

## AROMATIC AMINES

1. These are the derivatives of aromatic hydrocarbons in which a H of benzene ring has been replaced by an amine group,  $\text{-NH}_2$ .
2. Aromatic amines can be of two types:
  - a. Nucleus substituted amines or aryl amines (in which the amino group is directly attached to the aromatic nucleus).
  - b. Side-chain substituted amines or aryl alkyl amines or Aralkylamines (in which the amino group is present in the side chain of an aromatic compound).

They are also classified on the basis of number of groups attached to N-atom:

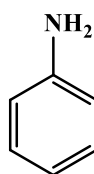
- i) Primary amine ( $1^\circ$ )
- ii) Secondary amine ( $2^\circ$ )
- iii) Tertiary amine ( $3^\circ$ )

### a Nucleus-substituted amines or aryl amines

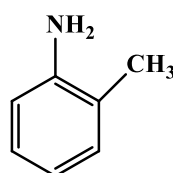
- i)  $1^\circ$  amines

Eg.-

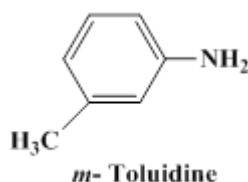
.Aniline (Aminobenzene)



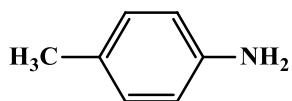
.*o*-Toluidine (*o*-Aminotoluene or 2-Methylaniline)



.*m*-Toluidine (*m*-Aminotoluene or 3-Methylaniline)

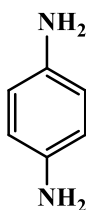


.*p*-Toluidine (*p*-Aminotoluene or 4-Methylaniline)

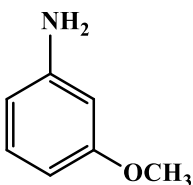


*p*-Toluidine

.*p*-Phenylenediamine (*p*-Diaminobenzene)



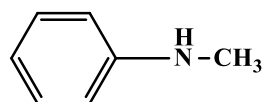
*m*-Anisidine (*m*-Methoxyaniline or 3-Methoxyaniline)



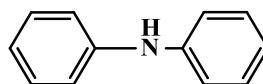
ii) 2° amines

Eg. -

.N-methylaniline



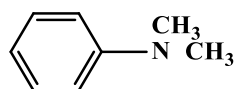
.Diphenylamine



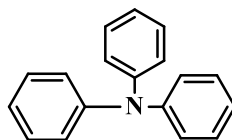
iii) 3° amines

Eg. -

.N,N- dimethylaniline



.Triphenylamine

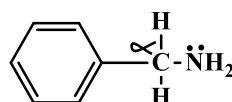


## b. Side-chain substituted amines or Arylalkylamine

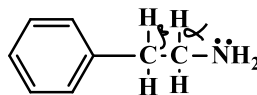
i) 1° amine

Eg.-

.α- Phenylmethyl amine (Benzyl amine)



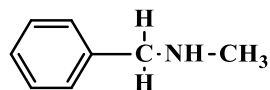
.β- Phenylethyl amine



ii) 2° amine

Eg.-

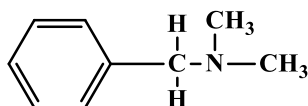
N-methylbenzyl amine



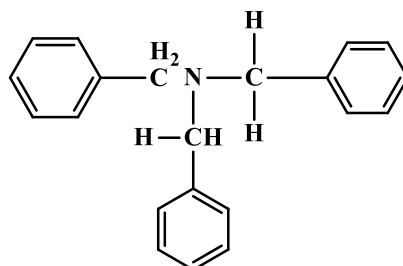
iii) 3° amine

Eg.-

.N,N- dimethylbenzyl amine



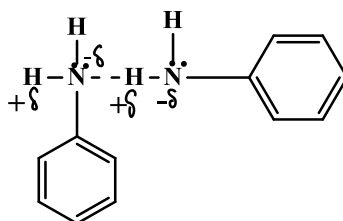
.Tribenzylamine



.The general formula for the three classes of aromatic amines are RNH<sub>2</sub>, R<sub>2</sub>NH and R<sub>3</sub>N, where R is an alkyl / arylalkyl group.

.The polar nature of N-H bond (due to the electronegativity difference of two atoms) results in the formation of H-bonds with other amine molecule or other H-bonding systems (eg. water). The implication of this are-

- High melting and boiling points compared to analogous alkanes.
- High solubility in aqueous media.

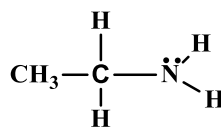
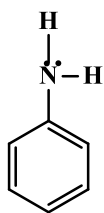


### Intermolecular Hydrogen bonding in aromatic amines

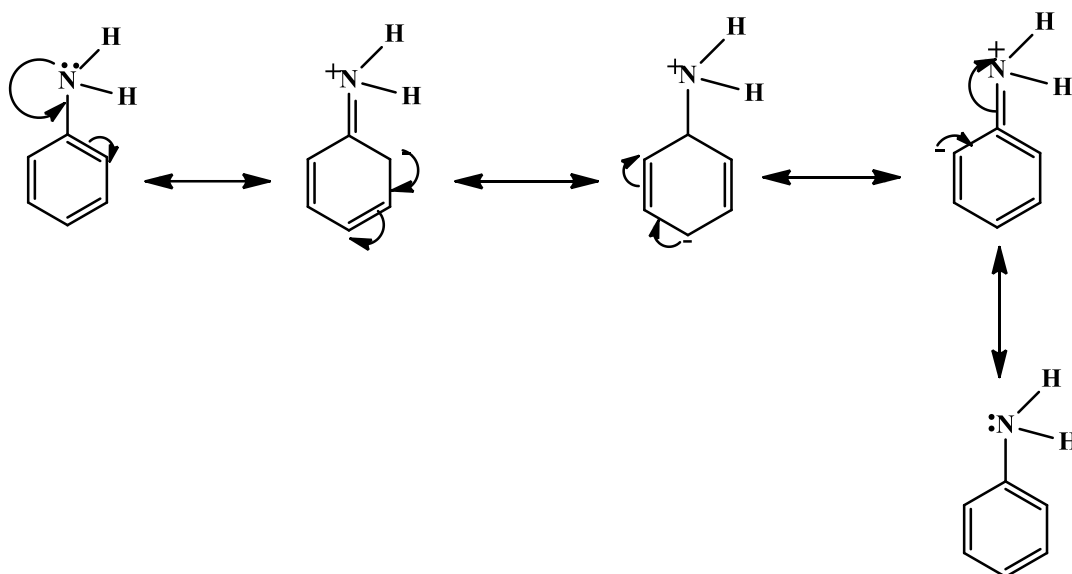
Aromatic amines in general are colourless liquids or solids. They turn brown in air due to oxidation.

### Basicity of Aromatic Amines

To compare the basicity of alkyl amines ( $\text{CH}_3\text{CH}_2\dot{\text{N}}\text{H}_2$ ) and aryl amine ( $\text{C}_6\text{H}_5\dot{\text{N}}\text{H}_2$ ), must consider the availability of lone pair of electrons on N. In case of ethyl amine, the lone pair of electron is localised on N-atom. In case of ethylamine, the lone pair of electron is localised on N-atom. In case of aniline, however, the lone pair is delocalised on the benzene ring. This decreases the electron density on N and makes aniline less basic than ethylamine.



The lone pair is localised on N-atom (no resonance structure)



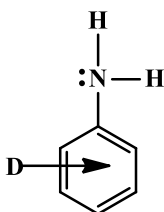
### Resonating structure of Aniline

(The lone pair of electron on N is delocalised on benzene ring)

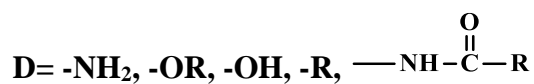
### Effect of substituent on Basicity:

.Substituted anilines are more or less basic than aniline depending on the nature of substituents.

1. Electron donating groups add electron density to the benzene ring, making the arylamine more basic than aniline.

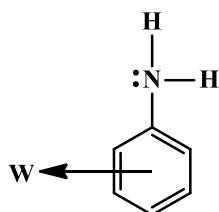


D= Electron donating group



**D makes the amine more basic than aniline.**

2. Electron withdrawing group removes electron density from benzene ring, making the arylamine less basic than aniline.



**W= Electron withdrawing group**

**W= -X, -CHO, -COOR, -NO<sub>2</sub>, -CN, -SO<sub>3</sub>H, -NR<sub>3</sub><sup>+</sup>, -COOH**

**W makes the amine less basic than aniline.**

**Note:** A substituent donates or withdraws electron density depends on the balance of its inductive and resonance effects.

: *p*- nitroaniline is less basic than aniline.

: *p*- methylaniline is more basic than aniline.

: *o*- phenylaniline is less basic than aniline.

: **Basicity**- *p*-toluidine > Aniline > *p*-nitroaniline.