OCR (B) Chemistry A-level

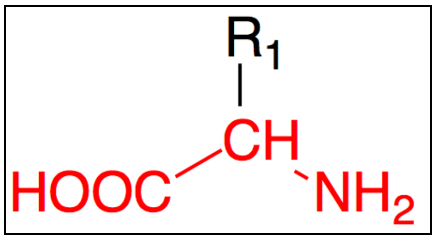
Storyline 7: Polymers and Life

Detailed Notes

Structure and Bonding: Proteins

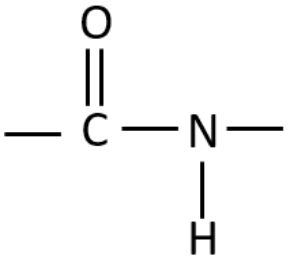
Amino Acids

α-amino acids are organic molecules containing a **carboxylic acid group** and an **amine group** bonded to the same carbon atom. Their general structure is shown below, where different amino acids have different chemical groups as the **'R' side chain**. The general formula for an α-amino acid is **$RCH(NH_2)COOH$**.

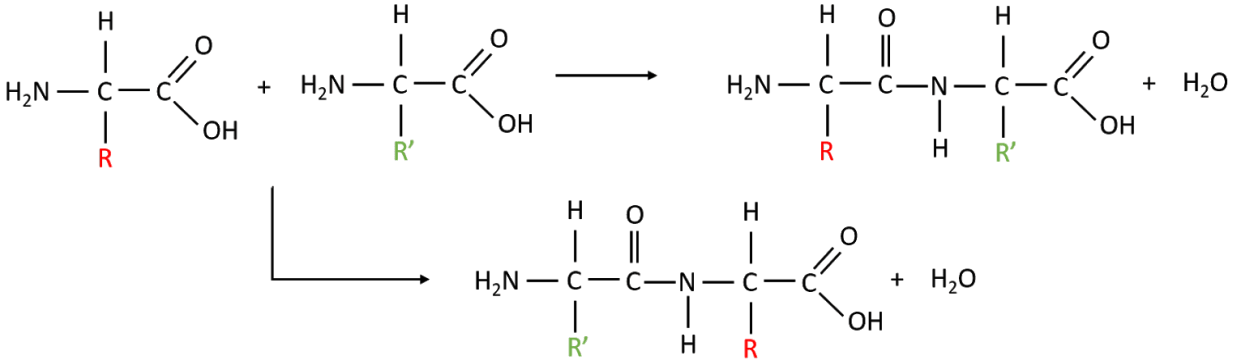


Peptide Bonds

A peptide bond is formed during a **condensation reaction** between **two amino acids**. A water molecule is lost. Proteins are chains of amino acids joined together by **peptide links**.



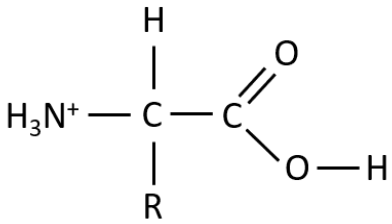
When two amino acids combine, a **dipeptide** is formed:



A **tripeptide** forms when three amino acids join together. A full chain of amino acid monomers results in a **protein**.

The **acid hydrolysis** of proteins is very similar to the acid hydrolysis of polyamides. When proteins are hydrolysed using acids, amino acids are formed. However, the **amine group**

accepts a proton to become **-NH_3^+**. The general structure of the product of protein hydrolysis in acidic conditions is shown below (where R represents any group):



Protein Structure

Proteins have complex structures that are held together by **hydrogen bonds, Van der Waals forces and sulfur-sulfur bonds (disulfide bonds)**. Proteins have different levels of structure.

Primary Structure - a single polypeptide chain of amino acids.

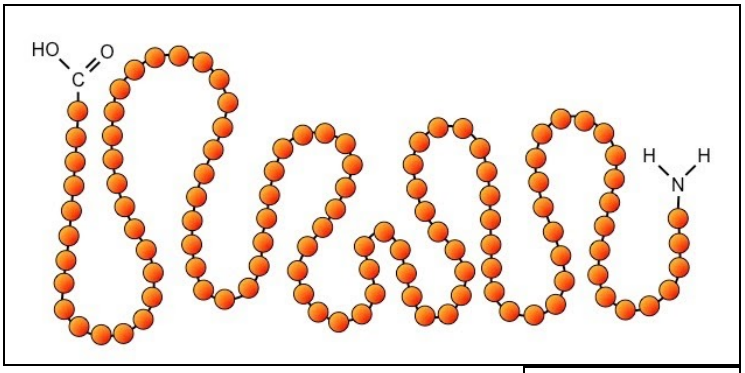


Image courtesy of BioNinja

Secondary Structure - an α-helix or β-pleated sheet held together by hydrogen bonds.

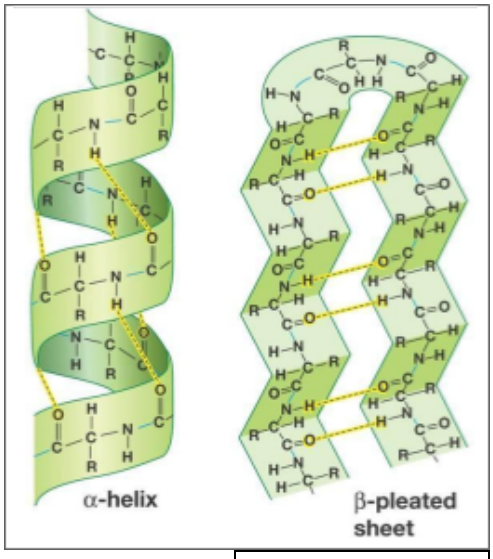


Image courtesy of hogayephd.com

Tertiary Structure - The polypeptide chain folds into a 3D shape with hydrogen and disulfide bonding.

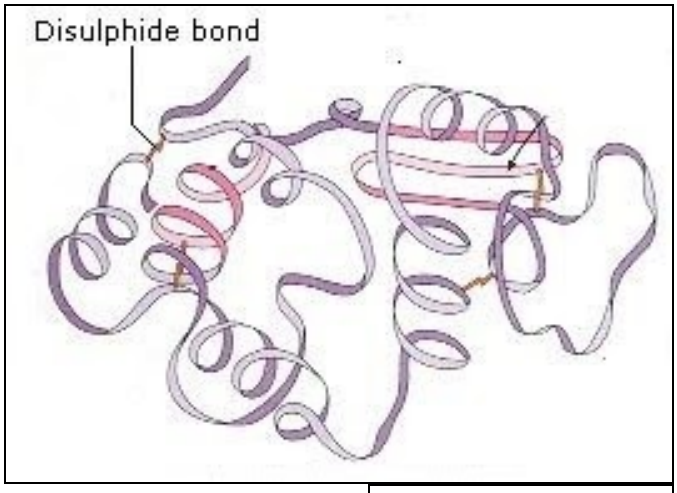


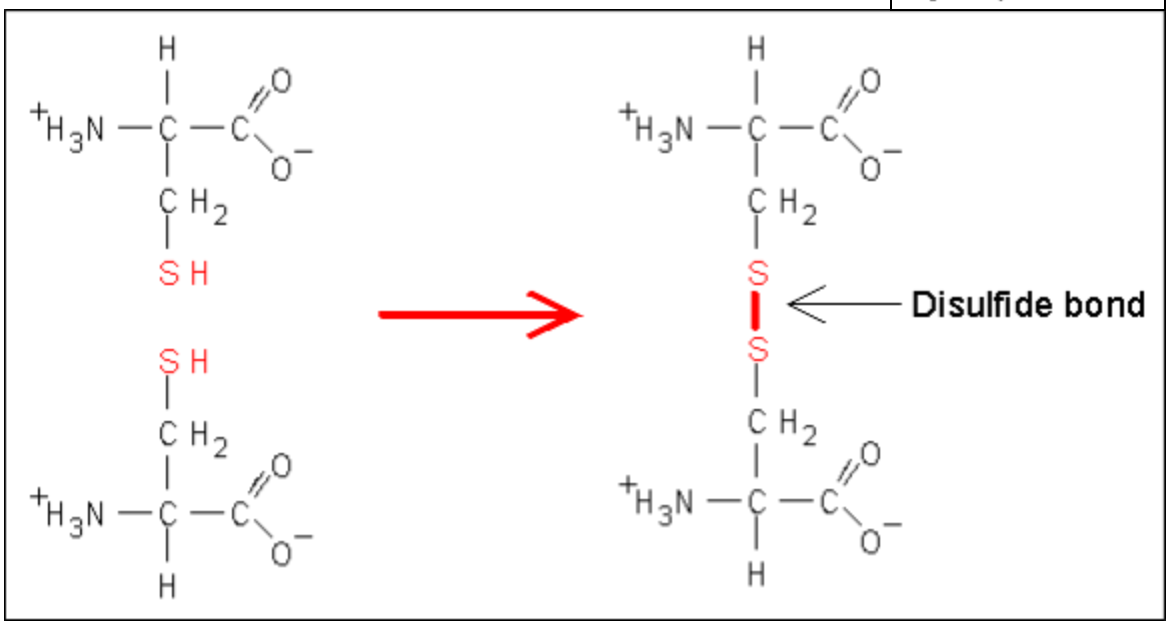
Image courtesy of knowhownutrition.co.uk

Disulfide Bonding

The sulfur-sulfur covalent bonds that hold tertiary structures together are known as a **disulfide bridge**. These bonds are strong so they help to stabilise the protein. During disulphide bond formation, two hydrogen atoms are lost.

Example:

Image courtesy of cbm.msoe.edu



Structure and Bonding: Nucleic Acids

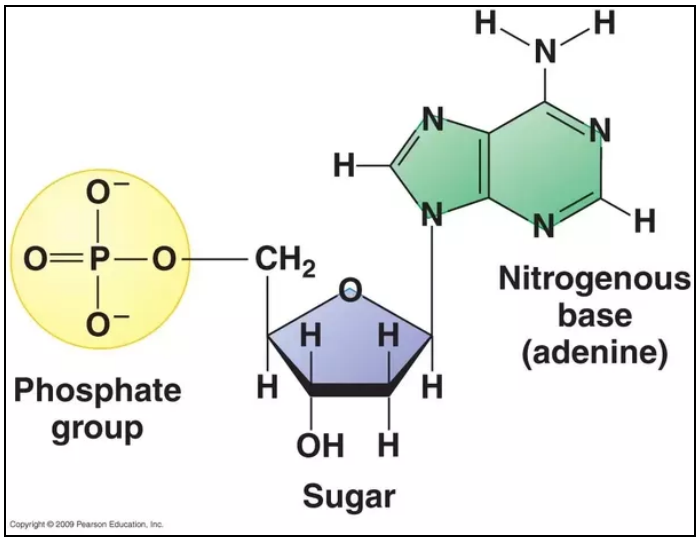
DNA and RNA

DNA (deoxyribonucleic acid) is a **condensation polymer** formed from a **sugar, a phosphate and a base**.

Nucleotides

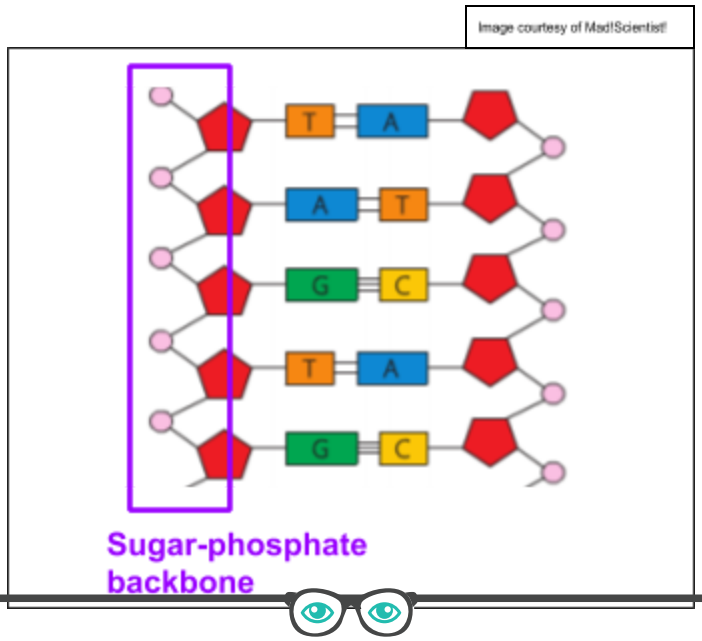
Nucleotides are each formed from one sugar, one nitrogenous base and one phosphate group. Nucleotides are the **monomers** of DNA and RNA.

Example:



The sugar present in the nucleotide that makes DNA is **2-deoxyribose** and in RNA is **ribose**. Sugar-phosphate bonds hold together multiple nucleotides into a **polynucleotide strand**, these bonds make up what is known as a **'sugar-phosphate backbone'**.

Example:



There are four possible bases that could be present in **DNA nucleotides**:

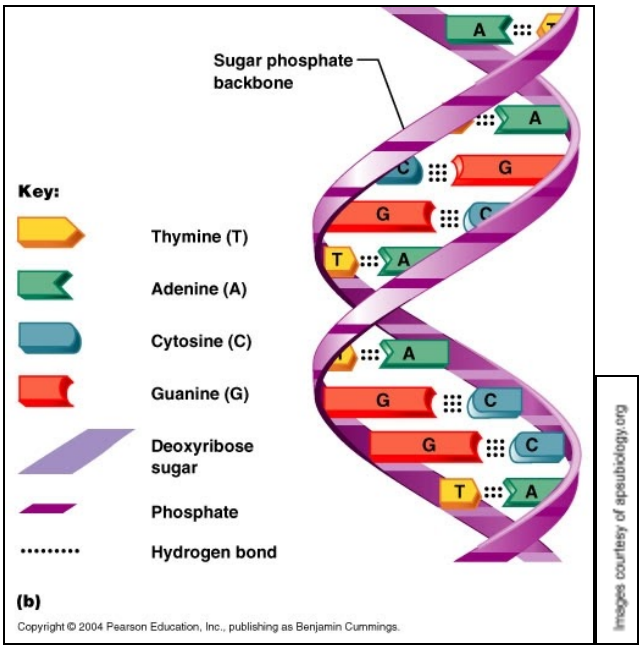
- Adenine (A)
- Cytosine (C)
- **Thymine (T)**
- Guanine (G)

The bases that could be present in **RNA nucleotides** are slightly different:

- Adenine (A)
- Cytosine (C)
- **Uracil (U)**
- Guanine (G)

These bases pair up and form **hydrogen bonds**. A **double helix** of DNA is formed from **two strands** of DNA joined together by **hydrogen bonds** between **complementary base pairs.**

Example:

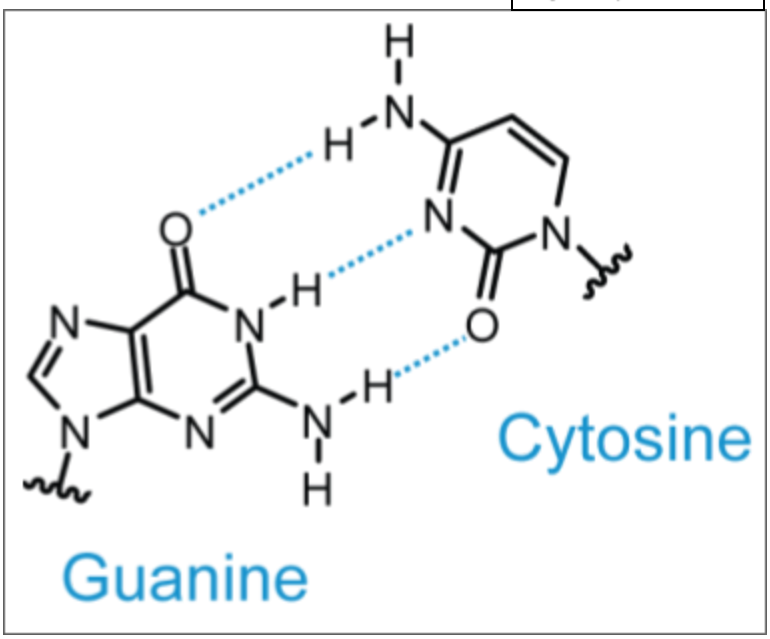


Complementary Bases

Guanine and cytosine form a complementary base pair with **three** hydrogen bonds.

Example:

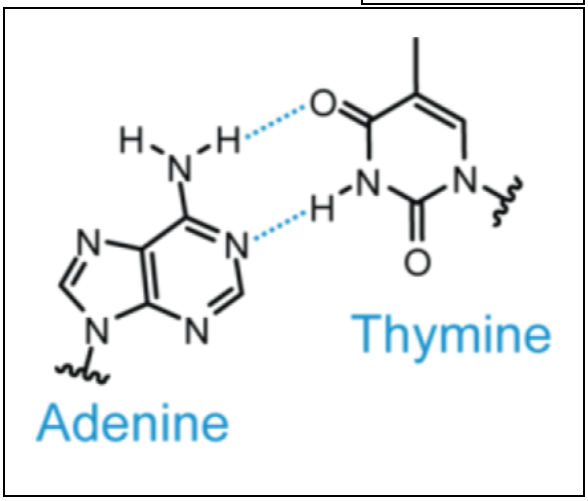
Image courtesy of cbm.mose.edu



Thymine and adenine form a complementary base pair with **two** hydrogen bonds.

Example:

Image courtesy of Wikipedia



How DNA codes for a Protein

DNA is made up of a long chain of nucleotides each with one of the four bases attached. These bases are in a specific sequence. Each base has another **complementary base** which it bonds to in the DNA double helix.

During **DNA transcription** (the process where DNA is used as a template to make RNA), the two strands of the helix are separated by breaking the hydrogen bonds between base pairs (this process is carried out by enzymes), and one strand is used as a template for an **RNA molecule**. The RNA nucleotide sequence is determined by the complementary base pairs of the DNA templates sequence.

The next step is **translation** (the process where RNA is used to form an amino acid sequence), RNA nucleotides are now grouped into threes, these base triplets are called **codons**. Each codon corresponds to a particular amino acid, so as the RNA molecule is read codon by codon (by enzymes), a particular **sequence of amino acids** is formed. These amino acids form a **polypeptide chain**, which then folds to form a **secondary** and then **tertiary protein structure**.

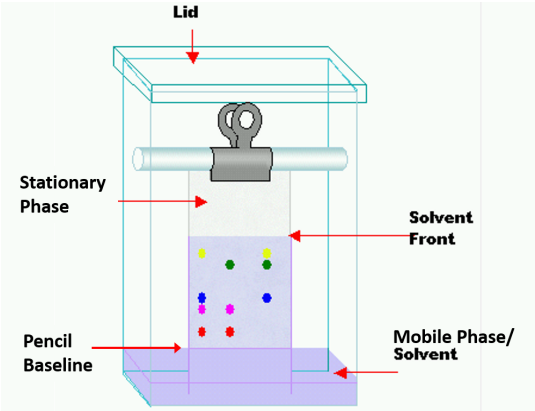
Molecular Recognition

For molecules to react and interact they need to collide with enough **energy** and in the correct **orientation**. For example, when an enzyme catalyses a reaction the **active site** and the **substrate** need to be complementary and make contact in the correct orientation with each other. The **active site/receptor site** of an enzyme and the substrate molecule are **complementary** in size and shape. Receptor sites can only bind specific molecules.

The part of a molecule that has a particular pharmaceutical or biological function is called a **pharmacophore**.

Paper Chromatography

In paper chromatography, the **mobile phase** is a solvent and the **stationary phase** is a piece of chromatography paper. A spot of the substance being analysed is put on the pencil **baseline** before the stationary phase is placed into the solvent.



'Paper chromatography', Wikipedia, CC BY-SA 3.0

The **Rf value** (or retention factor) can be calculated after chromatography is completed:

$$Rf = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent front}}$$

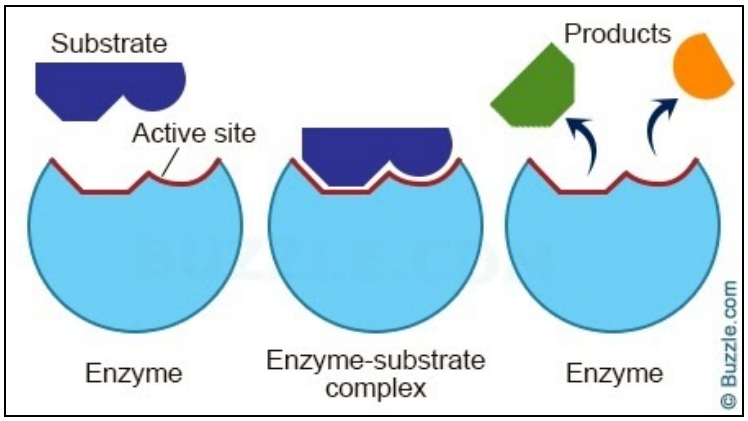
Substances are separated because different compounds have **different solubilities** in the solvent and **different attractions** to the stationary phase. **Paper chromatography** can be used to identify unknown amino acids. **UV light** is used to help view the traces on a **silica chromatography plate**.

Kinetics

Enzymes

Enzymes are proteins with a **tertiary structure** that act as **biological catalysts**. They contain **active sites** that are specific to the molecule they break down, called a **substrate**.

Example:



Enzymes are **stereospecific**, meaning they can only catalyse the reaction of a single enantiomer and will have no effect on the other optical isomer.

The rate of an enzyme-catalysed reaction will increase as temperature increases. However, at a high enough temperature, the rate then decreases due to the enzymes beginning to **denature.** Enzymes are said to be denatured when the substrate is no longer **complementary** to the **active site.** This occurs because enzymes are **tertiary proteins** so extremes of pH or high temperature may break **hydrogen bonds** and other **intermolecular forces** that maintain the enzyme's structure. If the 3D shape is altered, the enzyme may no longer be complementary to its substrate.

Each enzyme has an **optimal pH**, the pH at which the **rate of reaction** will be **fastest**. The further from this optimum then the **slower** the rate of reaction will be, until all the enzymes are **denatured**. This optimum pH often depends on the **environment** in which the enzymes are

found. For example, enzymes in the stomach often have an optimum pH of 2 (so they work well in the stomach acid).

The rate of an enzyme-catalysed reaction can be decreased by using **inhibitors**. **Competitive inhibitors** have a similar shape to the substrate molecule, so they are **complementary** to the active site of the enzyme. This means that the inhibitor will bind to the enzyme, **blocking** the **active site** from further substrate binding, so the enzyme cannot catalyse the reaction with its substrate.

When measuring the rates of enzyme-catalysed reactions in relation to the concentration of a substrate, a graph of **rate versus substrate concentrations** can be plotted. These graphs show that the rate increases very quickly as substrate concentration increases until the rate of reaction **plateaus** when all the **enzyme active sites** are already being used to catalyse the reaction so it cannot go any faster.

Equilibria (acid-base)

Reactions of Carboxylic Acids

Carboxylic acids are **weak acids** and therefore react with bases in **neutralisation** reactions to produce a **salt.**

Example:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

$$CH_3CH_2COOH + NH_3 \rightarrow CH_3CH_2COONH_4$$
(ammonia propanoate)

The reaction of a **metal** with a carboxylic acid will produce the corresponding **salt** and **hydrogen** gas. Whereas, the reaction with a **metal carbonate** will produce the **salt, carbon dioxide and water**.

Zwitterions

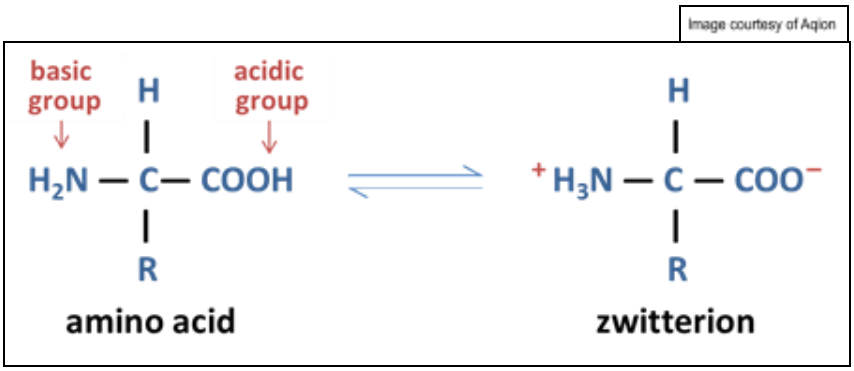
The two functional groups within a single molecule mean that amino acids can **behave as both acids and bases,** depending on the conditions of the reaction. The **carboxylic acid** group is acidic and will react with alkalis to donate a proton. The **amine group** is basic and will react with acids to accept a proton.

Zwitterions are **dipolar** ions with a positive charge in one part of the molecule and a negative charge in another part of the molecule. The zwitterionic form of an amino acid is the state in

which the **amine group** has a **positive** charge ($+NH_3$) and the **carboxyl group** has a **negative** charge (COO-).

Zwitterions form at the **isoelectric** point, which is the pH at which the **overall charge** of the molecule is **zero**.

Example:

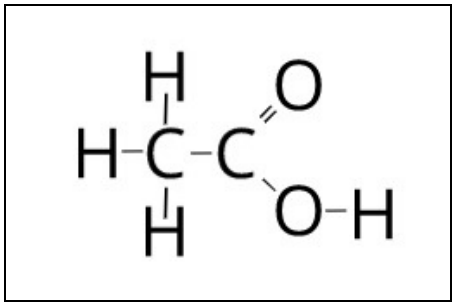


Organic Functional Groups

Carboxylic Acids

Carboxylic acids are organic compounds containing the **functional group -COOH,** made of a **carbonyl group (C=O)** and an **-OH acid group**. When naming carboxylic acids, the suffix **-anoic acid** is used. For example, a carboxylic acid containing a chain of four carbon atoms would be called butanoic acid.

Example: The displayed structure of ethanoic acid.



Dicarboxylic Acids

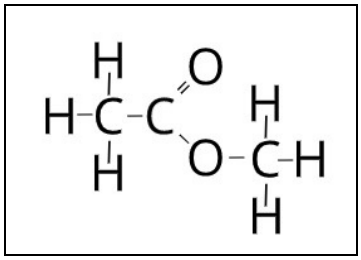
Dicarboxylic acids are chemical compounds that contain **two carboxylic acid** (-COOH) functional groups.

Esters

Esters have the functional group **-COO-**. They are named after the **alcohol and carboxylic acid** from which they are formed. For example, the ester formed from methanol and propanoic

acid is methyl propanoate and the ester formed from butanol and ethanoic acid is butyl ethanoate.

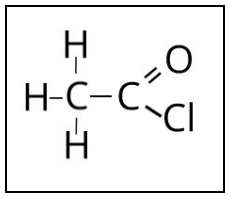
Example: The displayed structure of methyl ethanoate.

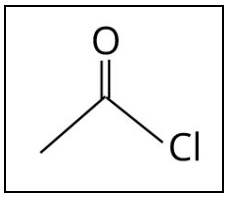


Acyl Chlorides

Acyl chlorides have the functional group **-COCl** and have the suffix **-oyl chloride**, with the stem of their name representing the longest chain of carbon atoms.

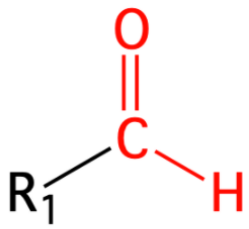
Example: The displayed structure and skeletal structure of ethanoyl chloride.





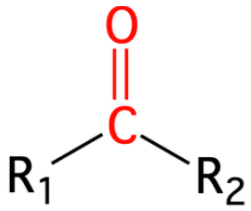
Aldehydes

Aldehydes are produced from the oxidation and distillation of **primary alcohols**. Aldehydes have a carbonyl group at the **end of the carbon chain** (the carbonyl group is only attached to **one other carbon atom**). This gives them the functional group **-CHO**.



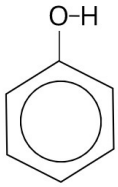
Ketones

Ketones also contain the **functional group -C=O,** a carbonyl group. They are produced from the oxidation of **secondary alcohols** with acidified potassium dichromate(VI). Ketones have a carbonyl group in the middle of a carbon chain (the carbonyl group is attached to **two other carbon atoms**).



Phenols

Phenols are organic compounds containing a **benzene ring** with an OH **alcohol group**. This makes them **aromatic alcohols**. Phenols are weak acids. They can be neutralised in a reaction with NaOH but will not react with carbonates.

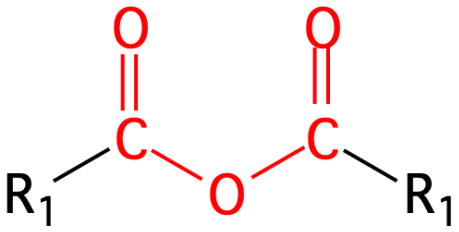


Diols

Diols are chemical compounds that contain **two hydroxyl** (-OH) functional groups.

Acid Anhydrides

Acid anhydrides are identified by their functional group **-COOCO-**, which consists of two carbonyl groups attached to an oxygen atom.



Amines

Amines are produced when one or more of the hydrogen atoms in ammonia is **replaced with an alkyl group**. They can be classified as **primary, secondary, or tertiary amines,** depending on how many alkyl groups are bonded to the nitrogen atom.

Example: Classification of amines

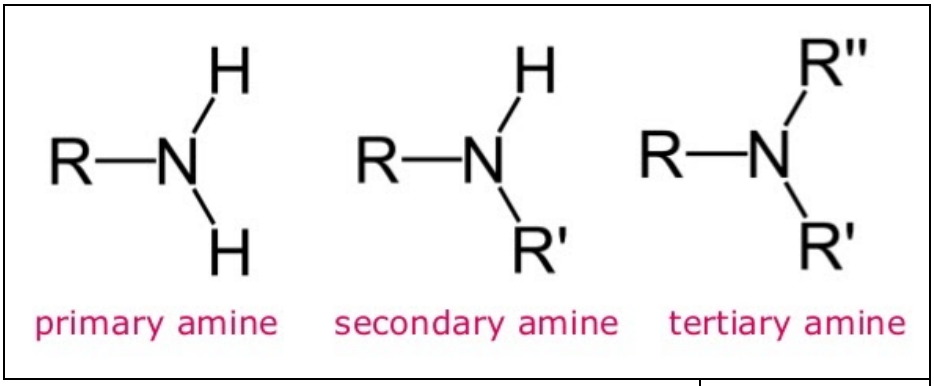


Image courtesy of SlideShare

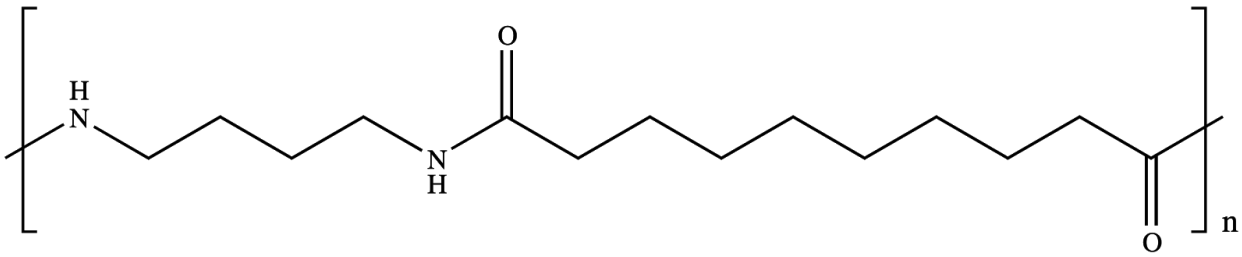
Diamines

Diamines are chemical compounds that contain **two amine** ($-NH_2$) functional groups.

Nylon Structures

Nylon structures are polymers made from **two monomers**, a diamine and a dicarboxylic acid, or by a diamine and a diacyl chloride joined by **amide linkages**. There are two types of nylon: **nylon 6,6** and **nylon 6,10**. The numbers show how many carbons there are in each of the monomers. In nylon 6,6 there are 6 carbons in both the amine and the carboxylic acid/diacyl chloride, whereas nylon 6,10 has 6 carbons in the amine and 10 in the carboxylic acid/diacyl chloride.

There is, however, an exception to this, **nylon 6**. This is made from **one monomer** which contains both the carboxylic acid/acyl chloride and amine functional group in one molecule. The 6 in the name is due to there being 6 carbons in the single monomer.



nylon-6,10

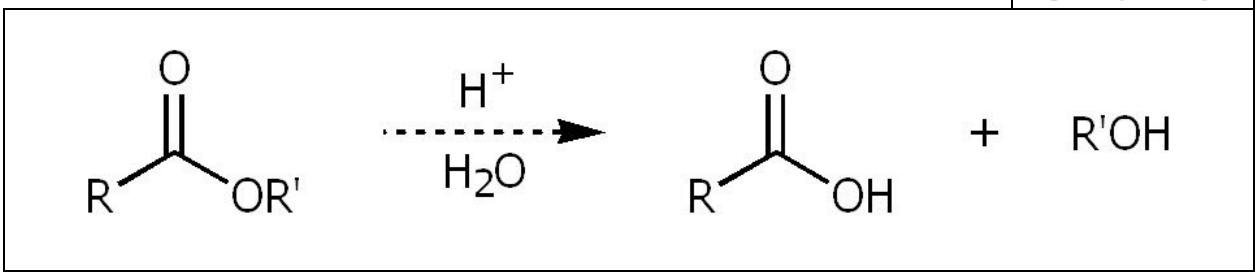
Organic Reactions

Hydrolysis of Esters

Ester hydrolysis is the **reverse reaction** to esterification, converting esters back into alcohols and carboxylic acids. This process is done by **adding water** but can be carried out under **different conditions** to produce different products.

Acidic Conditions

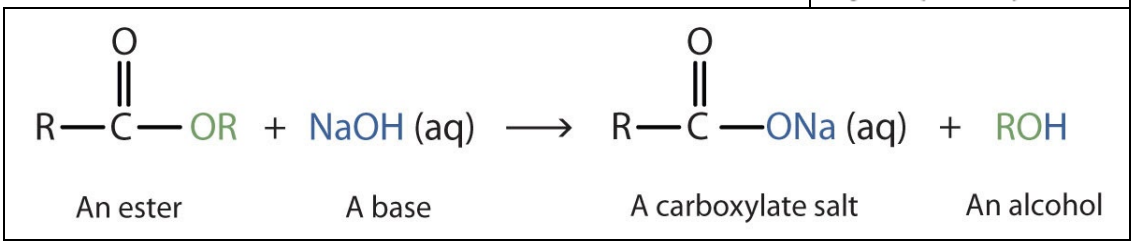
Image courtesy of SlidePlayer



The reaction conditions are heat and aqueous acid. This produces a simple reverse reaction back to the alcohol and carboxylic acid.

Alkaline Conditions

Image courtesy of Chemistry LibreTexts



The reaction conditions are heat and aqueous alkali. The carboxylic acid produced reacts further with the base to form a salt, so the final products are the carboxylate salt and alcohol.

The process of producing this salt is called **saponification**. Salts such as these are commonly used as **soaps** because they have **hydrophilic and hydrophobic** properties.

Reactions of Acyl Chlorides

The -COCl group makes acyl chlorides **very reactive** and so they react with a wide range of molecules to give a wide range of products:

+ Alcohol → Ester

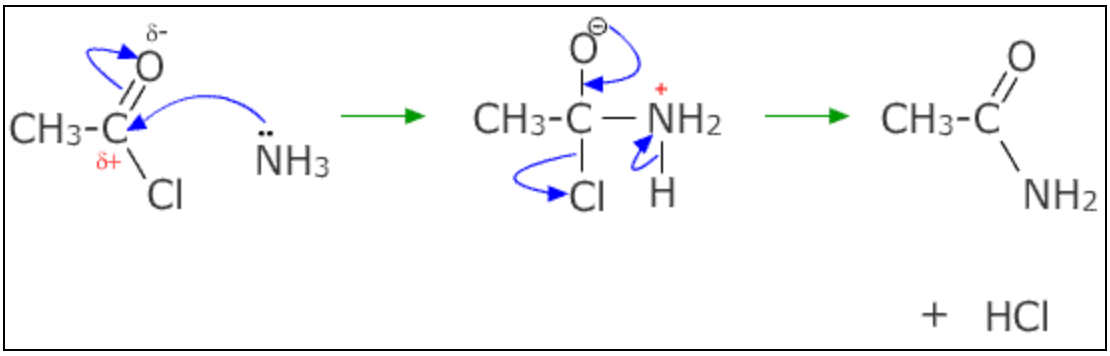
+ Ammonia → Amide

+ Amines → N-substituted Amide

Acyl chlorides react via **nucleophilic addition-elimination reactions**. In these reactions, the addition of a nucleophile leads to the elimination of a product under **aqueous conditions**. The mechanism for the reaction of ethanoyl chloride with ammonia is shown below:

Example: Nucleophilic addition-elimination mechanism

Image courtesy of alevelchem.com



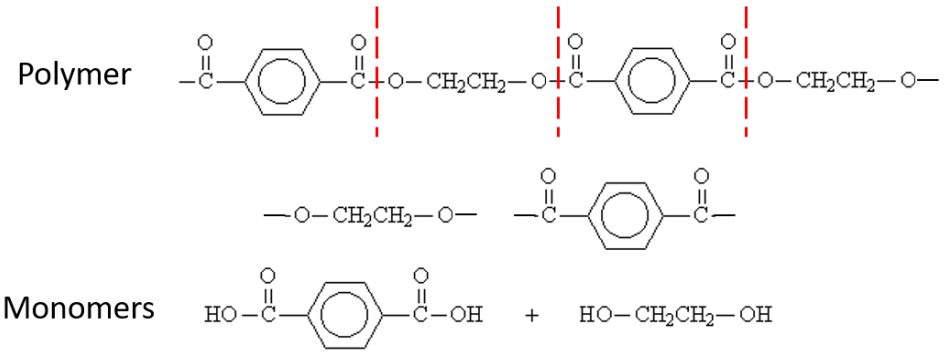
Acyl chlorides can be used in the **esterification of phenol**, which is not readily esterified by carboxylic acids.

Polymers

Differences Between Types of Polymerisation

Addition polymerisation	**Condensation polymerisation**
Monomers contain C=C double bonds.	Monomers contain -OH and -COOH or -COCl functional groups in polyesters. Monomers contain -NH_2 and -COOH or -COCl functional groups in polyamides.
Main chain of the polymer only contains C-C single bonds.	Main chain contains nitrogen or oxygen atoms as well as carbon atoms.
The polymer is the only product of the reaction.	The polymer and a small molecule (like water or HCl) are formed during the reaction.

To identify the **monomers** in a polymer, draw a line through the ester or amide linkages. Add OH or H to create the monomers.



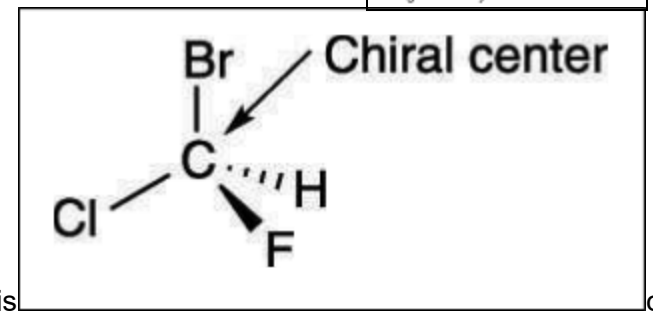
'Polymer Chemistry: Polymerization Reactions', Engineering LibreTexts, CC BY-NC-SA 3.0 US

Isomerism

Chiral Centres

A chiral centre is a carbon atom with **four different groups** bonded around it, so that the molecule has **no line of symmetry**.

Example:



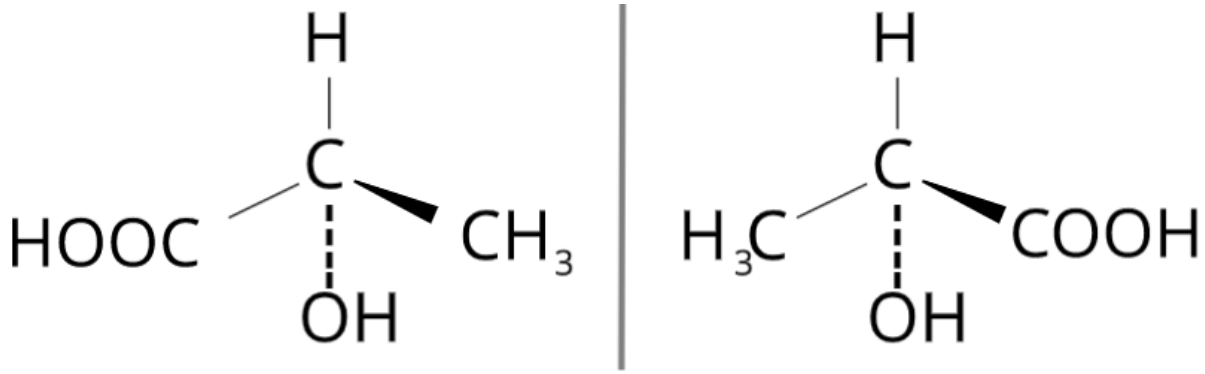
The chiral centre is commonly **indicated** using a * next to the asymmetric carbon.

Optical Isomerism

Optical isomerism is a type of **stereoisomerism** where molecules have the **same molecular and structural formula** but a different **spatial arrangement** of atoms.

The presence of a chiral centre leads to **two possible isomers** that are **non-superimposable mirror images** of each other. These are called **optical isomers**.

Example: Optical isomers of 2-hydroxypropanoic acid



The two different isomers are called **enantiomers** and are unique due to their effect on **plane polarised light**. Each enantiomer rotates plane polarised light **in opposite directions.**

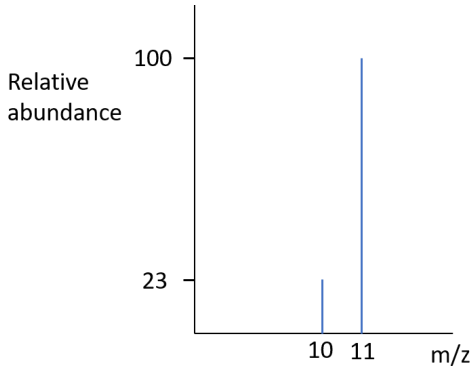
All amino acids, except **glycine**, contain a **chiral carbon** atom bonded to four separate groups. The R group on aminoethanoic acid (**glycine**) is just a hydrogen atom so the carbon is not bonded to four separate groups.

Since all other amino acids are chiral, they are **optically active**, so a solution of amino acids will **rotate plane-polarised monochromatic light**.

Modern Analytical Techniques

Mass Spectrometry

This is an **analytical technique** used to identify different molecules and find the overall relative molecular mass. During mass spectrometry, a **vaporised** sample (atoms or molecules) is turned into positive ions. The ions are then accelerated, deflected by a magnetic field and then detected. A graph is produced with the **mass to charge ratio (m/z)** on the x axis and **relative abundance** on the y axis:



The M^+ Peak

The molecular ion peak (**M^+**) is the peak with the **greatest mass to charge ratio**. The molecular mass (**Mr**) of a compound is equal to the m/z value of this peak. This is the peak that is furthest to the right on the spectrum. Other analytical techniques can be used to determine the empirical formula, then scaled up to the Mr value from mass spectrometry to give the molecular formula.

Fragmentation

Fragment ions are formed when an **unstable molecular ion breaks** up into a positive ion and an uncharged **free radical** (a species which contains an unpaired electron):

$M^+ \rightarrow X^+ + Y\bullet$

Only charged particles are detected so the free radical ($Y\bullet$) will not produce a line on the spectrum. Each line on the mass spectrum represents a different fragment ion. If **fragments** are present, this can also help to deduce the structure of the compound.

High Resolution Mass Spectrometry

High resolution mass spectrometry is a much **more sensitive** form of mass spectrometry which allows the Mr of a substance to be determined to **several decimal places**. Precise atomic masses can then be used to calculate the molecular formula of the compound being tested.

Once a molecular formula has been determined, you can predict **possible structures** of the compound. Knowledge of **general formulas** and **functional groups** aids this prediction.

NMR Spectroscopy

Nuclear Magnetic Resonance Spectroscopy is an **analytical technique** that allows the structure of a molecule to be determined by observing local magnetic fields around nuclei. Different chemical **environments** within a molecule are displayed as **different peaks** on a spectra print out.

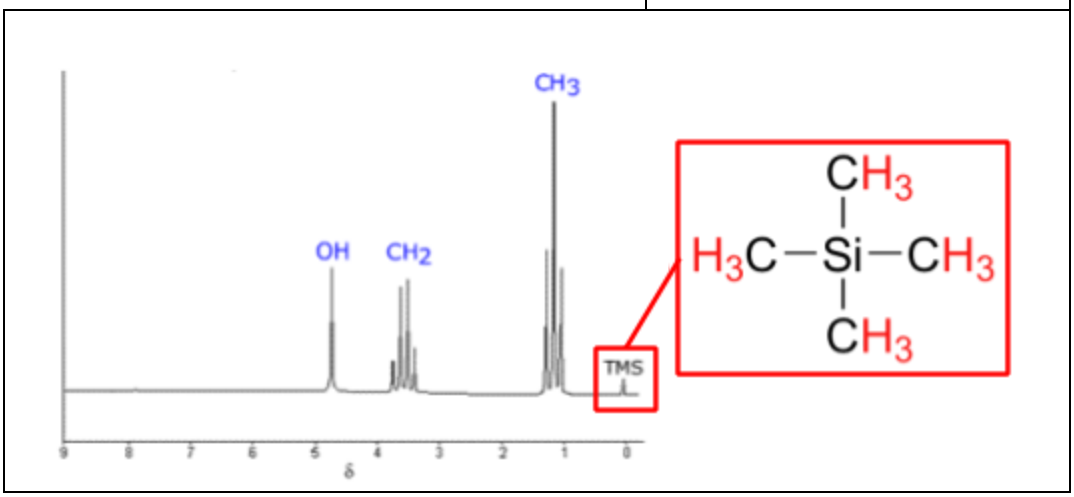
NMR Spectroscopy detects nuclei that have **spin**. Hydrogen, **^{1}H**, and carbon-13, **^{13}C**, both have spin and can be detected by NMR. **Deuterium** is an isotope of hydrogen with a mass number of 2. It can not be detected on a proton NMR spectra. For this reason, **deuterated solvents** are often used as they do not interfere with the compound's spectra.

Carbon-12 is the most common isotope of carbon but is not detected by NMR spectroscopy. This is why carbon-13 is used, however, carbon-13 only has an abundance of roughly 1.1%, so a greater quantity of sample will be needed to obtain a well resolved spectra.

The bond environment peaks are measured against a standard molecule, **tetramethylsilane, $Si(CH_3)_4$**, known as **TMS**. This is a standard molecule as it contains four **identical** carbon and hydrogen environments. It can be easily identified as it is seen as a peak at **δ=0 ppm** on the x-axis. TMS is also **inert** so it does not interfere with the compounds being analysed.

Example: A proton NMR spectra

Image courtesy of alevelchem.com and Chemistry LibreTexts

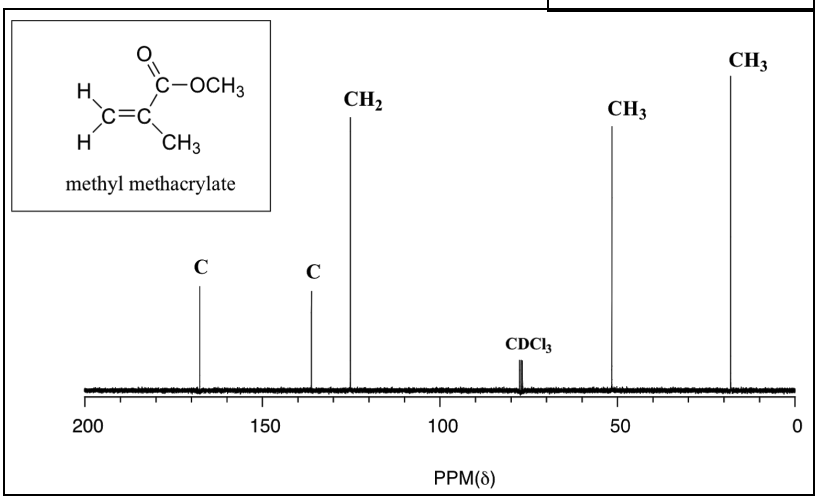


^{13}C NMR

^{13}C NMR spectroscopy analyses the different **carbon environments** in a molecule. The different environments are shown as peaks at different δ values.

Example:

Image courtesy of Chemistry LibreTexts



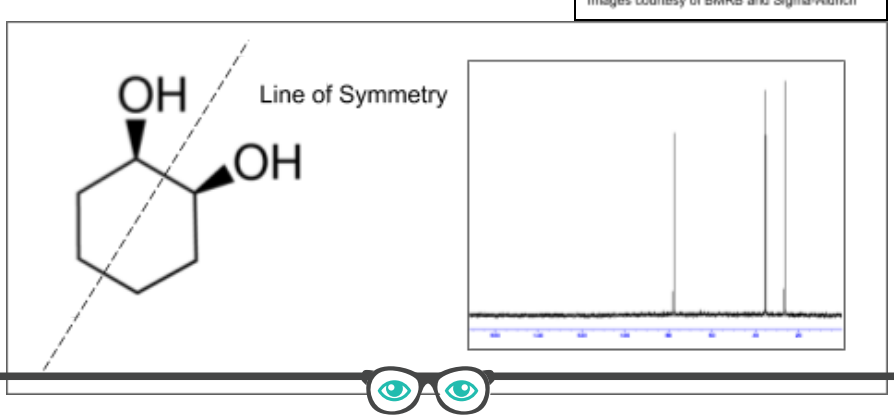
The scale on the x axis shows **chemical shift, δ**. It runs from right to left. Standard NMR chemical shift ranges will be provided for you on your data sheet in exams.
The **total magnetic field** experienced by a nucleus includes both the **external field** applied and the **local field** from neighbouring nuclei. The local field opposes the external field, so an increased electron density around a nucleus will **shield** it from the external field more and cause a **small chemical shift**. Conversely, a **reduced electron density** around a nucleus will cause it to be **deshielded** and hence have a **greater chemical shift**.

Electronegative atoms such as oxygen and nitrogen draw electron density towards themselves. This leaves adjacent carbon atoms more **deshielded.** Hence, carbon atoms neighbouring electronegative atoms have a higher shift. For this reason, carbonyl carbon atoms and those next to ester and alcohol functional groups are seen towards the left of the spectrum.

Molecules that have **symmetry** may display fewer δ peaks than the number of carbon atoms in the molecule. Therefore in these cases, it is important to look at the given **molecular formula** of the compound in order to decipher its **displayed structure**.

Example:

Images courtesy of BMRB and Sigma-Aldrich



This molecule, 1,2-cyclohexanediol, contains six carbon atoms but the NMR spectrum only has three peaks due to the symmetry of the molecule. Each peak corresponds to two identical carbon atoms.

^{1}H NMR (Proton NMR)

In ^{1}H NMR, the different **hydrogen environments** in a molecule are analysed and displayed as peaks on a spectrum. These peaks are also measured against the **TMS** standard.

The samples being analysed must be dissolved in a **non-hydrogen-containing solvent** so that the solvent doesn't produce any δ peaks on the spectrum. **CCl_4** is therefore a common solvent used along with **deuterated solvents** containing deuterium, an isotope of hydrogen. **Deuterium** has no spin so it will not be detected on an NMR spectrum.

^{1}H NMR spectra are more complex than ^{13}C spectra as the **integrals** of the peaks show the **relative intensity** of each δ value. These relative intensities correspond to the number of hydrogens in that certain environment within a molecule. The integral is the area below the peak. The **ratios** of the integrals on a spectrum can be used along with the molecular mass from mass spectrometry to work out the formula of a compound.

Different types of proton environment have different **chemical shift** values in the same way as for the ^{13}C spectra. The three protons in a methyl, $-CH_3$, group are all chemically identical so one peak with a **relative intensity** of 3 will be seen.

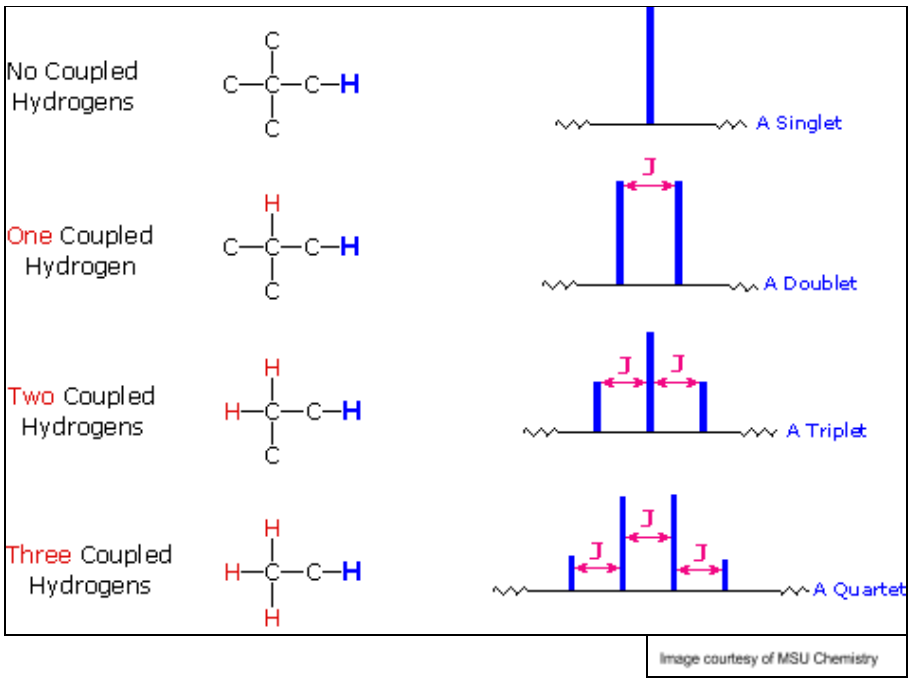
The chemical shift scale for proton NMR is much smaller than for ^{13}C. It typically runs from **0-10 ppm**. Again, chemical shift ranges for key functional groups will be provided on your data sheet in an exam.

Splitting Patterns

The peaks of a ^{1}H NMR spectra also inform **where each environment is positioned** within the molecule. Peaks are split into a **small cluster,** indicating how many hydrogens are on the **adjacent carbon atom** within the molecule. These smaller peaks are a **splitting pattern** and follow an **'n+1' rule**, where n is the number of identical hydrogen atoms on the adjacent carbon:

- **Singlet** = 0 H on adjacent carbon
- **Doublet** = 1 H on adjacent carbon
- **Triplet** = 2 H on adjacent atom
- **Quartet** = 3 H on adjacent carbon

Example:



There are some common **combinations of peaks and splitting patterns** that make deciphering the structure of the molecule easier. A **triplet-quartet** splitting pattern is a common combination as it represents a **-CH_2-CH_3** fragment. The two protons on the CH_2 group split the CH_3 peak into 3 (a triplet), by the **n+1 rule**. Likewise, the three protons on the CH_3 group split the CH_2 peak into 4 (a quartet). The **relative intensities** would be 3 and 2 for the triplet and quartet respectively.

Multiple fragments can be worked out from these peaks and **pieced together** to determine the **full molecule structure**.

Combined Techniques

The analytical techniques covered throughout the course can be used together to predict the structure of unknown compounds.