Organic Chemistry
CHEM 145

2 Credit hrs

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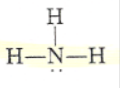
Amines and other Nitrogen Compounds

Structure and Classification of Amines

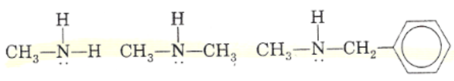
- **Amines** are compounds that derived from **ammonia** by replacement of one, two, or three hydrogens by alkyl or aryl groups.



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

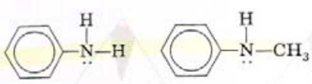
Ammonia

- **Aliphatic amines** contain *only alkyl* groups bonded directly to the nitrogen atom.



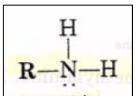
Aliphatic amines

- **Aromatic amines** are those in which one or more aryl groups are bonded directly to nitrogen.



Aromatic amines

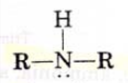
- According to the number of R or Ar groups *attached to the nitrogen atom*, **Amines** are classified as;



$R-\overset{H}{\ddot{N}}-H$

1° amine

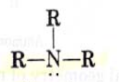
Primary (1°)



$R-\overset{H}{\ddot{N}}-R$

2° amine

Secondary (2°)



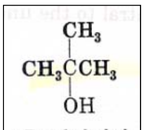
$R-\overset{R}{\ddot{N}}-R$

3° amine

Tertiary (3°)

Note

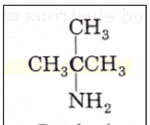
- *t*-butyl alcohol is a tertiary alcohol (because three carbons are attached to the carbinol carbon),



$CH_3\overset{CH_3}{\underset{OH}{C}}CH_3$

t-Butyl alcohol
(3° alcohol)

- *t*-butyl amine is a primary amine (because only one carbon is attached directly to the nitrogen atom).



$CH_3\overset{CH_3}{\underset{NH_2}{C}}CH_3$

t-Butylamine
(1° amine)

Nomenclature of Amines

- **Simple aliphatic amines** are named by listing, in alphabetical order, the alkyl groups attached to the nitrogen atom and adding the suffix *–amine.*

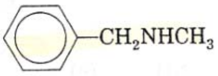
Alkylamine

CH_3NH_2

Methylamine

$CH_3NHCH_2CH_3$

Ethylmethylamine

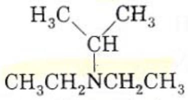


Benzylmethylamine

- **If two or three identical alkyl groups are attached to the nitrogen, the prefix *di-* or *tri-* is added to the name of the amine.**

CH_3NHCH_3

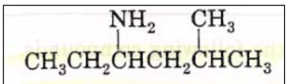
Dimethylamine



$CH_3CH_2\overset{\overset{H_3C\diagdown\ \diagup CH_3}{CH}}{\overset{|}{N}}CH_2CH_3$

Diethylisopropylamine

- **If the amine is complicated, the IUPAC system is used.**
  - In this system the amino group ($—NH_2$) is considered the substituent,
  - Its position on the chain is indicated by the lowest possible number.



$CH_3CH_2\overset{NH_2}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

3-Amino-5-methylhexane

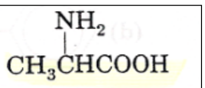
- **The amino group is also considered a substituent if it is part of a molecule that contains another functional group.**

$H_2NCH_2CH_2OH$

2-Aminoethanol

$H_2NCH_2CH_2CH_2OH$

3-Amino-1-propanol

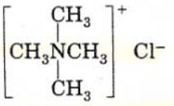


$CH_3\overset{NH_2}{\overset{|}{C}}HCOOH$

2-Aminopropanoic acid
(Alanine)

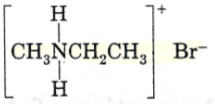
- **Amine salts are named by replacing the suffix *-amine* by *ammonium*, followed by the name of the anion, which is written as a second word.**

Alkylammonium + name of anion



$\left[CH_3\underset{CH_3}{\overset{CH_3}{N}}CH_3\right]^+ Cl^-$

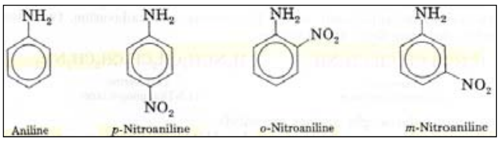
Tetramethylammonium chloride

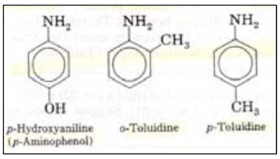


$\left[CH_3\underset{H}{\overset{H}{N}}CH_2CH_3\right]^+ Br^-$

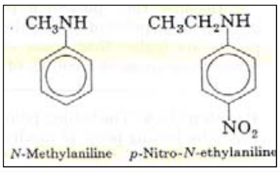
Ethylmethylammonium bromide

- **Aromatic amines are usually named as derivatives of aniline.**
  - **The prefixes ortho (*o*-), meta (*m*-), and para (*p*-) are used to locate the position of a substituent.**





- **If hydrocarbon groups are attached on the nitrogen atom,**
  - **The letter *N* is prefixed to the alkyl or aryl group name.**



Physical Properties of Amines

- **Low-molecular-weight aliphatic amines (methyl-, dimethyl-, and trimethylamines) are**
  - **Colorless gases.**
  - **Soluble in water.**
- **Amines containing 4 to 11 carbons atoms are liquids.**
- **Higher-molecular-weight amines are solids.**
- **Like ammonia, they form basic solutions.**
- **They have characteristically unpleasant odors that resemble the odors of ammonia and dead fish.**
- **Because they possess a polar $^{\delta-}$N—H $^{\delta+}$ bond, primary and secondary amines are capable of intermolecular hydrogen bonding.**
  - **Therefore their boiling points are**
    - **Higher than those of alkanes of comparable molecular weight.**
    - **Lower than those of alcohols of similar molecular weight.**

- Tertiary amines are also polar compounds, but because hydrogen is not bonded to nitrogen, these amines are incapable of intermolecular hydrogen bonding.
  - Therefore their boiling points are
    - Lower than primary and secondary amines of identical molecular weights.
    - Higher than those of alkanes of similar molecular weight.
- All amines are capable of forming hydrogen bonds with water.
- Amines with up to six carbons show appreciable solubility in water.

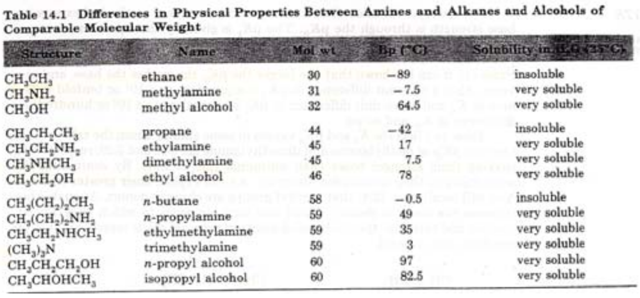
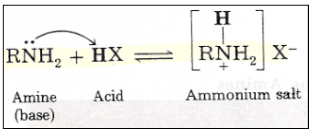


Table 14.1 Differences in Physical Properties Between Amines and Alkanes and Alcohols of Comparable Molecular Weight

Structure	Name	Mol wt	Bp (°C)	Solubility in H_2O (25°C)
CH_3CH_3	ethane	30	−89	insoluble
CH_3NH_2	methylamine	31	−7.5	very soluble
CH_3OH	methyl alcohol	32	64.5	very soluble
$CH_3CH_2CH_3$	propane	44	−42	insoluble
$CH_3CH_2NH_2$	ethylamine	45	17	very soluble
CH_3NHCH_3	dimethylamine	45	7.5	very soluble
CH_3CH_2OH	ethyl alcohol	46	78	very soluble
$CH_3(CH_2)_2CH_3$	*n*-butane	58	−0.5	insoluble
$CH_3(CH_2)_2NH_2$	*n*-propylamine	59	49	very soluble
$CH_3CH_2NHCH_3$	ethylmethylamine	59	35	very soluble
$(CH_3)_3N$	trimethylamine	59	3	very soluble
$CH_3CH_2CH_2OH$	*n*-propyl alcohol	60	97	very soluble
$CH_3CHOHCH_3$	isopropyl alcohol	60	82.5	very soluble

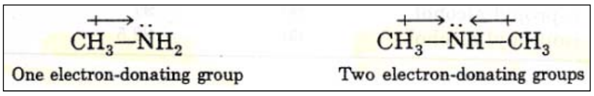
Basicity of Amines

- Amines are bases because the nitrogen atom has a nonbonded pair of electrons.
  - This nonbonded electron pair can be donated to an acid's proton to form an ammonium salt.



- The more available the electron pair on *N* is to an acid, the stronger the base, and vice versa.
- We can explain their greater basicity.

Methyl groups are electron donors, they increase the electron density about the nitrogen atom to which they are attached, and therefore the non-bonded electron pairs are made more available for reaction with an acid

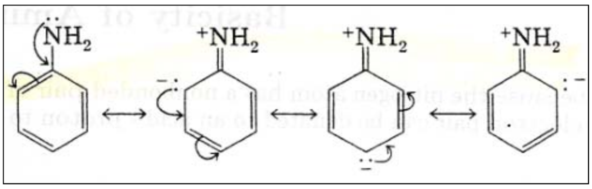


- **Aliphatic amines are more basic than aromatic amines.**
- **For example;**

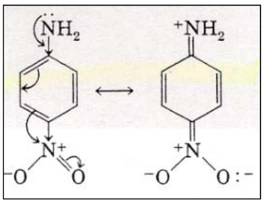
The basicity of aniline turns out to be almost a million times weaker than that of methylamine.

is attributed to resonance interactions.

- **The unshared pair of electrons in the resonance hybrid is not localized on the nitrogen atom in ammonia and aliphatic amines.**
- **It is distributed over the aromatic ring, thus making it less available for sharing in reaction with a Lewis acid.**



- **Nitroaniline is even *more weakly basic* than aniline.**
  - **because the *electron-withdrawing effect* of the *–NO_2* group on the ring.**
    - **lowers the electron density on the nitrogen atom,**
    - **making the electrons even less available for sharing with a Lewis acid**



Summary

- **Electron-releasing groups on the nitrogen atom of amines increase the basicity of amines,**
  and electron-withdrawing groups decrease the basicity.
- **Resonance effects in aromatic amines lower their basicity.**
- **Electron-withdrawing groups on the aromatic ring lower the basicity even more.**

Preparation of Amines

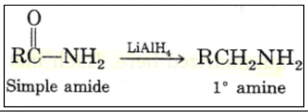
Reduction of Nitro Compounds, Nitriles and Amides;

- Catalytic hydrogenation works well with nitro compounds and nitriles to give *primary amines*.

$$CH_3CH_2NO_2 \xrightarrow{H_2/Pt} CH_3CH_2NH_2$$

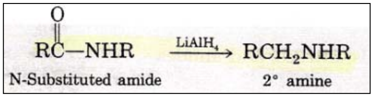
$$CH_3CH_2CN \xrightarrow{H_2/Pt} CH_3CH_2CH_2NH_2$$

- The carbonyl function of amides is reduced by **lithium aluminum hydride, $LiAlH_4$.**



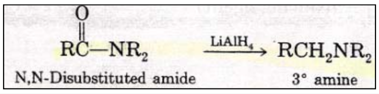
$$R\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} RCH_2NH_2$$

Simple amide 1° amine



$$R\overset{O}{\overset{\|}{C}}-NHR \xrightarrow{LiAlH_4} RCH_2NHR$$

N-Substituted amide 2° amine

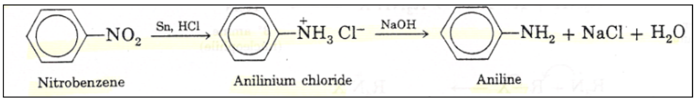


$$R\overset{O}{\overset{\|}{C}}-NR_2 \xrightarrow{LiAlH_4} RCH_2NR_2$$

N,N-Disubstituted amide 3° amine

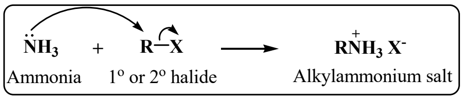
- **Aniline** is prepared by reduction of nitrobenzene.

The reducing agent most frequently used is tin and hydrochloric acid,



Alkylation of Ammonia;

- The non-bonded electron pair on the nitrogen makes ammonia an excellent nucleophile.
- Ammonia is capable of attacking primary or secondary alkyl halides in an S_N2 reaction to give an alkylammonium salt.



$$\ddot{N}H_3 + R-X \longrightarrow R\overset{+}{N}H_3\ X^-$$

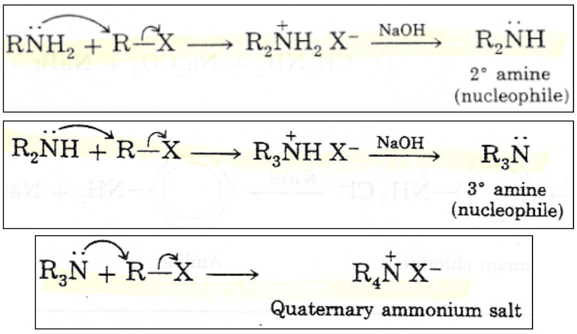
Ammonia 1° or 2° halide Alkylammonium salt

- Treatment of the alkylammonium salt with a strong base (NaOH) liberates the free amine.

$$R\overset{+}{N}H_3\ X^- \xrightarrow{NaOH} R\ddot{N}H_2 + NaX + H_2O$$

1° amine
(nucleophile)

➦ The net result is the replacement of a hydrogen of ammonia by an alkyl group, the reaction is called *alkylation of ammonia*.



$$R\ddot{N}H_2 + R{-}X \longrightarrow R_2\overset{+}{N}H_2\,X^- \xrightarrow{NaOH} R_2\ddot{N}H$$

2° amine
(nucleophile)

$$R_2\ddot{N}H + R{-}X \longrightarrow R_3\overset{+}{N}H\,X^- \xrightarrow{NaOH} R_3\ddot{N}$$

3° amine
(nucleophile)

$$R_3\ddot{N} + R{-}X \longrightarrow R_4\overset{+}{N}\,X^-$$

Quaternary ammonium salt

Conversion of Diazonium Salts

➡ **Aromatic diazonium salts** are useful for preparing a host of **substituted benzene derivatives**.