

AMINES

Structure Primary amines contain the NH_2 group.

<i>Classification</i>	primary (1°) amines secondary (2°) amines tertiary (3°) amines quarternary (4°) ammonium salts	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N}: \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{N}: \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{N}: \\ \\ \text{R} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{N}^+-\text{R} \\ \\ \text{R} \end{array}$
		1°	2°	3°	4°

Aliphatic methylamine, ethylamine, dimethylamine

Aromatic NH_2 group is **attached directly** to the benzene ring e.g. phenylamine

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

Aliphatic amines

$\text{C}_2\text{H}_5\text{NH}_2$	ethylamine
$(\text{CH}_3)_2\text{NH}$	dimethylamine
$(\text{CH}_3)_3\text{N}$	trimethylamine

Aromatic amines

$\text{C}_6\text{H}_5\text{NH}_2$	phenylamine (<i>aniline</i>)
-----------------------------------	--------------------------------

Q.1 Draw structures for all amines of molecular formula $\text{C}_4\text{H}_{11}\text{N}$.
Classify them as primary, secondary or tertiary amines.

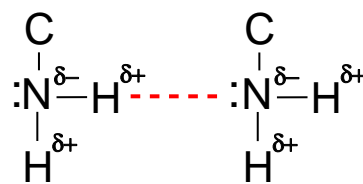
Properties The presence of the lone pair in 1° , 2° and 3° amines makes them ...

- **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.

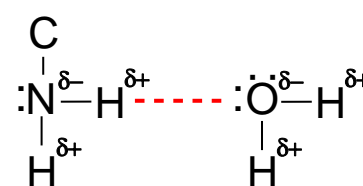
- Amines have higher boiling points than corresponding alkanes because of intermolecular hydrogen bonding.
- Quarternary ammonium salts are **ionic** - they exist as crystalline salts.



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

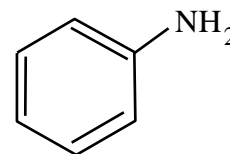
Basic properties

Bases The **lone pair** on nitrogen makes amines **basic**. $\text{RNH}_2 + \text{H}^+ \rightarrow \text{RNH}_3^+$

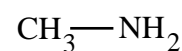
Strength

- 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. CH₃ groups) increase basicity as the electron density is increased



draw arrows to show the electron density movement

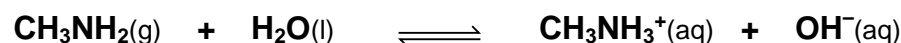
Measurement • the strength of a weak base is depicted by its K_b or pK_b value

- pK* and *pK_b*
- 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	<i>pK_b</i>	Comments
ammonia	NH ₃	4.76	
methylamine	CH ₃ NH ₂	3.36	methyl group is electron releasing
phenylamine	C ₆ H ₅ NH 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**

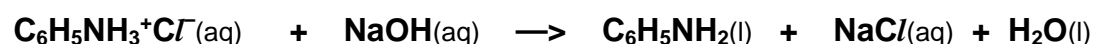


- Amines **react with acids to produce salts.**



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



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**

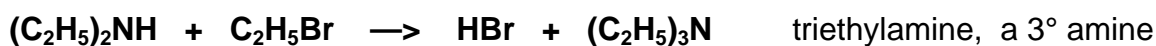
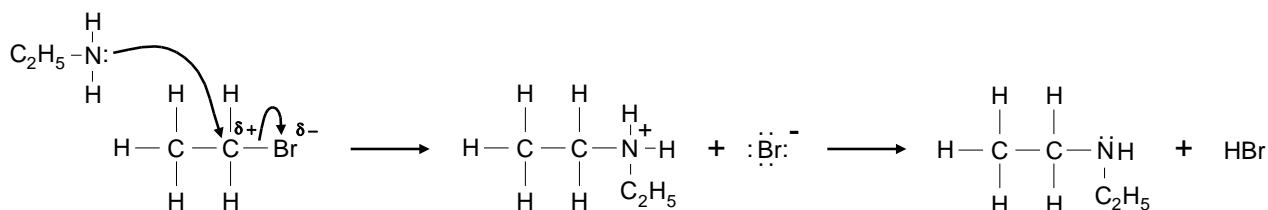
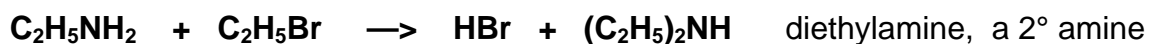
Haloalkanes Amines can be prepared from haloalkanes (see below and previous notes).

<i>Reagent</i>	Excess , alcoholic ammonia
<i>Conditions</i>	Reflux in excess, alcoholic solution under pressure
<i>Product</i>	Amine (or its salt due to a reaction with the acid produced)
<i>Nucleophile</i>	Ammonia (NH ₃)
<i>Equation</i>	$\text{C}_2\text{H}_5\text{Br} + \text{NH}_3(\text{aq / alc}) \longrightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{HBr} \quad (\text{or } \text{C}_2\text{H}_5\text{NH}_3^+\text{Br}^-)$

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



Uses

Quarternary ammonium salts with long chain alkyl groups are used as **cationic surfactants in fabric softening**. eg $[\text{CH}_3(\text{CH}_2)_{17}]_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$

Prepared from

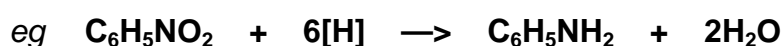
haloalkanes **Nucleophilic substitution** using ammonia ... see above

nitriles **Reduction of nitriles** using $\text{Li}^+\text{AlH}_4^-$ in **dry ether**



aromatic nitro compounds

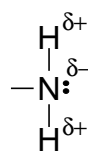
Reduction by refluxing with tin and conc. hydrochloric acid



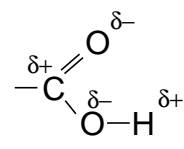
α - AMINO ACIDS

Structure Amino acids contain 2 functional groups

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

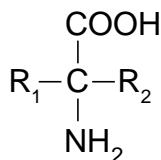


Amine

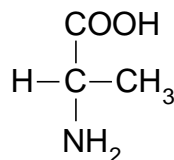


Carboxyl

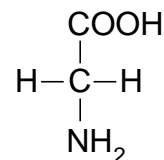
They all have a similar structure - the identity of R_1 and R_2 varies



general
structure



2-aminopropanoic acid
(Alanine)



2-aminoethanoic acid
(Glycine)

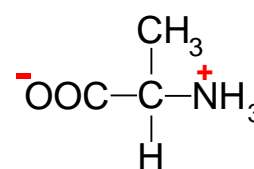
Optical

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

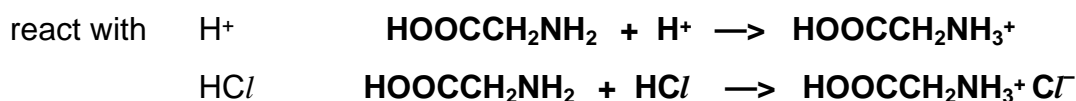


a zwitterion

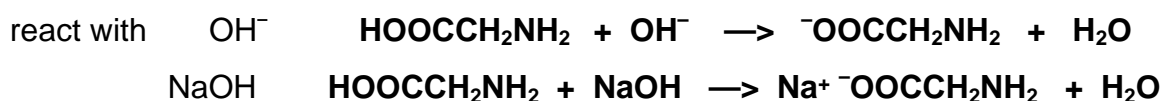
Acid/base properties

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

Basic properties:



Acidic properties:

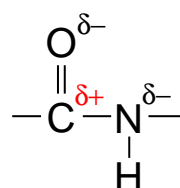


Q.2 Describe the arrangement of bonds in the amino acid $\text{H}_2\text{NCH}_2\text{COOH}$ around...
 the N atom in the NH_2
 the C atom in the COOH
 the C atom in the CH_2

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

PEPTIDES

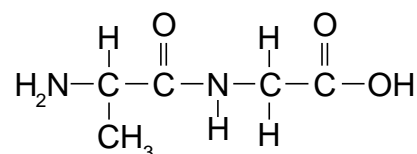
Formation • α -amino acids can join up together to form peptides via an **amide** or **peptide link**



the peptide link

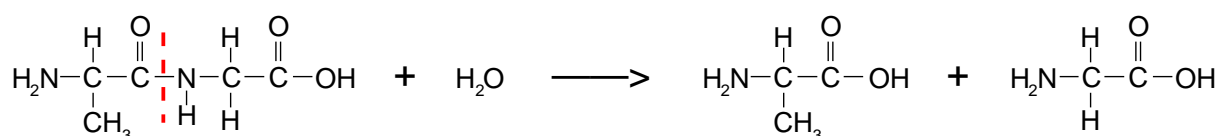
Structure Sequences of amino acids joined together by peptide links

- 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 $\text{C}=\text{O}$
- the $\text{C}-\text{N}$ bond next to the $\text{C}=\text{O}$ 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	$\text{COO}^- \text{Na}^+$
	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

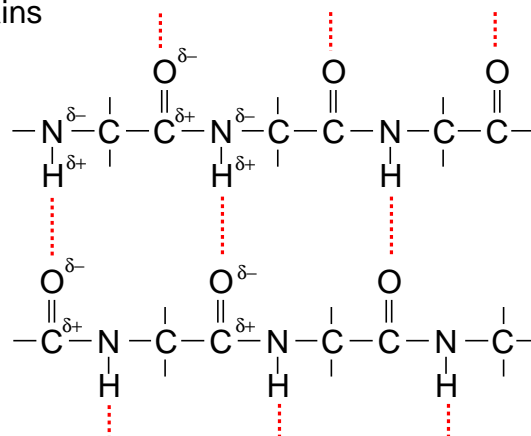
- 1 mol of amino acid **A**, 1 mol of amino acid **B** and 1 mol of amino acid **C**
- 1 mole of amino acid **A**, 2 mol of amino acid **B** and 1 mol of amino acid **C**

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

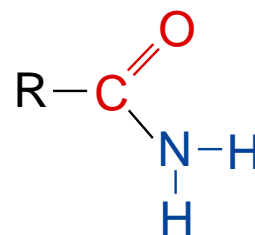


AMIDES - RCONH₂

Structure Based on a carboxylic acid (remove OH, add NH₂)

Primary (1°) amides two H's on the N

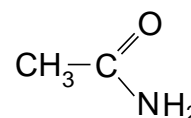
Secondary (2°) amides one H on the N



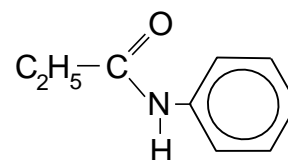
Appearance White crystalline solids

Nomenclature Named from the corresponding acid (**remove oic acid... add amide**)

(1°) **CH₃CONH₂** ethanamide (*acetamide*)



(2°) **C₂H₅CONHC₆H₅** N - phenyl propanamide
the N tells you that the substituent is on the nitrogen



Nylons are examples of polyamides. (*see polymers*)

Preparation Acyl chloride + ammonia (or amines for 2° amides) *see under carboxylic acids*



Chemical Properties

Hydrolysis general reaction $\text{CH}_3\text{CONH}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + \text{NH}_3$

acidic soln. $\text{CH}_3\text{CONH}_2 + \text{H}_2\text{O} + \text{HCl} \longrightarrow \text{CH}_3\text{COOH} + \text{NH}_4\text{Cl}$

alkaline soln. $\text{CH}_3\text{CONH}_2 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{NH}_3$

Identification Warming 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:

