I. AMINES

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.

For example:

$CH_3–NH_2$, $C_6H_5–NH_2$, $CH_3–NH–CH_3$, $CH_3–N(CH_3)_2$

Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore, sp^3 hybridised and the geometry of amines is pyramidal. Each of the three sp^3 hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C–N–E, (where E is

C or H) is less than 109.5°; for instance, it is 108° in case of trimethylamine as shown in Fig. 13.1.

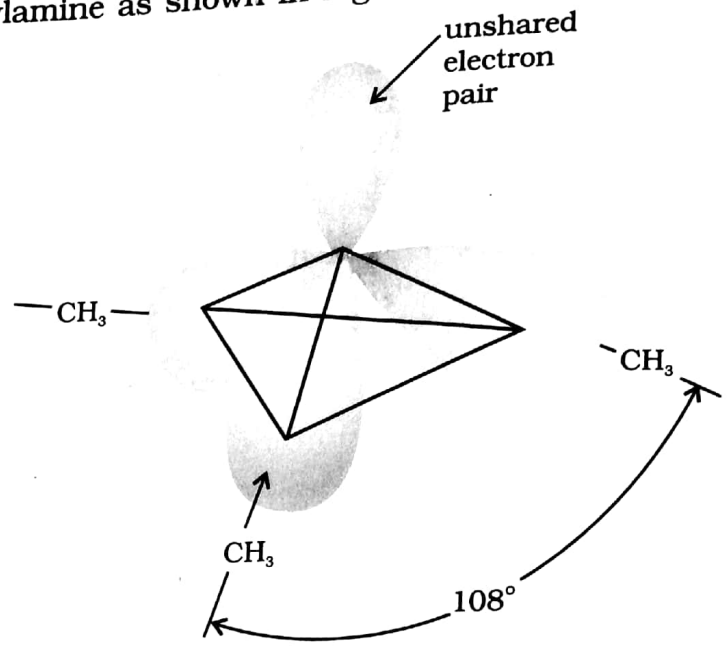
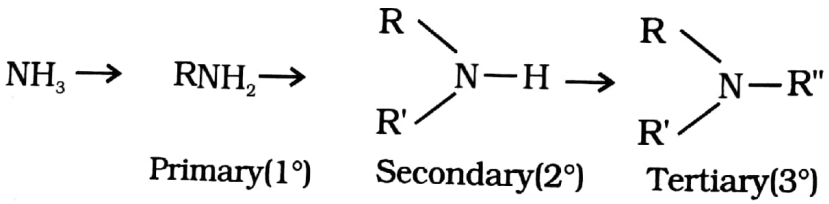


***Fig. 13.1** Pyramidal shape of trimethylamine*

13.2 Classification

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule. If one hydrogen atom of ammonia is replaced by R or Ar , we get RNH_2 or $ArNH_2$, a primary amine (1°). If two hydrogen atoms of ammonia or one hydrogen atom of R-NH_2 are replaced by another alkyl/aryl(R') group, what would you get? You get R-NHR', secondary amine. The second alkyl/aryl group may be same or different. Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine. Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.

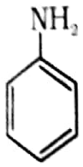
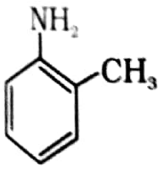
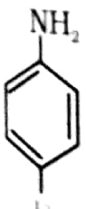
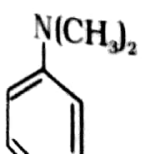


13.3 Nomenclature

In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g., methylamine). In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In IUPAC system, amines are named as **alkanamines**, derived by replacement of 'e' of alkane by the word amine. For example, CH_3NH_2 is named as methanamine. In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to the carbon atoms bearing –NH_2 groups and suitable prefix such as di, tri, etc. is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained. For example, H_2N–CH_2–CH_2–NH_2 is named as ethane-1, 2-diamine.

In arylamines, $-NH_2$ group is directly attached to the benzene ring. $C_6H_5NH_2$ is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name. While naming arylamines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'. Thus in IUPAC system, $C_6H_5-NH_2$ is named as benzenamine. Common and IUPAC names of some alkylamines and arylamines are given in Table 13.1.

Table 13.1: Nomenclature of Some Alkylamines and Arylamines

Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-Propylamine	Propan-1-amine
$CH_3-CH(NH_2)-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-N(H)-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3-N(CH_3)-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
$C_2H_5-N(C_2H_5)-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	*N,N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Aminotoluene
	*p*-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	*N,N*-Dimethylaniline	N,N-Dimethylbenzenamine