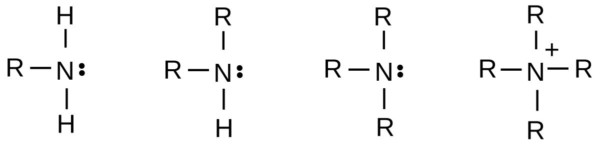
AMINES

Structure Contain the NH_2 group.

Classification **primary** (1°) amines
secondary (2°) amines
tertiary (3°) amines
quarternary (4°) **ammonium** salts



1° 2° 3° 4°

Aliphatic methylamine, ethylamine, dimethylamine

Aromatic NH_2 group is **attached directly** to the benzene ring (phenylamine)

Nomenclature Named after the groups surrounding the nitrogen + *amine*

Aliphatic amines		**Aromatic amines**	
$C_2H_5NH_2$	ethylamine	$C_6H_5NH_2$	phenylamine *(aniline)*
$(CH_3)_2NH$	dimethylamine		
$(CH_3)_3N$	trimethylamine		

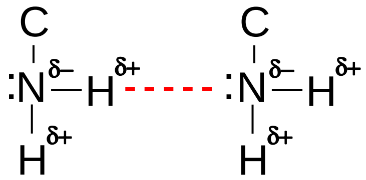
Q.1 *Draw structures for all amines of molecular formula $C_4H_{11}N$.*
Classify them as primary, secondary or tertiary amines.

Properties The presence of the lone pair in 1°, 2° and 3° amines makes them ...

- **Lewis bases -** they can be lone pair donors
- **Brønsted-Lowry bases** - can be proton acceptors
- **Nucleophiles -** provide a lone pair to attack a positive (electron deficient) centre

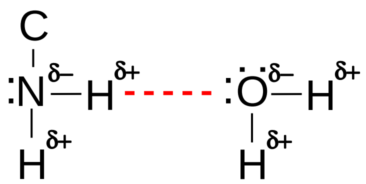
Physical properties

Boiling point
- Boiling points increase with molecular mass.
- Amines have higher boiling points than corresponding alkanes because of intermolecular hydrogen bonding.
- Quarternary ammonium salts are **ionic** - they exist as crystalline salts.



intermolecular hydrogen bonding in amines

Solubility
- Soluble in organic solvents.
- Lower mass compounds are soluble in water due to hydrogen bonding with the solvent.
- Solubility decreases as molecules get heavier.



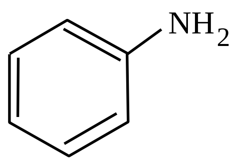
hydrogen bonding between amines and water

Basic properties

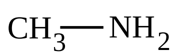
Bases The **lone pair** on nitrogen makes amines **basic**. $\mathbf{RNH_2 + H^+ \longrightarrow RNH_3^+}$

Strength
- depends on the availability of the lone pair and thus its ability to pick up protons
- the greater the electron density on the N, the better its ability to pick up protons
- this is affected by the groups attached to the nitrogen.

- electron withdrawing substituents (e.g. benzene rings) decrease basicity as the electron density on N is lowered.



- electron releasing substituents (e.g. CH_3 groups) increase basicity as the electron density is increased



draw arrows to show the electron density movement

Measurement • the strength of a weak base is depicted by its K_b or pK_b value *pK and pK_b values*

- the larger the K_b value the stronger the base
- the smaller the pK_b value the stronger the base.
- the pK_a value can also be used - ($pK_a + pK_b = 14$)
- the smaller the pK_b, the larger the pK_a.

Compound	*Formula*	*pK_b*	*Comments*
ammonia	NH_3	4.76	
methylamine	CH_3NH_2	3.36	methyl group is electron releasing
phenylamine	$C_6H_5NH_2$	9.38	electrons delocalised into the ring

strongest base **methylamine > ammonia > phenylamine** *weakest base*

Reactions

- Amines which dissolve in water **produce weak alkaline solutions**

$$CH_3NH_2(g) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

- Amines **react with acids to produce salts**.

$$C_6H_5NH_2(l) + HCl(aq) \longrightarrow C_6H_5NH_3^+Cl^-(aq)$$ *phenylammonium chloride*

This reaction allows one to dissolve an amine in water as its salt.

Addition of aqueous sodium hydroxide liberates the free base from its salt

$$C_6H_5NH_3^+Cl^-(aq) + NaOH(aq) \longrightarrow C_6H_5NH_2(l) + NaCl(aq) + H_2O(l)$$

Nucleophilic Character

Due to their **lone pair**, amines react as **nucleophiles** with

- haloalkanes *forming substituted amines* **nucleophilic substitution**
- acyl chlorides *forming N-substituted amides* **addition-elimination**

Haloalkanes Amines can be prepared from haloalkanes (see below and previous notes).

Reagent **Excess**, alcoholic ammonia

Conditions Reflux in excess, alcoholic solution under pressure

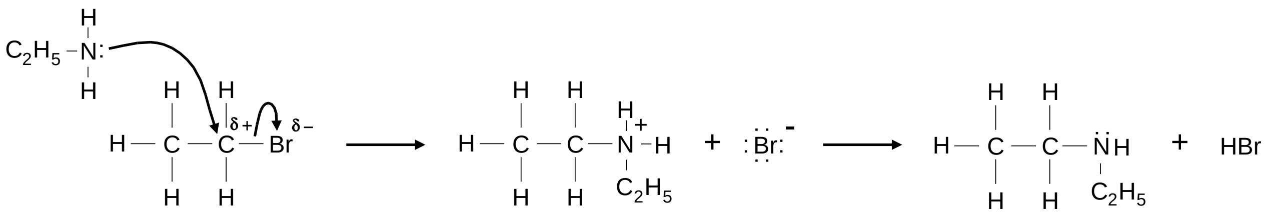
Product Amine (or its salt due to a reaction with the acid produced)

Nucleophile Ammonia (NH_3)

Equation $\mathbf{C_2H_5Br + NH_{3\,(aq\,/\,alc)} \longrightarrow C_2H_5NH_2 + HBr}$ (or $C_2H_5NH_3^+Br^-$)

Why excess ammonia? The amine produced is also a nucleophile and can attack another molecule of haloalkane to produce a secondary amine *(see mecahnism below)*. This in turn can react further producing a tertiary amine and, eventually an ionic quarternary amine. **By using excess ammonia, you ensure that all the haloalkane molecules react with ammonia rather than the newly produced haloalkane.**

Further reactions $\mathbf{C_2H_5NH_2 + C_2H_5Br \longrightarrow HBr + (C_2H_5)_2NH}$ diethylamine, a 2° amine



$\mathbf{(C_2H_5)_2NH + C_2H_5Br \longrightarrow HBr + (C_2H_5)_3N}$ triethylamine, a 3° amine

$\mathbf{(C_2H_5)_3N + C_2H_5Br \longrightarrow (C_2H_5)_4N^+ Br^-}$ tetraethylammonium bromide
a quarternary (4°) salt

Uses Quarternary ammonium salts with long chain alkyl groups are used as **cationic surfactants in fabric softening**. *eg* $[CH_3(CH_2)_{17}]_2N^+(CH_3)_2Cl^-$

Prepared from

haloalkanes Nucleophilic substitution using ammonia ... see above

nitriles **Reduction** of nitriles using **$Li^+AlH_4^-$** in **dry ether**

eg $\mathbf{CH_3CH_2CN + 4[H] \longrightarrow CH_3CH_2CH_2NH_2}$

aromatic nitro compounds **Reduction** by refluxing with **tin and conc. hydrochloric acid**

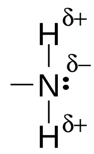
eg $\mathbf{C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O}$

α - AMINO ACIDS

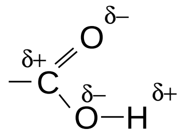
Structure

Amino acids contain 2 functional groups

- **amine** **NH_2**
- **carboxyl** **COOH**

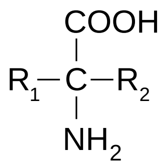


Amine

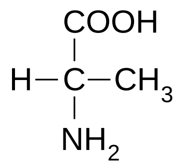


Carboxyl

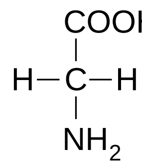
They all have a similar structure - the identity of R_1 and R_2 vary



general structure



2-aminopropanoic acid (Alanine)



2-aminoethanoic acid (Glycine)

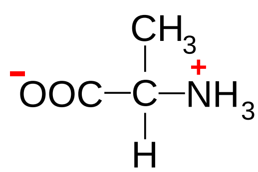
Optical Isomerism

Amino acids can exist as **optical isomers** if they have **different R_1 and R_2** groups

- optical isomers exist when a molecule contains an **asymmetric carbon** atom
- asymmetric carbon atoms have **four different atoms or groups** attached
- **two isomers** are formed
- one **rotates plane polarised light** to the left, one rotates it to the right
- **no optical isomerism with glycine** - two H's are attached to the C atom

Zwitterions

- a zwitterion is a **dipolar ion**
- it has a **plus and a minus charge** in its structure
- a proton from the COOH group moves to NH_2
- amino acids exist as **zwitterions** at a certain pH
- the pH value is called the **isoelectric point**
- produces increased inter-molecular forces
- melting and boiling points are higher



a zwitterion

Acid/base properties

- amino acids possess acidic and basic properties due to their functional groups
- they will form salts when treated with acids or alkalis.

Basic properties:

react with H^+ $\quad$ **$HOOCCH_2NH_2 + H^+ \longrightarrow HOOCCH_2NH_3^+$**

HCl $\quad$ **$HOOCCH_2NH_2 + HCl \longrightarrow HOOCCH_2NH_3^+\,Cl^-$**

Acidic properties:

react with OH^- $\quad$ **$HOOCCH_2NH_2 + OH^- \longrightarrow {}^-OOCCH_2NH_2 + H_2O$**

NaOH $\quad$ **$HOOCCH_2NH_2 + NaOH \longrightarrow Na^+\,{}^-OOCCH_2NH_2 + H_2O$**

Q.2 *Describe the arrangement of bonds in the amino acid H_2NCH_2COOH*

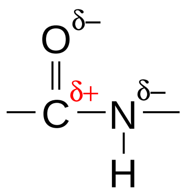
around... the N atom in the NH_2
the C atom in the COOH
the C atom in the CH_2

What change, if any, takes place to the arrangement around the N if the amino acid is treated with dilute acid?

PEPTIDES

Formation

- α-amino acids can join up together to form peptides via an **amide** or **peptide** **link**

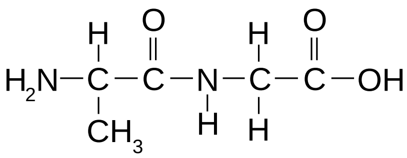


the peptide link

Structure

Sequences of amino acids joined together by peptide links

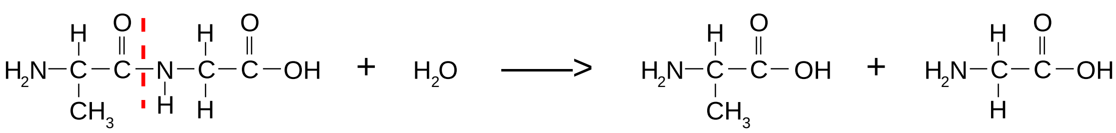
- 2 amino acids joined ***dipeptide***
- 3 amino acids joined ***tripeptide***
- many amino acids joined ***polypeptide***



a dipeptide

Hydrolysis

Peptides can be broken down into their constituent amino acids by **hydrolysis**



- attack takes place at the slightly positive C of the C=O
- the C-N bond next to the C=O is broken
- **hydrolysis with just water is not feasible**
- **hydrolysis in alkaline/acid conditions is quicker**
- hydrolysis in acid/alkaline conditions (e.g. NaOH) will produce salts

with	HCl	NH_2	will become	$NH_3^+Cl^-$
	H^+	NH_2	will become	NH_3^+
	NaOH	COOH	will become	COO^-Na^+
	OH^-	COOH	will become	COO^-

Q.3 *Draw structural isomers for the compounds produced when*

- *$H_2NCH_2CONHCH(CH_3)COOH$ is hydrolysed by water*

- *$H_2NCH_2CONHC(CH_3)_2COOH$ is hydrolysed in **acidic** solution*

- *$H_2NCH_2CONHCH(CH_3)COOH$ is hydrolysed in **alkaline** solution*

Q.4 *Write out possible sequences for the **original** peptide if the hydrolysis products are*

- *1 mol of amino acid **A**, 1 mol of amino acid **B** and 1 mol of amino acid **C***

- *1 mole of amino acid **A**, 2 mol of amino acid **B** and 1 mol of amino acid **C***

***How many** possible sequences are there for the **original** peptide if hydrolysis yields 1 mol of amino acid **A**, 1 mol of **B**, 1 mol of **C**, **1** mol of **D** and 1 mol of **E** ?*

Proteins

- **polypeptides with high molecular masses**
- chains can be lined up with each other
- the **C=O and N-H bonds are polar** due to a difference in electronegativity
- **hydrogen bonding** exists between chains

dotted lines ----------
represent hydrogen bonding