CHAPTER 11

AMINES
Learning Outcomes:
Draw structures and classify primary, secondary and tertiary amines.

11.1 INTRODUCTION

Learning Outcomes:

11.2 NOMENCLATURE

Learning Outcomes:

a) Draw the structures and name aliphatic and aromatic amines according to the IUPAC nomenclature (parent chain ≤ C_{10})
b) Give common names with parent chain ≤ C_{5}
c) Apply IUPAC rules to name primary, secondary and tertiary amines.

11.3 PHYSICAL PROPERTIES

Learning Outcomes:

a) Explain the physical properties:
   i. boiling point of
      - primary, secondary and tertiary amines.
      - amine with alkane, haloalkane, alcohol, carbonyl compound and carboxylic acid
   ii. Solubility of primary, secondary and tertiary amines.

b) Explain basicity in terms of:
   i. inductive effect
   ii. resonance effect

b) Compare the basicity of ammonia, aliphatic amines and aromatic amines in terms of inductive effect and resonance effect.
Amines are organic derivatives of ammonia, \( \text{NH}_3 \)

- **Primary amines**
  \[
  H - \text{N} - H - R
  \]

- **Secondary amines**
  \[
  H - \text{N} - R' - R
  \]

- **Tertiary amines**
  \[
  R'' - \text{N} - R' - R
  \]
CLASSIFICATION OF ALIPHATIC AND AROMATIC AMINES

i. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  $1^\circ$

ii. $\text{CH}_3\text{CH}_2\text{N} \equiv \text{H}$  $2^\circ$
   $\text{CH}_3$

iii. $\text{CH}_3\text{CH}_2\text{N} \equiv \text{CH}_3$
     $\text{CH}_3$  $3^\circ$

iv. $\text{C}_6\text{H}_5\text{N} \equiv \text{CH}_3$
    $\text{H}$  $2^\circ$

v. $\text{C}_6\text{H}_5\text{NH}_2$
   $1^\circ$

vi. $\text{C}_6\text{H}_5\text{N} \equiv \text{CH}_3$
     $\text{CH}_2\text{CH}_3$  $3^\circ$

Aliphatic amines

Aromatic amines
NOMENCLATURE

• In primary amines, the suffix ‘amine’ replaces the ‘e’ in the name of the parent alkane.

  i.  \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \)  1-propanamine

  3     2     1

• Secondary and tertiary amines are named as \( N \)-substituted derivatives of primary amines.

  ii.  \( \text{CH}_3\text{CH}_2\text{N} \equiv \text{H} \)  \( N \)-methylethamamine

  2     1
<table>
<thead>
<tr>
<th>Structure</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NH$_2$</td>
<td>Methanamine</td>
</tr>
<tr>
<td>CH$_3$CH(NH$_2$)CH$_3$</td>
<td>2-propanamine</td>
</tr>
<tr>
<td><img src="image" alt="Cyclopentanamine Structure" /></td>
<td>Cyclopentanamine</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CHCH$_2$CH$_3$</td>
<td>N-methyl-3-pentanamine</td>
</tr>
<tr>
<td><img src="image" alt="N-ethyl-N-methylethane Structure" /></td>
<td>N-ethyl-N-methylethane</td>
</tr>
</tbody>
</table>
When multiple functional groups are present and the \(-\text{NH}_2\) group does not take priority, it is named as an “amino” substituent.

\[
\text{NH}_2\text{CH}_2\text{COOH} \quad \text{2-aminoethanoic acid}
\]

Amino

(when amine becomes substituent)

\[
\text{H}_2\text{N}\quad \text{OH} \quad \text{NH}_2
\]

2,4-diaminophenol
- Aromatic amines are named as derivatives of aniline

\[ \text{Aniline} \]  
\[ \text{2,4,6-tribromoaniline} \]  
\[ \text{4-methylaniline} \]  
\[ \text{N-ethyl-N-methylaniline} \]
Most primary amines are named as alkylamines.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NH₂</td>
<td>methylamine</td>
</tr>
<tr>
<td>CH₃CH₂NH₂</td>
<td>ethylamine</td>
</tr>
<tr>
<td>CH₃CH₂CH₂NH₂</td>
<td>propylamine</td>
</tr>
<tr>
<td>CH₃NHCH₃</td>
<td>dimethylamine</td>
</tr>
<tr>
<td>CH₃NHCH₂CH₃</td>
<td>methylethylamine</td>
</tr>
</tbody>
</table>
Both **primary** and **secondary** amines can form intermolecular hydrogen bonds.

- **1° amine** can form **MORE H-bonding** than **2° amine**.
- **3° amines** cannot form hydrogen bonds to each other. Can only form weak Van der Waals (dipole-dipole forces) to each other.
The table below compares the boiling points of isomeric amines (same molar mass).

<table>
<thead>
<tr>
<th>AMINES</th>
<th>CLASS</th>
<th>Relative molecular mass</th>
<th>Boiling points/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂CH₂NH₂</td>
<td>1°</td>
<td>59</td>
<td>49</td>
</tr>
<tr>
<td>CH₃CH₂-NH-CH₃</td>
<td>2°</td>
<td>59</td>
<td>37</td>
</tr>
</tbody>
</table>
| CH₃  
  | CH₃-N-CH₃                | 3°    | 59                      | 4                 |

Boiling Point: CH₃CH₂CH₂NH₂ > CH₃CH₂NH(CH₃) > (CH₃)₃N
Amines have **higher boiling points** than alkanes or haloalkanes of similar relative molecular mass due to **intermolecular hydrogen bonding**.

<table>
<thead>
<tr>
<th>Amines</th>
<th>Type</th>
<th>Molar mass</th>
<th>Boiling points/°C</th>
<th>IMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂CH₂CH₃ butane</td>
<td>Alkane</td>
<td>58</td>
<td>-0.5</td>
<td>LDF</td>
</tr>
<tr>
<td>CH₃CH₂Cl chloroethane</td>
<td>Haloalakane</td>
<td>64.5</td>
<td>12.5</td>
<td>Dipole²</td>
</tr>
<tr>
<td>CH₃CH₂CH₂NH₂ 1-propanamine</td>
<td>Amine</td>
<td>59</td>
<td>48.6</td>
<td>H-bonding</td>
</tr>
</tbody>
</table>

Boiling point: Butane < Chloroethane < 1-propanamine
- 1-propanamine – can form two **hydrogen bonds**.
- Chloroethane – have **dipole-dipole force**.
- Butane – weak Van der Waals force only.
Amines have lower boiling points than alcohols or carboxylic acids of comparable molecular weight because......

- Hydrogen bond in amine, \( \text{RNH}_2 \) is weaker than the hydrogen bond in \( \text{ROH} \) and \( \text{RCOOH} \) because...
  
  Nitrogen is less electronegative than the oxygen.
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<tr>
<td>CH₃CH₂CH₂NH₂ 1-propanamine</td>
<td>Amine</td>
<td>59</td>
<td>48.6</td>
<td>H-Bonding</td>
</tr>
<tr>
<td>CH₃CH₂CH₂OH 1-propanol</td>
<td>Alcohol</td>
<td>60</td>
<td>97.2</td>
<td>H-bonding</td>
</tr>
<tr>
<td>CH₃COOH ethanoic acid</td>
<td>Carboxylic acid</td>
<td>60</td>
<td>118</td>
<td>H-bonded dimer</td>
</tr>
</tbody>
</table>

Boiling Point: Carboxylic acid > Alcohol > Amine > Haloalkane > Alkane
All amines including tertiary amines, are capable of forming hydrogen bonds with water molecules. Thus simple amines (amines of fewer than 5 carbons) are generally water soluble and dissolve to form basic aqueous solutions.
Comparison the solubility between 1°, 2° and 3° amine

1° amine forms 3 hydrogen bonds per a molecule

2° amine forms 2 hydrogen bonds per a molecule

3° amine forms 1 hydrogen bond per a molecule
The solubility: \[ 3^\circ < 2^\circ < 1^\circ \]

- **3° amine** forms 1 hydrogen bond per a molecule
- **2° amine** forms 2 hydrogen bonds per a molecule
- **1° amine** forms 3 hydrogen bonds per a molecule

→ As MORE number of H-bond can be formed with water, so the solubility increases.
An amine is a nucleophile (a Lewis base) because its **lone pair of non-bonding electrons on nitrogen**.

**Tips!**

*If acidity = ability to release \( H^+ \), so basicity = ability to accept \( H^+ \).*
Basicity: Inductive Effect

- An alkyl group is **electron donating group (EDG)**, and it **stabilises** the alkylammonium ion by **increasing e- density on N atom**.
- Hence, N atom is **more available** to accept H+.

```
\begin{align*}
\text{R-N} & \text{H} \quad + \quad \text{H-\text{OH}} \quad \leftrightarrow \quad \text{R-N}^+ \quad \text{H} \quad + \quad \text{OH}^- \\
\end{align*}
```

1° Amine

Stronger base

alkylammonium ion

Stabilised by the alkyl group
2° Amine    alkylammonium ion

**2° amine is more basic than 1° amine** because 2° amine has more alkyl group, R (EDG).

**But for 3° amine**, even tough it has most no. of alkyl group, R (EDG) it is **least basic** because the 3 alkyl groups, R are considered **bulky** hence give **greater steric effect**. N atom is **less available to accept H⁺**

**Strength as a base:**

Aromatic amine < NH₃ < 3° < 1° < 2°

**Increasing basicity**
Aromatic amines are less basic than aliphatic amine.

The lone pair electrons of nitrogen atom are delocalised and overlapped with the aromatic ring π electrons system make it less available for bonding to H⁺.

Arylamines are stabilised due to the 4 resonance structures.
Aromatic amines (e.g., aniline) are weaker bases than the corresponding aliphatic and cyclic amines.

Example:

\[
\begin{align*}
\text{Cyclohexylamine} & \quad pK_b = 3.36 \\
\text{Aniline} & \quad pK_b = 9.42
\end{align*}
\]
11.4 PREPARATION

Learning Outcomes:

a) Explain the preparation of:
   i. aromatic amines by reduction of nitro compounds using Zn/H⁺ or SnCl₂/H⁺ or Fe/H⁺
   ii. Primary aliphatic amines by reduction of nitriles using LiAlH₄ followed by H₃O⁺ or NaBH₄ in methanol or H₂/catalyst
   iii. Primary, secondary and tertiary amines by reductions of amides using LiAlH₄ followed by H₂O
   iv. Primary alkyl and aryl amines by Hoffmann’s degradation of primary amides

b) Outline the synthesis of primary, secondary, tertiary and aromatic amines.
- **Aromatic amines** can be prepared by reduction of nitro compounds using $\text{Zn}/\text{H}^+$ or $\text{SnCl}_2/\text{H}^+$ or $\text{Fe}/\text{H}^+$

![Chemical reaction diagram]

- Nitrobenzene $\rightarrow$ Aniline

**REDUCTION OF NITRO COMPOUNDS**
Nitriles are reduced to **primary aliphatic amines** by $\text{H}_2$/catalyst or $\text{LiAlH}_4$ followed by $\text{H}_3\text{O}^+$ or $\text{NaBH}_4$ in methanol.

Example:

\[
\begin{align*}
\text{R} - \text{C} &= \text{N} \quad \overset{\text{H}_2}{\xrightarrow{\text{catalyst (Pt, Ni, Pd)}}} \quad \text{RCH}_2\text{NH}_2
\end{align*}
\]
Reduction of an amide using LiAlH$_4$ followed by H$_2$O can yield a primary, secondary or tertiary amine depending on the type of amide used.
Example:

i. \[\text{CH}_3\overset{\text{O}}{\text{C}}\overset{\text{NH}_2}{\longrightarrow} \text{LiAlH}_4 \rightarrow \text{CH}_3\overset{\text{C}}{\text{NH}_2} + \text{H}_2\text{O}\]

Ethanamide (1° amide)

ii. \[\text{CH}_3\overset{\text{O}}{\text{C}}\overset{\text{NH}}{\longrightarrow} \text{LiAlH}_4 \rightarrow \text{CH}_3\overset{\text{C}}{\text{NH}} + \text{H}_2\text{O}\]

N-methylethanamide (2° amide)
On warming a primary amide with bromine in solution of NaOH, a primary amine is formed.

This reaction is used to synthesise primary alkyl and aryl amines.

The elimination of carbonyl group is shortening the length of carbon chain by one carbon atom.
Example:

\[
\text{CONH}_2 + \text{CO}_3^{2-} \rightarrow \text{Br}_2, \text{OH}^- \rightarrow \text{NH}_2 + \text{H}_2\text{O}
\]
Learning Outcomes:

a) Explain the reaction to distinguish classes of amines by using:
   i. Hinsberg’s test
   ii. Nitrous acid test

b) Distinguish classes of amines by using:
   i. Hinsberg’s test
   ii. Nitrous acid test

c) Explain the identification test of aniline using bromine water.

d) Explain the formation of dye by the coupling reaction of benzenediazonium chloride and phenol.

e) Outline the synthesis of compounds related to reactions of amines.
HINSBERG’S TEST

- This reaction is used to **differentiate** between $1^\circ$, $2^\circ$ and $3^\circ$ amines.
- Reagent: benzenesulphonyl chloride

\[
\text{Cl-S-} \quad \text{C=C} \quad \text{O} \\
\text{O} \\
\]

- Observation is different for each classes of amines.
Benzenesulphonyl chloride reacts with a 1° amine to form a **white precipitate** (N-substituted sulphonamides)

1° amine

\[ R-NH\textsubscript{2} + \text{Cl-S-SO}_2 \text{H} \xrightarrow{\text{excess NaOH}} R-N-S-SO_2\text{Na} \]

**water soluble salt**

(Clear solution)

\[ R-N-S-SO_2\text{H} \xrightarrow{\text{HCl}} R-N-S-SO_2\text{Na} \]

N-substituted benzenesulphonamides

(White precipitate)
Benzenesulphonyl chloride reacts with a 2° amines to form a white precipitate ($N,N$-disubstituted sulphonamide).

2° Amine

Excess NaOH

$N,N$-disubstituted benzenesulphonamides (White precipitate)

HCl

No reaction (White precipitate remains)
3° amine do not give visible reaction with benzenesulphonyl chloride.

\[ \text{3° amine} \quad \text{Cl-S-} \quad \text{OH}^- \quad \text{no reaction} \quad \text{HCl} \quad \text{R}_3\text{NH}^+\text{Cl}^- \]

(2 layers formed)

water soluble salt (clear solution)
### SUMMARY OF HINSBERG’S TEST

<table>
<thead>
<tr>
<th>Classes of Amines</th>
<th>Addition of NaoH</th>
<th>Addition of HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°</td>
<td>Clear solution</td>
<td>White precipitate</td>
</tr>
<tr>
<td>2°</td>
<td>White precipitate</td>
<td>White precipitate</td>
</tr>
<tr>
<td>3°</td>
<td>2 layers formed</td>
<td>Clear solution</td>
</tr>
</tbody>
</table>
Nitrous acid (HNO₂) is a weak and unstable acid.

It is always prepared in situ, by treating cold sodium nitrite (NaNO₂) with an aqueous solution of a cold dilute hydrochloride acid (<5°C).

Nitrous acid reacts with all classes of amines.

Nitrous acid test can be used to distinguish:
- 1° aliphatic and 1° aromatic amines
- 1° aliphatic and 2° aliphatic amines
Primary aliphatic amines react with nitrous acid to yield highly unstable aliphatic diazonium salts.

\[
R-\text{NH}_2 + \text{NaNO}_2, \text{HCl} \rightarrow [R-N\equiv NC\text{Cl}^-] \rightarrow C=C + \text{ROH} + \text{RX} + \text{N}_2
\]

**Observation:**
Formation of gas bubbles (N\textsubscript{2})
Primary arylamines react with nitrous acid to give arenediazonium salts (stable).

Observation:
Clear solution @ No formation of gas bubbles (N₂) unless T > 5°C
Form secondary N-nitrosamines as yellow oil, which is stable under the reaction conditions.

\[ \text{R'} \quad \text{R-N-H} \quad \xrightarrow{\text{NaNO}_2, \text{HCl}} \quad 0 \text{ to } 5^\circ \text{C} \quad \text{R'} \quad \text{R-N-N=O} \]

**Observation:**

Yellow oil formed.
Reaction of **primary aliphatic amines**:  

\[ \text{RNH}_2 + \text{O} = \text{N}-\text{OH} \rightarrow \text{R-OH} + \text{H}_2\text{O} + \text{N}_2(\text{g}) \]

**Bubble gas**

Reaction of **secondary aliphatic/aromatic amines**:  

\[ \text{R}_2\text{N}-\text{H} + \text{HO}-\text{N}=\text{O} \rightarrow \text{R}_2\text{N}-\text{N}=\text{O} + \text{H}_2\text{O} \]

**yellow oil**

Reaction of **tertiary aliphatic amines**:  

\[ \text{R}_2\text{N}-\text{R} + \text{HO}-\text{N}=\text{O} \rightarrow \text{R}_2\text{N}^+-\text{R} + \text{H}_2\text{O} \]

\[ \text{HCl}^- \]

**Clear solution**

**water soluble salt**
Aniline reacts with aqueous bromine to yield white precipitates.

NH₂ group is an activating and ortho-para directors group.

\[
\text{Cylindrical} \quad \xrightarrow{3\text{Br}_2(\text{aq}) \text{ (room temperature)}} \quad \text{NH}_2 \quad \xrightarrow{\text{Br}} \quad \text{NH}_2 \quad \xrightarrow{\text{Br}} \quad \text{NH}_2 \quad \xrightarrow{\text{Br}} \quad + \quad 3\text{HBr}
\]

(2,4,6-tribromoaniline)

Observation:

White precipitate formed.
Primary arylamines react with nitrous acid to give arenediazonium salts which are stable at 0 °C.

Arenediazonium salts also undergo coupling reaction with aromatic compounds with strong electron donating group, such as –OH and –NR₂ at the para position to yield azo compounds.

Azo compounds are usually intensely coloured and relatively inexpensive compounds, they are used as dyes.
Arenediazonium salt