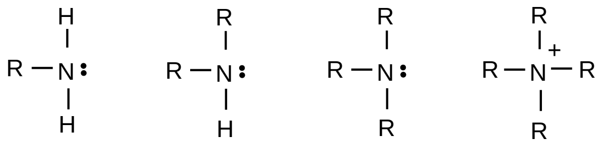
AMINES

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

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

e.g.	$C_2H_5NH_2$	ethylamine	$(CH_3)_2NH$	dimethylamine
	$(CH_3)_3N$	trimethylamine	$C_6H_5NH_2$	phenylamine *(aniline)*

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

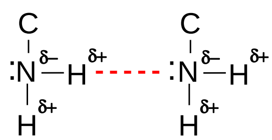
Properties The presence of the lone pair in 1°, 2° and 3° amines makes them ...

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

Physical properties

Boiling point

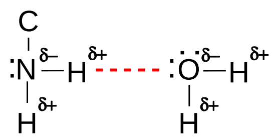
- Boiling points increase with molecular mass.
- Amines have higher boiling points than corresponding alkanes because of intermolecular hydrogen bonding.
- Quarternary ammonium salts are ionic - exist as salts.



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 the molecules get heavier.



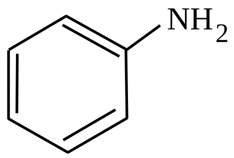
hydrogen bonding between amines and water

Basic properties

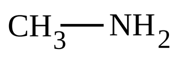
Bases The **lone pair** on nitrogen makes amines **basic**. $RNH_2 + H^+ \longrightarrow RNH_3^+$

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 pK_b value
- the smaller the pK_b the stronger the base.
- the pK_a value can also be used; it is worked out by applying $pK_a + pK_b = 14$.
- 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** *weekest 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

$$C_6H_5NH_3^+Cl^-{}_{(aq)} + NaOH_{(aq)} \longrightarrow C_6H_5NH_{2(l)} + NaCl_{(aq)} + H_2O_{(l)}$$

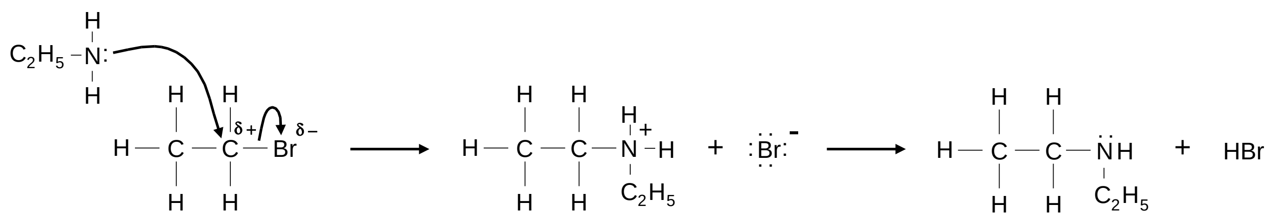
Nucleophilic Character Due to their **lone pair**, amines react as **nucleophiles** with

- 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	Aqueous, alcoholic ammonia
Conditions	Reflux in aqueous, 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 $C_2H_5NH_3^+Br^-$)

Problem The amine produced is also a nucleophile (lone pair on the N) and can attack another molecule of haloalkane to produce a secondary amine. This in turn is a nucleophile and can react further producing a tertiary amine and, eventually an ionic quarternary amine.



$\mathbf{C_2H_5NH_2 + C_2H_5Br \longrightarrow HBr + (C_2H_5)_2NH}$ 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 4° salt

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

Preparation from

haloalkanes Nucleophilic substitution using ammonia ... see above

nitriles **Reduction** of nitriles using $\mathbf{Li^+AlH_4^-}$ in **dry ether**

e.g. $\mathbf{CH_3CH_2CN + 4[H] \longrightarrow CH_3CH_2CH_2NH_2}$

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

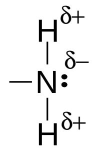
e.g. $\mathbf{C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O}$

AMINO ACIDS

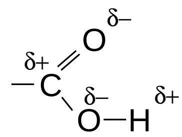
Structure

Amino acids contain 2 functional groups

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

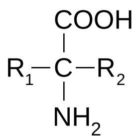


Amine

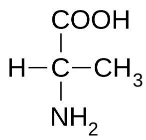


Carboxyl

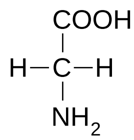
They all have a similar structure - the identity of R_1 and R_2 vary



general structure



2-aminopropanoic acid (Alanine)



2-aminoethanoic acid (Glycine)

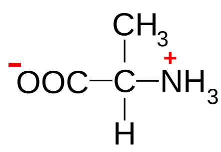
Optical Isomerism

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
- **glycine doesn't exhibit optical isomerism** as there are two H attached to the C atom

Zwitterions

- a zwitterion is a **dipolar ion**
- it has a **plus and a minus charge** in its structure
- amino acids exist as zwitterions
- 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^+ **$HOOCCH_2NH_2 + H^+ \longrightarrow HOOCCH_2NH_3^+$**

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

Acidic properties:

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

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

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?

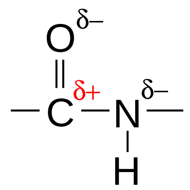
Peptide formation

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

PEPTIDES

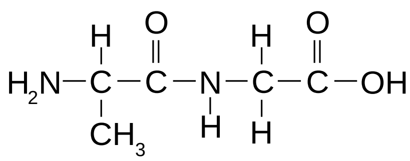
Structure

Sequences of amino acids joined together by peptide links



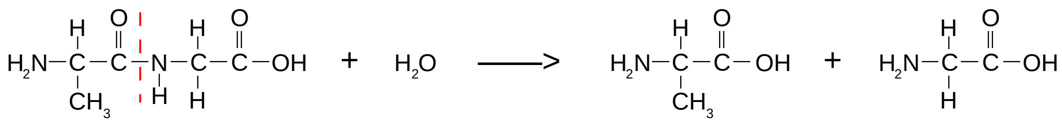
the peptide link

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



a dipeptide

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 mole of amino acid* ***A****, 1 mole of amino acid* ***B*** *and 1 mole of amino acid* ***C***

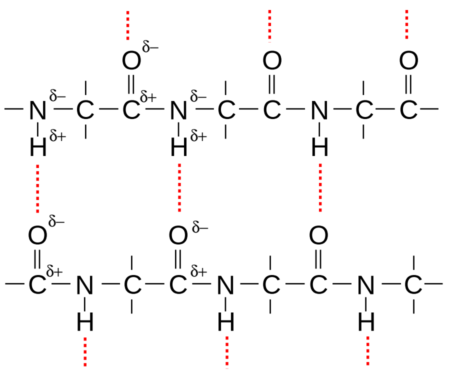
- *1 mole of amino acid* ***A****, 2 moles of amino acid* ***B*** *and 1 mole of amino acid* ***C***

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



AMIDES - $RCONH_2$

Structure of amides

Nomenclature White crystalline solids named from the corresponding acid (remove oic acid, add amide)

CH_3CONH_2	ethanamide *(acetamide)*	
$C_2H_5CONHC_6H_5$	N - phenyl propanamide -	the N tells you the substituent is on the nitrogen

Nylons are examples of polyamides. (see under polymers)

Preparation Acyl chloride + ammonia (see above)

Chemical Properties

Hydrolysis

general reaction $CH_3CONH_2 + H_2O \longrightarrow CH_3COOH + NH_3$

acidic soln. $CH_3CONH_2 + H_2O + HCl \longrightarrow CH_3COOH + NH_4Cl$

alkaline soln. $CH_3CONH_2 + NaOH \longrightarrow CH_3COONa + NH_3$

Identification Warming an amide with **dilute sodium hydroxide** solution and testing for the **evolution of ammonia** using moist red litmus paper is used as a simple test for amides.

Reduction Reduced to primary amines: $CH_3CONH_2 + 4[H] \longrightarrow CH_3CH_2NH_2 + H_2O$