Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry (2026-27 / New NCERT)

Chapter 9: Amines

Class 12th Chemistry – Organic Chemistry – Nitrogen-Containing Compounds

What you will master in this chapter

Amines are nitrogen analogues of alcohols and ethers: replace one or more H atoms of NH_3 by alkyl/aryl groups and you have an amine. In this chapter you will (i) classify amines as $1°$, $2°$, $3°$ or quaternary; (ii) name them by both common and IUPAC systems; (iii) understand the pyramidal sp^3 geometry that gives nitrogen its lone pair and basicity; (iv) prepare amines by six routes – nitro reduction, ammonolysis, nitrile/amide reduction, Gabriel synthesis and Hoffmann bromamide degradation; (v) explain the rich basicity trends (alkyl vs aryl, gas vs aqueous phase, +I, +M, $-M$, solvation and steric effects); (vi) master the named tests – carbylamine, Hinsberg, nitrous acid – and the electrophilic substitution chemistry of aniline; and (vii) handle benzenediazonium chloride and its conversions (Sandmeyer, Gattermann, coupling) which are exam staples for JEE and NEET every year.

Contents

1 Structure, Classification and Nomenclature

Amines are derivatives of ammonia in which one, two or all three N–H bonds are replaced by N–C bonds to alkyl or aryl groups. Because nitrogen still retains its lone pair, every amine behaves as both a *base* (proton acceptor) and a *nucleophile* (electron-pair donor). These two properties drive almost every reaction in the chapter.

1.1 Structure of Amines

In an amine, nitrogen is sp^3 hybridised. Three of the four sp^3 orbitals form σ-bonds to H or C; the fourth holds the lone pair. The molecule is therefore **pyramidal** (not planar), and the C–N–E bond angle is slightly less than the perfect tetrahedral 109.5° because the lone pair occupies more space than a bond pair.

Geometry around N in amines

Hybridisation of N:	sp^3
Shape:	Pyramidal (umbrella)
Bond angle C–N–C in $(CH_3)_3N$:	108°
Lone pair:	Occupies the fourth sp^3 orbital

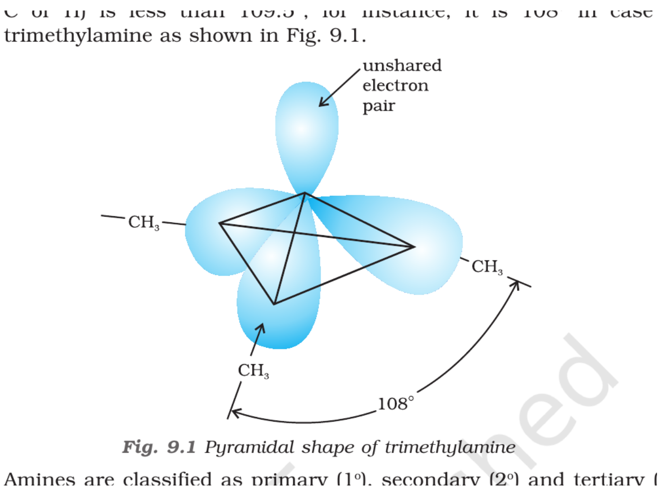

trimethylamine as shown in Fig. 9.1.

Fig. 9.1 Pyramidal shape of trimethylamine

Amines are classified as primary (1°), secondary (2°) and tertiary (

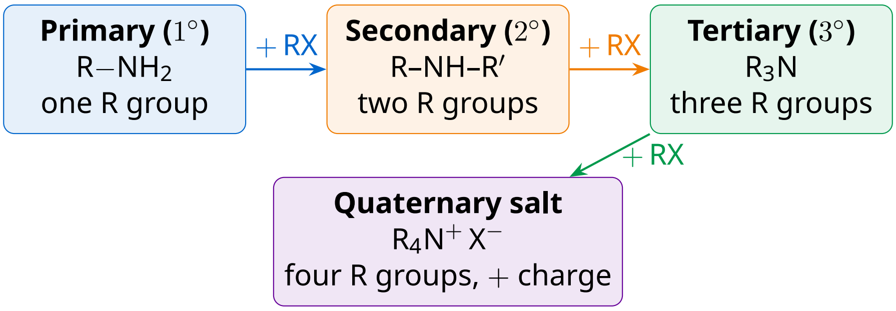
Fig. 9.1 (NCERT): Pyramidal shape of trimethylamine showing the three sp^3 C–N bonds and the unshared electron pair sticking out of the apex.

Why 108°, not 109.5°?

A lone pair feels only one nucleus (its own N), whereas a bond pair is shared by two nuclei. The lone pair therefore spreads out and pushes the three N–C bonds slightly closer together, compressing the bond angle by about 1.5°. This is exactly the VSEPR explanation you learnt in Class 11 for the bent shape of water and the pyramidal shape of NH_3.

1.2 Classification – 1°, 2°, 3° and Quaternary

Amines are classified by counting how many of the three N–H bonds of NH_3 have been replaced by R/Ar groups.



If the R groups on the nitrogen are all identical, the amine is called **simple** (e.g. trimethylamine); if they differ, it is **mixed** (e.g. ethylmethylamine). Note that this classification is *by nitrogen*, not by carbon – which is the opposite of how we label alcohols. $(CH_3)_3C-NH_2$ is therefore a **primary** amine even though the C bearing the NH_2 is tertiary.

Classify by nitrogen, not by carbon

Students often look at the carbon and call $(CH_3)_3C-NH_2$ a tertiary amine because the carbon is tertiary. **Wrong**. The $-NH_2$ still has two H atoms on N, so only one of the three N–H bonds has been replaced – it is a **primary amine**. The same trap appears with isopropylamine, *tert*-butylamine and neopentylamine.

1.3 Nomenclature – Common and IUPAC

Two parallel naming systems coexist; both are tested.

Aliphatic amines

- *Common:* write the alkyl group(s) followed by *amine* as one word – CH_3NH_2 = methyl**amine**. When two or three identical groups sit on N, use the prefix *di* or *tri* – $(CH_3)_3N$ = trimethyl**amine**.
- *IUPAC:* drop the final "-e" of the parent alkane and append "-amine" – CH_3NH_2 = methan**amine**; $CH_3CH_2CH_2NH_2$ = propan-1-amine.
- If two or more amino groups are present, retain the "-e" and use *di-amine/triamine* with locants – $H_2N-CH_2CH_2-NH_2$ = ethane-1,2-diamine.
- For 2° and 3° amines, the largest alkyl group is the parent; smaller substituents on N take the locant prefix **N-** – $CH_3NHC_2H_5$ = N-methylethanamine; $(C_2H_5)_3N$

= N,N-diethylethanamine.

Aromatic amines (arylamines)

- The simplest is $C_6H_5NH_2$ (aniline). “Aniline” is itself an accepted IUPAC name.
- Strict IUPAC name: replace “-e” of arene with “-amine” – $C_6H_5NH_2$ = benzen**amine**; 4-bromoaniline = 4-bromobenzenamine.

Quick reference – common vs IUPAC names

Structure	Common	IUPAC
CH_3NH_2	Methylamine	Methanamine
$CH_3CH_2NH_2$	Ethylamine	Ethanamine
$(CH_3)_2CHNH_2$	Isopropylamine	Propan-2-amine
$CH_3NHC_2H_5$	Ethylmethylamine	N-Methylethanamine
$(CH_3)_3N$	Trimethylamine	N,N-Dimethylmethanamine
$H_2N(CH_2)_6NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
$C_6H_5NH_2$	Aniline	Benzenamine (Aniline)
$C_6H_5N(CH_3)_2$	N,N-Dimethylaniline	N,N-Dimethylbenzenamine

The “-e” drop trick. For mono-amines, *drop* the “-e” of the alkane: ethane → ethan-amine. For *di*-amines and tri-amines, *keep* the “-e” because the next letter is a consonant: ethane-1,2-diamine, not “ethan-1,2-diamine”. For mixed amines, list N-substituents *alphabetically* before the parent name – e.g. $CH_3CH_2-N(CH_3)-CH(CH_3)_2$ is N-methyl-N-(propan-2-yl)ethanamine.

2 Preparation of Amines

The syllabus tests six standard preparations. Master the reagents, the connectivity (does the product have the same number of carbons as the starting material, one more, or one less?), and the stereochemistry/selectivity caveats.

2.1 Reduction of Nitro Compounds

Nitro compounds ($R-NO_2$, $Ar-NO_2$) reduce to primary amines under two standard conditions.

Nitro → primary amine

$$\mathrm{Ar{-}NO_2} \xrightarrow{H2,\ Ni/Pd/Pt} \mathrm{Ar{-}NH_2}$$

$$\mathrm{Ar{-}NO_2} \xrightarrow{Sn\ or\ Fe\ +\ HCl} \mathrm{Ar{-}NH_2}$$

Same carbon count. Works for both aromatic ($ArNO_2$) and aliphatic (RNO_2) nitro compounds.

The Fe/HCl combination is preferred industrially because the $FeCl_2$ generated hydrolyses to release fresh HCl, so the reaction is catalytic in acid. The single most-asked example is nitrobenzene → aniline.

Choice of reducing agent matters

H_2/Ni at high pressure will also reduce C = C bonds. If your substrate has both a nitro group *and* a C = C, use Fe/HCl (or Sn/HCl) instead – these reduce $-NO_2$ but leave alkenes untouched.

2.2 Ammonolysis of Alkyl Halides

Treating an alkyl/benzyl halide with an ethanolic solution of NH_3 in a sealed tube at 373 K substitutes $-X$ by $-NH_2$. Because the freshly-formed primary amine is itself a nucleophile, it attacks another alkyl halide molecule and the process repeats.

Ammonolysis cascade

$$\mathrm{RX} \xrightarrow{NH3} \mathrm{RNH_2} \xrightarrow{RX} \mathrm{R_2NH} \xrightarrow{RX} \mathrm{R_3N} \xrightarrow{RX} \mathrm{R_4N^+X^-}$$

Reactivity order of halides: RI $>$ RBr $>$ RCl. Yield of 1° amine ↑ when NH_3 is in *large excess*.

"Ammonolysis gives only 1° amine" – wrong

Ammonolysis always produces a *mixture* of 1°, 2°, 3° amines plus quaternary ammonium salt. Excess ammonia merely *biases* the mixture towards the primary amine. The reaction does *not* work cleanly for aryl halides because nucleophilic substitution on an aromatic ring is unfavourable.

2.3 Reduction of Nitriles and Amides

These two routes are "carbon-changing": nitrile reduction adds one carbon to the amine; amide reduction keeps the carbon count the same.

Nitrile / amide → amine

Nitrile (ascent of series, $+1$ C):

$$\mathrm{R{-}CN} \xrightarrow{LiAlH4\ or\ H2/Ni} \mathrm{R{-}CH_2{-}NH_2}$$

Amide (same C count):

$$\mathrm{R{-}CONH_2} \xrightarrow{LiAlH4} \mathrm{R{-}CH_2{-}NH_2}$$

Both give 1° amine only – clean, no mixture.

Why nitrile reduction is called “ascent of amine series”

The starting material R – CN has n carbons in R plus 1 more in CN. After reduction, the new amine R – CH_2 – NH_2 has $n+1$ carbons. So if you want propan-1-amine (3 C) starting from a halide route, you pick ethyl bromide (2 C), convert to ethyl cyanide CH_3CH_2CN, then reduce. Compare with amide reduction: butanamide (4 C) $\rightarrow$ butan-1-amine (4 C).

2.4 Gabriel Phthalimide Synthesis

This is the cleanest route to pure 1° amines – no mixture, no over-alkylation. The trick is to “protect” nitrogen with two carbonyls so the alkylated intermediate cannot react with another RX.

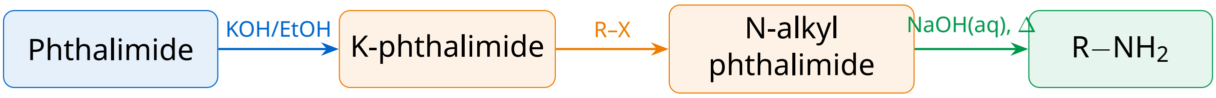
Gabriel synthesis – three steps

Step 1: Phthalimide $\xrightarrow{KOH/EtOH}$ Potassium phthalimide

Step 2: K-phthalimide $\xrightarrow{R-X}$ N-alkyl phthalimide

Step 3: N-alkyl phthalimide $\xrightarrow{NaOH(aq),\ \Delta}$ R$-$$NH_2$ + phthalate

Result: a pure primary amine, identical carbon count to the alkyl halide.



Gabriel does not work for aniline-type amines

Aryl halides (e.g. chlorobenzene) do not undergo nucleophilic substitution with the phthalimide anion – the C–X bond on sp^2 carbon is too strong and the aromatic ring resists S_N2. Therefore **aromatic primary amines like aniline cannot be prepared by Gabriel synthesis.** For aniline, you use nitrobenzene + Sn/HCl, or the Hoffmann bromamide route on benzamide.

2.5 Hoffmann Bromamide Degradation

Treating an amide with Br_2 in NaOH (aq) or NaOH/EtOH produces a primary amine with *one carbon less* than the amide. Mechanistically, an alkyl/aryl group migrates from the carbonyl carbon onto the nitrogen with simultaneous loss of Br^- and CO_2.

Hoffmann bromamide – “-1 C amine factory”

$$\text{R–CONH}_2 + 4\,\text{NaOH} + \text{Br}_2 \longrightarrow \text{R–NH}_2 + \text{Na}_2\text{CO}_3 + 2\,\text{NaBr} + 2\,\text{H}_2\text{O}$$

Carbon count: amide (n C) → amine ($n-1$ C). Always gives 1° amine.

Spot Hoffmann in conversion problems

If a problem asks you to convert acetamide (CH_3CONH_2, 2 C) to methylamine (CH_3NH_2, 1 C), the carbon count drops by 1 – this is the unmistakable signature of Hoffmann bromamide. Likewise benzamide → aniline (7 C → 6 C).

2.6 Comparing the Six Preparation Routes

Method	Reagents	ΔC	Notes
Nitro reduction	H_2/Ni or Sn-Fe/HCl	0	Best for aromatic amines (aniline)
Ammonolysis of RX	NH_3, sealed tube, 373 K	0	Gives mixture; needs excess NH_3
Nitrile reduction	$LiAlH_4$ or H_2/Ni	$+1$	Ascent of series; pure 1°
Amide reduction	$LiAlH_4$	0	Pure 1°, no mixture
Gabriel synthesis	phthalimide, KOH, RX, NaOH	0	Cleanest 1° route; not for aryl
Hoffmann bromamide	Br_2 + NaOH on amide	-1	Always 1°; works for $ArNH_2$

Carbon-count mnemonic – “A G + 1 H -1”

For “add 1 carbon” problems, think **C**yanide (nitrile reduction = **C**+1). For “lose 1 carbon” problems, think **H**offmann ($H-1$). For “same C count”, everything else (nitro, ammonolysis, amide, Gabriel).

3 Physical Properties

3.1 State, Solubility, Odour

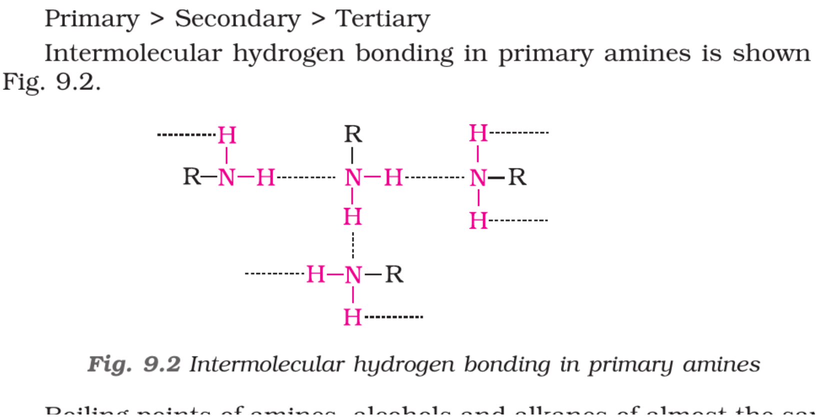
- Lower aliphatic amines (CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$) are **gases** with a sharp fishy smell.
- Amines with ≥ 3 C are **liquids**; higher members are **solids**.
- Aniline and other arylamines are colourless when freshly prepared but *darken on storage* due to atmospheric oxidation.
- Lower amines are water-soluble because N–H ...O hydrogen bonds form with

water. Solubility decreases as the alkyl chain grows (the hydrophobic "tail" wins).

- Amines dissolve in alcohols, ethers and benzene.

3.2 Boiling Points and Hydrogen Bonding

Primary and secondary amines self-associate via N–H …N hydrogen bonds (just like water, but weaker because N is less electronegative than O). Tertiary amines have no N–H, so they cannot self-associate.



Primary > Secondary > Tertiary

Intermolecular hydrogen bonding in primary amines is shown Fig. 9.2.

***Fig. 9.2** Intermolecular hydrogen bonding in primary amines*

Boiling points of amines, alcohols and alkanes of almost the sa

Fig. 9.2 (NCERT): Intermolecular hydrogen bonding in primary amines. Each –NH_2 donates two H atoms and accepts via the N lone pair, weaving a network of N–H …N bonds.

Boiling-point order at fixed molar mass

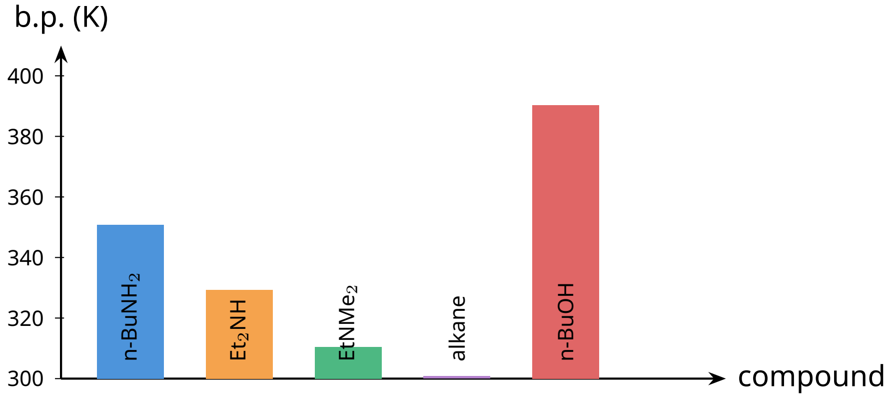
For three amines of the same molar mass (e.g. all $C_4H_{11}N$):

$$\boxed{\text{Primary} > \text{Secondary} > \text{Tertiary}}$$

because 1° has 2 N–H bonds for H-bonding, 2° has 1, and 3° has 0.

Boiling points (Table 9.2) – compounds of ≈ 73 g/mol

Compound	Molar mass (g/mol)	b.p. (K)
n-$C_4H_9NH_2$ (1°)	73	350.8
$(C_2H_5)_2NH$ (2°)	73	329.3
$C_2H_5N(CH_3)_2$ (3°)	73	310.5
$C_2H_5CH(CH_3)_2$ (alkane)	72	300.8
n-C_4H_9OH (alcohol)	74	390.3



The alcohol sits highest because O–H ...O bonds are stronger than N–H ...N (O is more electronegative). The alkane has no H-bonding at all, so it sits at the bottom.

Three-line rule for boiling-point comparisons at the same molar mass: (1) **O–H** bond present ⇒ highest b.p. (alcohol, carboxylic acid); (2) **N–H** bond present ⇒ middle b.p. with $1^\circ > 2^\circ$ amine; (3) no H-bond donor ⇒ lowest b.p. (3° amine, ether, alkane). Note that for *water-solubility* even 3° amines remain reasonably soluble in the low-molar-mass range because water can still donate an H to the lone pair on N – so $1^\circ \approx 2^\circ \approx 3^\circ$ for solubility, but $1^\circ > 2^\circ > 3^\circ$ for boiling point.

4 Basicity of Amines

Basicity is the single most-tested concept in this chapter. Every JEE and NEET paper carries at least one question of the form "arrange the following amines in increasing/decreasing order of basic strength". To solve such questions reliably, you must know *four* competing effects: (i) inductive ($+I$), (ii) resonance ($+M$ / $-M$), (iii) solvation of the cation, and (iv) steric hindrance.

4.1 K_b and pK_b

An amine ionises in water:

$$\mathrm{R{-}NH_2 + H_2O \rightleftharpoons R{-}NH_3^{+} + OH^{-}}$$

Definition of K_b and pK_b

$$K_b = \frac{[\mathrm{R{-}NH_3^{+}}][\mathrm{OH^{-}}]}{[\mathrm{R{-}NH_2}]} \qquad \mathrm{p}K_b = -\log_{10} K_b$$

Higher K_b = lower pK_b = stronger base.

The pK_b rule of thumb

For ammonia, p$K_b = 4.75$. Anything with p$K_b < 4.75$ is a stronger base than ammonia; anything with p$K_b > 4.75$ is weaker. Aliphatic amines sit in the range $3.0 - 4.2$ (stronger than NH_3); aniline sits at p$K_b \approx 9.4$ (much weaker than NH_3).

4.2 Table of pK$_b$ Values (NCERT Table 9.3)

Amine	pK$_b$ (aq. 298 K)
Methanamine CH_3NH_2	3.38
N-Methylmethanamine $(CH_3)_2NH$	3.27
N,N-Dimethylmethanamine $(CH_3)_3N$	4.22
Ethanamine $C_2H_5NH_2$	3.29
N-Ethylethanamine $(C_2H_5)_2NH$	3.00
N,N-Diethylethanamine $(C_2H_5)_3N$	3.25
Ammonia NH_3 (reference)	**4.75**
Phenylmethanamine $C_6H_5CH_2NH_2$ (benzylamine)	4.70
Benzenamine $C_6H_5NH_2$ (aniline)	9.38
N-Methylaniline $C_6H_5NHCH_3$	9.30
N,N-Dimethylaniline $C_6H_5N(CH_3)_2$	8.92

4.3 Alkanamines vs Ammonia – The Four Effects

In the **gas phase**, only inductive effect matters. Each alkyl group pushes electrons towards N ($+I$), making the lone pair more available and stabilising the conjugate acid RNH_3^+ by dispersing the positive charge.

Gas-phase basicity – expected order

$$\boxed{3^\circ > 2^\circ > 1^\circ > \mathrm{NH_3}} \quad \text{(gas phase, pure } +I \text{ effect)}$$

In **aqueous solution**, three new effects start to compete:

(i) Solvation of the cation. The smaller and less substituted the substituted-ammonium ($R_nNH_{4-n}{}^+$) cation, the more N–H bonds it has available for H-bonding with water, the better solvated and more stable it is. So solvation favours $NH_4^+ > 1^\circ > 2^\circ > 3^\circ$ – the *opposite* of the $+I$ trend.

(ii) Steric hindrance. Bulky R groups around N make it geometrically harder for water to reach the lone pair, both in the amine and in the cation. This penalises tertiary amines.

(iii) Hyperconjugation. Minor; usually ignored at this level.

The net order is the *tug of war* between $+I$ (favours more substitution) and solvation $+$ steric (favours less substitution). The result depends on which alkyl group:

Aqueous-phase basicity orders (memorise these two!)

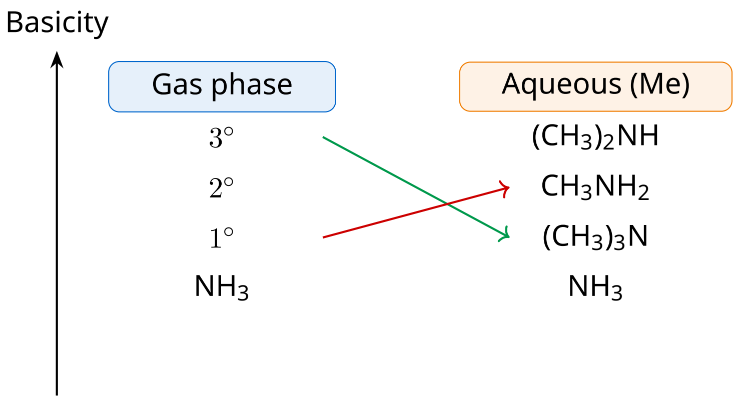
Methyl series:

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

Ethyl series:

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

Notice: for the larger ethyl group, the 3° amine sneaks above the 1° because the extra ethyl provides extra $+I$ that outpaces the solvation penalty.



The Me-series "hump" rule

In the **methyl series in water**, secondary tops the order: $2^\circ > 1^\circ > 3^\circ > NH_3$. Read it as "two methyls give the best balance" – enough $+I$ to push electron density, not enough bulk to block solvation. This is the textbook trick question.

4.4 Arylamines vs Ammonia – Resonance Wins

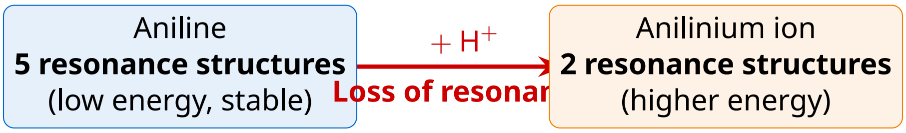
Aniline ($C_6H_5NH_2$) has $pK_b = 9.38$ – about ten thousand times less basic than NH_3. The reason is **lone-pair conjugation** with the benzene ring.

Why aniline is a weak base

The nitrogen lone pair is delocalised into the benzene ring through five resonance structures (one with the lone pair on N, four with the negative charge on the *ortho* and *para* ring carbons). This delocalisation *lowers* the energy of aniline.

When aniline accepts a proton, the lone pair becomes a N – H bond and the resonance is *lost*. The anilinium cation has only two (Kekule) resonance structures, so it is much less stabilised than neutral aniline.

Net effect: loss of resonance energy on protonation makes the equilibrium $ArNH_2 + H^+ \rightleftharpoons ArNH_3{}^+$ shift to the left ⇒ weaker base.



Aryl substituents that change aniline basicity

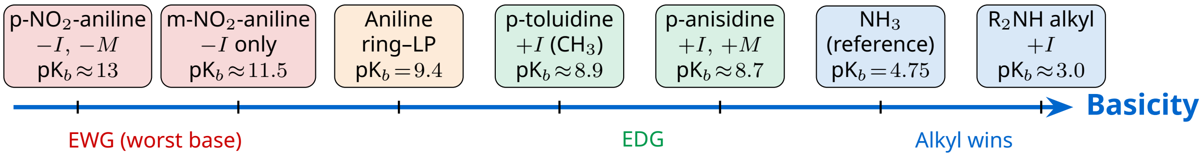
Electron-releasing groups (EDG, $+I$ or $+M$): $-CH_3$, $-OCH_3$, $-OH$, $-NH_2$, $-NR_2$
⇒ *increase* basicity. Example: p-toluidine $>$ aniline.

Electron-withdrawing groups (EWG, $-I$ or $-M$): $-NO_2$, $-SO_3H$, $-COOH$, $-CN$, $-X$ (halogen)
⇒ *decrease* basicity. Example: p-nitroaniline $\ll$ aniline.

Position of substituent matters too

Don't compare two arylamines by group type alone. **Order matters: meta-NO_2-aniline is more basic than para-NO_2-aniline** because at the para position, the $-NO_2$ group is conjugated with the lone pair (full $-M$); at meta, only the $-I$ effect operates. The same logic applies to OCH_3: p-anisidine (p-methoxyaniline) is *more* basic than aniline (both $+I$ and $+M$ act); m-anisidine is only slightly more basic (only $+I$).

The complete basicity ranking for substituted anilines on a single basicity axis:



Three-line rule for ranking aryl amines

For any list mixing alkyl and aryl amines:

1. Alkyl ($1°, 2°, 3°$) amines beat NH_3.
2. NH_3 beats aryl amines (no resonance for NH_3, big resonance loss for $ArNH_2$).
3. Within aryl: EDG-substituted $>$ unsubstituted $>$ EWG-substituted.

Default ranking: alkyl 2° $>$ alkyl 1° $>$ NH_3 $>$ $ArNH_2$ (e.g. aniline) $>$ $ArNH_2$ with EWG (e.g. p-nitroaniline).

"Alkyl pushes, aryl pulls"

Alkyl groups *push* electron density to N → amine more basic. Aryl ring *pulls* the lone pair into itself by resonance → amine less basic. A nitro group on the aryl ring *pulls even harder* (combining $-I$ and $-M$ from ring + NO_2) → very weak base.

5 Chemical Reactions of Amines

The reactions split into five families: (1) basic / salt formation, (2) alkylation, (3) acylation, (4) carbylamine and Hinsberg tests, (5) reaction with HNO_2, (6) electrophilic substitution on arylamines.

5.1 Salt Formation with Mineral Acids

$$R{-}NH_2 + HCl \longrightarrow R{-}NH_3^+\,Cl^-$$

The salt is water-soluble (ionic), but insoluble in ether. Treatment with NaOH regenerates the free amine. This is the basis of the standard **separation procedure** for amines from neutral organics:

Acid wash separation

A mixture of an amine and a neutral hydrocarbon is shaken with dilute HCl. The amine forms a water-soluble ammonium salt and partitions into the aqueous layer; the hydrocarbon stays in the organic layer. Separate the layers, then basify the aqueous one with NaOH to recover the free amine.

5.2 Alkylation

Amines react with alkyl halides exactly like in the ammonolysis preparation: each successive alkylation moves the amine up the substitution ladder ($1^\circ \to 2^\circ \to 3^\circ \to$ quaternary salt). The reaction is therefore useful for *making* mixed/tertiary amines, but is a nuisance when you want a pure 1° amine.

5.3 Acylation – Making Amides

Acylation of 1° and 2° amines

$$R{-}NH_2 + R'COCl \xrightarrow{pyridine} R\text{–}NH\text{–}COR' + HCl$$

$$R{-}NH_2 + R'COOCOR' \xrightarrow{pyridine} R\text{–}NH\text{–}COR' + R'COOH$$

The base (pyridine) mops up the HCl or carboxylic-acid by-product (R′COOH), pushing equilibrium to the right.

Benzoylation is the special case where the acylating agent is benzoyl chloride (C_6H_5COCl). The product is a benzamide:

$$CH_3NH_2 + C_6H_5COCl \longrightarrow CH_3NHCOC_6H_5 + HCl$$

This is called the **Schotten–Baumann reaction** (NCERT does not name it but JEE often asks).

Tertiary amines have no N–H bond, so they cannot acylate – shake an unknown amine with C_6H_5COCl, and if no amide precipitates, the unknown is 3°.

5.4 Carbylamine (Isocyanide) Test

The classic test for **primary amines only**. Heat a primary amine with $CHCl_3$ and ethanolic KOH; you get a *horrible fishy / putrid* smelling isocyanide R – N = C.

Carbylamine reaction – test for 1° amine

$$\mathrm{R{-}NH_2} + \mathrm{CHCl_3} + 3\,\mathrm{KOH} \xrightarrow{\Delta} \mathrm{R{-}NC} + 3\,\mathrm{KCl} + 3\,\mathrm{H_2O}$$

Secondary and tertiary amines give NO reaction. The terrible smell is the positive result.

> **"Carbylamine catches only the first born"**
>
> 1° amine → isocyanide. $2^\circ, 3^\circ$ → nothing. Use the smell of isocyanide as the unmistakable positive flag.

5.5 Reaction with Nitrous Acid (HNO_2)

Nitrous acid is generated *in situ* from $NaNO_2$ + HCl. The three classes of amines react in three completely different ways – making this a powerful diagnostic test *and* the key step in diazotisation.

Reaction of HNO_2 with amines

(a) Aliphatic 1°: unstable diazonium, immediately decomposes

$$\mathrm{R{-}NH_2} \xrightarrow{HNO2} \mathrm{R{-}N_2}^{+} \xrightarrow{H2O} \mathrm{R{-}OH} + \mathrm{N_2}\uparrow$$

Quantitative N_2 evolution is used in *Van Slyke amino acid estimation*.

(b) Aromatic 1° (e.g. aniline): stable diazonium at 273–278 K

$$\mathrm{Ar{-}NH_2} \xrightarrow{NaNO2/HCl,\ 273\text{–}278\ K} \mathrm{Ar{-}N_2}^{+}\mathrm{Cl}^{-} + 2\,\mathrm{H_2O}$$

(c) Secondary amines (aliphatic or aromatic): N-nitrosoamine, a yellow oily liquid

$$\mathrm{R_2NH} \xrightarrow{HNO2} \mathrm{R_2N{-}NO}$$

(d) Tertiary amines: no reaction (aliphatic); only nitrosation of the para position (aromatic).

Why diazonium chemistry rules the dye industry

The fact that $Ar-N_2^+$ is stable at 0–5 °C but not at room temperature is exactly what the dye industry needs. Chemists prepare the diazonium salt cold, then react it on demand with phenols or amines to make azo dyes whose colour can be tuned by changing the substituents. The orange of methyl orange, the red of para-red, the yellow of butter yellow – all azo dyes born from this reaction.

5.6 Hinsberg's Test (Distinguishing 1°, 2°, 3°)

Benzenesulphonyl chloride $C_6H_5SO_2Cl$ reacts differently with each class. Modern labs use p-toluenesulphonyl chloride for the same purpose.

Hinsberg's reagent reactions

1°: $R{-}NH_2 + C_6H_5SO_2Cl \rightarrow C_6H_5SO_2{-}NHR$ (soluble in NaOH)
2°: $R_2NH + C_6H_5SO_2Cl \rightarrow C_6H_5SO_2{-}NR_2$ (insoluble in NaOH)
3°: $R_3N + C_6H_5SO_2Cl \rightarrow$ no reaction.

Why 1° sulphonamide dissolves in NaOH, but 2° doesn't

The N–H of a sulphonamide is unusually acidic because the lone pair on N can delocalise into the strong electron-withdrawing sulphonyl group. So in 1° sulphonamide, the remaining H is removed by NaOH to give a soluble sodium salt. In 2° sulphonamide there is no N–H, so no acid–base reaction, so no dissolution.

1° **amine**	2° **amine**	3° **amine**
Product: $C_6H_5SO_2NHR$ soluble in NaOH	Product: $C_6H_5SO_2NR_2$ insoluble in NaOH	No reaction (no N–H)

5.7 Electrophilic Substitution in Arylamines

The $-NH_2$ group of aniline is a powerful *ortho*- and *para*-directing *activator* because its lone pair donates into the ring by resonance. Aniline is therefore so reactive that direct bromination/nitration over-substitutes or oxidises the ring.

(a) Bromination of aniline. Aniline reacts with Br_2-water at room temperature to give 2,4,6-tribromoaniline as a white precipitate (no Lewis acid catalyst needed – the ring is too activated).

$$C_6H_5NH_2 + 3\,Br_2(aq) \longrightarrow \text{2,4,6-tribromoaniline} + 3\,HBr$$

(b) Nitration of aniline. Direct nitration with HNO_3/H_2SO_4 is messy because:

- the NH_2 group gets oxidised by hot HNO_3 to give a tarry mess;

- the strong acid protonates NH_2 to NH_3^+, which is now *meta*-directing (the NH_3^+ group is $-I$, $-M$). So the product is a mixture of ortho/para/meta nitroanilines.

To get clean p-nitroaniline as the major product, **protect the NH_2 as acetanilide first**, nitrate, then hydrolyse back:

$$\begin{aligned} C_6H_5NH_2 &\xrightarrow{(CH3CO)2O} C_6H_5NHCOCH_3 \\ &\xrightarrow{HNO3/H2SO4} \text{p-}O_2N\text{–}C_6H_4\text{–}NHCOCH_3 \\ &\xrightarrow{H3O+} \text{p-}O_2N\text{–}C_6H_4\text{–}NH_2 \end{aligned}$$

(c) Sulphonation of aniline. Aniline + conc. $H_2SO_4 \rightarrow$ anilinium hydrogen sulphate $\xrightarrow{453\text{–}473\,K}$ p-aminobenzenesulphonic acid (**sulphanilic acid**). This exists as a *zwitterion*: $H_3N^+-C_6H_4-SO_3^-$.

(d) Friedel–Crafts on aniline: does not work. The Lewis acid catalyst ($AlCl_3$) coordinates to the lone pair on N, generating a positively-charged $ArNH_2-AlCl_3$ adduct. The $-NH_2-AlCl_3^+$ group is now a powerful deactivator (like NH_3^+), so the ring is too electron-poor to undergo Friedel–Crafts alkylation/acylation.

A favourite trap question: "Can you alkylate aniline using $CH_3Cl/AlCl_3$?" – the answer is **no**. To install an alkyl group ortho/para to NH_2, either (i) protect the NH_2 first as acetanilide, then do F–C on the protected substrate; or (ii) start from the alkylated nitrobenzene and reduce.

> **Why acetanilide is the universal aniline protector**
>
> $-NHCOCH_3$ (acetamido group) is still ortho/para directing because the N still has a lone pair, but it is far less activating than $-NH_2$ because the lone pair is partly delocalised into the carbonyl. So the ring is reactive enough to take one electrophile, but *not* reactive enough to over-substitute, get oxidised or trip up Friedel–Crafts.

6 Diazonium Salts

The second half of the chapter focuses on **arenediazonium salts**, $Ar-N_2^+X^-$. They are the most versatile intermediates in aromatic chemistry and are the gateway to substituents ($-F$, $-I$, $-CN$, $-OH$) that cannot be installed by direct electrophilic substitution.

6.1 Preparation of Benzenediazonium Chloride

Diazotisation – aniline to diazonium

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \xrightarrow{273\text{–}278\,K} C_6H_5{-}N_2^+\,Cl^- + NaCl + 2\,H_2O$$

Conditions: $NaNO_2$ + HCl (gives HNO_2 in situ); temperature 0–5 °C (273–278 K). Higher temperature decomposes the salt to phenol.

Why arenediazonium is stable but alkanediazonium is not

$Ar{-}N_2^+$ is stabilised by resonance: the positive charge on the terminal N can be delocalised onto the ring carbons. Alkanediazonium $R{-}N_2^+$ has no aromatic ring to share the charge – the C–N bond simply heterolyses, ejecting $N_2(g)$ and leaving a carbocation that quickly reacts with water. That is why aliphatic 1° amines + $HNO_2 \rightarrow$ alcohols + N_2, but aromatic 1° amines give a usable diazonium salt.

6.2 Physical Properties

Benzenediazonium chloride: colourless crystalline solid, water-soluble, stable only in cold solution. Decomposes when dry or warmed:

$$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{\Delta} C_6H_5OH + N_2\uparrow + HCl$$

Benzenediazonium fluoroborate ($C_6H_5N_2^+\,BF_4^-$) is far more stable and can be isolated as a dry solid; it is used in the Schiemann reaction (see below).

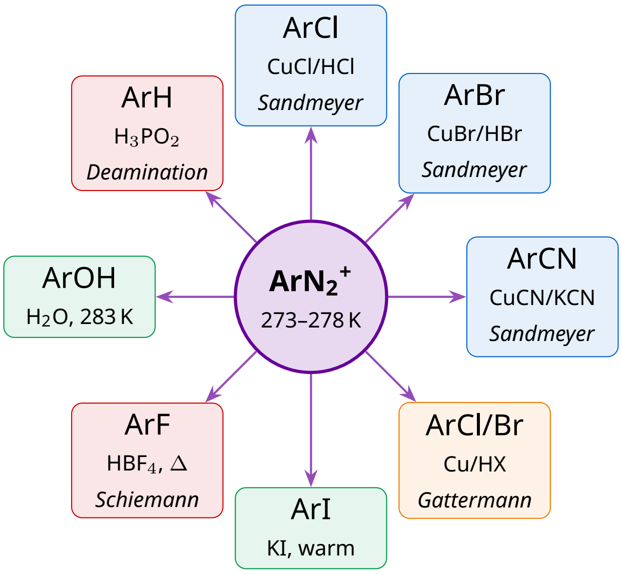
6.3 Chemical Reactions – Two Big Families

Diazonium reactions fall into two categories:

- **A. Displacement of N_2**: the $-N_2^+$ group is one of the best leaving groups in organic chemistry. Substituents (Cl, Br, I, F, CN, OH, NO_2, H) replace $-N_2^+$, with $N_2(g)$ escaping.
- **B. Retention of $-N{=}N-$**: the diazonium group is kept and N_2^+ acts as an electrophile, coupling to electron-rich arenes (phenol, aniline) to give azo dyes.

6.4 Displacement of $-N_2^+$ (Sandmeyer, Gattermann, Schiemann...)

The displacement reactions are best memorised as a “hub-and-spoke” diagram with ArN_2^+ at the centre:



Master list – replacing $-N_2^+$

Replacement	Reagent	Reaction name
$-N_2^+ \longrightarrow -Cl$	CuCl/HCl	Sandmeyer
$-N_2^+ \longrightarrow -Br$	CuBr/HBr	Sandmeyer
$-N_2^+ \longrightarrow -CN$	CuCN/KCN	Sandmeyer
$-N_2^+ \longrightarrow -Cl$ or $-Br$	Cu powder + HCl/HBr	Gattermann
$-N_2^+ \longrightarrow -I$	KI (no Cu needed)	– (warm)
$-N_2^+ \longrightarrow -F$	HBF_4, then Δ	Balz–Schiemann
$-N_2^+ \longrightarrow -OH$	H_2O, warm to 283 K	Hydrolysis
$-N_2^+ \longrightarrow -H$	H_3PO_2 or C_2H_5OH	“Deamination”
$-N_2^+ \longrightarrow -NO_2$	$NaNO_2$/Cu, HBF_4 salt	–

Sandmeyer vs Gattermann – a one-line difference

Both install Cl or Br on the ring. **Sandmeyer uses Cu(I) salt** (CuCl/CuBr); **Gattermann uses Cu metal powder**. Sandmeyer gives higher yields, but Gattermann uses cheaper reagents. JEE Main has asked exactly this distinction.

“F needs Boron, I needs Potassium”–

For $-F$ substitution, use **HBF_4** (Balz–Schiemann). For $-I$, use **KI** (no copper needed; iodide is nucleophilic enough on its own).

6.5 Retention – Coupling Reactions and Azo Dyes

When the diazonium salt is mixed with an electron-rich aromatic compound (phenol or aniline) in mildly basic / mildly acidic conditions, the diazonium ion attacks the *para* position of the partner ring as an electrophile. The product is an **azo compound** Ar–N=N–Ar′, almost always brightly coloured.

Coupling reactions

With phenol (in dilute NaOH):

$$C_6H_5{-}N_2{}^+Cl^- + C_6H_5{-}OH \longrightarrow \text{p-hydroxyazobenzene (orange)}$$

With aniline (in dilute acid):

$$C_6H_5{-}N_2{}^+Cl^- + C_6H_5{-}NH_2 \longrightarrow \text{p-aminoazobenzene (yellow)}$$

Why azo dyes are coloured

The extended Ar–N=N–Ar′ system pushes the HOMO–LUMO gap into the visible range. Tweaking the substituent on either ring ($-OH$, $-NMe_2$, $-NO_2$, $-SO_3H$) shifts the absorption to a different wavelength – which is how chemists tune textile dyes from yellow through orange, red, violet to blue.

6.6 Importance of Diazonium Salts in Synthesis

The diazonium toolbox

Diazonium salts let you install groups you cannot install directly:

- $-F$, $-I$ (cannot be done by direct halogenation of benzene)
- $-CN$ (chlorobenzene won't undergo SN; diazonium + CuCN will)
- $-OH$ (phenol from aniline)
- $-H$ (use H_3PO_2 to "remove" an $-NH_2$ after using it as a directing group)

This is why an aniline group is often used as a *temporary directing group* in multi-step synthesis – install it, exploit its ortho/para direction, then diazotise and remove.

Two worked syntheses students must memorise:

(i) p-Nitrotoluene → 2-bromobenzoic acid.

$$\text{p-MeC}_6\text{H}_4\text{NO}_2 \xrightarrow{KMnO4,\ OH-} \text{p-HOOC-C}_6\text{H}_4\text{-NO}_2 \xrightarrow{Sn/HCl} \text{p-HOOC-C}_6\text{H}_4\text{-NH}_2$$

$$\xrightarrow{NaNO2/HCl,\ 273\,K} \text{p-HOOC-C}_6\text{H}_4\text{-N}_2^+\text{Cl}^- \xrightarrow{CuBr/HBr} \text{2-bromobenzoic acid}$$

(ii) Benzene to p-bromoaniline.

$$C_6H_6 \xrightarrow{HNO3/H2SO4} C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2 \xrightarrow{(CH3CO)2O} C_6H_5NHCOCH_3$$

$$\xrightarrow{Br2/CH3COOH} \text{p-Br-acetanilide} \xrightarrow{H3O+} \text{p-bromoaniline}$$

7 Distinguishing Tests – Lab-Style Summary

A standalone summary that students should memorise verbatim for the practical and theory papers.

Test	1° amine	2° amine	3° amine
Carbylamine ($CHCl_3$/KOH)	Fishy isocyanide smell	No reaction	No reaction
Hinsberg ($C_6H_5SO_2Cl$)	Sulphonamide, soluble in NaOH	Sulphonamide, insoluble in NaOH	No reaction
HNO_2 ($NaNO_2$/HCl, cold)	Alkyl: N_2 gas $+$ alcohol; aryl: diazonium salt	Yellow oily N-nitrosamine	No reaction (aryl: para nitrosation)
Acetic anhydride	Acetanilide-type amide	N,N-disubst. amide	No reaction

A primary amine is the only class that gives all three of (i) carbylamine smell, (ii) NaOH-soluble sulphonamide, and (iii) N_2 gas (alkyl) or stable diazonium (aryl) with HNO_2. If you see all three positives in a viva, it must be 1°.

8 Quick Reference Summary

8.1 Key formulas and constants

Master cheat sheet

Geometry of N in amine: sp^3, pyramidal, $\angle$CNC $\approx 108^\circ$.

Basicity: $K_b = \dfrac{[RNH_3^+][OH^-]}{[RNH_2]}$; $pK_b = -\log K_b$; smaller pK_b = stronger base.

Diazotisation: $ArNH_2 \xrightarrow{NaNO2/HCl,\ 0\text{–}5^\circ C} ArN_2^+Cl^-$.

ΔC of preparations: nitro=0, ammonolysis=0, nitrile=$+1$, amide=0, Gabriel=0, Hoffmann=-1.

8.2 Order of basicity – one-page memorisation chart

Phase / series	Order
Gas phase, alkyl	$3^\circ > 2^\circ > 1^\circ > NH_3$
Aqueous, methyl	$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
Aqueous, ethyl	$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
Alkyl vs aryl	alkyl $1^\circ/2^\circ/3^\circ > NH_3 > ArNH_2$ (e.g. aniline)
Substituted aniline	EDG-aniline $(+I, +M)$ $>$ aniline $>$ EWG-aniline $(-I, -M)$

8.3 Reagent-to-product flash table

Substrate	Reagent	Product
$ArNO_2$	Sn/HCl	$ArNH_2$
RX	NH_3, 373 K	RNH_2 (mixture)
RCN	$LiAlH_4$	RCH_2NH_2 ($+1$ **C**)
$RCONH_2$	$LiAlH_4$	RCH_2NH_2
$RCONH_2$	Br_2/NaOH	RNH_2 (-1 **C**)
RNH_2	$CHCl_3$/KOH	RNC (foul smell, 1° only)
RNH_2	$C_6H_5SO_2Cl$	Hinsberg test
$ArNH_2$	$NaNO_2$/HCl, 273 K	$ArN_2^+Cl^-$
ArN_2^+	CuCl/HCl	ArCl (Sandmeyer)
ArN_2^+	Cu/HBr	ArBr (Gattermann)
ArN_2^+	KI	ArI
ArN_2^+	HBF_4, Δ	ArF (Schiemann)
ArN_2^+	H_3PO_2	ArH (deamination)
ArN_2^+	H_2O, 283 K	ArOH
ArN_2^+	phenol/NaOH	p-hydroxyazobenzene (orange)
ArN_2^+	aniline/HCl(dil.)	p-aminoazobenzene (yellow)

8.4 Five red-flag traps to avoid

Five traps that students fall into every year

1. Classifying amines by carbon, not nitrogen. ($(CH_3)_3CNH_2$ is 1°, not 3°.)
2. Picking the gas-phase basicity order for aqueous solution. (Use the Me-series "hump".)
3. Forgetting that aniline cannot undergo Friedel–Crafts.
4. Trying to use Gabriel synthesis to make aniline. (Aryl halides + phthalimide anion: no reaction.)

5. Forgetting that diazonium decomposes above $\approx 5\,^{\circ}$C – always keep the bath cold.

Where amines hide in plain sight

The smell of rotting fish is dimethylamine and trimethylamine. The bitter taste of unripe coffee is caffeine, an alkaloid amine. Adrenaline and noradrenaline (the fight-or-flight hormones), histamine (the allergy molecule), dopamine, serotonin – all are biologically active 1° or 2° amines. Novocaine, lidocaine, procaine and most local anaesthetics are tertiary amine salts. Nylon-6,6 is a polyamide – made by condensing hexane-1,6-diamine with adipic acid. Quaternary ammonium salts ($R_4N^+X^-$) are the active surfactants in hair conditioners and fabric softeners. *Every shelf in every chemist's shop has an amine on it.*

End of Chapter 9 – Amines

NCERT 2026-27 syllabus • Collegedunia NCERT Revision Notes