Amines and nitro compounds

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Amines

= **organic derivatives of ammonia** in which one or more of the hydrogen atoms is replaced by an alkyl or by aromatic group (R)

- ammonia NH_3
- primary amine $R_1\text{-}NH_2$
- secondary amine $R_1\text{-}NH\text{-}R_2$
- tertiary amine $R_1\text{-}N(R_2)\text{-}R_3$
- quarternary ammonium cation $N(R)_4^+$

  (choline, acetylcholine)

Properties of amines

- C_1-C_5 amines are soluble in water (H-bonds)
- **low MW**: gases, sharp penetrating odour similar to ammonia
- amines with **increasing MW**: liquids and solids, they smell like decaying fish
- diamines are responsible for the odour of decaying animal tissue:
  - H_2N-$(CH_2)_4$-NH_2 = **putrescine**
  - H_2N-$(CH_2)_5$-NH_2 = **cadaverine**

Amines

- classification of amines ≠ classification of alcohols!

  t-butylamine = primary amine
  t-butylalcohol = tertiary alcohol

- N-containing heterocyclic compounds, e.g.
  - *piperidine = secondary alicyclic amine*
  - *indole = secondary aromatic amine*
- **suffix**: -amine (alkyl amine or hydrocarbon amine)
- **prefix**: amino- or alkylamino hydrocarbon

  3-(N-methylamino)pentane

Exercise

- CH_3-CH_2-NH_2
- CH_3-$CH(NH_2)$-CH_3
- CH_3-CH_2-$N(CH_3)$-C_6H_5
- CH_3-$CH(NH_2)$-CH_2-CH_3
- CH_3-$CH(NH_2)$-CH_2-OH
- H_2N-$(CH_2)_3$-NH_2
- CH_3-CH_2-CH_2-$CH(CH_3)$-$N(CH_3)_2$
- CH_3-CH_2-$CH(NH_2)$-$COOH$

Exercise

- C_6H_5-NH_2 = aniline !
- C_6H_5-NH-CH_3
- C_6H_5-$N(CH_3)_2$
- $(CH_3)_2NH$
- CH_3-CH_2-CH_2-$N(CH_3)$-CH_2-CH_3
- C_6H_{11}-NH_2
- H_2N-C_6H_4-$COOH$
- C_6H_5-CH_2-NH_2

Reactions of amines

- many chem. properties reflect the reactivity of the unshared pair of electrons on „N" (= **base**)
  - $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$
    methylammonium ion
- amines are completely protonated in the reaction with a strong acid → ammonium salts (more soluble in water)
  - $CH_3NH_2 + HCl \rightarrow CH_3NH_3^+ + Cl^-$
  - *drugs containing –NH_2 are often given in the form of salts to improve their solubility in body fluids*
- some detergents contain quarternary ammonium salts, they are used as germicides (for med. istruments)

Reactions of amines

- alkyl substituted amines are stronger bases than ammonia:
  - $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ $K_b = 1{,}8 \times 10^{-5}$
  - $CH_3\text{-}NH_2$ $K_b = 4{,}6 \times 10^{-4}$
  - $(CH_3)_2\text{-}NH$ $K_b = 4{,}7 \times 10^{-4}$
- aromatic amines are weaker bases:
  - $C_6H_{11}\text{-}NH_2$ $K_b = 4{,}6 \times 10^{-4}$
  - $C_6H_5\text{-}NH_2$ $K_b = 4{,}3 \times 10^{-10}$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Reaction of amines with HNO_2

- it is used in cassifying unknown amines:
  - primary amines → diazonium salts (unstable)
    $R\text{-}NH_2 + HNO_2 \rightarrow R\text{-}N{\equiv}N^+ \rightarrow N_2 + \text{alcohol}$
  - secondary amines → N-nitrosamines (yellow oily comp.)
    $R_1\text{-}NH\text{-}R_2 + HNO_2 \rightarrow R_1R_2N\text{-}N{=}O + \text{water}$
  - tertiary amines + HNO_2 → no reaction
- **aromatic primary amines** react with HNO_2 in a reaction called **DIAZOTATION**

  ⇒ diazonium salts stabilized by the aromatic ring

$$C_6H_5\text{-}NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5\text{-}N{\equiv}N^+\ Cl^- + NaCl + 2H_2O$$

benzenediazonium chloride

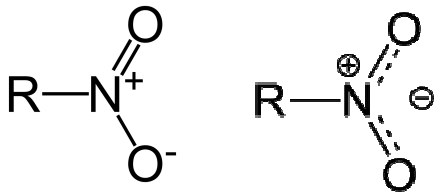
Reactions of amines

- diazonium salts are used for preparation of **AZO DYES**
  by the reaction with a phenol or an aromatic amine (= **coupling reaction**)
- example of azo dyes: *methylorange*
- azo compounds: **-N=N-**
- examples:
  - C_6H_5-N=N-C_6H_5 azobenzene
  - C_6H_5-N=N-C_6H_4-CH_3 toluene-4-azobenzene

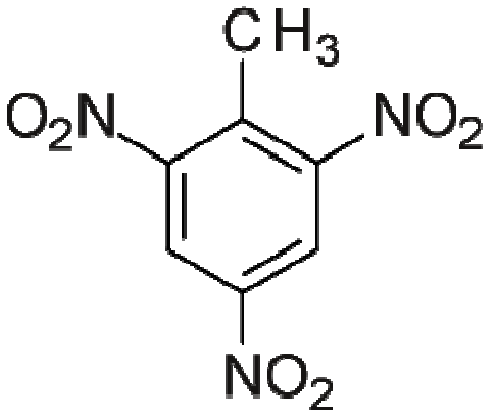
Exercise

• CH_3-CH_2-CH_2-NH_2	• propylamine
• C_6H_5-NH-C_6H_5	• diphenylamine
• $N(CH_3)_3$	• trimethylamine
• $CH_3(CH_2)_2$-$N(CH_3)$-CH_2CH_3	• ethyl methyl propylamine
• C_6H_5-$N(CH_3)_2$	• dimethyl phenyl amine (N, N-dimethylaniline)
• H_2N-C_6H_4-COOH	• 4-aminobenzoic acid
• CH_3-NH-CH_2-CH_2-CH_3	• methyl propyl amine
• H_2N-CH_2-CH_2-OH	• 2-aminoethanol

Nitro compounds



- <u>functional group</u>: **-NO_2** (= nitro group)
- only <u>prefix</u>: **nitro-** *(there is no suffix used)*
- <u>preparation</u>: **by nitration**
  (nitration mix = HNO_3 + H_2SO_4)
- **<u>examples:</u>**
  - CH_3-NO_2 — nitromethane
  - O_2N-CH_2-CH_2-NO_2 — 1,2-dinitroethane
  - CH_3-$CH(NO_2)$-CH_3 — 2-nitropropane
  - O_2N-$C(CH_3)_3$ — 2-nitro-2-methylpropane
  - C_6H_5-NO_2 — nitrobenzene *(yellow liquid)*
  - H_3C-C_6H_4-NO_2 — p-nitrotoluene



TNT

= 2,4,6-trinitrotoluene

http://en.wikipedia.org/wiki/Trinitrotoluene

Properties of nitro compounds

- low MW: liquids of a sweet odour
- some **nitroarenes** are solid crystalline substances
- high b.p., *water insoluble,* ***often highly explosive***
- the most important reaction: **reduction**

C_6H_5-NO_2	**nitrobenzene**
C_6H_5-N=O	nitrozobenzene
C_6H_5-NH-OH	N-phenylhydroxylamine
C_6H_5-N=N-C_6H_5	azobenzene
C_6H_5-NH-NH-C_6H_5	hydrazobenzene
C_6H_5-NH_2	**aniline**