

4. Amines, Amides and Amino Acids

Naming

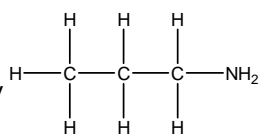
Amines

These end in **-amine**.

There is, however, rather confusingly two ways of using this suffix.

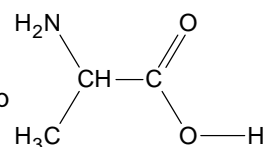
The exam board tend to use the common version where the name stem ends in **-yl** propylamine.

The IUPAC version of the same chemical is propan-1-amine. (This is used in the same way as naming alcohols)



propylamine
Or propan-1-amine

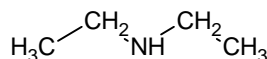
If there is another priority functional group as well as the amine group then the prefix amino is used.



2-aminopropanoic acid.

If the amine is secondary and has two alkyl groups attached to the nitrogen, then each chain is named and the smaller alkyl group is preceded by an **-N** which plays the same role as a number in positioning a side alkyl chain

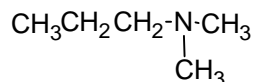
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$
N-methylpropylamine (common name)
N-methylpropan-1-amine (IUPAC name)



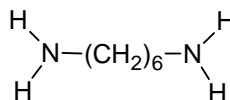
In the common naming version if the chain lengths are the same an **-N** is not used

Diethylamine (common name- does not use N if chains are same length)
N-ethylethanamine (IUPAC name does still use N)

If a tertiary amine similar rules apply, and each alkyl side group is given an **N**



N,N-dimethylpropylamine (common name)
N,N-dimethylpropan-1-amine (IUPAC name)

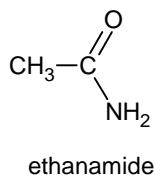


It could also be named
1,6-diaminohexane

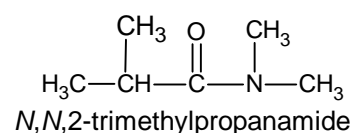
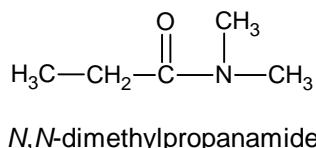
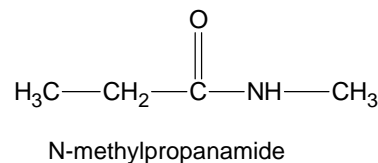
hexane-1,6-diamine

Amides

Add **-amide** to the stem name



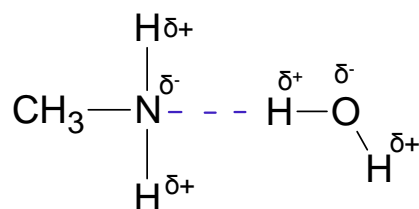
Secondary and tertiary amides are named differently to show the two (or three) carbon chains. The smaller alkyl group is preceded by an **-N** which plays the same role as a number in positioning a side alkyl chain



Properties of Amines

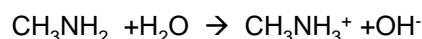
Amines have a characteristic fishy smell

Small amines can form hydrogen bonds with water and therefore can dissolve readily in water.

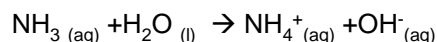


Base Properties

Primary aliphatic amines act as Bronsted-Lowry Bases because the lone pair of electrons on the nitrogen is readily available for forming a dative covalent bond with a H⁺ and so accepting a proton.



Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and so make it a stronger base.

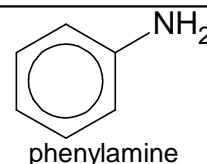


Secondary amines are stronger bases than primary amines because they have more alkyl groups that are substituted onto the N atom in place of H atoms. Therefore more electron density is pushed onto the N atom (as the inductive effect of alkyl groups is greater than that of H atoms).

One might expect using the same trend that tertiary amine would be the strongest amine base but the trend does not hold. The tertiary amines and corresponding ammonium salts are less soluble in water and this makes them less strong bases than the secondary amines. (This point will not be examined)

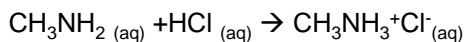
Base strength of aromatic amines

Primary aromatic amines such as Phenylamine do not form basic solutions because the lone pair of electrons on the nitrogen delocalise with the ring of electrons in the benzene ring. This means the N is less able to accept protons.

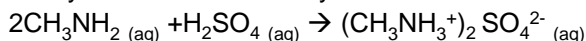


Reactions with acids

Amines as bases react with acids to form ammonium salts.



Methylamine methylammonium chloride



Addition of NaOH to an ammonium salt will convert it back to the amine

The ionic salts formed in this reaction means that the compounds are soluble in the acid.

e.g. Phenylamine is not very soluble in water but phenylammonium chloride is soluble

These ionic salts will be solid crystals, if the water is evaporated, because of the strong ionic interactions.

Making a basic buffer from an amine

Basic buffers can be made from combining a weak base with a salt of that weak base

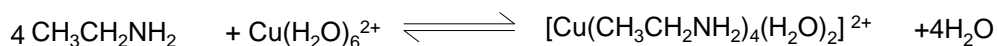
e.g. Ammonia and ammonium chloride

Methylamine and methylammonium chloride

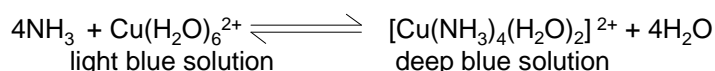
Ethylamine and ethylammonium chloride

Formation of complex ions

The lone pair of electrons on the nitrogen enable amines to act as ligands and form dative covalent bonds into transition metal ions to form coloured complex ions.

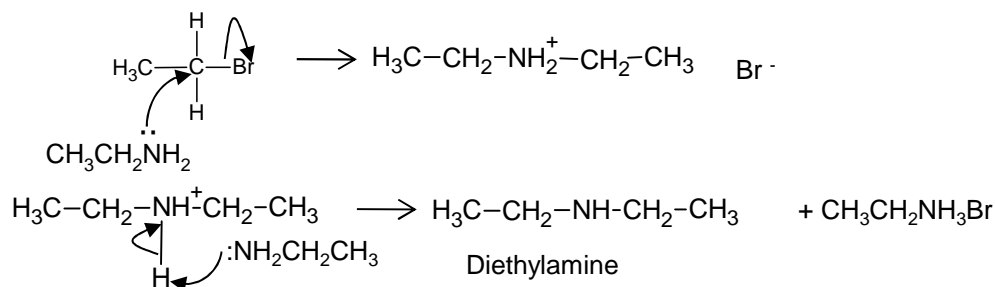
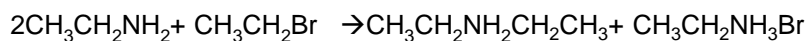


This is a similar ligand exchange reaction to the one where ammonia acts as the ligand



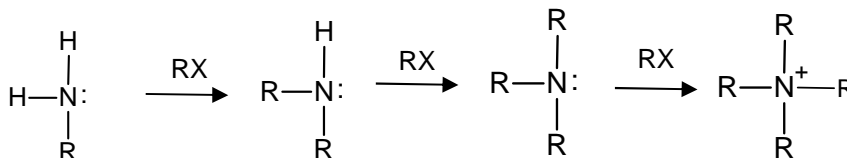
Reaction of primary Amines with halogenoalkanes forming secondary amines

Amines will react with halogenoalkanes in a similar way to the reaction of ammonia with halogenoalkanes via a nucleophilic substitution reaction



The secondary amine formed can also then react with more halogenoalkane to form a tertiary amine and subsequently on to what is called a quaternary ammonium salt

Where RX is the haloalkane

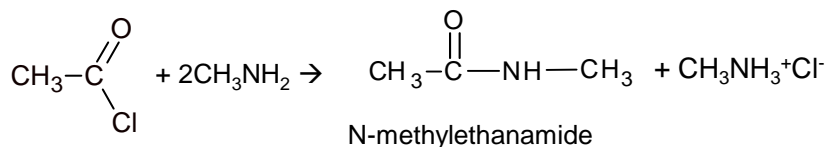


Reaction with primary amines with acyl chlorides

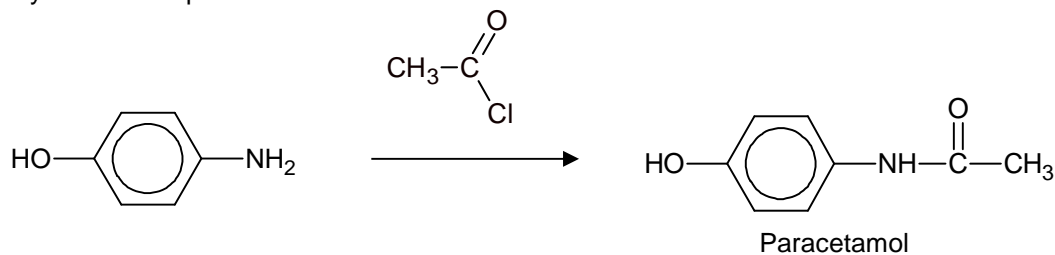
Change in functional group: **acyl chloride** \rightarrow **secondary amide**

Reagent: **primary amine**

Conditions: **room temp.**



Paracetamol is made by the reaction of an aromatic amine with an acyl chloride to produce an amide



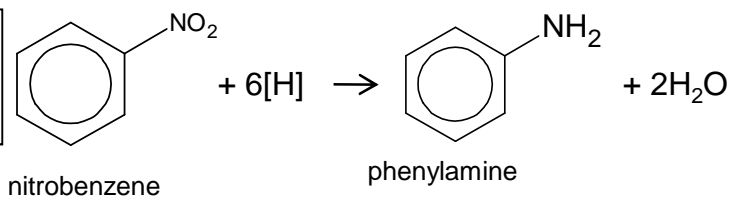
Reducing nitroarenes to aromatic amines

The nitro group on an arene can be reduced an amine group as follows

Reagent: Sn and HCl or Fe and HCl

Conditions: Heating

Mechanism: reduction

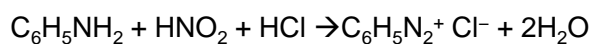
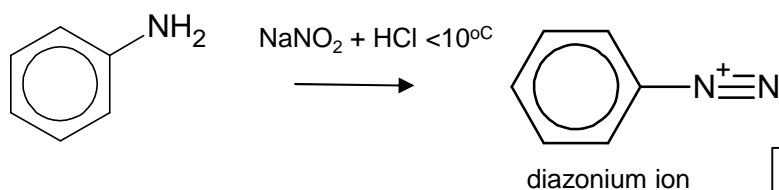


As the reaction is carried out in HCl the salt $C_6H_5NH_3^+Cl^-$ will be formed. Reacting this salt with NaOH will give phenylamine.

The phenylamine formed in this reaction is best separated from the reaction mixture by steam distillation.

Synthesis of azo dyes

Step 1: reaction of an aromatic amine with nitrous acid at $<10^\circ C$, forming a diazonium ion,

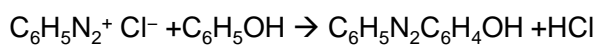
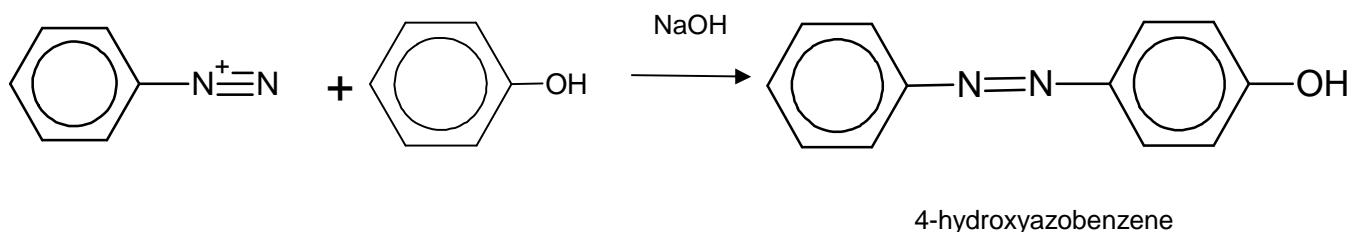


Nitrous acid is generated *in situ* from $NaNO_2/HCl$.

Below $0^\circ C$ the temperature is too low and the reaction would be too slow

If the diazonium ion is allowed to heat above $10^\circ C$ it reacts with water to form phenol and N_2 gas
 $C_6H_5N_2^+ + H_2O \rightarrow C_6H_5OH + N_2 + H^+$

Step 2: coupling of diazonium ion with a phenol under alkaline conditions;



Azo dyes are used for dyes, pigments and colourings

Polymers

There are two **types** of **polymerisation**: **addition** and **condensation**

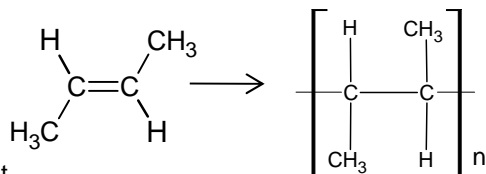
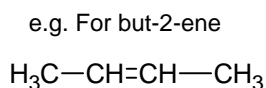
Addition Polymerisation

An **addition polymer** forms when unsaturated monomers react to form a polymer
Monomers contain C=C bonds

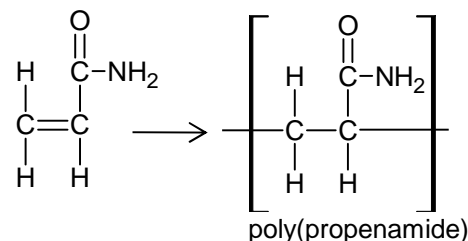
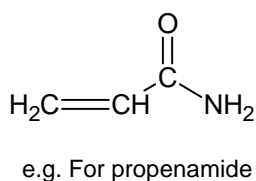
Poly(alkenes) are chemically inert due to the strong C-C and C-H bonds and **non-polar** nature of the bonds and therefore are non-biodegradable.

Chain forms when same basic unit is repeated over and over.

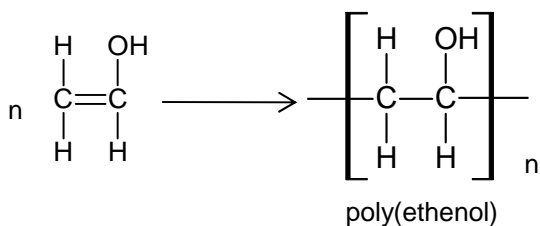
You should be able to draw the polymer repeating unit for any alkene



It is best to first draw out the monomer with groups of atoms arranged around the double bond



Poly(ethenol)



The addition polymer poly(ethenol) has good solubility in water because it can form many strong hydrogen bonds with water. This makes it a useful polymer for uses such as soluble laundry bags and liquid detergent capsules.

Condensation Polymerisation

The two most common **types** of condensation polymers are **polyesters** and **polyamides** which involve the formation of an **ester** linkage or an **amide** linkage.

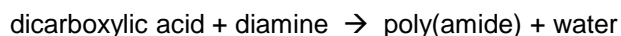
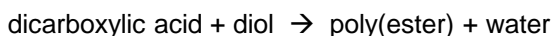
In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g. H_2O or HCl .

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di-carboxylic acid, diol, diacyl chloride.

Forming polyesters and polyamide uses these reactions we met earlier in the course

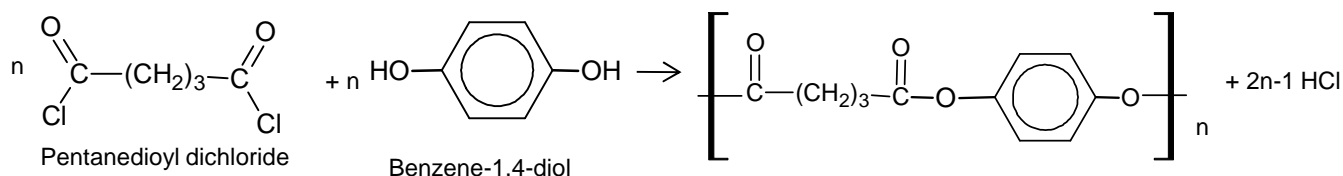
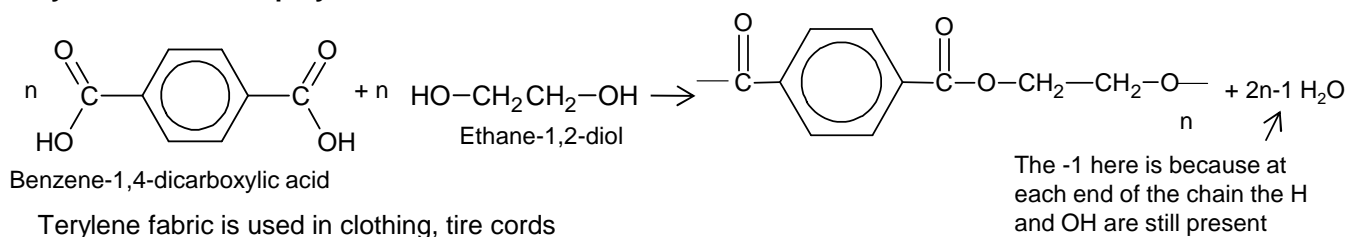


If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:

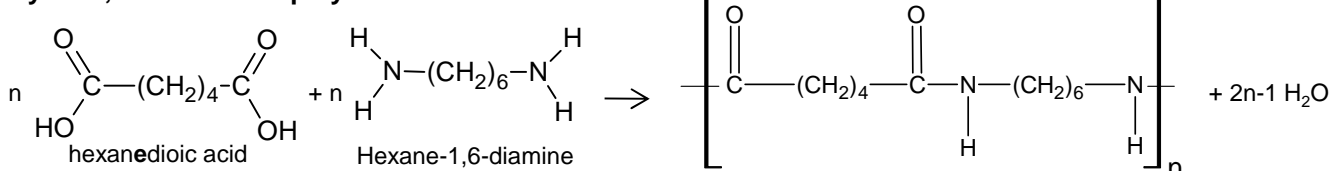


Using the carboxylic acid to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous HCl fumes.

Terylene- a common polyester

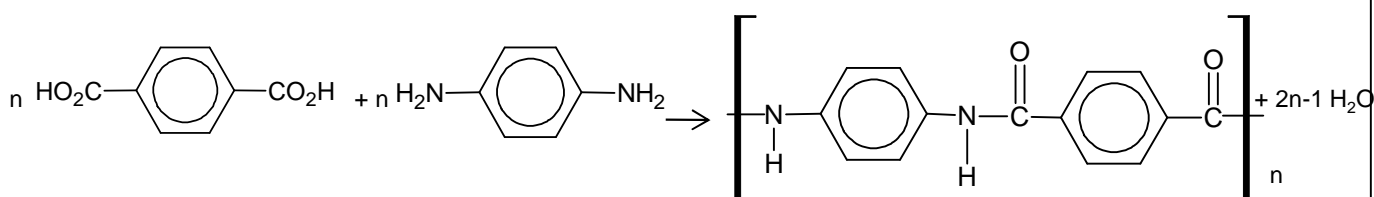


Nylon 6,6 - a common polyamide



The 6,6 stands for 6 carbons in each of the monomers. Different length carbon chains produce different polyamides

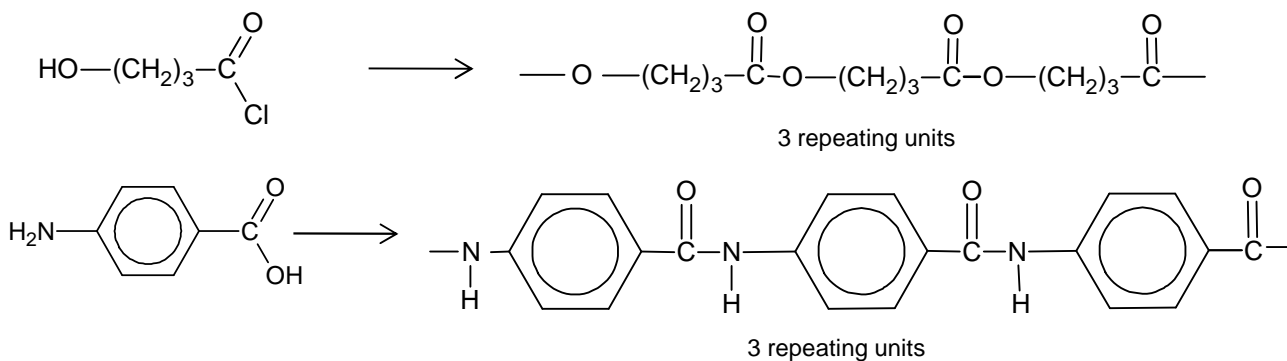
Kevlar- a common polyamide



Note on classification for condensation polymers

If asked for **type of polymer**: It is polyamide or polyester
Whereas **type of polymerisation** is **condensation**

It is also possible for polyamides and polyesters to form from **one** monomer, if that monomer contains both the functional groups needed to react



Chemical reactivity of condensation polymers

polyesters and polyamides can be broken down by **hydrolysis** and are, therefore, biodegradable

The reactivity can be explained by the presence of **polar bonds** which can attract attacking species such as nucleophiles and acids

Polyesters can be hydrolysed by acid and alkali

With HCl a polyester will be hydrolysed and split up into the original dicarboxylic acid and diol

With NaOH a polyester will be hydrolysed and split up into the diol and dicarboxylic acid salt.

Polyamides can be hydrolysed by aqueous acids or alkalis.

With HCl a polyamide will be hydrolysed and split up into the original dicarboxylic acid and diamine salt

With NaOH a polyamide will be hydrolysed and split up into the diamine and dicarboxylic acid salt

Intermolecular bonding between condensation polymers chains

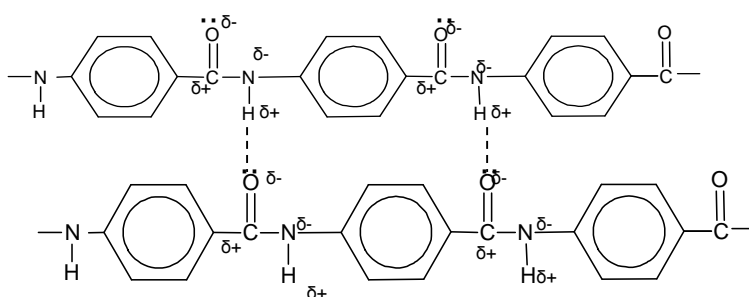
Polyesters have permanent dipole bonding between the $C^{\delta+}=O^{\delta-}$ groups in the different chains in addition to the London forces between the chains.

Polyamides (and proteins) have **hydrogen bonding** between the lone pairs on oxygen in $C^{\delta+}=O^{\delta-}$ groups and the H in the $N^{\delta-}-H^{\delta+}$ groups in the different chains.

There are also **Permanent dipole-permanent dipole forces** because the polar $C=O$ bond and polar $C-N$ bond

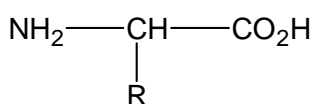
There are also **London forces** which are large because there are many electrons in the molecule

Polyamides will therefore have higher melting points than polyesters.



Amino Acids

General structure of an amino acid

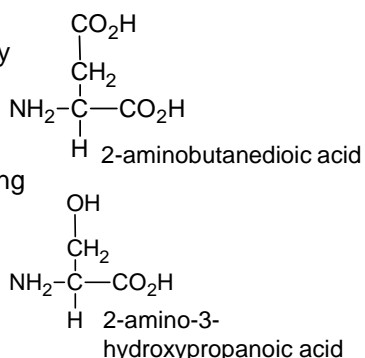
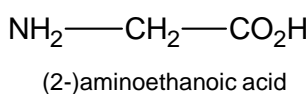


The R group can be a variety of different things depending on what amino acid it is.

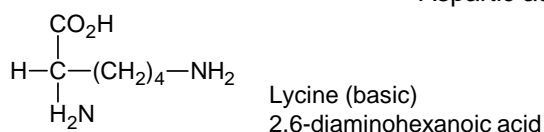
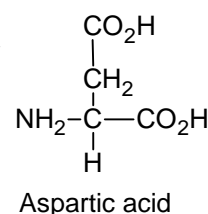
The simplest amino acid is glycine, where the R is an H $\text{NH}_2 - \text{CH}_2 - \text{CO}_2\text{H}$

Naming amino acids

You do not need to know any common names for the 20 essential amino acids. We should, however, be able to name given amino acids using IUPAC organic naming



Some amino acids have an extra carboxylic acid or an amine group on the R group. These are classed as acidic or basic (respectively) amino acids

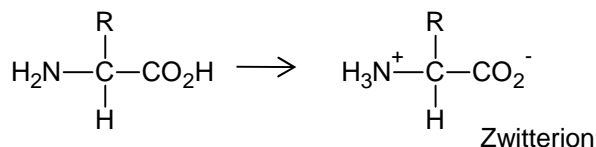


Zwitterions

The no charge form of an amino acid never occurs.
The amino acid exists as a dipolar zwitterion.

Amino acids are often **solids**

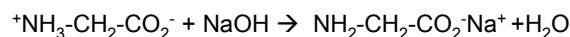
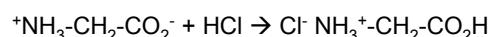
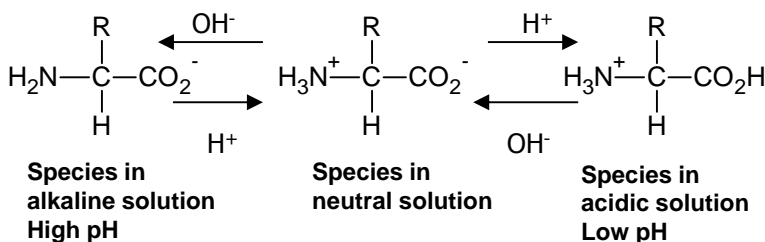
The **ionic interaction** between zwitterions explains the relatively high melting points of amino acids as opposed to the weaker hydrogen bonding that would occur in the no charge form.



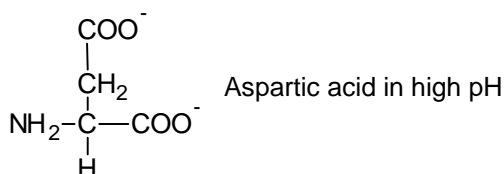
Acidity and Basicity

The amine group is basic and the carboxylic acid group is acidic.

Amino acids act as weak buffers and will only gradually change pH if small amounts of acid or alkali are added to the amino acids.



The extra carboxylic acid or amine groups on the R group will also react and change form in alkaline and acid conditions



Chromatography of Amino Acids

A mixture of amino acids can be separated by chromatography and identified from the amount they have moved.

$$R_f \text{ value} = \frac{\text{distance moved by amino acid}}{\text{distance moved by the solvent}}$$

Each amino acid has its own R_f value. Compare an unknown amino acid's R_f value with known values in a data book to identify the amino acid

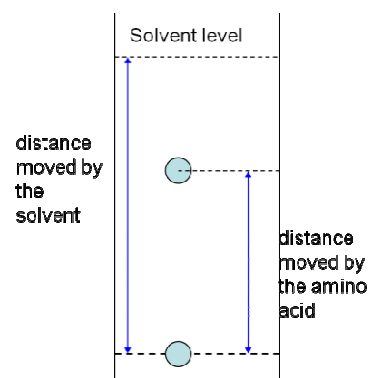
Method

Take chromatography paper and draw a pencil line 1.5cm from bottom.

With a capillary tube put a small drop of amino acid on pencil line
Roll up paper and stand it in a large beaker.

The solvent in the beaker should be below the pencil line.
Allow to stand for 20 mins and mark final solvent level

Spray paper with ninhydrin and put in oven

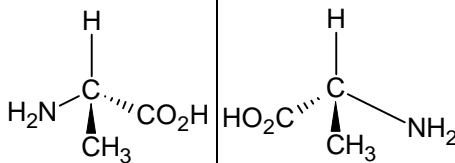


If ninhydrin is sprayed on an amino acid and then heated for 10 minutes then red to blue spots appear. This is done because amino acids are transparent and cannot be seen.

Optical Activity

All amino acids, except glycine, are chiral because there are four different groups around the C

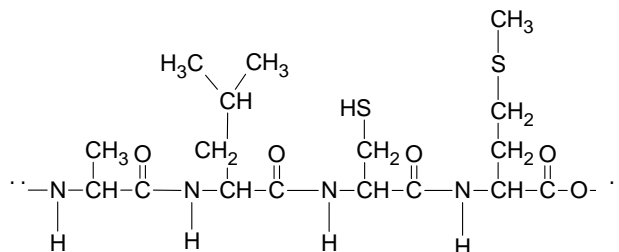
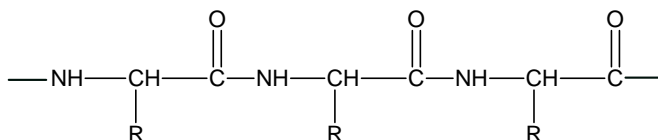
They rotate plane polarised light.



Optical isomers have similar physical and chemical properties, but they rotate plane polarised light in different directions.

Proteins

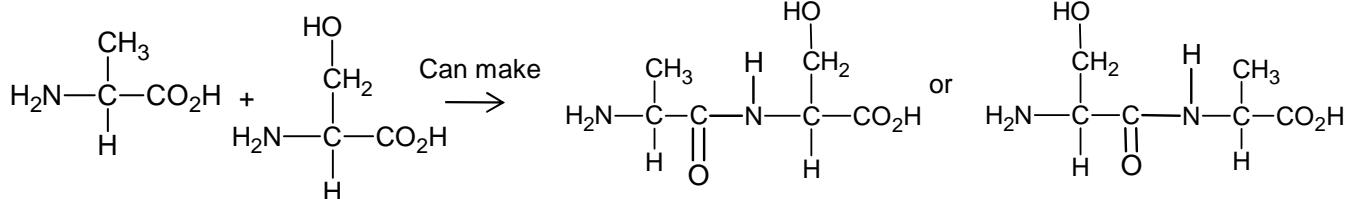
Proteins are polymers made from combinations of amino acids. The amino acids are linked by peptide links, which are the amide functional group.



Dipeptides

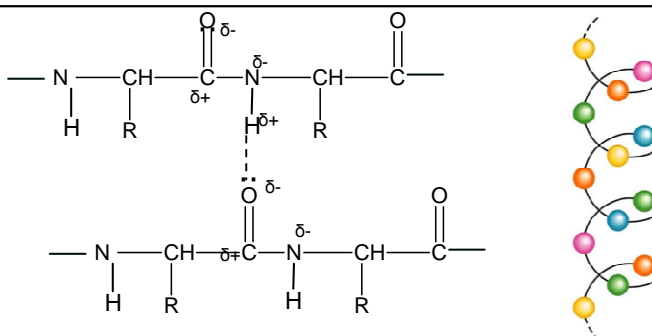
Dipeptides are simple combination molecules of two amino acids with one amide (peptide) link.

For any two different amino acids there are two possible combinations of the amino acids in the dipeptide.



Importance of hydrogen bonding in proteins

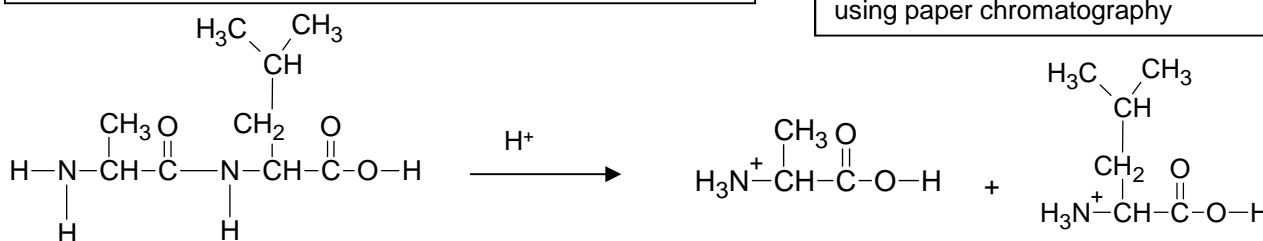
The 3D arrangement of amino acids with the polypeptide chain in a corkscrew shape is held in place by Hydrogen bonds between the H of $\text{---N}^{\delta-}\text{---H}^{\delta+}$ group and the $\text{---O}^{\delta-}$ of $\text{C}^{\delta+}=\text{O}^{\delta-}$.



Hydrolysis of di-peptides/proteins

If proteins are heated with dilute acid or alkali they can be hydrolysed and split back in to their constituent amino acids.

The composition of the protein molecule may then be deduced by using paper chromatography



Other reactions of amino acids

The carboxylic acid group and amine group in amino acids can undergo the usual reactions of these functional groups met in earlier topics. Sometimes questions refer to these.

e.g. Esterification reaction

