Amines
1 – Nomenclature, Properties and Applications

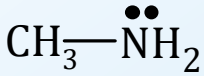
Dr. Sapna Gupta

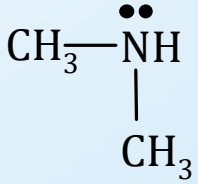
Amines

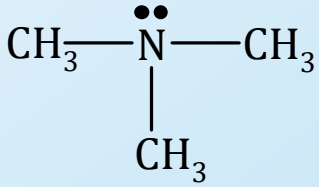
Amines are organic derivatives of ammonia, NH_3 with alkyl groups substituting the hydrogens.

The nitrogen atom has a lone pair of electrons, making amines both basic and nucleophilic.

Amines are classified as 1^o (RNH_2), 2^o (R_2NH), 3^o (R_3N)





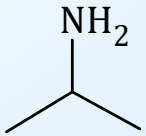


Nomenclature - Aliphatic - Primary

For IUPAC nomenclature change the suffix **-e** of the parent alkane to -**amine**. The general nomenclature follows the alkylamine naming. Below I have given the general names in italics.

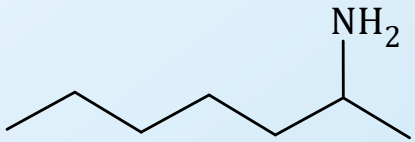
CH_3NH_2	$CH_3CH_2NH_2$	$CH_3CH_2CH_2NH_2$
methanamine	ethanamine	propanamine
methylamine	*ethylamine*	*propylamine*

In case of primary amines and long alkane chains, find the longest chain and give it the base name and locant number to amine group.

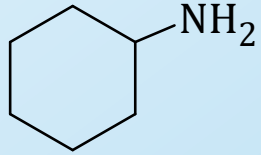


2-propanamine

Isopropylamine



2-heptanamine



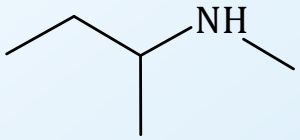
cyclohexanamine

cyclohexylamine

Nomenclature - Secondary and Tertiary

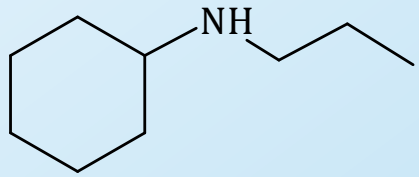
In case of secondary and tertiary amines, identify the long alkane chain; the smaller alkyl group is written as a substituent on the nitrogen as N-alkyl group. For the general name name both the alkyl substituents alphabetically and end with amine. Again, the general names are given in italics.

CH_3NHCH_3	$CH_3CH_2NHCH_3$	$CH_3CH_2CH_2NHCH_3$
N-methylmethanamine	N-methylethanamine	N-methylpropanamine
Dimethyl amine	*ethylmethylamine*	*methyl propylamine*



2-methyl-N-methyl propanamine

methyl-sec-butylamine



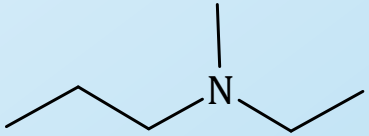
N-propylcyclohexanamine

cyclohexylpropylamine

$(CH_3)_3N$

N, N-dimethylmethanamine

trimethylamine

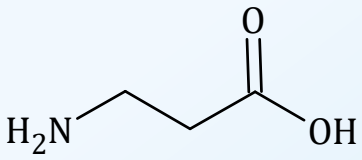


N-ethyl-N-methylpropanamine

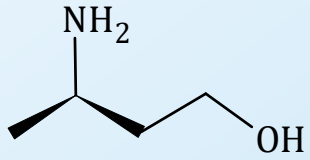
ethylmethylpropylamine

Nomenclature – with Substituents

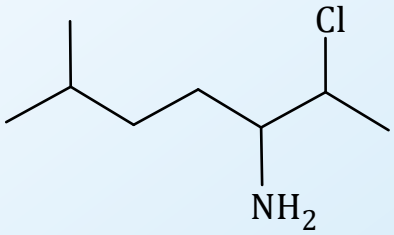
Among the various functional groups discussed in the text, -NH_2 is not in any order of precedence. It is named alphabetically just like any other alkyl or halide group.



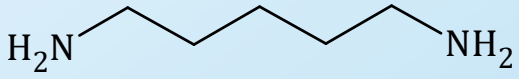
3-aminopropanoic acid



(R) – 3-aminobutan-1-ol



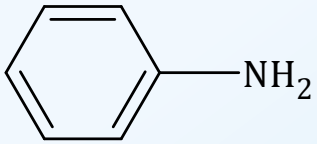
3-amino-2-chloro-6-methylheptane



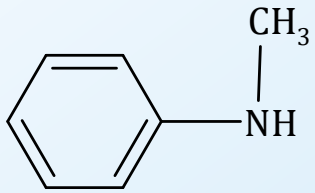
1,5-pentanediamine

Nomenclature - Aromatic

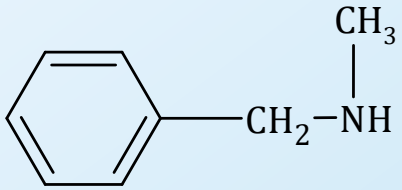
When an amine group on benzene is present then use aniline as the base name unless there are other substituents taking precedence.



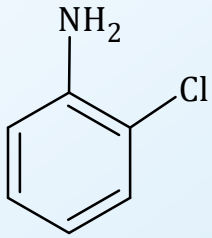
aniline



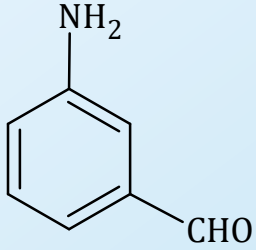
N-methylaniline



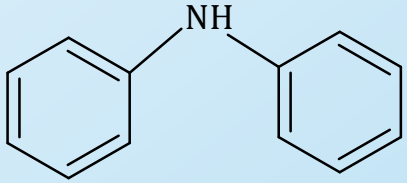
N-methylbenzylamine



O-chloroaniline



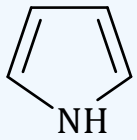
m-aminobenzaldehyde



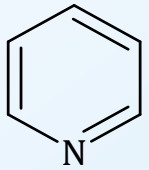
N-phenylaniline

Nomenclature - Heterocyclic

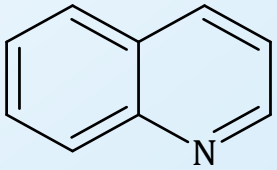
There can be one N or two Ns in one ring. The ring can be aromatic or not.



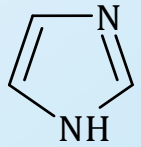
pyrrole



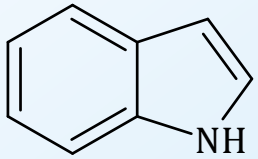
pyridine



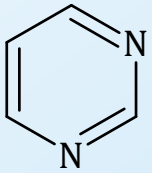
quinoline



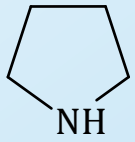
imidazole



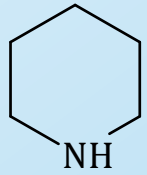
indole



pyrimidine



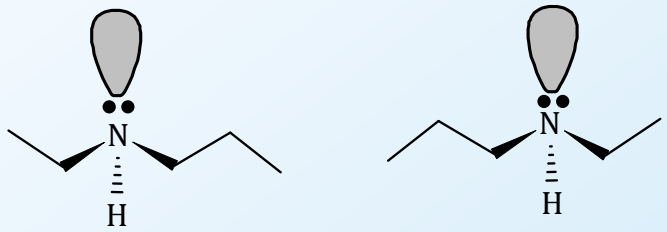
pyrrolidine



piperidine

Chirality of Amines

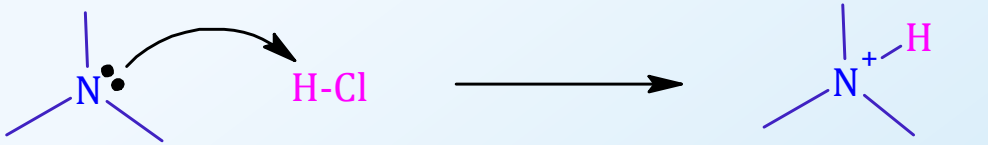
- Consider the unshared pair of electrons on nitrogen as a fourth group, then the arrangement of groups around N is approximately tetrahedral.



- An amine with three different groups bonded to N is chiral and exists as a pair of enantiomers and, in principle, can be resolved.
- In practice, however, they cannot be resolved because they undergo pyramidal inversion, which converts one enantiomer to the other.
- But if there are

Basicity of Amines

The lone pair of electrons on nitrogen makes amines basic and they react with acids to form acid–base salts.



Base Acid Ammonium salt

- Amines are stronger bases than alcohols, ethers, or water.
- Most simple alkylammmonium ions have pKa's of 10 to 11.
- In general alkyl amines are stronger than ammonia. The more alkyl groups, the stronger the base.

	NH_3	CH_3NH_2	$CH_3CH_2NH_2$
pK_a	0.26	10.64	10.81

- In aqueous phase the basicity of amines is 2>1>3. This is because H of N is stabilized by hydrogen bonding.

	$(CH_3)_2NH$ >	CH_3NH_2 >	$(CH_3)_3N$
pK_a	10.98	10.64	9.81

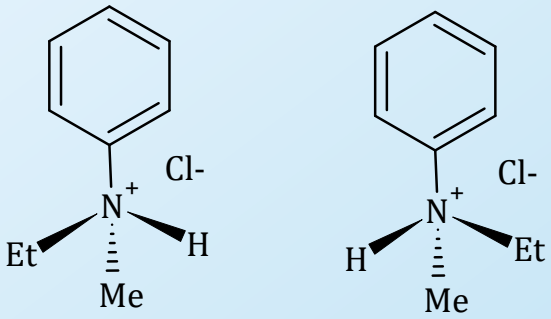
Nomenclature – Quarternary Salts

When four groups are bonded to nitrogen, the compound is named as a salt of the corresponding amine. Generally, amines form ammonium salts. Ammonium salts are quarternary salts.

$Me_4N^+Cl^-$: Tetramethyl ammonium chloride

$PhNH_3^+Cl^-$: Phenylammonium chloride

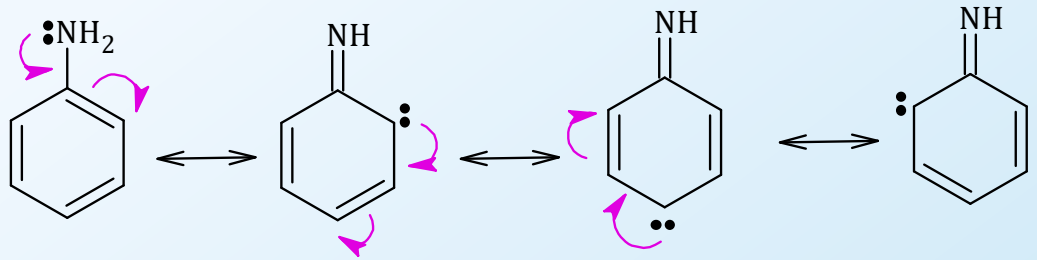
If ammonium salts have four different groups, they can be chiral since N is sp^3 hybridized and thus a tetrahedral.



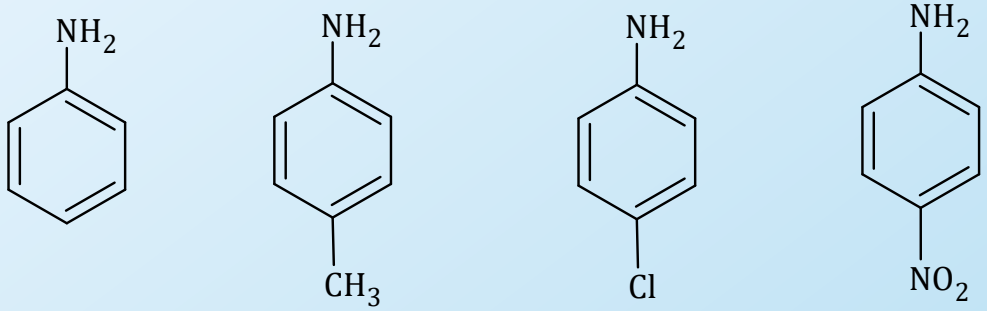
Basicity of Arylamines

Aromatic amines basic in nature but less than aliphatic amines.

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



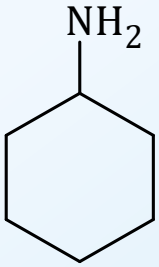
- Substituted arylamines can be more basic or less basic than aniline
- Electron-donating substituents (such as $-CH_3$, $-NH_2$, $-OCH_3$) increase the basicity of the corresponding arylamine
- Electron-withdrawing substituents (such as –Cl, $-NO_2$, –CN) decrease arylamine basicity



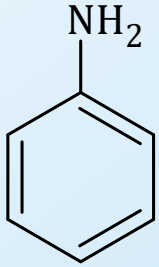
pK_a	4.63	5.08	4.15	1.0

Basicity – More Amines

Aliphatic amines are stronger bases than aromatic because they don't have the double bonds to undergo resonance, so the electrons on N are available for reaction.

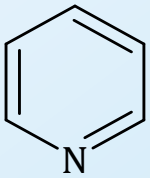


Cyclohexylamine $pK_a = 10.66$

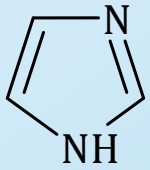


Aniline $pK_a = 4.63$

Heterocyclic amines have variable strength as bases depending on whether the N has electrons available for donation or not.



Pyridine $pK_a = 5.25$



Imidazole $pK_a = 6.95$

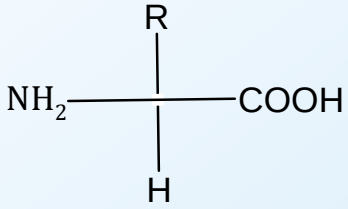
Physical Properties of Amines

1) Boiling point: Amines have high boiling points due to hydrogen bonding. However, boiling point decreases from primary to tertiary ($1^o > 2^o > 3^o$) due to decreasing hydrogen bonding. And boiling point increases with molecular weight of amines.
2) Solubility in water: Primary more than secondary than tertiary due to hydrogen bonding, however solubility in water decreases with increasing molecular weight.
3) Odor: Amines are foul smelling compounds.
   - Fish smell: trimethyl amine
   - Cadaverine: 1,5-hexanediamine
   - Putrascene: 1,4-butanediamine

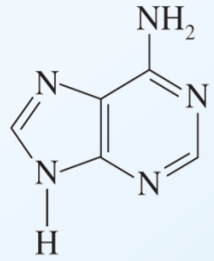
Amines in Nature

There are many natural products that contain nitrogen in aliphatic and aromatic form.

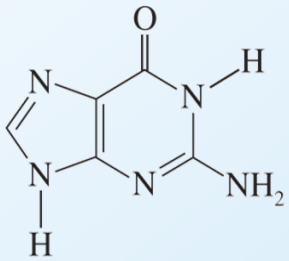
- Amino Acids (20)



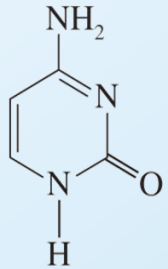
- Nuclear bases (5)



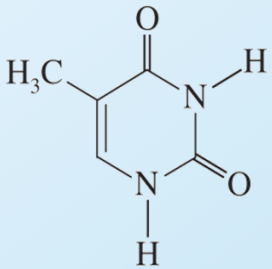
Adenine
(A)



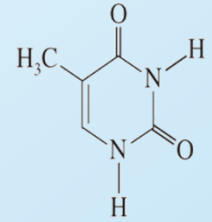
Guanine
(G)



Cytosine
(C)



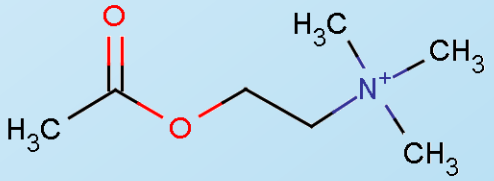
Thymine
(T)



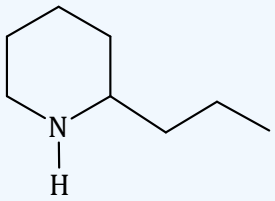
Thymine
(T)

midines

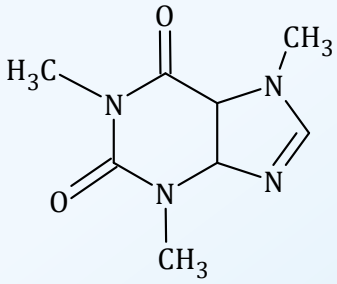
- Neurotransmitters *(more examples on next slide):* Acetylcholine (shown below) is the common neurotransmitter in our bodies. But neurotransmitters taken as medicine or recreationally can be medically useful but are usually addictive and in some cases toxic.



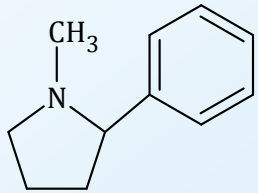
Alkaloids - examples



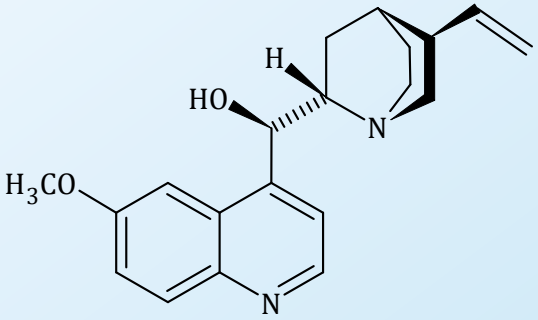
coniine



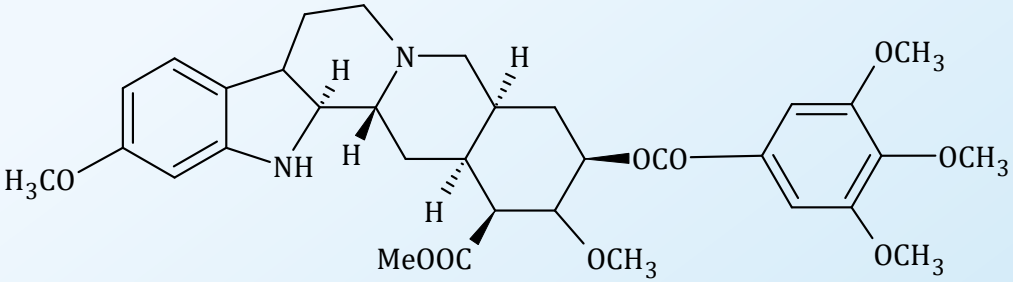
caffeine



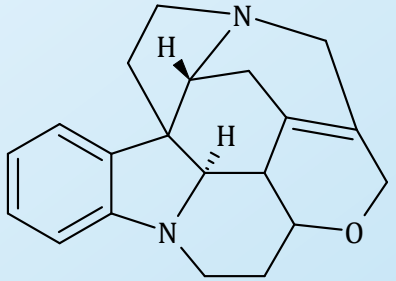
nicotine



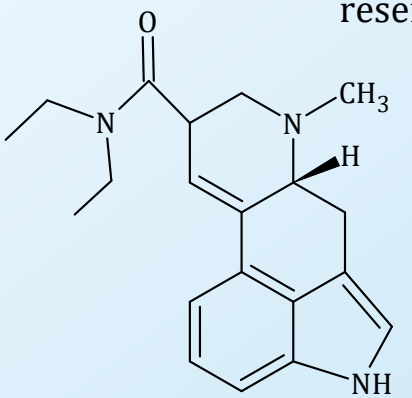
quinine



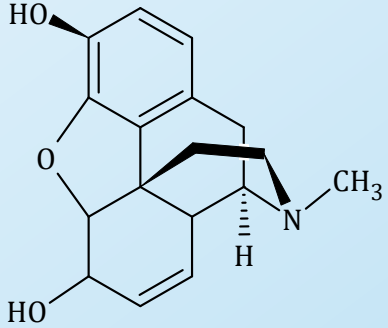
reserpine



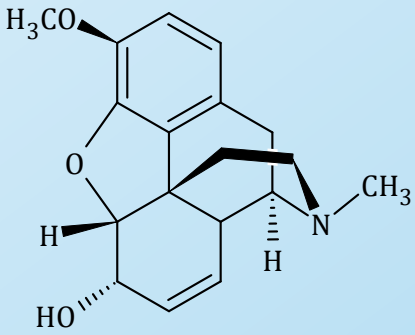
strychnine



LSD



Morphine

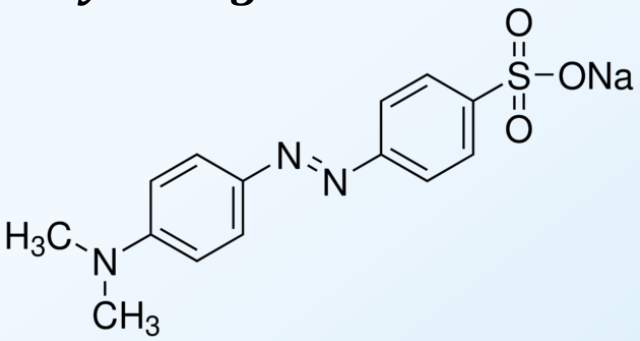


Codeine

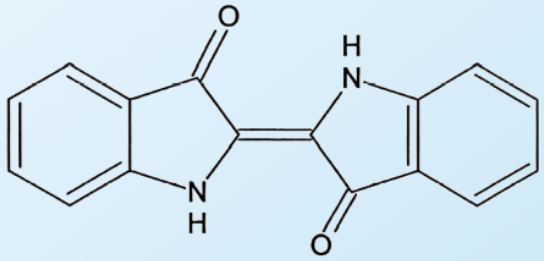
Amines - Dyes

Amines are important functional group in natural and synthetic dyes.

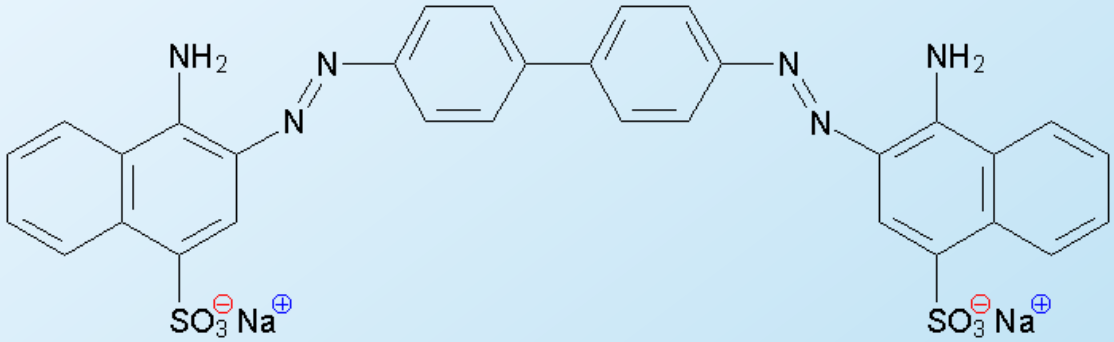
Methyl orange



Indigo



Congo Red



Key Words/Concepts

- Nomenclature
- Physical properties
- Basicity of amines