

19. Amines, Amides, Amino Acids and proteins

Naming

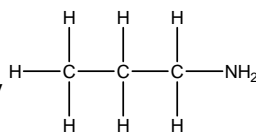
Amines

These end in **-amine**.

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

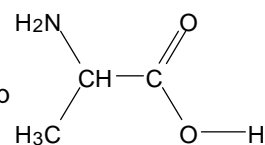
The exam board tend to use the common version where the name stem ends in **-yl** propylamine.

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

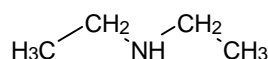
If there is another priority functional group as well as the amine group then the prefix amino is used.



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)

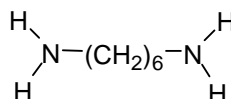


In the common naming version if the chain lengths are the same an **-N** is not used

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**

$\text{CH}_3\text{CH}_2\text{CH}_2\text{-N-CH}_3$
|
 CH_3
N,N-dimethylpropylamine (common name)
N,N-dimethylpropan-1-amine (IUPAC name)

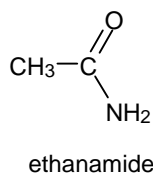


hexane-1,6-diamine

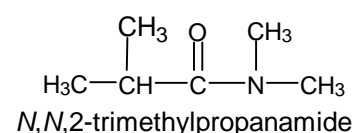
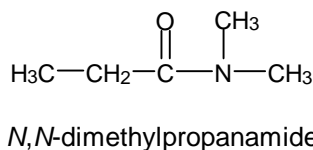
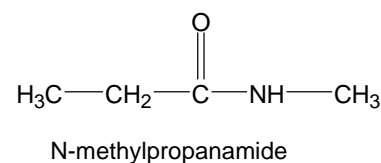
It could also be named
1,6-diaminohexane

Amides

Add **-amide** to the stem name



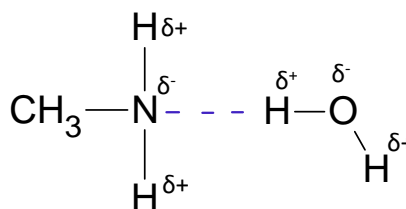
Secondary and tertiary amides are named differently to show the two (or three) carbon chains. The smaller alkyl group is preceded by an **-N** which plays the same role as a number in positioning a side alkyl chain



Properties of Amines

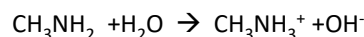
Amines have a characteristic fishy smell

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

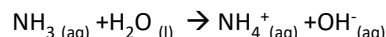


Base Properties

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.

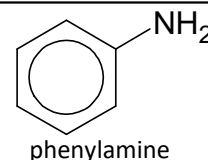


Secondary amines are stronger bases than primary amines because they have more alkyl groups that are substituted onto the N atom in place of H atoms. Therefore more electron density is pushed onto the N atom (as the inductive effect of alkyl groups is greater than that of H atoms).

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)

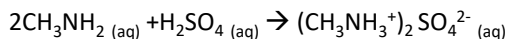
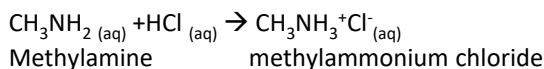
Base strength of aromatic amines

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.



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

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

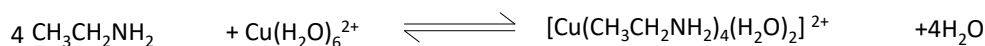
The ionic salts formed in this reaction means that the compounds are soluble in the acid.
e.g. Phenylamine is not very soluble in water but phenylammonium chloride is soluble

Making a basic buffer from an amine

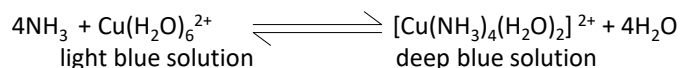
Basic buffers can be made from combining a weak base with a salt of that weak base
e.g. Ammonia and ammonium chloride
Methylamine and methylammonium chloride
Ethylamine and ethylammonium chloride

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.

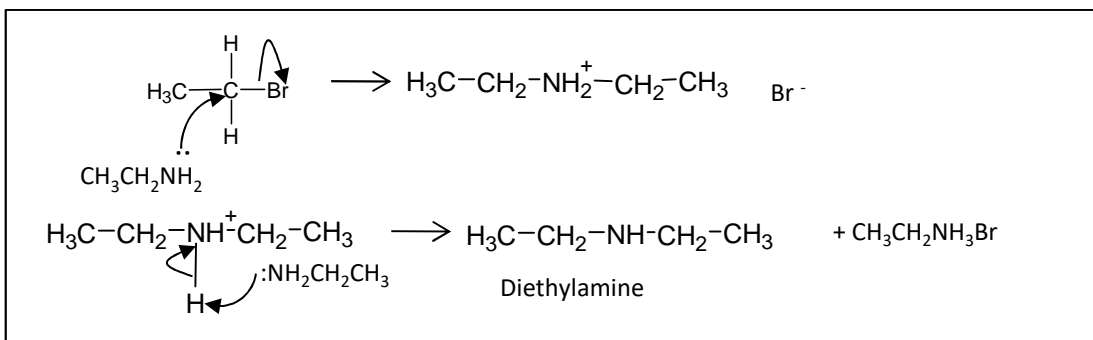
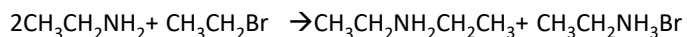


This is a similar ligand exchange reaction to the one where ammonia acts as the ligand



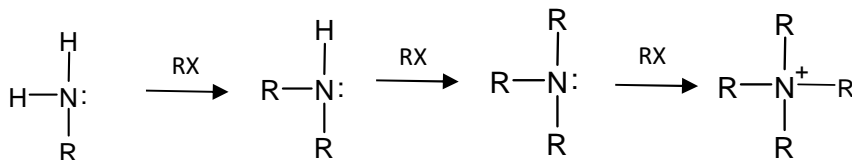
Reaction of primary Amines with halogenoalkanes forming secondary amines

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

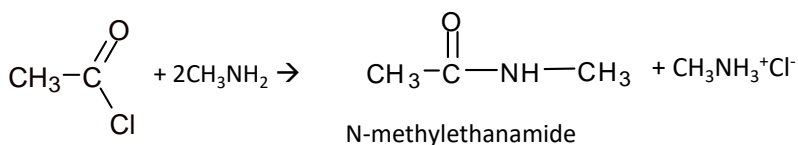


Reaction with primary amines with acyl chlorides

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

Reagent: **primary amine**

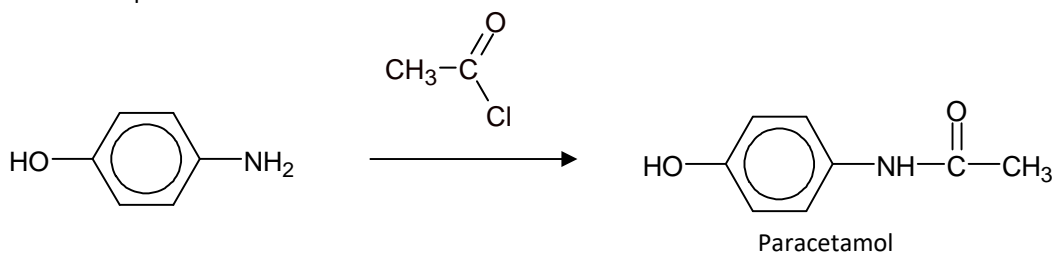
Conditions: **room temp.**



Forming Amides

Aliphatic amines and phenylamine can react with acyl chlorides to form amides in a nucleophilic addition-elimination reaction- see chapter 15C for more details.

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

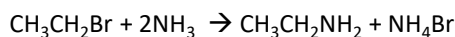


The preparation of primary aliphatic amines

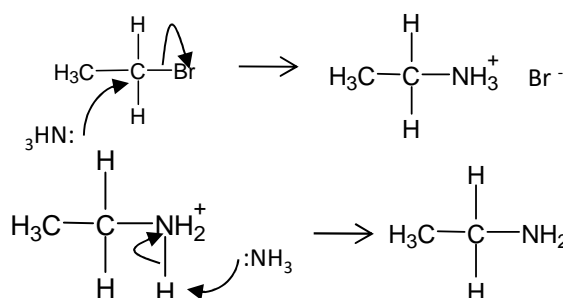
1. Forming a primary amine in a one step reaction of halogenoalkanes with ammonia

Primary amines can be formed by the **nucleophilic substitution** reaction between halogenoalkanes and ammonia in a **one step reaction**. However, as the lone pair of electrons is still available on the N in the amine formed, the primary amine can react in the same nucleophilic way in a successive series of reactions forming secondary, tertiary amines and quaternary ammonium salts.

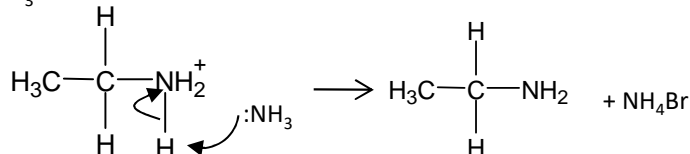
This is therefore not a good method for making a primary amine because of the further reactions. It would mean the desired product would have to be separated from the other products.



Ammonia dissolved in ethanol is the initial nucleophile



In the first step of the mechanism the nucleophile attacks the halogenoalkane to form an intermediate



In the second step of the mechanism a second ammonia removes a proton from the intermediate (acts as base) to form the amine

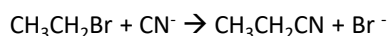
Using an **excess of Ammonia** can limit the further subsequent reactions and will **maximise the amount of primary amine** formed

2. Preparing Amines from Nitriles

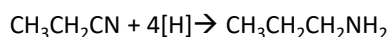
Using the method above of reacting halogenoalkanes and ammonia is not an efficient method for preparing a high yield of the primary amine because of the further substitution reactions that occur.

A better method is to use the following reactions

Step 1. convert **halogenoalkane to nitrile** by using KCN in ethanol (heat under reflux)



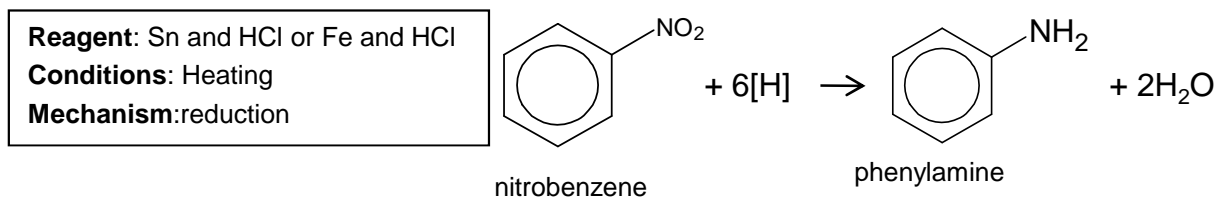
Step 2. reduce **nitrile to amine** by using **LiAlH₄ in ether** or by reducing with H₂ using a Ni catalyst



A disadvantage of this method is that it is a two step reaction that may therefore have a low yield. Also KCN is toxic.

Reducing nitroarenes to aromatic amines

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

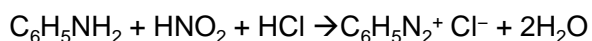
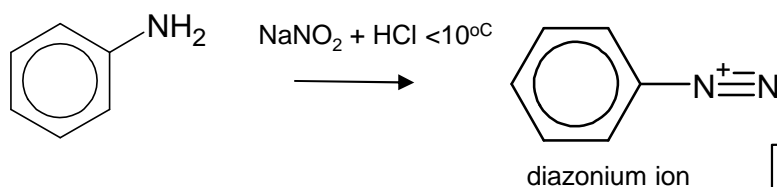


As the reaction is carried out in HCl the salt $C_6H_5NH_3^+Cl^-$ will be formed. Reacting this salt with NaOH will give phenylamine.

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,

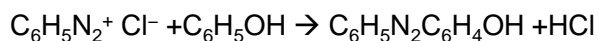
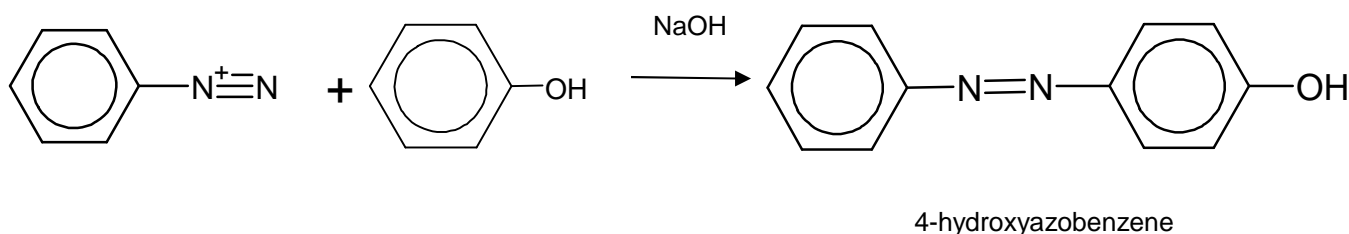


Nitrous acid is generated *in situ* from $NaNO_2/HCl$.

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;

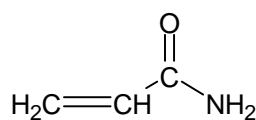


Azo dyes are used for dyes, pigments and colourings

Addition Polymerisation

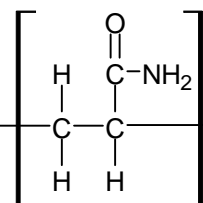
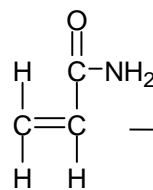
An addition polymer forms when unsaturated monomers react to form a polymer
Monomers contain C=C bonds

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.



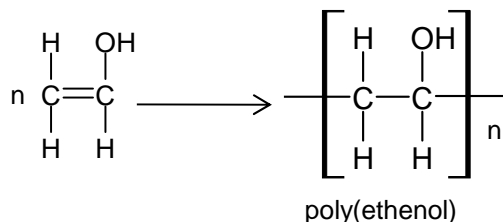
e.g. For propenamide

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



poly(propenamide)

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 (Liquitabs).

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. H₂O or HCl.

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

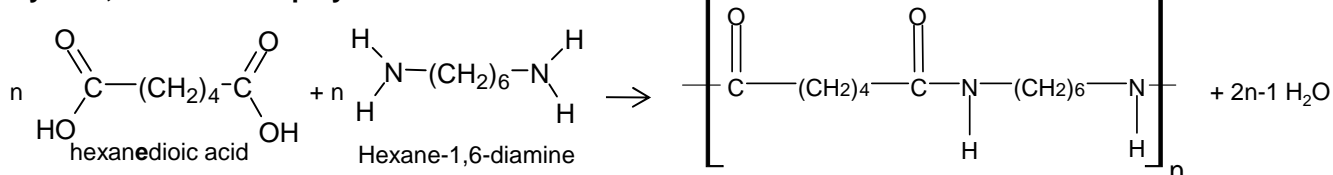
Forming polyamide uses these reactions we met earlier in the course



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

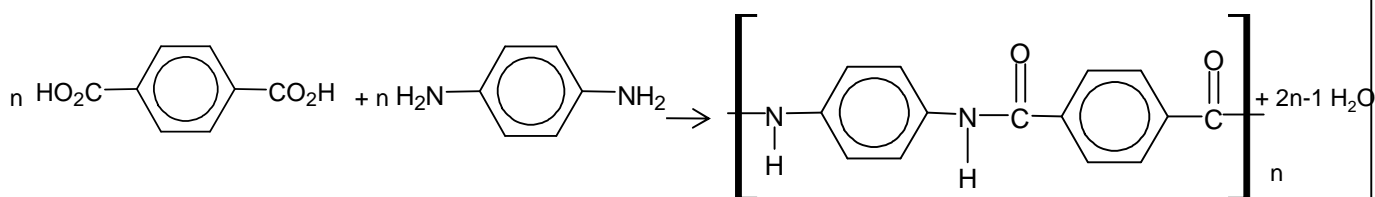


Nylon 6,6 - a common polyamide



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

Kevlar- a common polyamide

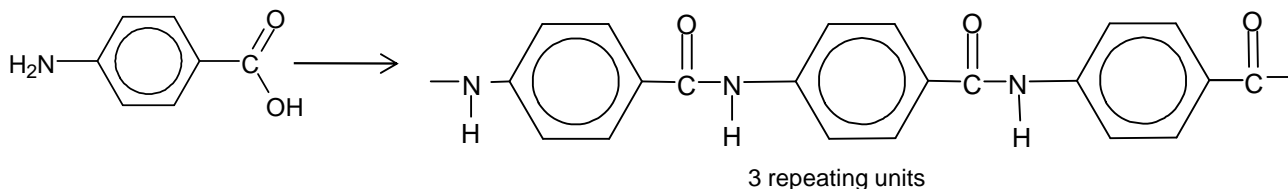
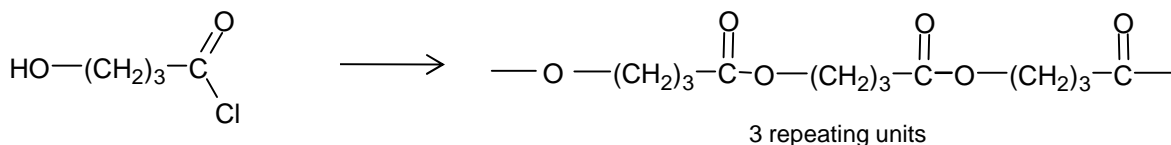


Note on classification for condensation polymers

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

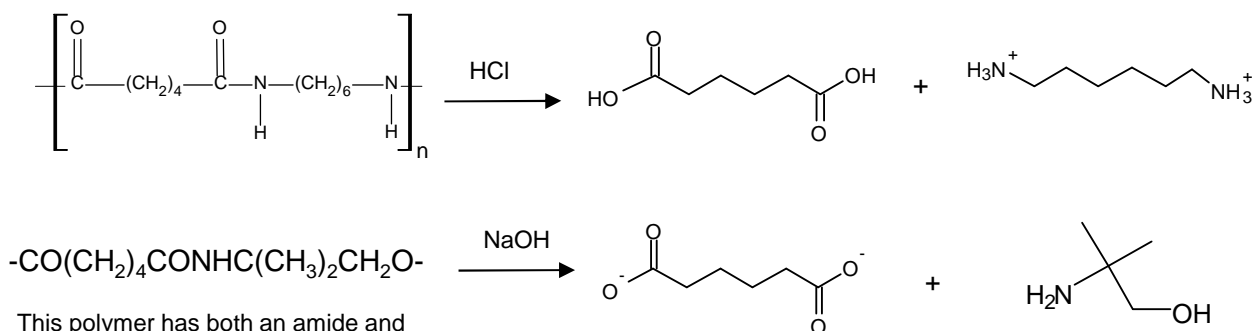
polyesters and polyamides can be broken down by **hydrolysis** and are, therefore, biodegradable

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

Hydrolysis

Polyesters and polyamides can be hydrolysed by acid and alkali

The hydrolysis will result in the original monomers forming- although the carboxylic acid or amine group will be in salt form depending on whether the conditions are alkaline or acidic



This polymer has both an amide and ester link

Intermolecular bonding between condensation polymers chains

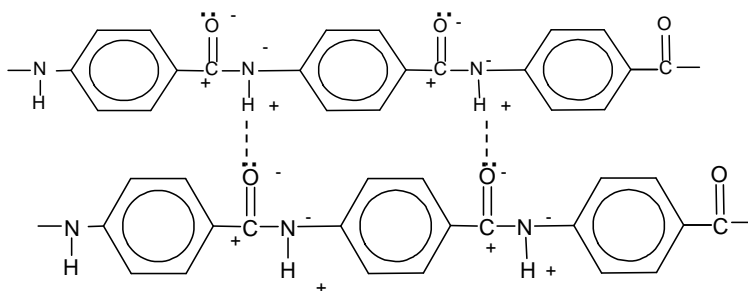
Polyesters have permanent dipole forces between the C⁺=O⁻ groups in the different chains in addition to the London forces between the chains.

Polyamides (and proteins) have **hydrogen bonding** between the lone pairs on oxygen in C⁺=O⁻ groups and the H in the N⁻-H⁺ groups in the different chains.

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

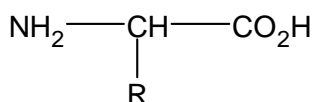
There are also **London forces** which are large because there are many electrons in the molecule

Polyamides will therefore have higher melting points than polyesters.



Amino Acids

General structure of an amino acid

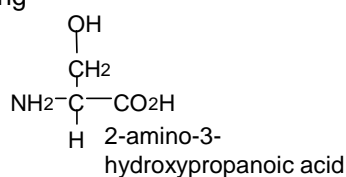
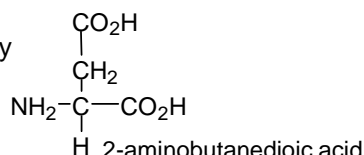
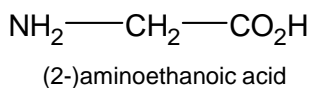


The R group can be a variety of different things depending on what amino acid it is.

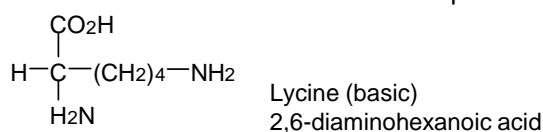
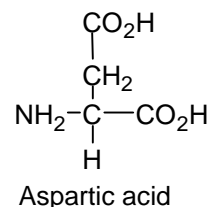
The simplest amino acid is glycine, where the R is an H $\text{NH}_2 - \text{CH}_2 - \text{CO}_2\text{H}$

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

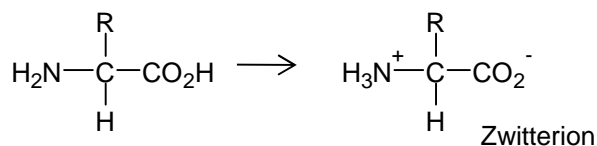


Zwitterions

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

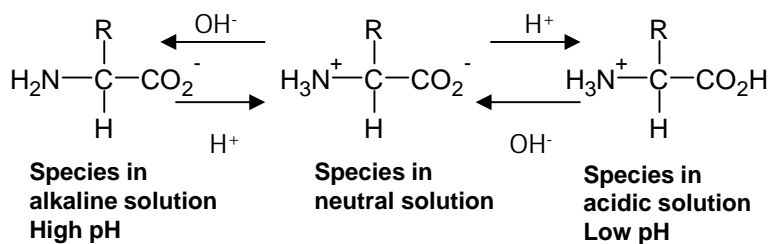
Amino acids are often **solids**

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.

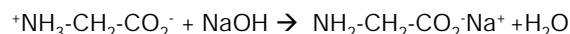
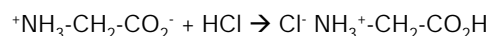


Acidity and Basicity

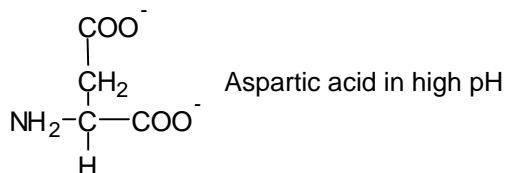
The amine group is basic and the carboxylic acid group is acidic.



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.



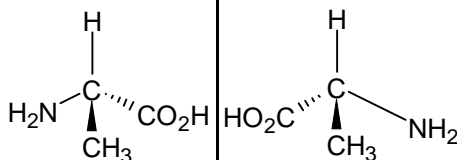
The extra carboxylic acid or amine groups on the R group will also react and change form in alkaline and acid conditions



Optical Activity

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

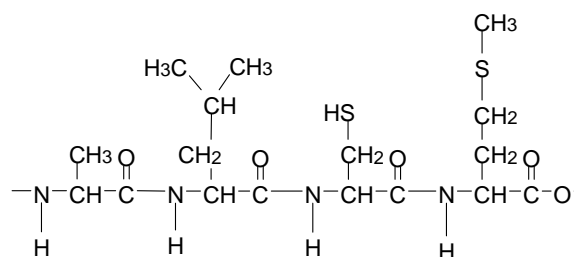
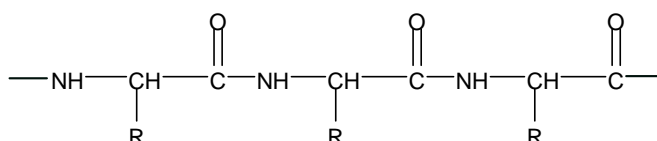
They rotate plane polarised light.



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

Proteins

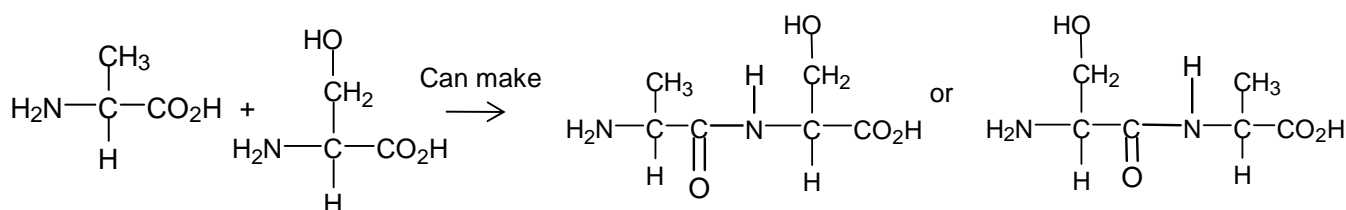
Proteins are polymers made from combinations of amino acids. The amino acids are linked by peptide links, which are the amide functional group.



Dipeptides

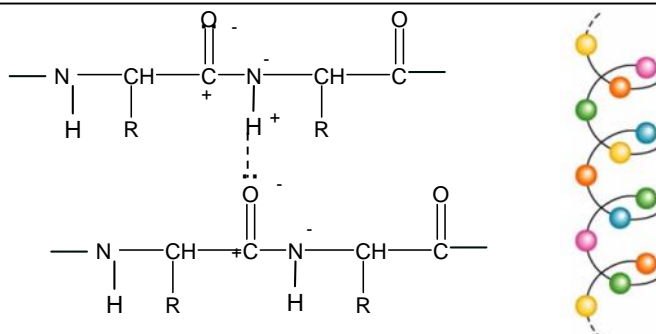
Dipeptides are simple combination molecules of two amino acids with one amide (peptide) link.

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 $-N^+H^-$ group and the $-O^-$ of $C=O$



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

