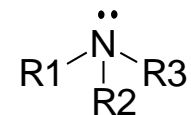


## Amines

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## Amines

- **Amines** are organic compounds that contain a nitrogen atom attached to at least one alkyl or aryl (aromatic) substituent.



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## Types of amines

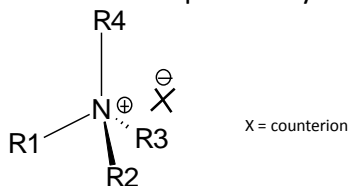
- **primary amines** arise when one of three hydrogen atoms in ammonia is replaced by an organic substituent.
- **Secondary amines** have two organic substituents bound to N together with one H.
- In **tertiary amines** all three hydrogen atoms are replaced by organic substituents.

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Type of amine	Structure
Primary	$\begin{array}{c} \text{R1} - \overset{\cdot\cdot}{\text{N}} - \text{H} \\   \\ \text{H} \end{array}$
Secondary	$\begin{array}{c} \text{R1} - \overset{\cdot\cdot}{\text{N}} - \text{H} \\   \\ \text{R2} \end{array}$
Tertiary	$\begin{array}{c} \text{R1} - \overset{\cdot\cdot}{\text{N}} - \text{R3} \\   \\ \text{R2} \end{array}$

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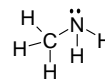
- If there are four alkyl substituents on the nitrogen, the species has a charged nitrogen center, and necessarily come with a negative counterion.
- It is known as quaternary ammonium salts.



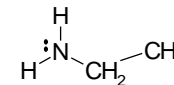
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## IUPAC NOMENCLATURE

- Lower amines are named with the suffix -*amine*.



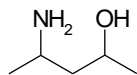
Methylamine



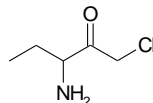
Ethylamine

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- Amines have the prefix *amino* as a functional group, if the parent chain contains other functional groups which rank higher than the amine group.



4-Amino-pentan-2-ol



3-Amino-1-chloro-pentan-2-one

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## Physical properties

- Thus the boiling point of amines is higher than those of the corresponding alkanes, but generally lower than those of the corresponding alcohols.
- Methyl-, dimethyl-, trimethyl-, and ethylamine are gases under standard conditions, whereas diethylamine and triethylamine are liquids.
- Most other common alkyl amines are liquids; high-molecular-weight amines are, solids.

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- Gaseous amines possess a characteristic ammonia smell, liquid amines have a distinctive "fishy" smell.
- Most aliphatic amines display some solubility in water, reflecting their ability to form hydrogen bonds.
- Solubility decreases with the increase in the number of carbon atoms, especially when the carbon atom number is greater than 6.
- Aliphatic amines display significant solubility in organic solvents, especially polar organic solvents.

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## Boiling points of various amines

type	formula	boiling point (°C)
primary	CH <sub>3</sub> NH <sub>2</sub>	-6.3
primary	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	16.6
primary	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	48.6
secondary	(CH <sub>3</sub> ) <sub>2</sub> NH	7.4
tertiary	(CH <sub>3</sub> ) <sub>3</sub> N	3.5

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- The boiling point of methylamine is -6.3°C, whereas ethane's boiling point is much lower at -88.6°C.
- The reason for the higher boiling points of the primary amines is that they can form hydrogen bonds with each other as well as van der Waals dispersion forces and dipole-dipole interactions.

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## Hydrogen bonding in amines

- The hydrogen bonding isn't as efficient as it is in, say, water, because there is a shortage of lone pairs.
- Some slightly positive hydrogen atoms won't be able to find a lone pair to hydrogen bond with.
- There are twice as many suitable hydrogens as there are lone pairs.

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- The boiling points of the primary amines increase as you increase chain length because of the greater amount of van der Waals dispersion forces between the bigger molecules.
- The boiling point of the secondary amine is a little lower than the corresponding primary amine with the same number of carbon atoms.
- Secondary amines still form hydrogen bonds, but having the nitrogen atom in the middle of the chain rather than at the end makes the permanent dipole on the molecule slightly less.

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- In a tertiary amine there aren't any hydrogen atoms attached directly to the nitrogen. That means that hydrogen bonding between tertiary amine molecules is impossible. That's why the boiling point is much lower.

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## Solubility in water

- The small amines of all types are very soluble in water. In fact, the ones that would normally be found as gases at room temperature are normally sold as solutions in water - in much the same way that ammonia is usually supplied as ammonia solution.
- All of the amines can form hydrogen bonds with water - even the tertiary ones.

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- Although the tertiary amines don't have a hydrogen atom attached to the nitrogen and so can't form hydrogen bonds with themselves, they can form hydrogen bonds with water molecules just using the lone pair on the nitrogen.

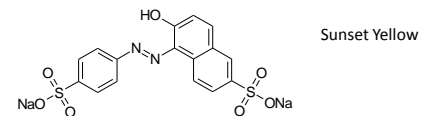
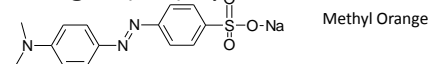
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- Solubility falls off as the hydrocarbon chains get longer - noticeably so after about 6 carbons. The hydrocarbon chains have to force their way between water molecules, breaking hydrogen bonds between water molecules.

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## Use of amines

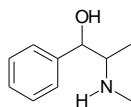
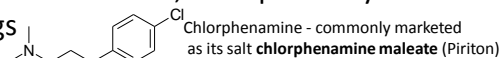
- Dyes: Primary aromatic amines are used as a starting material for the manufacture of di-nitrogen (azo) dyes.



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## Use of amines

- Drugs: Many drugs are designed to mimic or to interfere with the action of natural amine neurotransmitters, exemplified by the amine drugs



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