

Edexcel IAL Chemistry A-level

Topic 19: Organic Nitrogen Compounds: Amines, Amides, Amino Acids and Proteins Detailed notes

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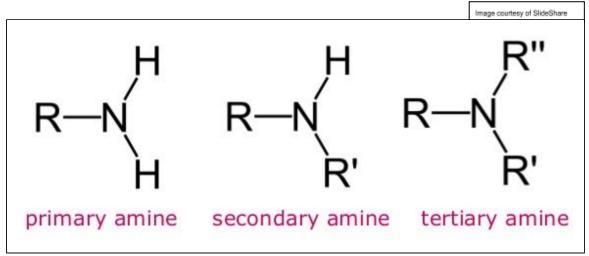




Aliphatic Amines

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. Amines are **miscible** with water as a result of the **hydrogen bonding** which occurs between water molecules and the δ + **hydrogen atoms** in the amine group.

Example: Classification of amines

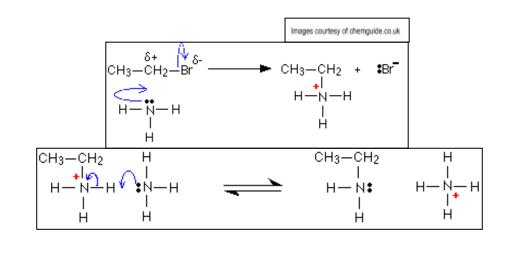


Amines can be produced by nucleophilic substitution or by the reduction of nitriles:

Nucleophilic Substitution

Amines can be produced from the nucleophilic substitution reaction between a halogenoalkane with ammonia in a sealed tube. One mole of halogenoalkane reacts with two moles of ammonia, producing a primary amine and an ammonium salt (ammonium ion and halide ion).

Example: Nucleophilic substitution of bromoethane with ammonia

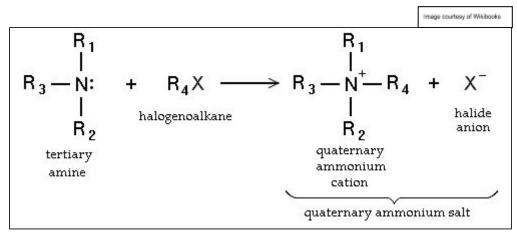






This substitution reaction can continue until **all the hydrogen atoms have been replaced** with amine groups. Following this, an additional substitution can occur, producing a **quaternary ammonium salt**.

Example:

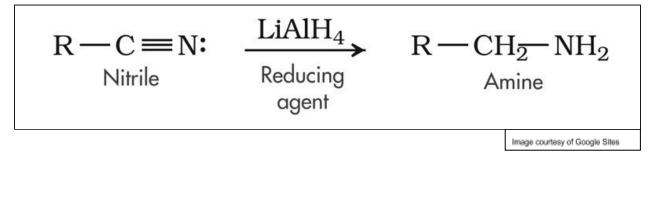


The multiple possible substitutions mean that a **mixture of products** is produced. Therefore, the reaction has **low efficiency** and the reaction **conditions** have to be changed so that only a single substitution occurs. Ammonia can be added **in excess** in order to achieve only the primary amine, or the mixture of products can be **separated using fractional distillation**.

Reduction of Nitriles

Amines can be produced by the reduction of nitriles by hydrogenation. This reduction requires the reducing agent LiAlH₄, and acidic conditions, or a combination of hydrogen with a nickel catalyst (catalytic hydrogenation).

Example:



Amine Base Properties

Amines are **weak bases** because the **lone electron pair** on the nitrogen atom can accept protons. The base strength of amines depends on **how available** the electron pair is on the nitrogen atom.

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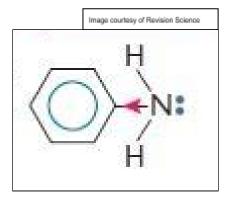
The more available the electron pair is, the more likely it is to accept a proton, meaning the amine is a stronger base.

The Inductive Effect

In an organic molecule, different functional groups can affect how available a lone electron pair is by changing **electron density** around the bond.

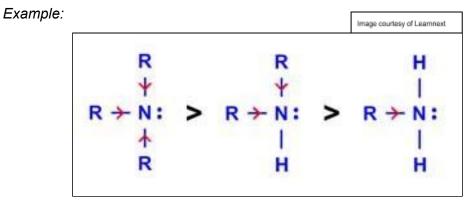
1. **Benzene rings** - draw electron density **away** from the nitrogen making the lone pair 'less available'





Negative inductive effect

2. Alkyl groups - push electron density towards the nitrogen atom making the lone pair 'more available'. More alkyl groups means more 'pushing'.



Positive inductive effect

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Therefore, aliphatic amines are stronger bases and aromatic amines are weaker bases.

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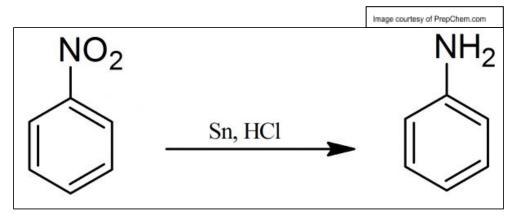




Aromatic Amines

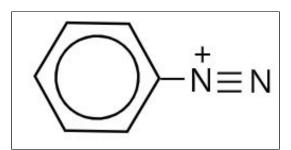
Aromatic amines can be produced from the **reduction of nitrobenzene** using **concentrated hydrochloric acid** (HCI) and a **tin catalyst**. Aromatic amines consist of an amine group and a benzene ring.

Example:



Reactions of Aromatic Amines

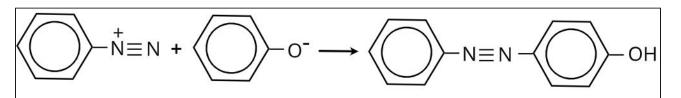
Benzenediazonium ions are formed when primary aromatic compounds react with **nitric(III)** acid (nitrous acid) at temperatures **below 10°C**. Diazonium ions are ions that contain an N_2^+ group.



Structure of a benzenediazonium ion

Benzenediazonium chloride reacts with phenol in a **coupling reaction**. Coupling reactions are organic reactions that involve the joining together of two chemical species in an **alkaline solution**.

First, a solution of sodium phenoxide is produced by dissolving phenol in sodium hydroxide. Next, the solution is cooled and added to benzenediazonium chloride. A **yellow-orange solution/precipitate** is formed. The product is known as an **azo compound**.



The coupling reaction between a benzenediazonium ion and a phenoxide ion





Azo compounds form brightly coloured compounds, so they are regularly used in dyes.

Reactions of Primary Aliphatic Amines and Aromatic Amines

Amines as Bases

Amines react with water to form an **alkaline solution**. The lone pair of electrons on the amine's nitrogen atom can **accept a hydrogen** from a water molecule, therefore acting as a base. This releases **OH**⁻ **ions** into the solution.

Example:

$$\mathrm{CH_3CH_2NH_2} + \mathrm{H_2O} \rightarrow \mathrm{CH_3CH_2}^+\mathrm{NH_3} + \mathrm{OH^-}$$

To produce Salts

Amines react with acids to form an ammonium salt. Again, the amine acts as a base and accepts a proton to form a **quaternary ammonium salt**.

Example:

$$\mathrm{CH_3CH_2CH_2CH_2NH_2} + \mathrm{HCI} \rightarrow \mathrm{CH_3CH_2CH_2CH_2^+NH_3\,CI^-}$$

Butylamine + hydrochloric acid \rightarrow butylammonium chloride

Reaction with Copper(II) ions

In topic 18 it was learnt that ammonia can react with copper aqua ions to form an **octahedral complex.** Similarly, aliphatic and aromatic amines can react in the same way. In solution, the copper ions will react with water to form a **copper aqua ion**. The amine then acts as a base to **accept protons** from the water ligands to give a **blue precipitate** of $Cu(OH)_2(H_2O)_4$ along with an ammonium salt.

Example:

$$[\operatorname{Cu}(\operatorname{H_2O})_6]^{2+} + 2\operatorname{CH_3CH_2NH_2} \rightarrow [\operatorname{Cu}(\operatorname{H_2O})_4(\operatorname{OH})_2] + 2\operatorname{CH_3CH_2NH_3^+}$$

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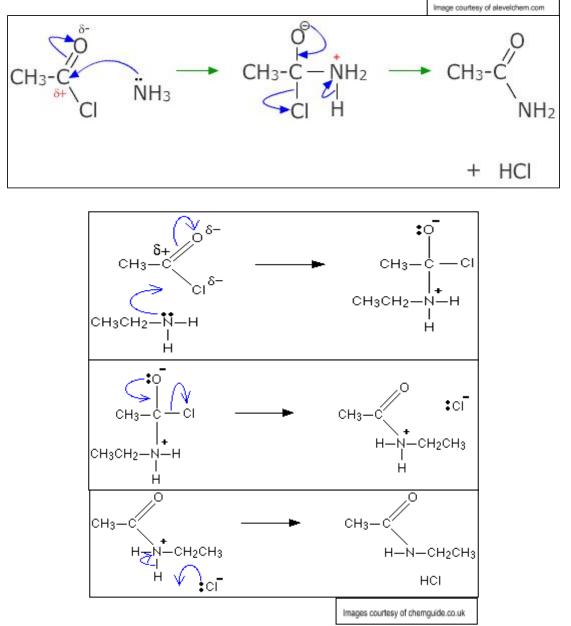
Amides





Amines can undergo **nucleophilic addition-elimination** reactions with **acyl chlorides** to produce **amides** and **N-substituted amides**.

Mechanism



This same reaction mechanism can also occur with **acid anhydrides** to produce an amide and a carboxylic acid.

N-substituted Amides

When **naming** N-substituted amides, they are treated in a similar way to **esters**. The **prefix** indicates the length of the carbon chain bonded to the **nitrogen** atom only and the **suffix** indicates the carbon chain which contains the **carbonyl** bond.

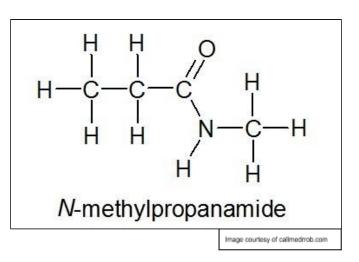
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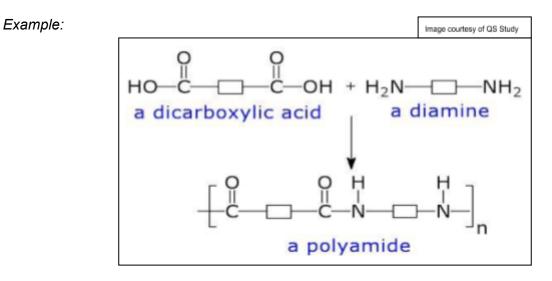


Example:



Polyamides

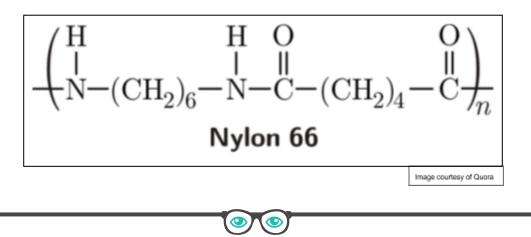
Polyamides are condensation polymers generally formed in a reaction between a **dicarboxylic acid and a diamine**. A molecule of water is removed, leaving an **amide linkage**.



-CONH- is the amide linkage

Examples of polyamides include nylon-6,6 made from 1,6-diaminohexane and hexanedioic acid.

Example:



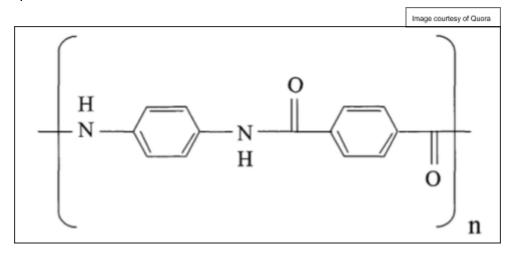
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Kevlar is another common polyamide made from benzene-1,4-dicarboxylic acid and 1,4-diaminobenzene.

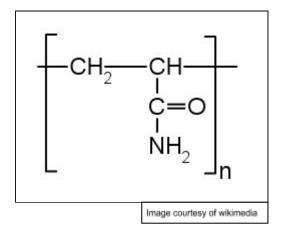
Example: Repeat unit of kevlar

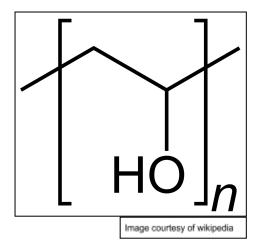


Polyamides are commonly formed from long chain molecules which makes them strong.

Polyamides may also be formed by **addition polymerisation** reactions of monomers that contain both an **amide functional group** and **unsaturated carbon bonds**.

Examples: The repeat unit of the polymers poly(propenamide) (left) and poly(ethenol) (right).





Properties

Polyamides have **high strength** and **resilience**. They are commonly used in carpets, clothing and plastics, amongst other things. They are generally **soluble** in water, since the amide functional group can form **hydrogen bonds** with water.



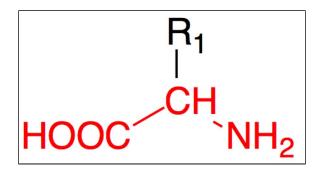


Poly(ethenol) is also a water-soluble polymer. This is due to the presence of the alcohol group which can also form **hydrogen bonds** with water. This property, along with its high tensile strength, means it is used in **soluble laundry bags** and **liquid-detergent capsules**.

Amino Acids

Chirality

 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.



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**.

Zwitterions

The two functional groups within a single molecule mean that amino acids can **react as both acids and bases**, depending on the conditions of the reaction.

A zwitterion is a **dipolar ion**. This means it has 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⁻).

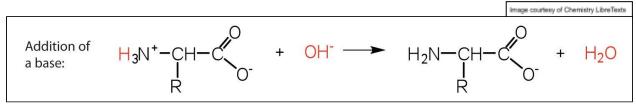
In **acidic conditions (low pH)**, the COO⁻ group is more likely to accept a hydrogen ion, producing a **positive (acidic) end** to the molecule.

Example:	Addition of an acid:	H ₃ N ⁺ −CH−C ^O R	+ H*		H ₃ N+	-CH-COH	
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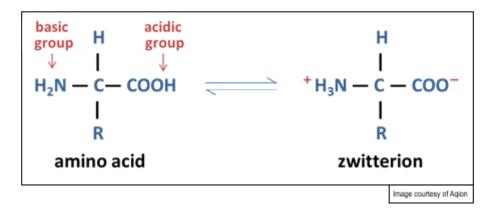
In **basic conditions (high pH)**, the hydrogen ion in the NH_3^+ group is more likely to be lost, producing a **negative (basic) end** to the molecule.

Example:



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

Example:



Thin-layer chromatography can be used to identify unknown amino acids. UV light is used to help view the traces on the silica plate.

Proteins

Proteins are another form of condensation polymer formed from sequences of amino acids joined together by **peptide bonds**.

