Organic nitrogen compounds

Amines, amides, amino acids and proteins, polyamides and other polymers, the preparation and basicity of amines, and diazonium coupling to make azo dyes.

Naming

- **Amines** have the group $-NH_2$ (primary): butylamine ($CH_3CH_2CH_2CH_2NH_2$), butan-1-amine, **phenylamine** ($C_6H_5NH_2$).
- **Amides** have $-CONH_2$: ethanamide (CH_3CONH_2). An **N-substituted amide** has an alkyl group on nitrogen: N-methylethanamide.
- **Amino acids** have both $-NH_2$ and $-COOH$: aminoethanoic acid (glycine), 2-aminopropanoic acid (alanine). A **α-amino acid** has both on the same carbon, $RCH(NH_2)COOH$.

Amines

Basicity

The nitrogen has a **lone pair** that accepts H^+, so amines are **bases**.

- With **water**: $CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$, an alkaline solution.
- With **acids**: $CH_3CH_2NH_2 + HCl \longrightarrow CH_3CH_2NH_3^+Cl^-$, a salt that dissolves in water.

Small amines are **miscible with water** because they form hydrogen bonds with it.

Relative basicity: aliphatic amine $>$ NH_3 $>$ phenylamine.

- In **aliphatic amines** the alkyl group **pushes electrons** towards the nitrogen, increasing its electron density, so the lone pair is **more available** to accept H^+.
- In **phenylamine** the lone pair on nitrogen is **delocalised into the benzene ring**, so it is **less available**, so phenylamine is a weaker base than ammonia.

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Other reactions

Reagent	Product
Halogenoalkane	Secondary amine (and then further substitution to tertiary amines and a quaternary salt)
Ethanoyl chloride	**N-substituted amide**: $CH_3CH_2NH_2 + CH_3COCl \rightarrow CH_3CONHCH_2CH_3 + HCl$
Copper(II) ions	Ligand exchange: a **deep blue** complex ion $[Cu(RNH_2)_4(H_2O)_2]^{2+}$ forms (like ammonia)

Preparation

- **Primary aliphatic amines** from **halogenoalkanes**: heat with an excess of ammonia in ethanol under pressure. Excess ammonia reduces further substitution.
- By **reduction of nitriles**: $RCN + 4[H] \rightarrow RCH_2NH_2$, using $LiAlH_4$ in dry ether, or hydrogen with a nickel catalyst.
- **Aromatic amines** from **nitro compounds** by reducing them with **tin and concentrated hydrochloric acid** (then adding alkali to free the amine from its salt):

$$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$$

Diazonium ions and azo dyes

Phenylamine reacts with **nitrous acid** (HNO_2, made in situ from sodium nitrite and hydrochloric acid) at **below 5 °C** (ice bath) to form a **benzenediazonium ion**:

$$C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^- + 2H_2O$$

The diazonium ion is **unstable above 5 °C** and decomposes to give nitrogen and phenol.

It undergoes a **coupling reaction** with an alkaline solution of **phenol** (or another aromatic compound activated by an $-OH$ or $-NH_2$ group) to form an **azo compound**, which has the **azo group** $-N=N-$ joining two benzene rings. Azo compounds are strongly **coloured** (yellow, orange or red) because of an extended **delocalised** system, and are used as **dyes**.

> **Two conditions to remember: keep the temperature below 5 °C when making the diazonium salt, and use alkaline solution of phenol for coupling.**

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Amides

Amides can be prepared from **acyl chlorides**, with concentrated ammonia (primary amides) or with amines (N-substituted amides).

Polymers

Condensation polymers: polyamides

Polyamides form from a **dicarboxylic acid** (or diacyl chloride) and a **diamine**, with loss of H_2O (or HCl) at each **amide (peptide) link**, $-CONH-$.

Nylon-6,6 is made from **hexane-1,6-diamine** and **hexanedioic acid** (or hexanedioyl dichloride, which is more reactive and makes the reaction fast at room temperature):

$$n\,H_2N(CH_2)_6NH_2 + n\,ClOC(CH_2)_4COCl \rightarrow [-HN(CH_2)_6NHCO(CH_2)_4CO-]_n + 2n\,HCl$$

The polymer has **hydrogen bonds between chains** (between $N-H$ and $C=O$) and **strong London forces**, giving **strength, high melting temperature and resistance to stretching**, so it can be used for fibres, ropes and clothing.

Proteins are polyamides of amino acids, formed in the same way.

Addition polymers with hydrogen bonding

- **Poly(propenamide)** from $CH_2=CHCONH_2$. Repeat unit $[-CH_2-CH(CONH_2)-]$.
- **Poly(ethenol)** from (indirectly) hydrolysis of poly(ethenyl ethanoate). Repeat unit $[-CH_2-CH(OH)-]$. It is **soluble in water** because the $-OH$ groups form **hydrogen bonds** with water. It is used for **soluble laundry bags** and **liquid-detergent capsules (liquitabs)**.

> **NOTE**
>
> Poly(ethenol) cannot be made from ethenol directly, because ethenol is unstable and changes to ethanal.

Amino acids

An amino acid contains a basic $-NH_2$ group and an acidic $-COOH$ group. In the solid state and in solution near neutral pH, it exists as a **zwitterion**, $^+H_3N-CHR-COO^-$, which has both a positive and a negative charge but no overall charge. This explains why amino acids are **soluble in water** and have **high melting temperatures**, like ionic compounds.

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Condition	Form
Acid (low pH)	$^{+}H_3N-CHR-COOH$ (cation)
Neutral	$^{+}H_3N-CHR-COO^{-}$ (zwitterion)
Alkali (high pH)	$H_2N-CHR-COO^{-}$ (anion)

- Amino acids (except glycine) have a **chiral** carbon, so they are **optically active**.
- They form **peptide bonds** by **condensation**: $H_2NCH_2COOH + H_2NCH_2COOH \rightarrow H_2NCH_2CONHCH_2COOH + H_2O$. A **dipeptide** forms, and a long chain is a **polypeptide** (protein).

> **TRY IT**
>
> Draw the dipeptide formed from glycine and alanine, with glycine at the N-terminus.

$H_2NCH_2-CO-NH-CH(CH_3)-COOH$. The $-CONH-$ link is the peptide bond.

Core Practical 15 is an analysis of inorganic and organic unknowns using the tests in this specification.

Note Academy