1. General Introduction and Structure

Amines are considered organic derivatives of ammonia (NH_3), obtained by replacing one, two, or all three hydrogen atoms with alkyl and/or aryl groups. They occur naturally in proteins, vitamins, alkaloids, and hormones.

Structure of Amines

Like ammonia, the nitrogen atom in amines is sp^3 **hybridized**.

- The geometry is **pyramidal** due to the presence of one unshared (lone) pair of electrons on the nitrogen atom.
- The $C-N-C$ or $C-N-H$ bond angle is slightly less than the standard tetrahedral angle of 109.5° (e.g., it is 108° in trimethylamine) due to lone pair-bond pair repulsion.

2. Classification and Nomenclature

Classification

Amines are classified based on the number of alkyl or aryl groups attached to the nitrogen atom:

1. **Primary (1°) Amine:** One hydrogen of NH_3 is replaced by an alkyl/aryl group ($R-NH_2$).
2. **Secondary (2°) Amine:** Two hydrogens are replaced ($R-NH-R'$).
3. **Tertiary (3°) Amine:** All three hydrogens are replaced (R_3N).

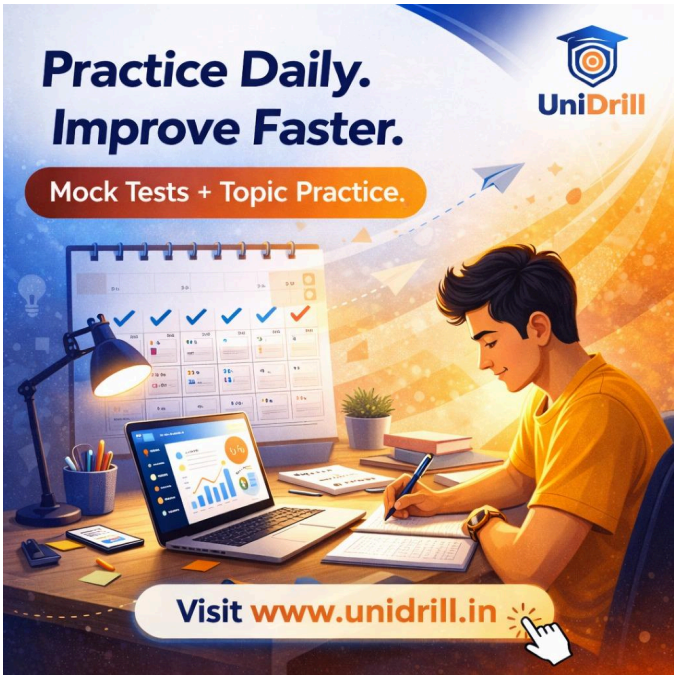
Nomenclature

- **Common System:** Named by prefixing the alkyl group to "amine" (e.g., methylamine). Secondary and tertiary amines use prefixes like *di-* or *tri-* for identical groups.
- **IUPAC System:** Named by replacing the 'e' of the parent alkane with **-amine** (e.g., Methanamine).
    - For 2° and 3° amines, the largest alkyl group is chosen as the parent chain, and the smaller groups are treated as N-substituents (e.g., $CH_3-NH-CH_2CH_3$ is N-Methylethanamine).
    - The simplest aromatic amine is aniline ($C_6H_5NH_2$), which is accepted in IUPAC nomenclature, though it can also be called Benzenamine.

3. Methods of Preparation of Amines

1. **Reduction of Nitro Compounds:**
   Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided Ni, Pd, or Pt, or by reduction with metals in acidic medium.
   $$R-NO_2+3H_2 \xrightarrow{Pd/Ethanol} R-NH_2+2H_2O$$
   (Note: Reduction with Iron scrap and HCl is preferred because $FeCl_2$ formed gets hydrolyzed to release HCl, meaning only a small amount of HCl is needed).
2. **Ammonolysis of Alkyl Halides:**
   An alkyl halide undergoes nucleophilic substitution with an ethanolic solution of ammonia. This yields a mixture of 1°, 2°, 3° amines, and a quaternary ammonium salt. (The 1° amine is the major product if NH_3 is taken in large excess).
   $$R-X+NH_3 \rightarrow R-NH_2 \xrightarrow{R-X} R_2NH \xrightarrow{R-X}$$
3. **Reduction of Nitriles:**
   Reduced to primary amines using H_2/Ni, $Na(Hg)/C_2H_5OH$, or $LiAlH_4$. Used to ascend the amine series (adding one carbon).
   $$R-C\equiv N \xrightarrow{H_2/Ni} R-CH_2NH_2$$

4. **Reduction of Amides:**
   Reduced with $LiAlH_4$ to yield primary amines.
   $R-CONH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2NH_2$
5. **Gabriel Phthalimide Synthesis:**
   Used for the preparation of **pure primary aliphatic amines**. Phthalimide reacts with ethanolic KOH, followed by an alkyl halide, and then alkaline hydrolysis.
   (Cannot be used for aromatic primary amines because aryl halides do not undergo nucleophilic substitution easily).
6. **Hoffmann Bromamide Degradation Reaction:**
   An amide is treated with bromine in an aqueous or ethanolic solution of $NaOH$. It yields a primary amine with **one carbon atom less** than the parent amide.
   $R-CONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2$



4. Physical Properties

- **Boiling Points:** Primary and secondary amines can form intermolecular hydrogen bonds. Tertiary amines cannot (no N-H bond). Thus, the order of boiling points for isomeric amines is:
  1° **Amine >** 2° **Amine >** 3° **Amine**
  (Note: Amines have lower boiling points than corresponding alcohols or carboxylic acids because N is less electronegative than O, making the N-H hydrogen bond weaker than the O-H bond).
- **Solubility:** Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. Solubility decreases with an increase in the molar mass of the hydrophobic alkyl chain. Aromatic amines are generally insoluble in water.

5. Basic Character & Chemical Properties

Amines behave as Lewis bases due to the unshared electron pair on nitrogen. The basic strength is expressed using K_b or pK_b values (Larger K_b / Smaller pK_b = stronger base).

Basic Character Trends

- **Aliphatic Amines vs Ammonia:** Aliphatic amines are **more basic** than NH_3 because the electron-releasing (+I) effect of alkyl groups increases the electron density on the nitrogen atom.
- **Aromatic Amines vs Ammonia:** Aniline and other aromatic amines are **less basic** than NH_3. The lone pair on nitrogen is in conjugation with the benzene ring, making it less available for protonation.
- **Basic Order in Aqueous Solution:** Depends on +I effect, steric hindrance, and solvation (hydration) effect.
  - For Methyl substituted amines: $2^\circ > 1^\circ > 3^\circ > NH_3$
  - For Ethyl substituted amines: $2^\circ > 3^\circ > 1^\circ > NH_3$

Chemical Properties

1. **Alkylation & Acylation:** Primary and secondary amines react with acid chlorides,

anhydrides, and esters by nucleophilic substitution to form amides.

2. **Carbylamine Reaction (Isocyanide Test):** **Only primary amines** (aliphatic and aromatic) react with chloroform ($CHCl_3$) and ethanolic KOH upon heating to form foul-smelling isocyanides (carbylamines).
   $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC +$
3. **Reaction with Nitrous Acid (HNO_2):**
   - 1° Aliphatic amines: Form unstable diazonium salts which liberate N_2 gas and form alcohols.
   - 1° Aromatic amines: Form stable diazonium salts at low temperatures (273-278 K).
4. **Reaction with Arylsulphonyl Chloride (Hinsberg's Test):**
   Benzenesulphonyl chloride reacts with 1° and 2° amines to form sulphonamides.
   - 1° amine product: Soluble in alkali (due to acidic hydrogen attached to N).
   - 2° amine product: Insoluble in alkali (no acidic hydrogen).
   - 3° amine: Does not react.
5. **Electrophilic Substitution in Aromatic Amines:**
   The $-NH_2$ group is highly activating and ortho-para directing.
   - **Bromination:** With bromine water, it yields 2,4,6-tribromoaniline (white ppt). To get a monosubstituted product, the $-NH_2$ group is first protected by acetylation with acetic anhydride.
   - **Nitration:** Direct nitration yields a significant amount of meta-nitroaniline (due to the formation of the anilinium ion in the strongly acidic medium). Protection by acetylation is required for para-major products.

6. Aliphatic & Aromatic Diazonium Salts

General Formula: $R-N_2^+X^-$ (where R is an alkyl or aryl group, and X^- is an anion like Cl^-, HSO_4^-, BF_4^-). Aliphatic diazonium salts are highly unstable. Aromatic diazonium salts are stable for a short time at low temperatures (273-278 K) due to resonance stabilization.

Method of Preparation (Diazotization)

Aniline is treated with nitrous acid (produced in situ from $NaNO_2$ and mineral acid) at 0-5°C.

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2^+Cl^-$

Physical Properties

Colorless, crystalline solids. Readily soluble in water and stable in cold water but react with warm water. They decompose easily in the dry state.

Chemical Properties

1. **Reactions Involving Displacement of Nitrogen:**
   - **Sandmeyer Reaction:** Displacement by Cl^-, Br^-, or CN^- using $Cu(I)$ salts (

Cu_2Cl_2/HCl, Cu_2Br_2/HBr, $CuCN/KCN$).

- **Gatterman Reaction:** Displacement by Cl^- or Br^- using copper powder in presence of corresponding halogen acid (Cu/HCl, Cu/HBr).
- **Replacement by Iodide Ion:** Simply warming the salt with aqueous Potassium Iodide (KI).
- **Replacement by Fluoride Ion (Balz-Schiemann Reaction):** Treating with fluoroboric acid (HBF_4) forms a precipitate, which on heating yields fluorobenzene.
- **Replacement by H (Reduction):** Mild reducing agents like hypophosphorous acid (H_3PO_2) or ethanol reduce the salt to benzene.
- **Replacement by Hydroxyl Group:** Warming the aqueous solution up to 283 K yields phenol.

2. **Reactions Involving Retention of Diazo Group (Coupling Reactions):**
The diazonium ion acts as an electrophile and reacts with electron-rich aromatic rings like phenols and anilines to form brightly colored azo compounds ($-N=N-$), widely used as dyes.
   - Coupling with Phenol: Yields p-hydroxyazobenzene (orange dye) in a basic medium (pH 9-10).
   - Coupling with Aniline: Yields p-aminoazobenzene (yellow dye) in an acidic medium (pH 4-5).

Importance of Diazonium Salts in Synthesis

They are excellent intermediates for introducing $-F$, $-Cl$, $-Br$, $-I$, $-CN$, $-OH$, and $-NO_2$ groups into the aromatic ring. This is highly valuable because direct halogenation with fluorine or iodine is difficult, and groups like cyano cannot be introduced directly by nucleophilic substitution of chlorobenzene.