI WOMEN'S COLLEGE, WANDIWASH

AMINES

Class : II UG CHEMISTRY

Mrs.S. PREMA

Assistant Professor

Department of Chemistry

SWAMY ABEDHANADHA EDUCATIONAL TRUST, WANDIWASH

Amines

Amines are carbon – hydrogen – nitrogen compounds.

Amines occurs widely in living organisms.

Many amines are naturally occurring compounds that are very active physiologically.

Numerous drugs used for the treatment of mental illness, hay fever, heart problems, and other physical disorders are amines.

Bonding Characteristics of Nitrogen Atoms in Organic Compounds

An understanding of the bonding characteristics of the Nitrogen atom is a prerequisite to our study of amines.

Nitrogen is a member of Group VA of the periodic table; it has five valence electrons

and it will form three covalent bonds to complete its octet of electrons.

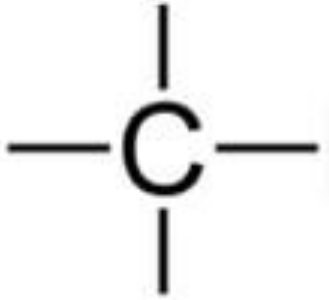
In Organic Chemistry,

carbon forms four bonds.

4 valence electron

4 covalent bond

No nonbonding electron pair

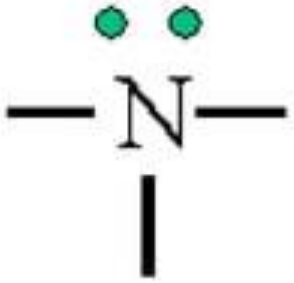


nitrogen forms three bonds

5 valence electron

3 covalent bond

1 nonbonding electron pair



Oxygen forms two bonds

6 valence electron

2 covalent bond

2 nonbonding electron pair

Structure and Classification of Amines

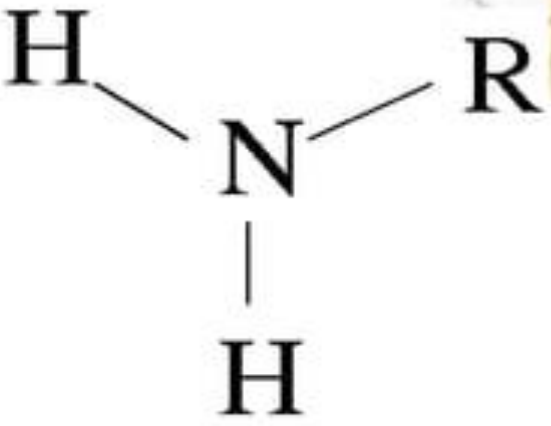
An Amine is an organic derivative of **ammonia** (NH_4) in which one or more **alkyl**, **cycloalkyl**, or **aryl** groups are attached to the **nitrogen** atom.

Amines are classified as **primary** (1^0), **secondary** (2^0), or **tertiary** (3^0) on the basis of how many hydrocarbon groups are bonded to the ammonia nitrogen atom.

Primary Amine

Is an amine in which the nitrogen atom is bonded to one hydrocarbon group and two hydrogen atoms.

The generalized formula for a primary amine is **RNH_2**.



The functional group present in a primary amine, the NH_2 group is called an **Amino group.**

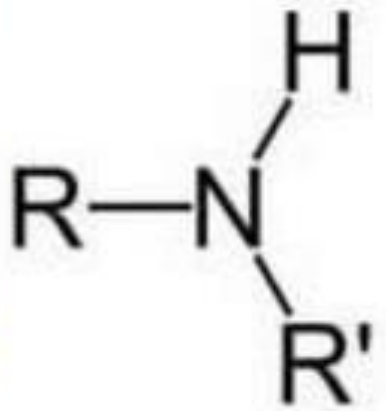
An Amino group is the NH_2 functional group.

$CH_3 - NH_2$

Secondary Amine

Is an amine in which the nitrogen atom is bonded to two hydrocarbon groups and one hydrogen atom.

The generalized formula for a secondary amine is $\mathbf{R_2NH}$.

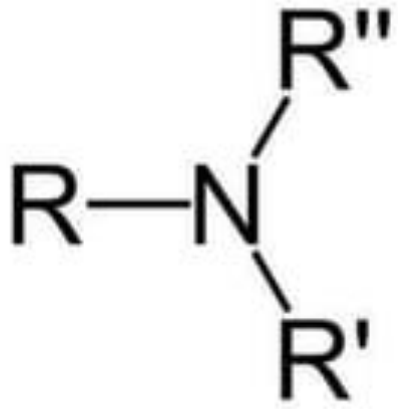


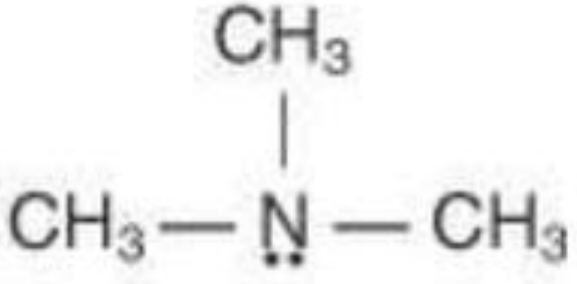
$CH_3 - NH - CH_3$

Tertiary Amine

Is an amine in which the nitrogen atom is bonded to three hydrocarbon groups and no hydrogen atom.

The generalized formula for a tertiary amine is **R_3N.**





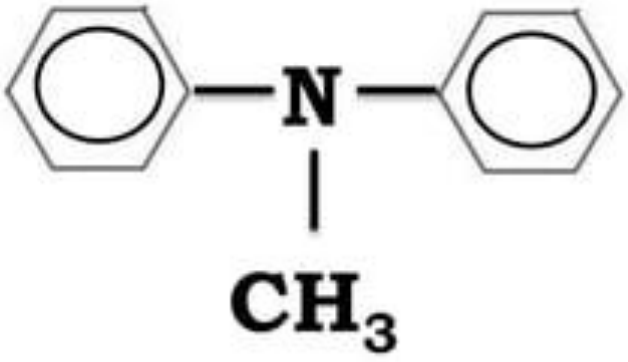
Classify Amines each of the following Amines as a Primary, Secondary, or Tertiary

1) $CH_3 - NH$ 

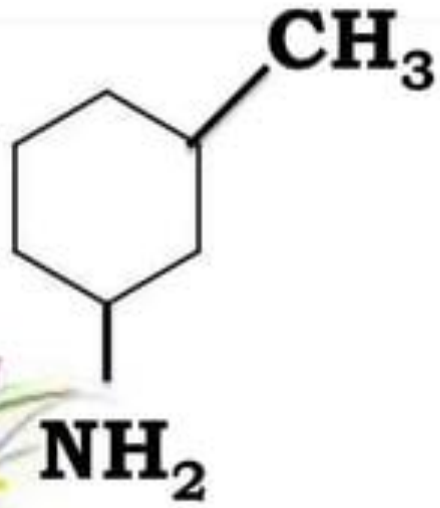
This is a secondary amine because the nitrogen is bonded to both a methyl group and phenyl group

2) $CH_3 - N(CH_3) - CH_3$

Here we have a tertiary amine because the nitrogen atom is bonded to three methyl groups.

3) 

This is also a tertiary amine; the nitrogen atom is bonded to two phenyl groups and a methyl group.

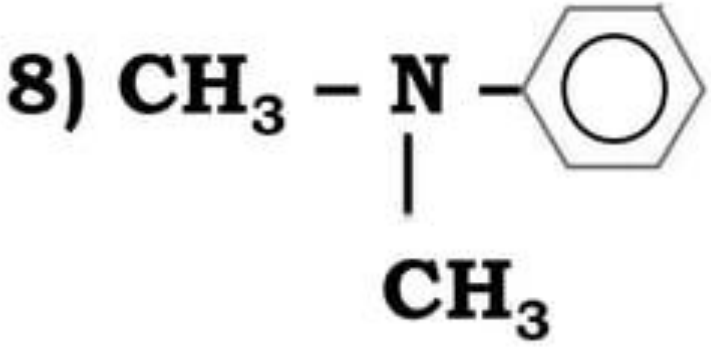
4) 

This is a primary amine. The nitrogen atom is bonded to only one carbon atom.

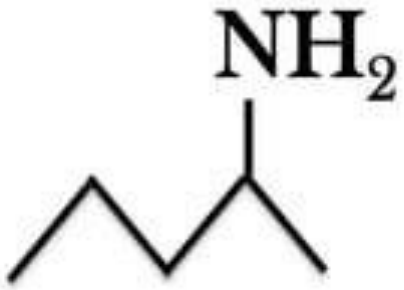
5) $CH_3 - CH_2 - CH_2 - NH_2$ 1^0

6)  1^0

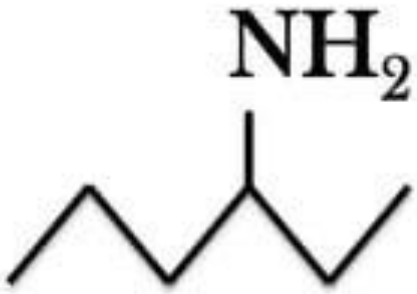
7) $CH_3 - NH - CH_2 - CH_3$ 2^0

8)  3^0

1) 1^0



2) 1^0



3) 1^0

4) 2^0

5) 3^0

Physical Properties of Amines

The methylamines (mono-, di-, tri-) and ethylamine are gases at room temperature and have ammonia-like odors.

Most other amines are liquid, and many have odor resembling that of raw fish.

A few amines, particularly diamines, have strong, disagreeable odors.

The foul odor arising from dead fish and decaying flesh is due to amines released by the bacterial decomposition of protein.

Diamines putrescine and cadaverine are two "odoriferous" compounds.

$H_2N-(CH_2)_4-NH_2$ $H_2N-(CH_2)_5-NH_2$

Putrescine
1,4-butanediamine

Cadaverine
1,5-pentanediamine

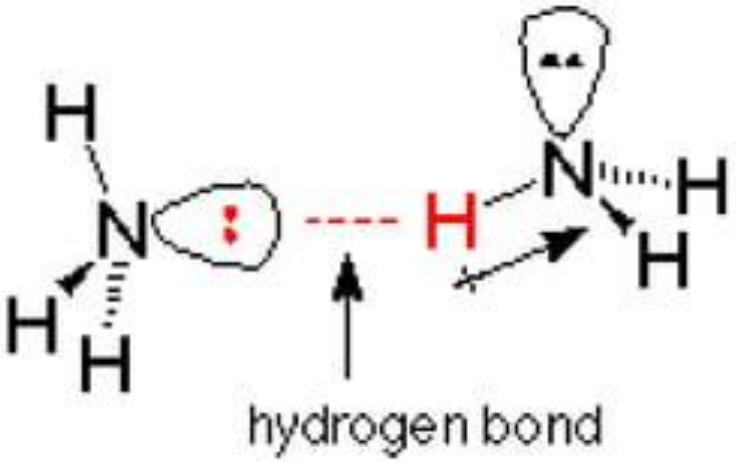
The simples amines are irritating to the skin, eyes, and mucous membranes and are toxic by ingestion.

Aromatic amines are generally toxic.

Many amines are readily absorbed through the skin and affect both the blood and the nervous system.

The boiling points of amines are intermediate between those of alkanes and alcohols of similar molecular mass.

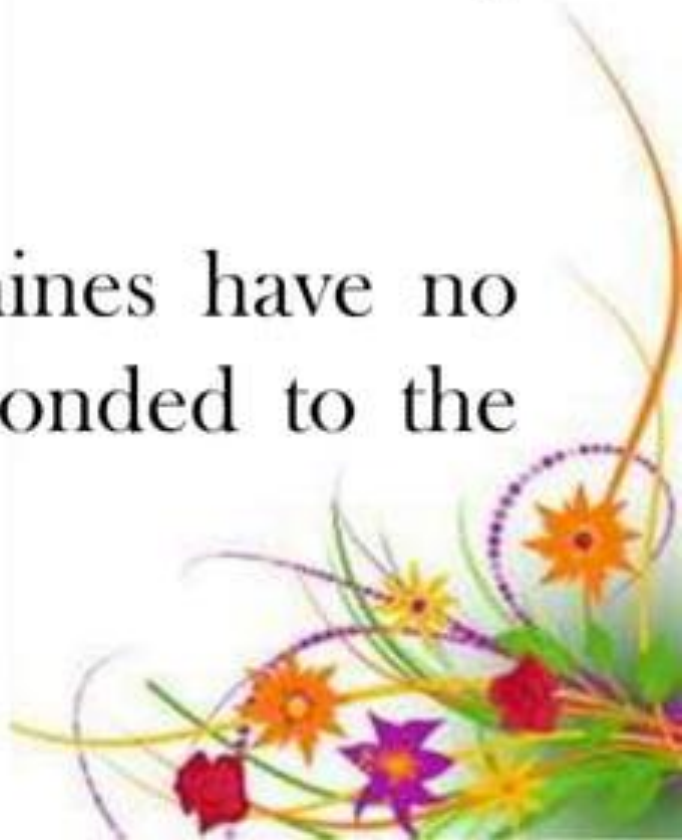
Amines are higher than alkane boiling point, because hydrogen bonding is possible between amine molecules but not between alkane molecules.



Intermolecular hydrogen bonding of amines involves the hydrogen atoms and nitrogen atoms of the amino group.

Tertiary amines have lower boiling point than primary and secondary amines because intermolecular hydrogen bonding is not possible in tertiary amines.

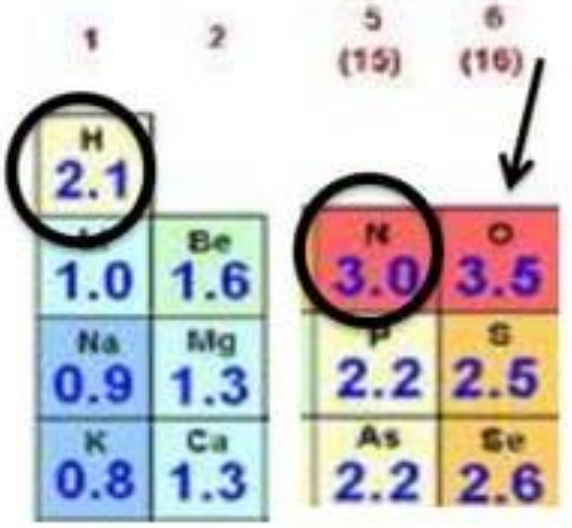
Secondary and tertiary amines have no hydrogen atoms directly bonded to the nitrogen atom.



The boiling point of amines are lower than those of corresponding alcohols, because N – H bonds are weaker than O – H bonds.

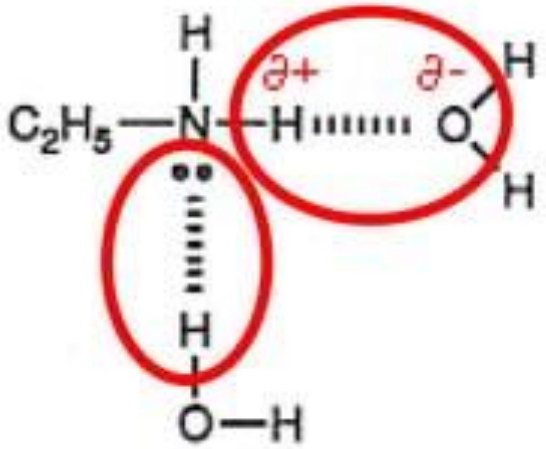
Note: The difference in hydrogen-bond strength results from electronegativity differences, nitrogen is less electronegative than oxygen.

Element	Electronegativity values	Difference
Nitrogen	3.0	0.9
Hydrogen	2.1	
Oxygen	3.5	1.4
Hydrogen	2.1	



Amines with fewer than six carbon atoms are infinitely soluble in water.

This solubility results from hydrogen bonding between the amines and water.



Even tertiary amines are water-soluble, because amine nitrogen atom has a nonbonding electron pair that can form a hydrogen bond with a hydrogen atom of water.

Basicity of Amines

Amines, like ammonia, are **weak bases.**

Ammonia's weak-base behavior results from its accepting a proton (H^+) from water to produce ammonium ion (NH_4^+) and hydroxyl ion (OH^-)

$$NH_3 + HOH = NH_4^+ + OH^-$$

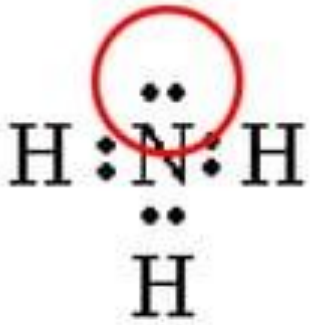
ammonia — Ammonium ion — Hydroxide ion

Amines behave in a similar manner.

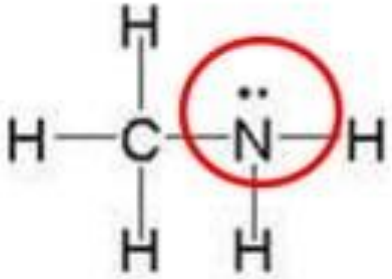
$$CH_3 - NH_2 + H\,OH = CH_3 + \overset{+}{N}H_3 + OH^-$$

Methylamine — Methylammonium ion — Hydroxide ion

Amines, like ammonia, have a pair of unshared electrons on the nitrogen atom present.

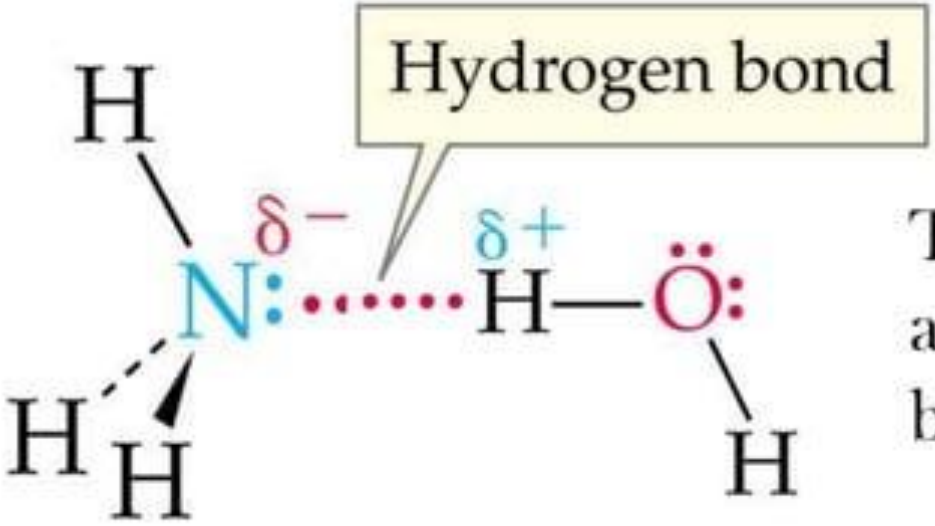


ammonia



amine

These unshared electrons can accept a hydrogen ion from water.



Thus, both amines and ammonia produce basic aqueous solution

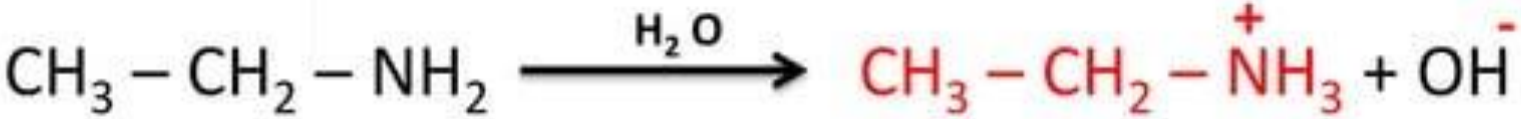
The result of the interaction of an amine with water is a basic solution containing **substituted ammonium ions** and hydroxide ions.

A substituted ammonium ion is an ammonium ion in which one or more alkyl, cycloalkyl, or aryl groups have been substituted for hydrogen atom.

Substituted ammonium ions always contain one or more hydrogen atom than their "parent" amine. They also always carry a +1 charge, whereas the "parent" amine is a neutral molecule.

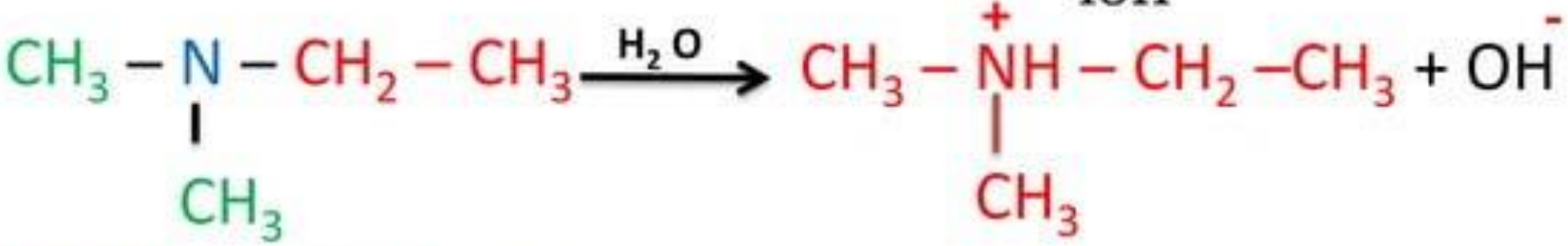
Naming the positive ion that results from the interaction of an amine with water is based on the following two rules:

Rule 1: For alkylamine, the ending of the name of the amine is changed from amine to ammonium ion



Ethylamine

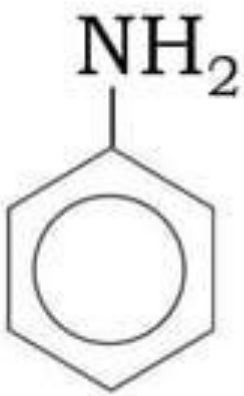
Ethylammonium ion



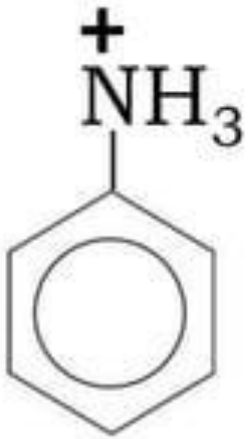
Ethyldimethylamide

Ethyldimethylammonium ion

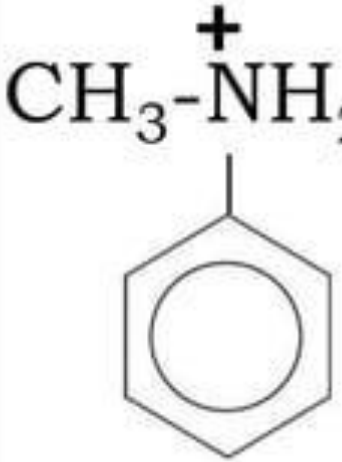
Rule 2: For aromatic amines, the final ***–e*** of the name of the amine is replaced by ***–ium*** ion.



Aniline

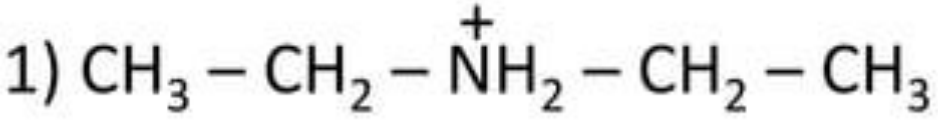


Anilinium ion



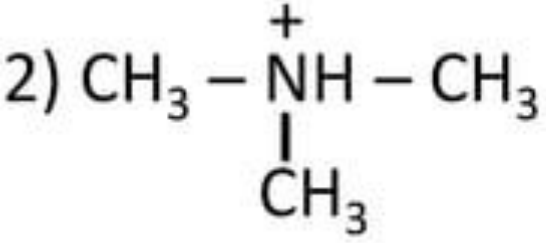
N – methylanilinium ion

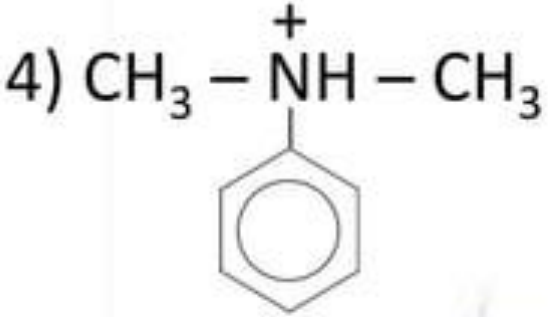
Name the following substituted ammonium or substituted anilinium ions.

1) 

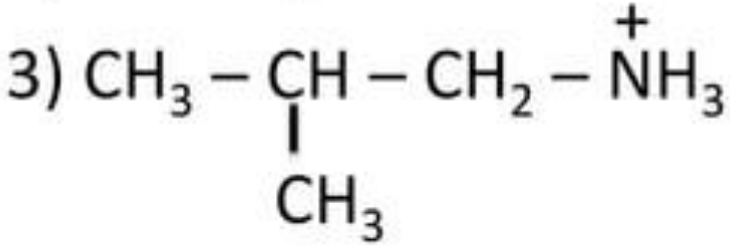
1) diethylammonium ion

2) trimethylammonium ion

2) 

4) 

3) isobutylammonium ion

3) 

4) N,N dimethylanilinium ion

5) $CH_3 - CH_2 - NH_2 - CH_3$

5) Ethylmethylammonium ion

6) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - NH_3$

6) Isopropylammonium ion

7) $CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{NH}} - CH_2 - CH_3$

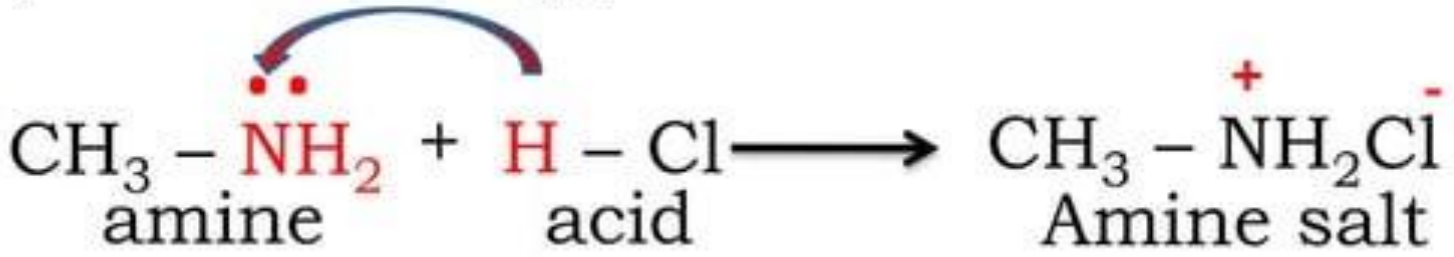
7) Diethylmethylammonium ion

8) $NH_2 - CH_2 - CH_2 - CH_3$

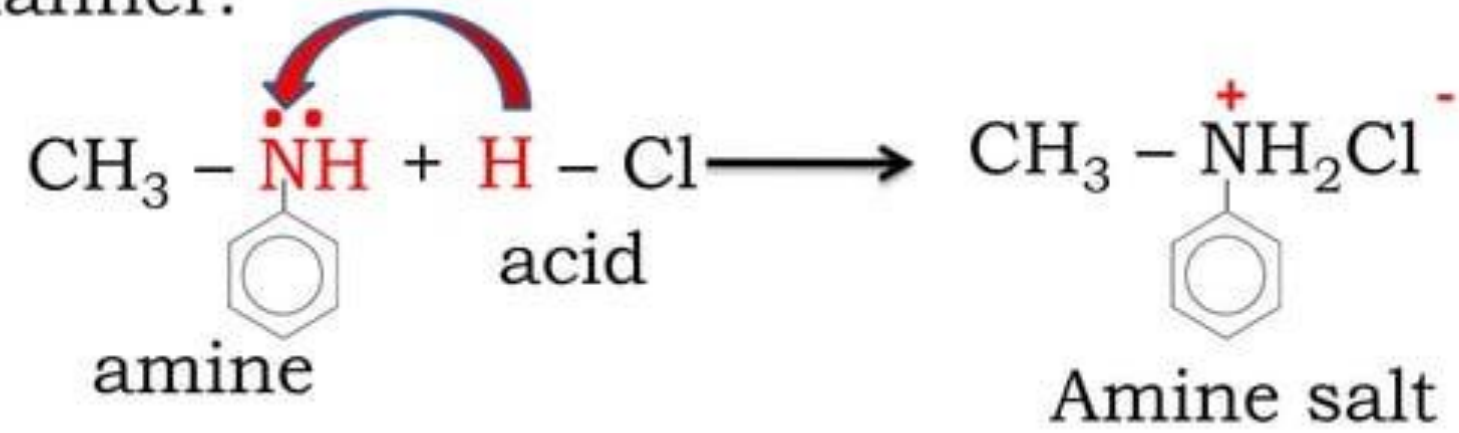
8) N-propylanilinium ion

Amine Salt

The reaction of an acid with a base (neutralization) produces a salt.



Aromatic amines react with acids in a similar manner.



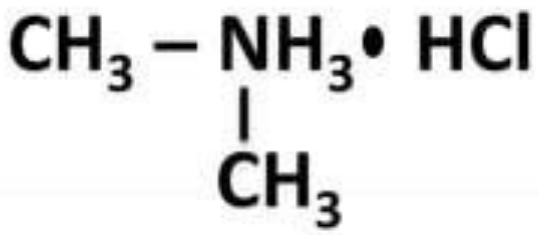
An amine salt is an organic compound in which the positive ion is a mono-, di-, or trisubstituted ammonium ion ($\mathbf{RNH_3^+}$, $\mathbf{R_2NH_2^+}$, or $\mathbf{R_3NH^+}$) and the negative ion comes from an acid.

Amine salt can be obtained in crystalline form (odorless, white crystals) by evaporating the water from the acidic solutions in which amine salt are prepared.

Amine salt are named using standard nomenclature procedures for ionic compound.

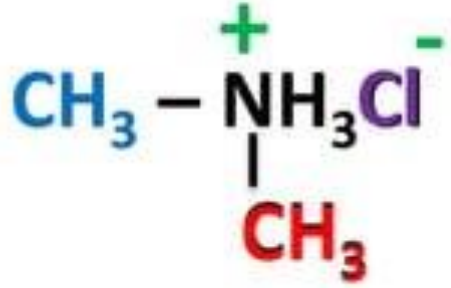
The name of the positive ion, the substituted ammonium or anilinium ion, is given first and followed by a separate word for the name of the negative ion.

An older system for amine slats, still used in the pharmaceutical industry, treat amine salts as amine- acid complexes rather than as ionic compound.



Dimethylamine hydrochloride

Rather than as



dimethylammonium chloride

Many people unknowingly use acids to form amine slats when they put vinegar or lemon juice on fish.

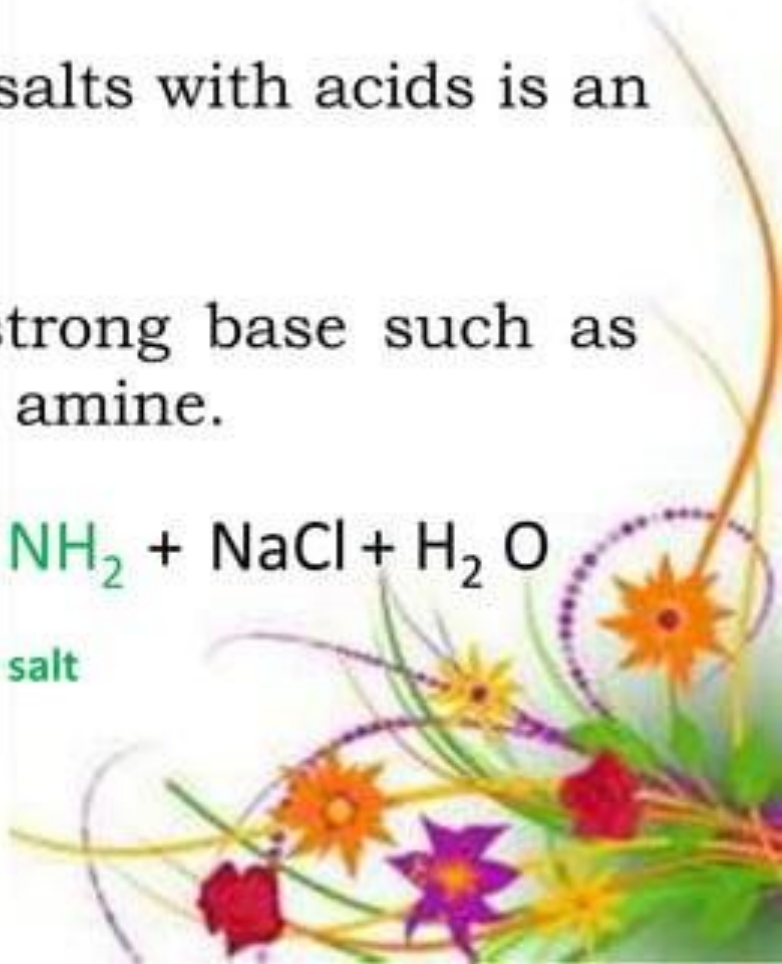
Such action converts amines in fish (often smelly compounds) to salts, which are odorless.

The process of forming amine salts with acids is an easily reversed process.

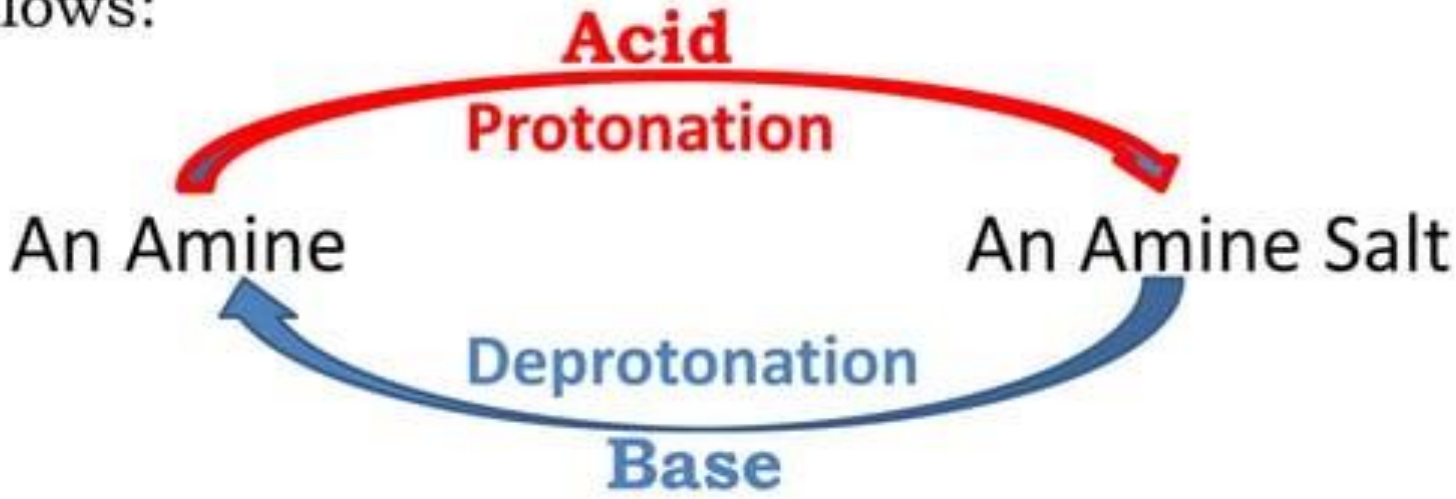
Treating amine salts with a strong base such as NaOH regenerates the "parent" amine.

$$CH_3 - NH_3\,Cl + NaOH \rightarrow CH_3 - NH_2 + NaCl + H_2O$$

Amine salt base Amine salt



The "opposite nature" of the processes of amine salt formation from an amine and the regeneration of the amine from its amine salt can be diagrammed as follows:

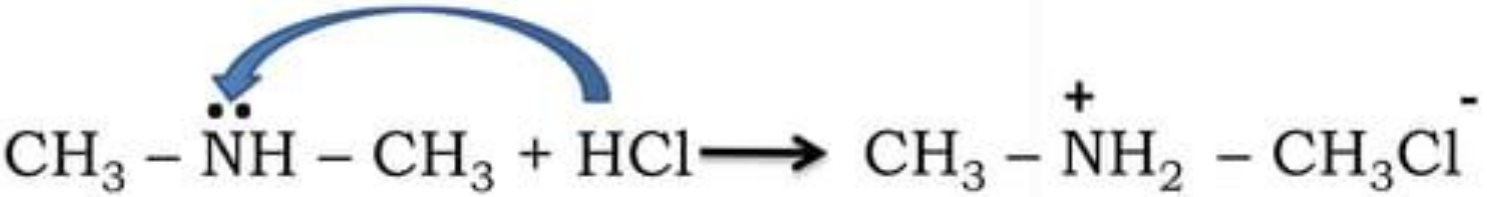


An amine gains hydrogen ion to produce an amine salt when treated with an acid (protonation.

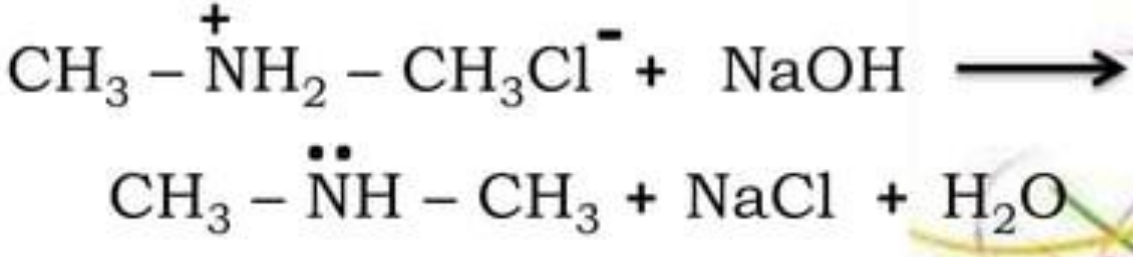
An amine salt loses a hydrogen ion to produce an amine when treated with a base (deprotonation reaction)

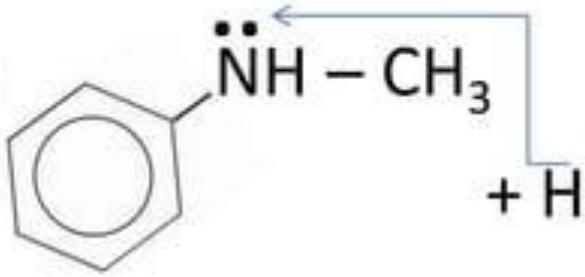
Write the structures of the products that forms when each of the following reactions involving amines or amine salts takes place.

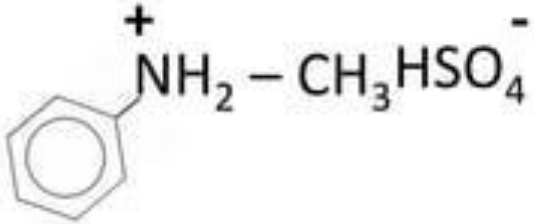
1) $CH_3 - NH - CH_3 + HCl \longrightarrow$



2) $CH_3 - \overset{+}{N}H_2 - CH_3Cl^-$



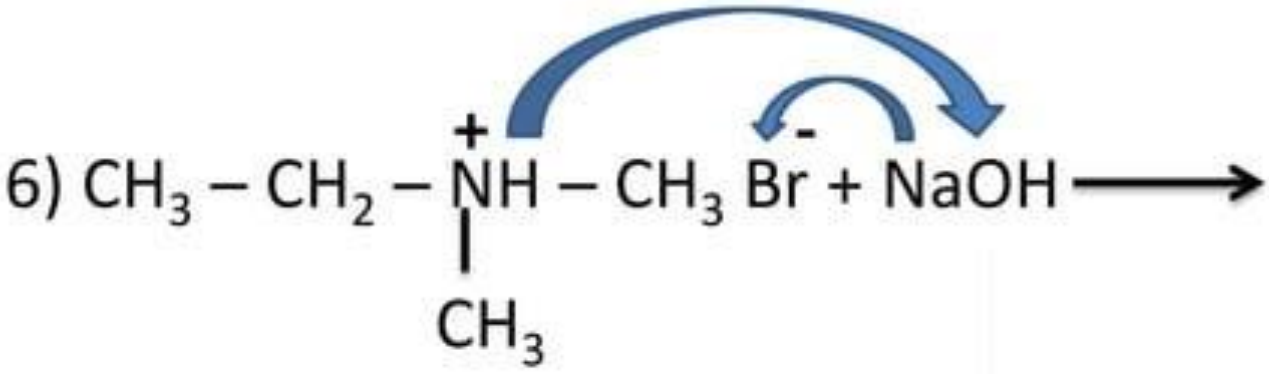
3) 

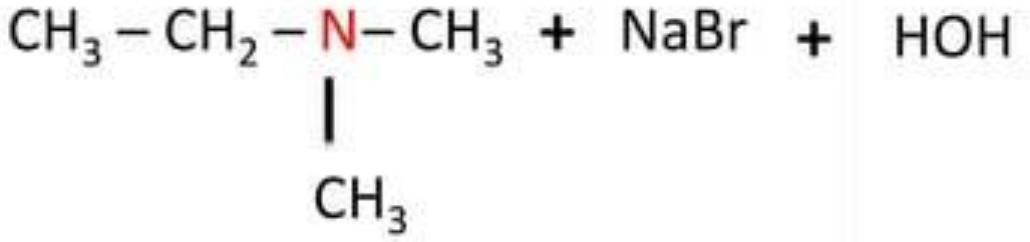


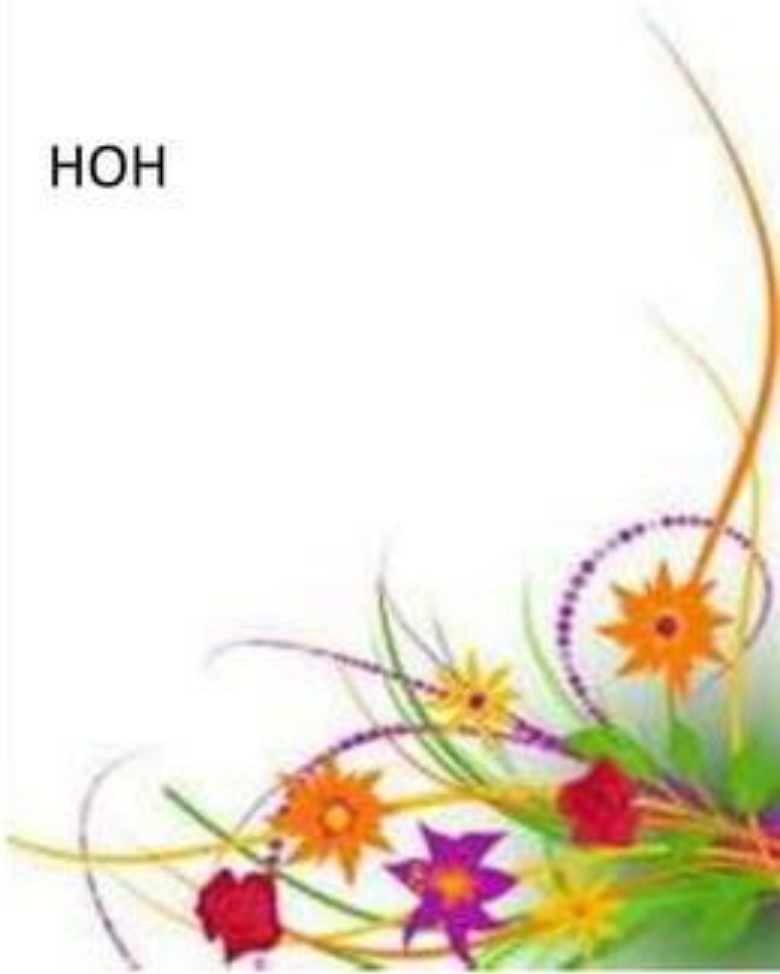
4) $CH_3 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}} - CH_3 + HCl \longrightarrow$ $CH_3 - CH_2 - \overset{+}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}}H - CH_3Cl^-$

5) $CH_3 - CH_2 - NH_2 - H_2SO_4 \longrightarrow$

$CH_3 - CH_2 - \overset{+}{N}H_3HSO_4^-$


6) $CH_3 - CH_2 - \overset{+}{N}H - CH_3\ \overset{-}{Br} + NaOH \longrightarrow$
CH_3


$CH_3 - CH_2 - N - CH_3 + NaBr + HOH$
CH_3



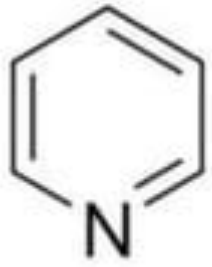
Heterocyclic Amines

Heterocyclic amine is an organic compound in which nitrogen atoms of amine group are part of either an aromatic or a nonaromatic ring system.

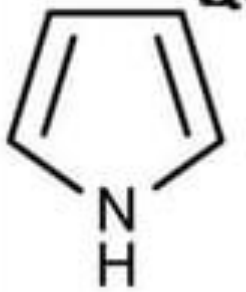
Heterocyclic amine are the most common type of heterocyclic organic compound

Heterocyclic amines are the first heterocyclic compounds we have encountered that have nitrogen heteroatoms.

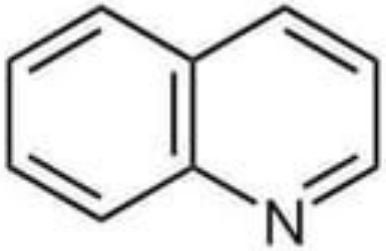
Selected Structural Formulas of Heterocyclic amines that serve as "parent" molecule for complex amine derivatives.



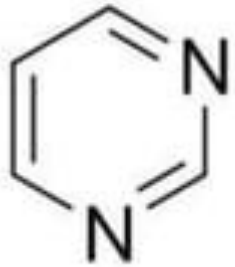
Pyridine



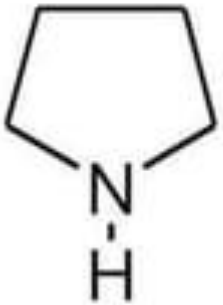
Pyrrole



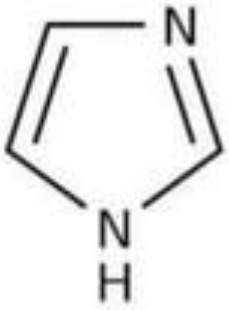
Quinoline



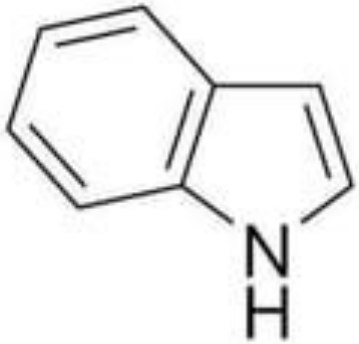
Pyrimidine



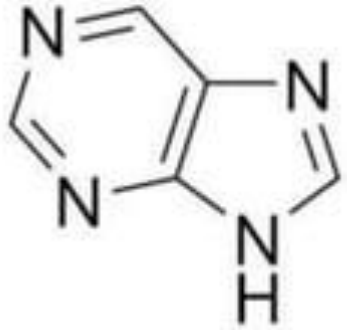
Pyrrolidine



Imidazole



Indole

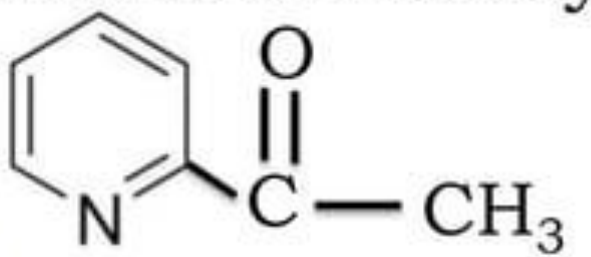


Purine

Heterocyclic amines often have strong odor, some agreeable and others disagreeable.

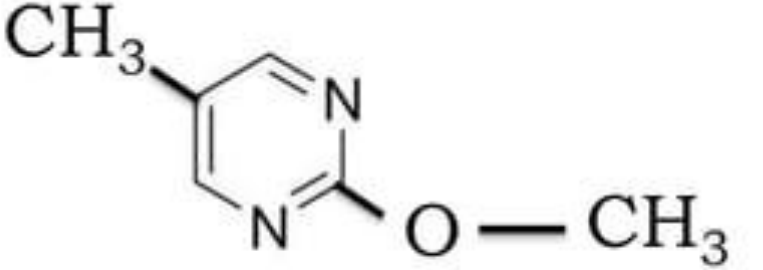
The pleasant aroma of many heat-treated food is caused by heterocyclic amines formed during the treatment.

The compounds responsible for the pervasive odors of poop popcorn and hot peanut are heterocyclic amines.



Methyl- 2- pyridyl ketone

odor of popcorn



2-Methoxy-5-methylpyrazine

odor of peanut

Isomerism for Amines

Constitutional isomerism in amines can arise from several causes.

1. **Different carbon atom arrangements produce isomers, as in**

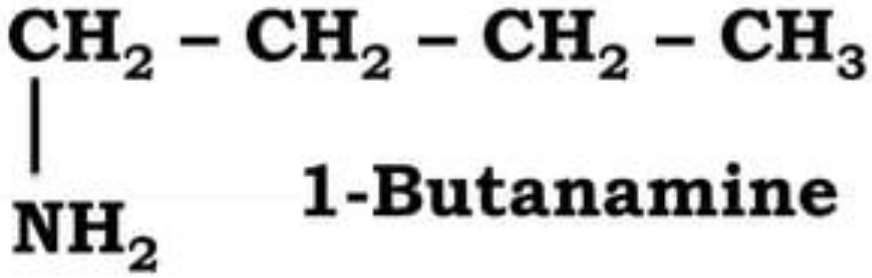
$CH_3 - CH_2 - CH_2 - CH_2 - CH_2\ NH_2$

1-Pentanamine **$C_5\ H_{11} - NH_2$**

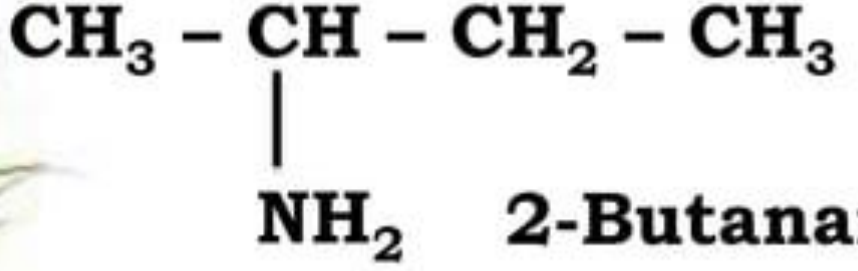
$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - NH_2$$

2 Methyl-1-butanamine **$C_5\ H_{11} - NH_2$**

2) Different positioning of the nitrogen atom on a carbon chains is another cause for isomerism.



1-Butanamine

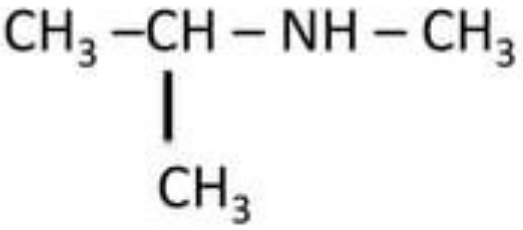


2-Butanamine

3) For secondary and tertiary amines, different partitioning of carbon atoms among the carbon chains present produces constitutional isomers.

$CH_2 – CH_2 – NH – CH_2 – CH_3$ **N-Ethylethanamine**

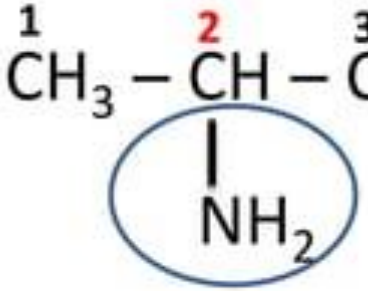
$CH_3 – CH_2 – CH_2 – NH – CH_3$ **N-Methyl -1- propanamine**



N-Methyl -2-propanamine

Nomenclature for Amines

A. Naming Primary Amines



2- butan amine

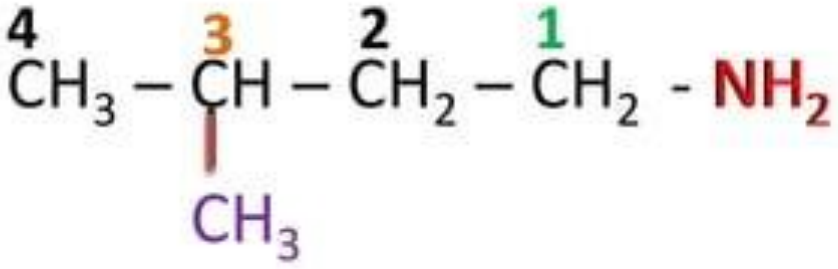
1	methane
2	ethane
3	propane
4	butane
5	pentane

1. Select as the parent carbon chain the longest chain to which the nitrogen atom is attached.

2. Name the parent chain by changing the ***–e*** ending of the corresponding alkane name to –amine.

3. Number the parent chain from the end nearest the nitrogen atom.

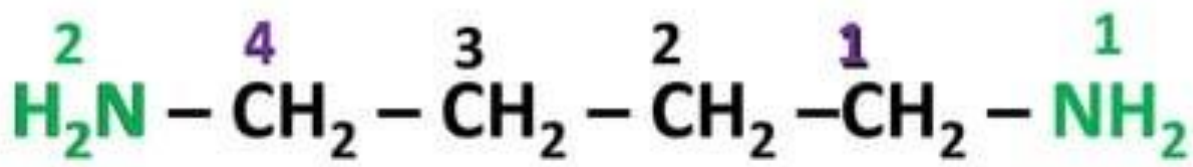
4. The position of attachment of the nitrogen atom is indicated by a number in front of the parent chain name.



1	methane
2	ethane
3	propane
4	butane
5	pentane

3 - Methyl - 1 - butanamine

In diamines, the final **–*e*** of the carbon chain name is retained for ease pronunciation.



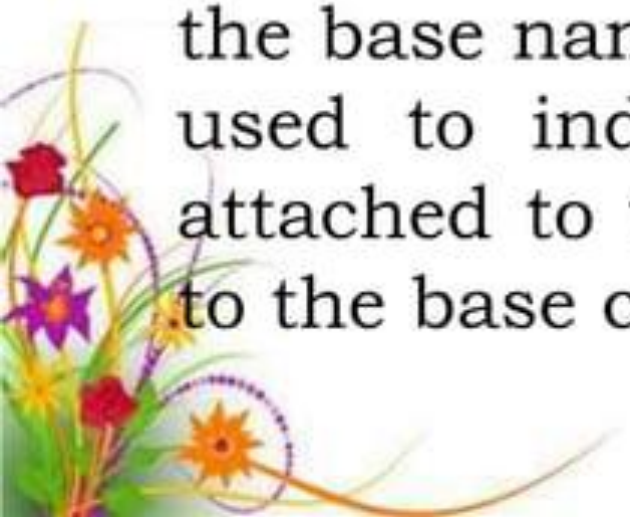
1 ,4- butane di amine

1	methane
2	ethane
3	propane
4	butane
5	pentane

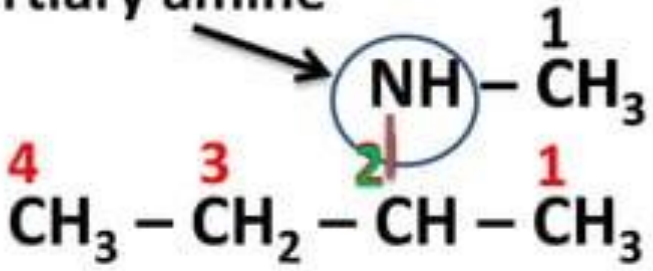
Secondary and Tertiary Amines are named as N- substituted primary amines.

The largest carbon group bonded to the nitrogen is used as the parent amine name.

The names of the other group attached to the nitrogen are appended to the front of the base name, and N- or N,N- prefixes are used to indicate that those groups are attached to the nitrogen atom rather than to the base carbon chain.

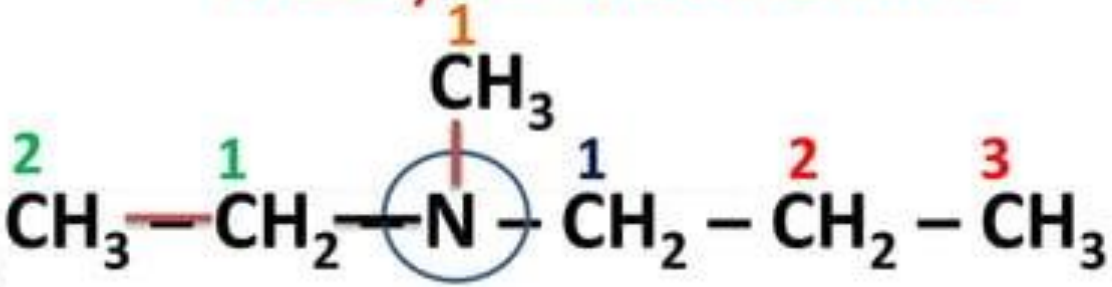


Tertiary amine

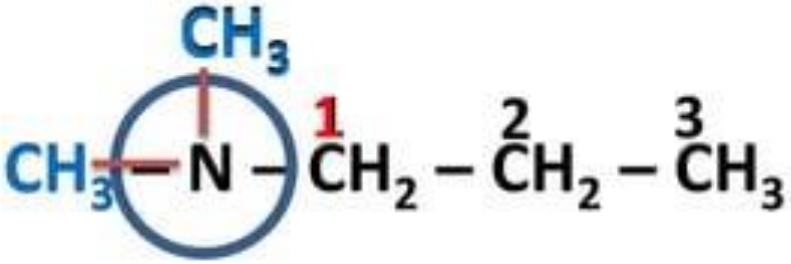


1	methane
2	ethane
3	propane
4	butane
5	pentane

***N*-Methyl-2-butanamine**



N- Ethyl- *N*- methyl-1-propanamine



1	methane
2	ethane
3	propane
4	butane
5	pentane

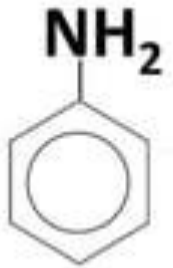
***N*- methyl *N*- methyl 1- propanamine**

Di

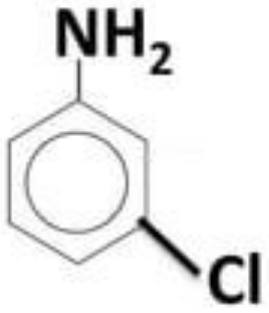
N,N – Dimethyl – 1 - propanamine

Simplest aromatic amine, a benzene ring bearing an amino group, is called ***aniline.***

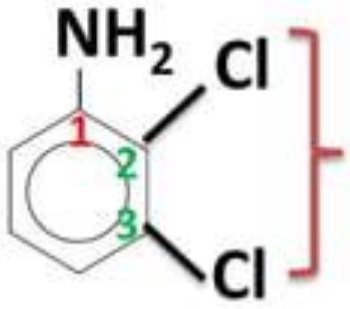
Other simple aromatic amines are named as derivatives of aniline.



Aniline

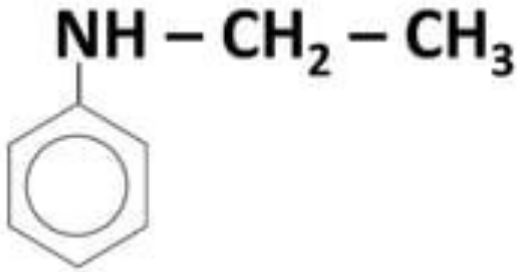


m - Chloroaniline

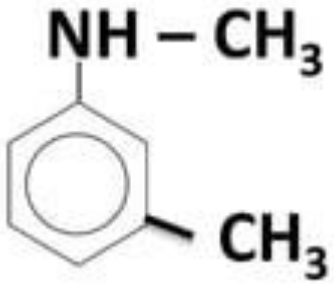


2 – 3, dichloroaniline

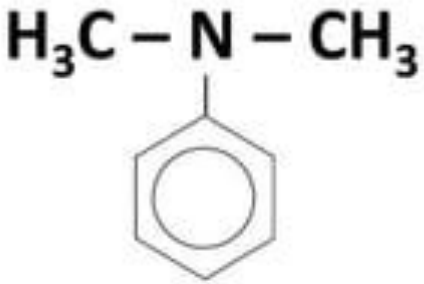
In secondary and tertiary aromatic amines, the additional group or groups attached to the nitrogen atom are located using a capital ***N-***



N- Ethylaniline



3,N Dimethylaniline

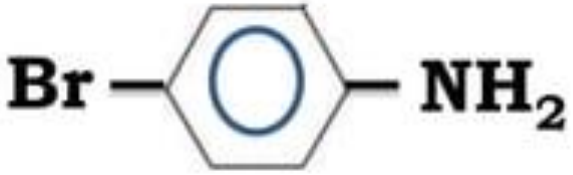


N- N Dimethylaniline

Assign IUPAC name to each of the following amines.

1) $CH_3 - CH_2 - NH - (CH_2)_4 - CH_3$

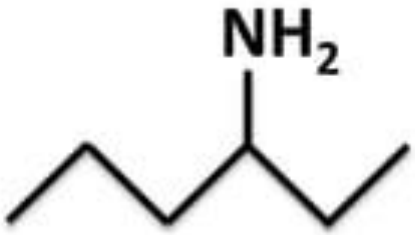
N-ethyl-1-pentanamine

2)  4-bromoaniline

3) $H_2N - CH_2 - CH_2 - NH_2$

1,2-Ethanediamine

4)  N,N - Dimethylethanamine

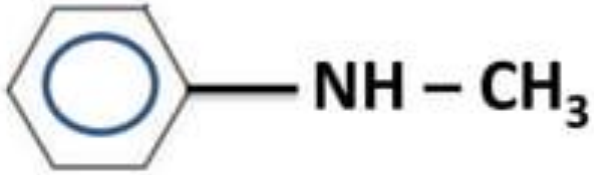
5) 

3- Hexanamine

6) $CH_3 - CH_2 - CH_2 - NH - CH_2 - CH_2 - CH_3$

N- Propyl-1-propanamine

7) $CH_3 - N(CH_3) - CH_3$ N,N- Dimethylmethanamine

8) 

N- Methylaniline