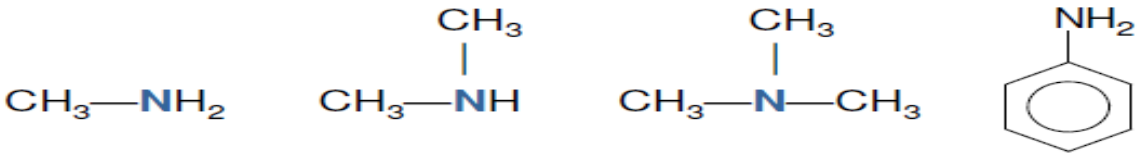
Amines

Are derivatives of ammonia NH3.

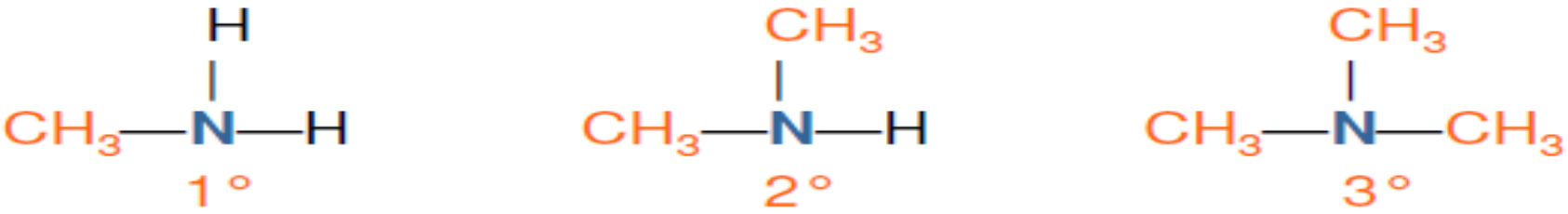
Contain N attached to one or more alkyl or aromatic groups.



Classification of Amines

Amines are classified as primary, secondary, or tertiary.

- In a primary (1°) amine, one carbon group is bonded to the nitrogen atom.
- A secondary (2°) amine has two carbon groups.
- A tertiary (3°) amine has three carbon groups.

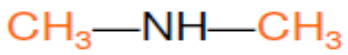


Naming Simple Amines

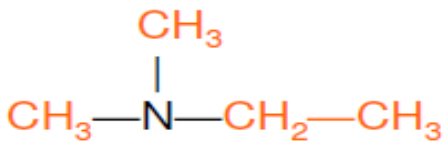
Simple amines

- Are named as alkylamines.
- List the names of the alkyl groups bonded to the N atom in alphabetical order in front of *amine*.

ethylamine



dimethylamine

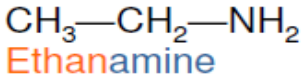


ethyldimethylamine

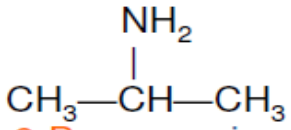
IUPAC Names of Amines

In the IUPAC system,

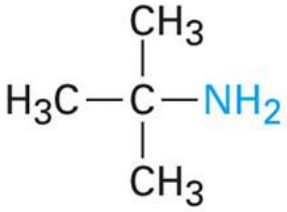
- Amines are named as alkanamines.
- The *-e* in the alkane name of the longest chain is changed to *-amine*.
- The chain is numbered to locate the amine group and substituents.



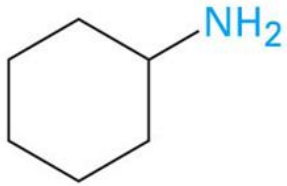
Ethanamine



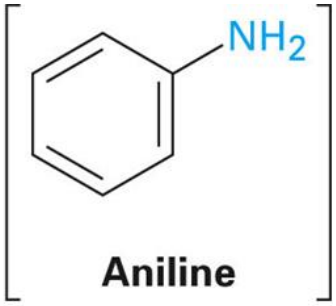
2-Propanamine



***tert*-Butylamine**



Cyclohexylamine

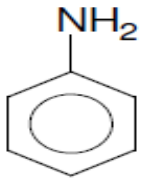


Aniline

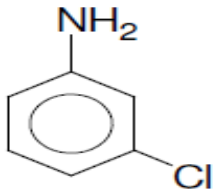
Aromatic Amines

The amine of benzene is aniline.

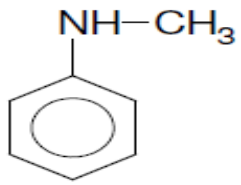
Alkyl groups on the N use the prefix *N*- and the alkyl name.



Aniline



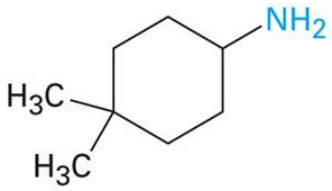
3-chloroaniline



N-methylaniline

IUPAC Names – "-amine" Suffix

The suffix -*amine* can be used in place of the final -*e* in the name of the parent compound ■



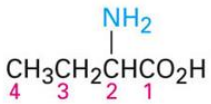
4,4-Dimethylcyclohexanamine

$H_2NCH_2CH_2CH_2CH_2NH_2$

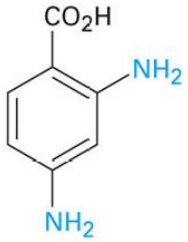
1,4-Butanediamine

IUPAC Names – Amines With More Than One Functional Group

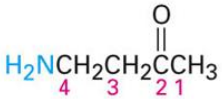
Consider the —NH_2 as an *amino* substituent on the parent molecule ■



2-Aminobutanoic acid



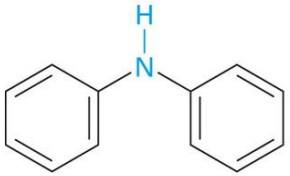
2,4-Diaminobenzoic acid



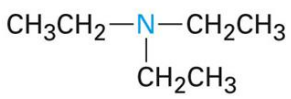
4-Amino-2-butanone

IUPAC Names – Multiple Alkyl Groups

- Symmetrical secondary and tertiary amines are named by adding the prefix *di-* or *tri-* to the alkyl grou



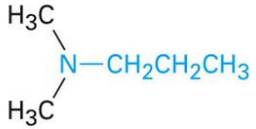
Diphenylamine



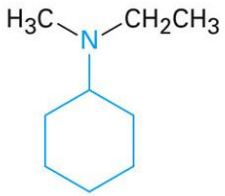
Triethylamine

IUPAC Names – Multiple, Different Alkyl Groups

- Named as *N*-substituted primary amines
  - Largest alkyl group is the parent name, and other alkyl groups are considered *N*-substituents



***N,N*-Dimethylpropylamine**



***N*-Ethyl-*N*-methylcyclohexylamine**

Properties of Amines

Bonding to N is similar to that in ammonia ■

N is sp^3-hybridized ■

C–N–C bond angles are close to 109° tetrahedral value ■

Trimethylamine

Boiling Points of Amines, Alcohols, and Alkanes

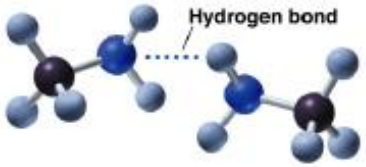
The boiling points of amines are

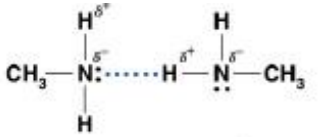
- Higher than alkanes.
- Lower than alcohols of similar mass.

Hydrogen Bonding for Amines

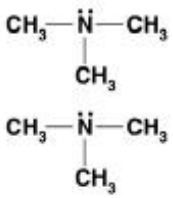
The polar N-H bond

- Provides hydrogen bonding in 1° and 2° amines, but not 3°.
- In amines is not as polar as the O-H bonds in alcohols.





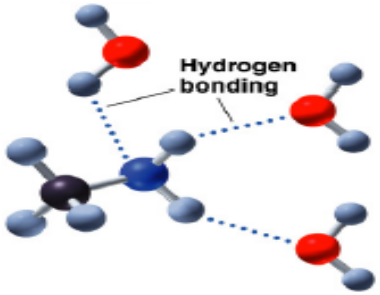
No hydrogen bonds in 3° amines

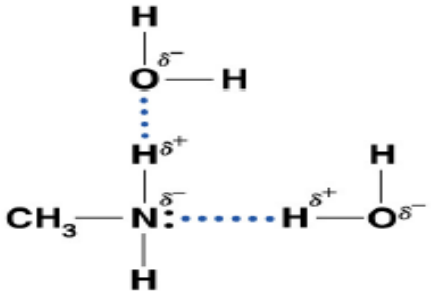


Solubility in Water

Amines are soluble in water

- If they have 1-5 carbon atoms.
- Because the N atom in smaller amines forms hydrogen bonds with the polar O-H bond in water.





Amines React as Bases

Amines are

- Bronsted-Lowry bases that attract a H^+ from H_2O to the N atom.
- Weak bases in water.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

ammonium hydroxide

$$CH_3—NH_2 + H_2O \rightleftharpoons CH_3—NH_3^+ + OH^-$$

methylammonium hydroxide

Neutralization forms Amine Salts

An amine salt

- Forms when an amine is neutralized by acid.
- Is named by replacing the *amine* part of the name with *ammonium* followed by the name of the negative ion.

$$CH_3—NH_2 + HCl \rightleftharpoons CH_3—NH_3^+Cl^-$$

methylamine — methylammonium chloride

Basicity of Amines

The lone pair of electrons on nitrogen makes amines basic and nucleophilic ■

They react with acids to form acid–base salts and they react with electrophiles ■

An amine (a Lewis base) **An acid** **A salt**

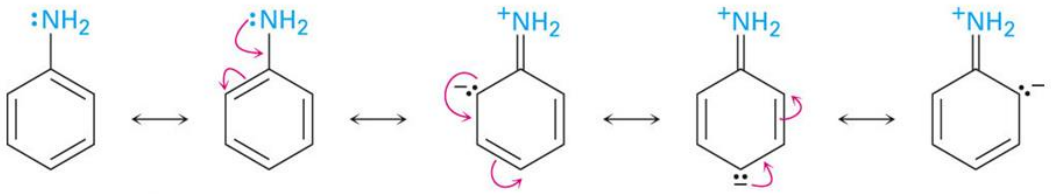
Relative Basicity

Amines are stronger bases than alcohols,ethers,or water ■

Amines establish an equilibrium with water in which the amine becomes protonated and hydroxide is produced

Basicity of Substituted Arylamines

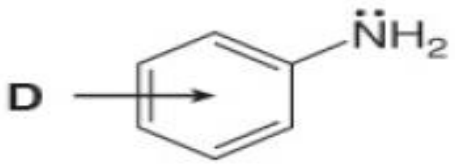
The N lone-pair electrons in arylamines are delocalized by interaction with the aromatic ring π electron system and are less able to accept H^+ than are alkylamines



Substituted Arylamines

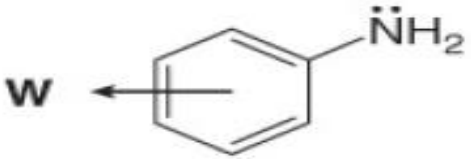
- Can be more basic or less basic than aniline
- Electron-donating substituents (such as —CH_3, —NH_2, —OCH_3) increase the basicity of the corresponding arylamine
- Electron-withdrawing substituents (such as —Cl, —NO_2, —CN) decrease arylamine basicity

- Electron donors increase basicity.



D
$-NH_2$
$-OH$
$-OR$
$-NHCOR$
$-R$

- Electron withdrawers decrease basicity.



W	
$-X$	$-CN$
$-CHO$	$-SO_3H$
$-COR$	$-NO_2$
$-COOR$	$-NR_3^+$
$-COOH$	