Amines

Chapter 11

1432-2011

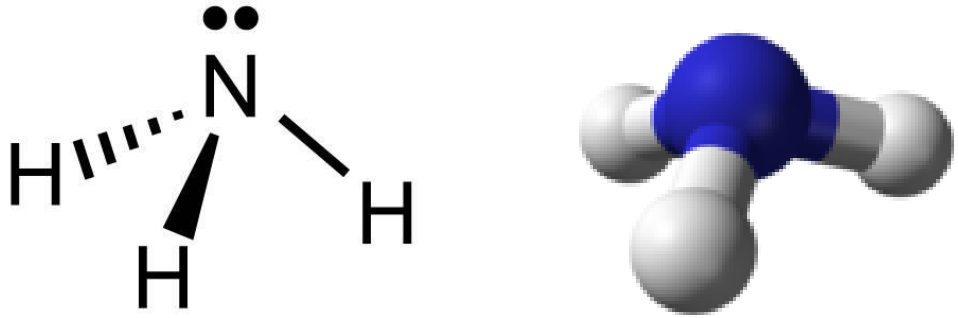
Dr. Seham ALTERARY

Chapter out lines:

- Structure and Classification of Amines.
- Nomenclature of Amines.
  - Aliphatic amines
  - Aromatic amines
- Physical properties of Amines.
- Basicity of Amines.

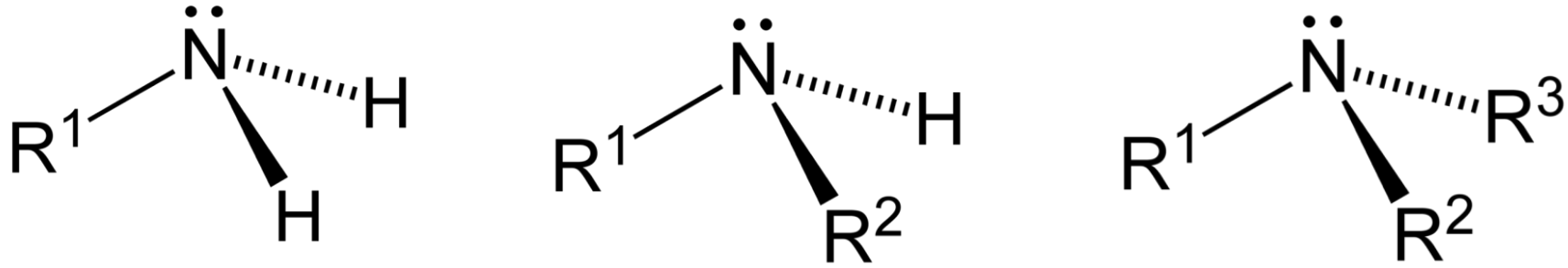
Amines

✓Amines are organic compounds and function group that contain a basic ***nitrogen atom*** with a ***lone pair***.



Ammonia structure

✓Amines are derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group.

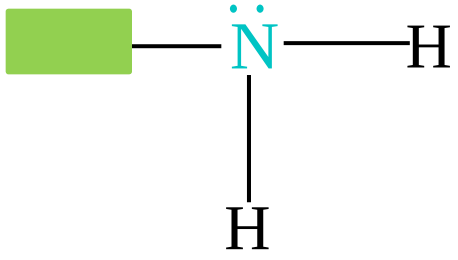


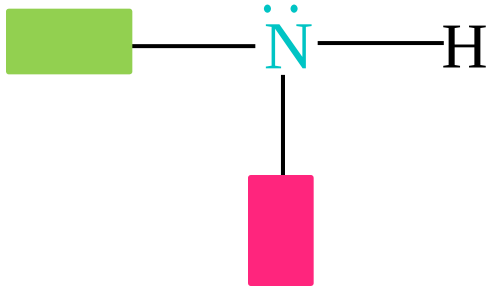
Structure and classification of amines

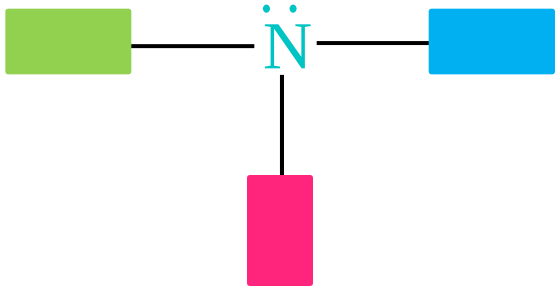
Aliphatic amines:

- Contain only alkyl groups bonded directly to the nitrogen atom.

•Amines are classified as primary (1°), secondary (2°), or tertiery(3°) according to the number of R or Ar attached to the ***nitrogen atom***.







primary amine(1°), Secondary amine (2°), Tertiary amine (3°)

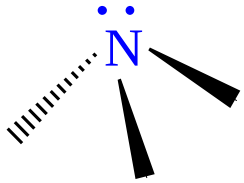
Examples

$CH_3CH_2NH_2$

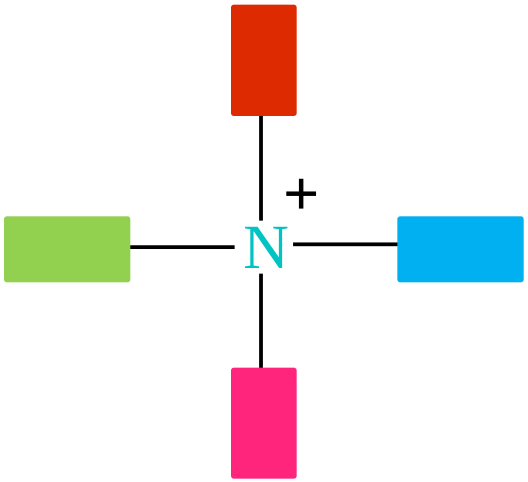
$(CH_3CH_2)_2NH$

$(CH_3CH_2)_3N$

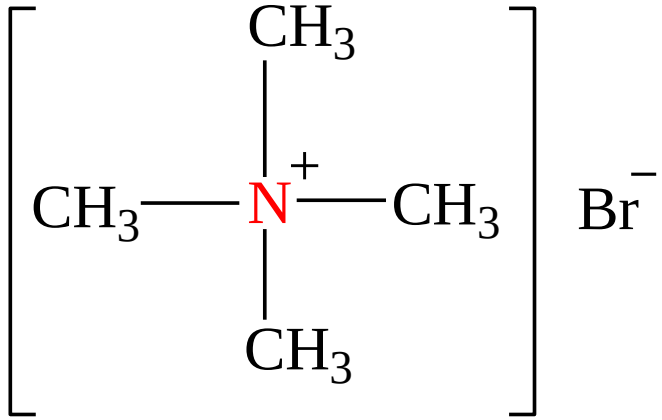
- Each amine N atom has a lone pair of electrons.



- The lone pair is responsible in large part for the chemistry of amines.
- When a fourth group bonds to the nitrogen through this lone pair, the product is a ***quaternary ammonium ion***, which has a positive charge and forms ionic compounds with anions.



Example:



A quaternary ammonium ion R_4N^+

Nomenclature of Amines

1. Common Nomenclature for primary amines :

➢Name primary amines by naming the alkyl group, followed by the word "amine". This should be written all as one word; named as ***alkylamines***.

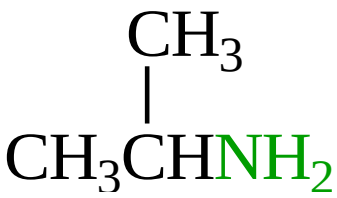
Examples:

CH_3NH_2

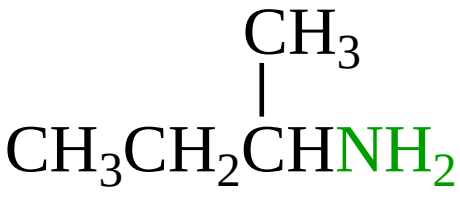
Methylamine

$CH_3CH_2NH_2$

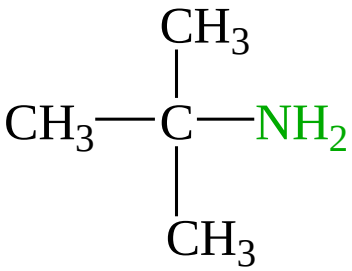
Ethylamine



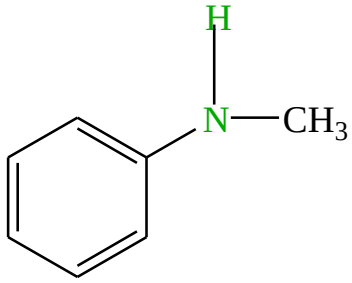
Isopropylamine



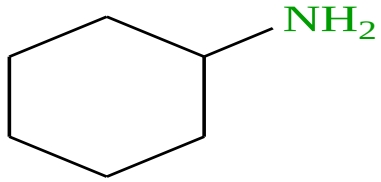
Sec-butylamine



t-butyl amine



Methylphenylamine



cyclohexylamine

2. Common Names for Secondary Amines

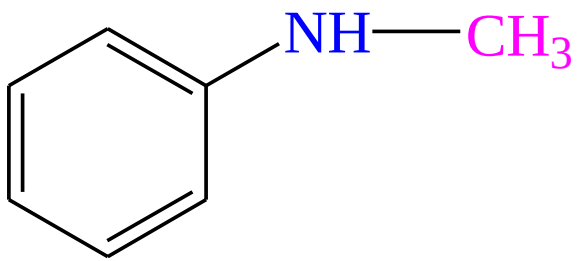
- Amines which have two alkyl groups attached to the nitrogen are called ***secondary amines***.

- ***Secondary amines*** are usually named by listing both of the alkyl groups that are attached to the nitrogen, followed by the name "amine."

Examples:

$CH_3CH_2NHCH_2CH_2CH_3$

Ethylpropylamine

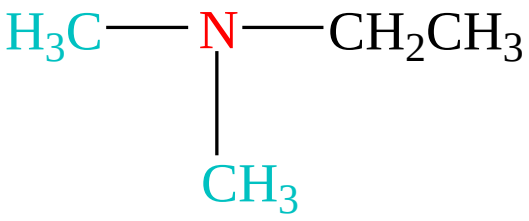


Methylphenylamine

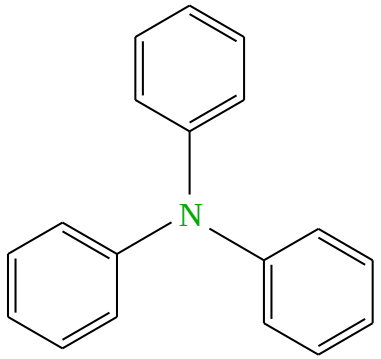
3. Common Names for teritary Amines

- Amines which have three alkyl groups attached to the nitrogen atom are called tertiary amines.
- These also are named by naming each of the alkyl groups attached to the nitrogen, followed by the word "amine."

Examples:



Dimethylethylamine



Triphenylamine

IUPAC Nomenclature:

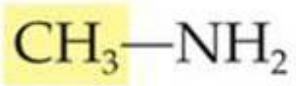
1. Aliphatic amines

- Primary alkyl amines (1°)

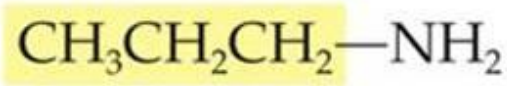
are named by identifying the alkyl group attached to nitrogen and adding the suffix -amine to the alkyl group name.

The "amino" ($-NH_2$) substituent on a parent alkane.

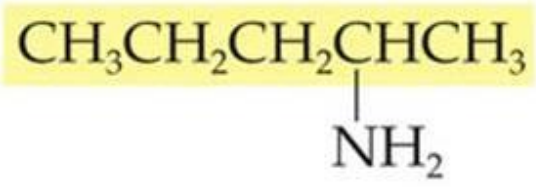
Examples:



Methanamine



1-Propanamine



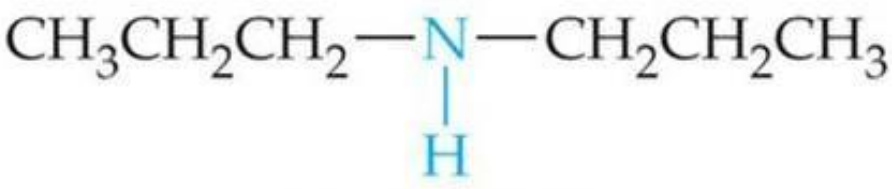
2-Pentanamine

secondary (2°) & tertiary (3°) amines

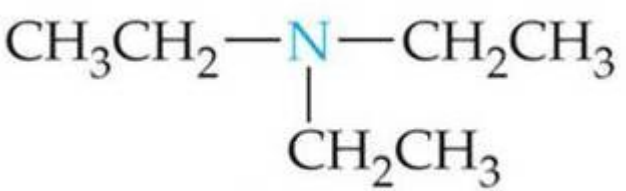
a. Incase of identical groups

- (those possessing two or three identical groups on the nitrogen, respectively) are named by adding the appropriate prefix, di- or tri-, to the alkyl group name along with the suffix -amine.

Examples:



Dipropylamine



Triethylamine

b. Incase of different groups

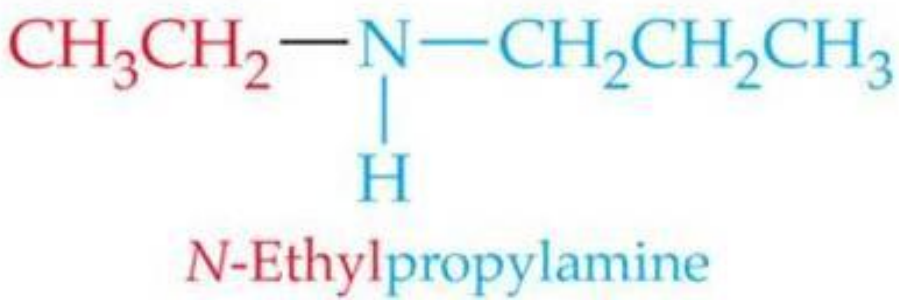
- When R groups in 2° or 3° amines are different, the compounds are named as N-substituted derivatives of a 1° amine.

• The parent compound is chosen as the 1° amine that contains the largest of the R groups.

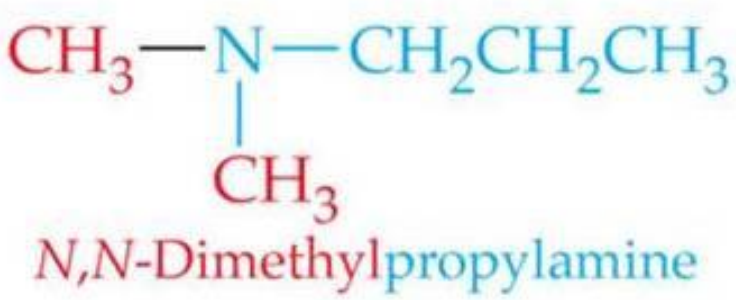
- All other groups are considered to be N-substituents.

The following compounds are named as propylamines because the propyl group in each is the largest alkyl group:

Examples for naming more complex alky and aryl amines:



N-Ethylpropylamine

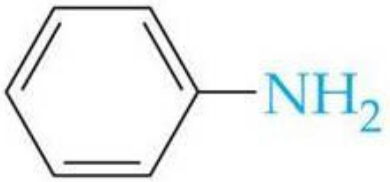


N,N-Dimethylpropylamine

Nomenclature of Amines.

Aromatic amines

- The simplest aromatic amine is known by the common name **aniline**.

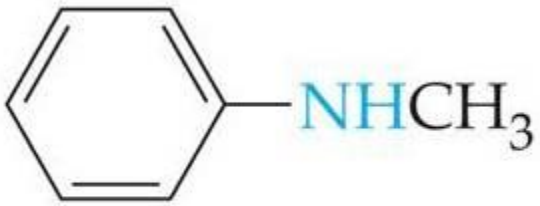


Aniline

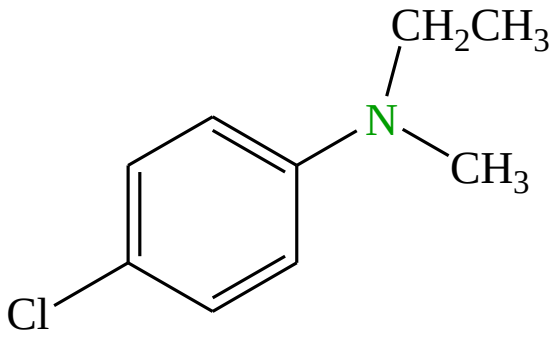
- "Aniline" is the IUPAC and common name for the aromatic amine $C_6H_5NH_2$, which is used a parent compound for other aromatic amines.

- The $-NH_2$ functional group is an **amino group**, and when this group is a substituent, amino- is used as a prefix.

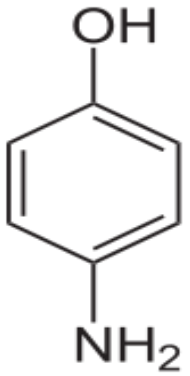
Examples:



N-Methylaniline

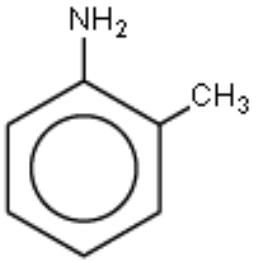


P-chloro-N-ethyl-N-methylaniline

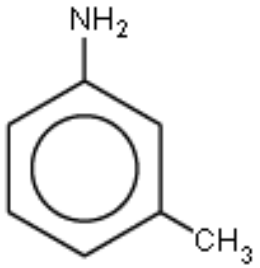


P-aminophenol

Examples

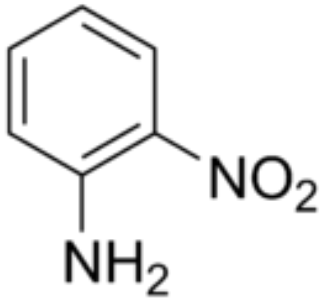


o-toluidine
(*o*-methylaniline)



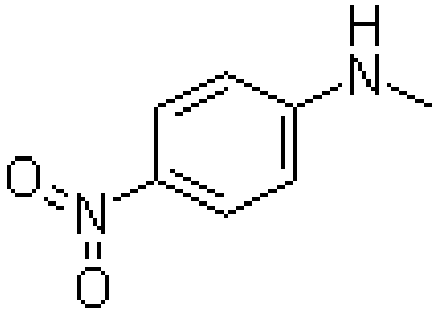
m-toluidine
(*m*-methylaniline)

p-toluidine
(*p*-methylaniline)

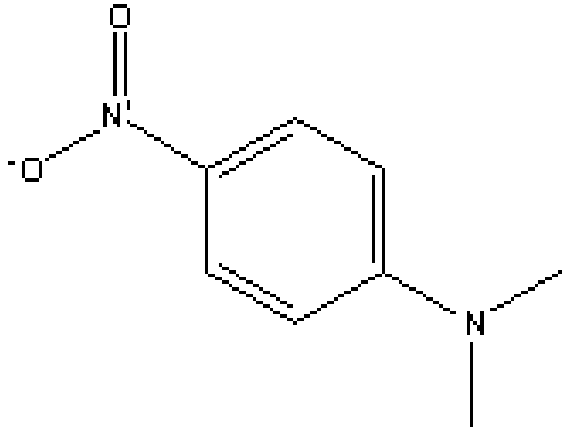


0-nitroaniline

2-nitrobenzenamine

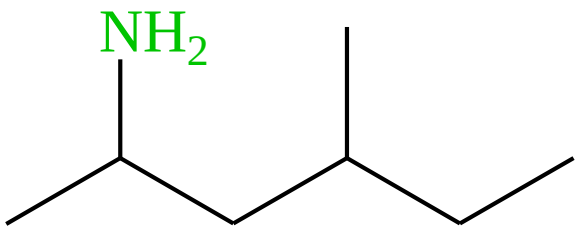


4-Nitro-N-methylaniline

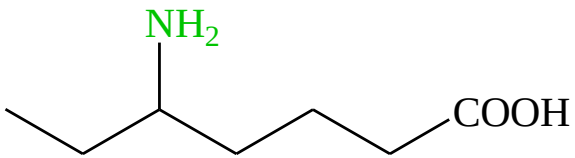


p-Nitro-N,N-dimethylaniline

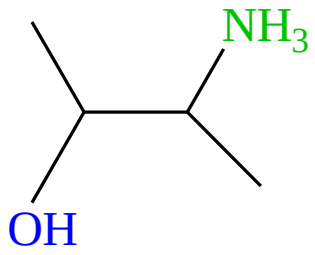
Examples



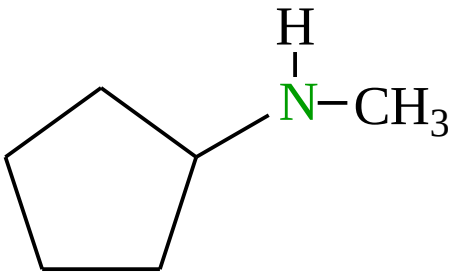
2-Amino-4-methylhexane



5-Aminoheptanoic acid

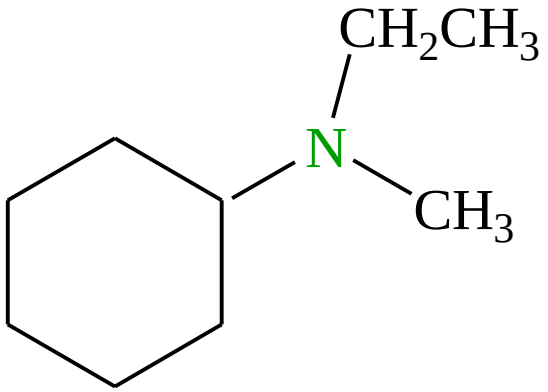


3-Amino-2-butanol



IUPAC N-Methylcyclopent**an**amine

Common cyclopent**yl**methylamine



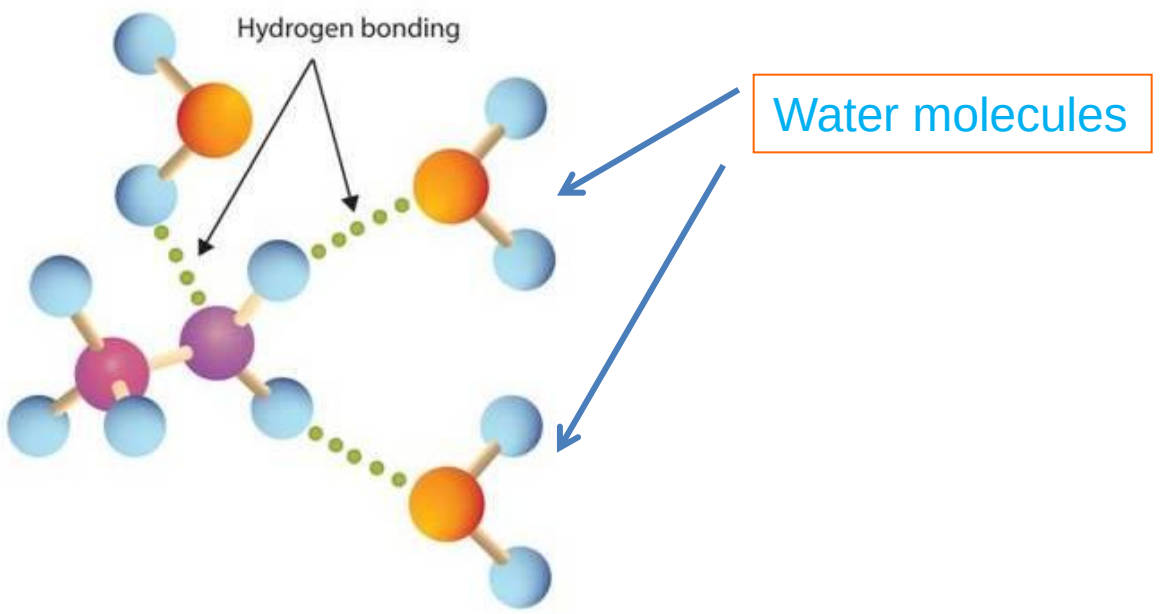
N-Ethyl- N- Methyl cyclohex**an**amine

cyclohex**yl**Ethylmethyl amine

Physical properties of Amines.

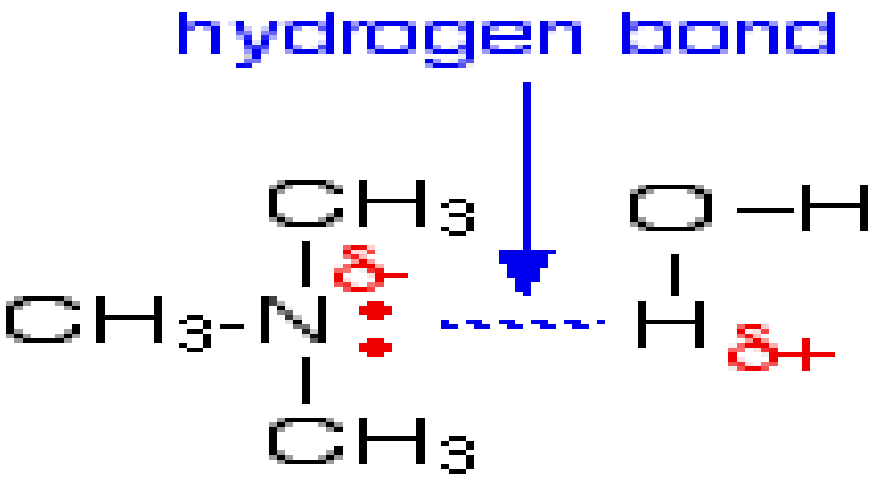
1. *Solublilty in water.*

- Amines with small alkyl groups are very **soluble in water**.
- This is because hydrogen bonding occurs between the amine and water molecules:



- The larger the alkyl chain and the more of them there are, the less soluble the amine is in water.

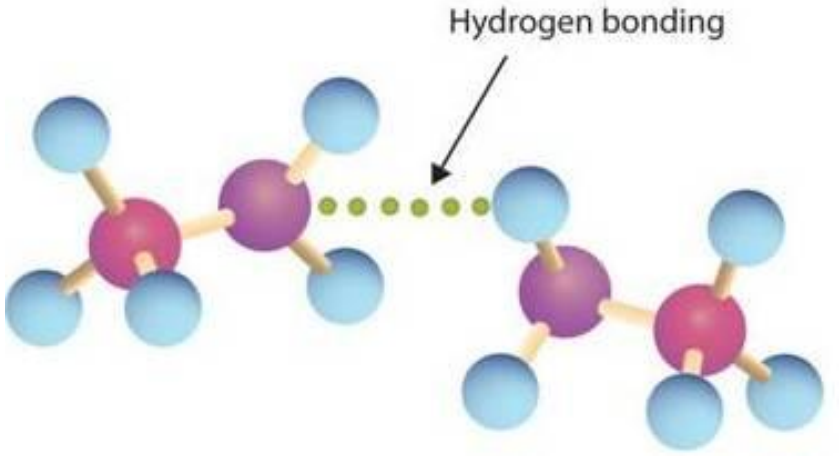
○ Although the tertiary amines don't have a hydrogen atom attached to the nitrogen and **so can't form hydrogen bonds with themselves**,

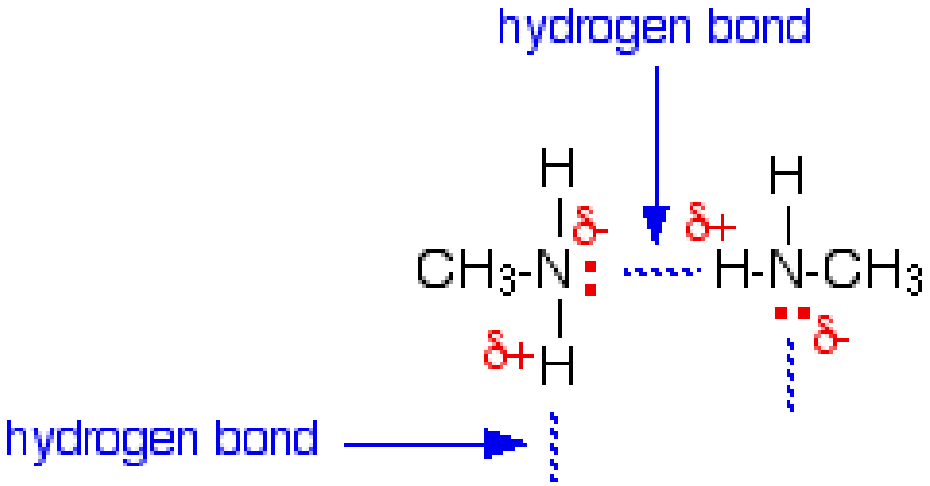


○ they can form hydrogen bonds with water molecules just using the lone pair on the nitrogen.

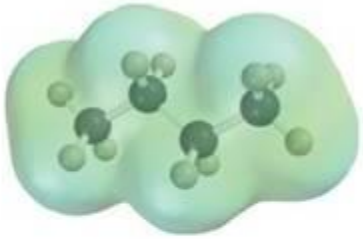
2. *Boiling point*

- Because they possess a polar N-H bond, primary and secondary amines are capable of intermolecular hydrogen bonding.



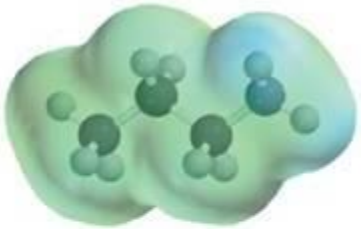


The boiling points of primary and secondary amines are **higher than** those of alkanes or ethers of similar molar mass but are lower than those of alcohols.



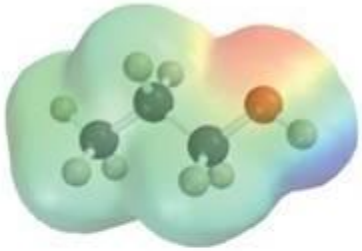
$CH_3CH_2CH_2CH_3$

Butane, bp 0 °C
MW = 58



$CH_3CH_2CH_2NH_2$

Propylamine, bp 48 °C
MW = 59



$CH_3CH_2CH_2OH$

Propanol, bp 97 °C
MW = 60

Basicity of Amines

- Amines are basic because they possess a pair of unshared electrons, which they can share with other atoms.

- These unshared electrons create an electron density around the nitrogen atom. The greater the electron density, the more basic the molecule.

- Groups that donate or supply electrons will increase the basicity of amines while groups that decrease the electron density around the nitrogen decrease the basicity of the molecule.

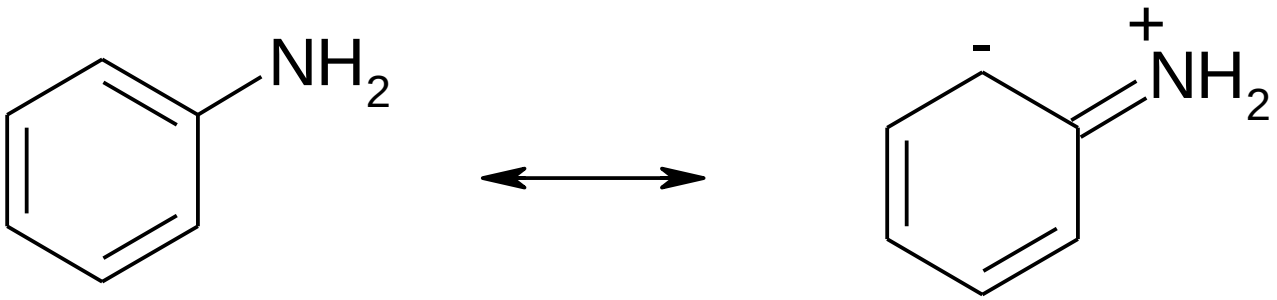
$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$$

Most basic — Least basic

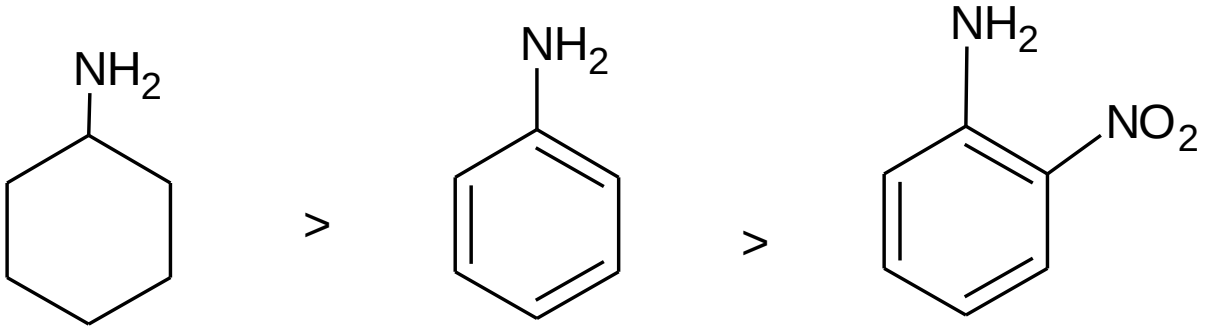
Increase basicity

- Aromatic amines are **less basic strength** than aliphatic amines.

- This is because the **lone pair e-** of **N** **can overlap with the pi-molecular orbital** of the benzene ring. It is thus less available to co-ordinate with a proton.



- Aliphatic amines are considerably more basic than aromatics amines.



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Page: 375; problems 14.4

Page: 379; problems 14.7