Unit

13

Amines

Objectives

After studying this Unit, you will be able to

- describe amines as derivatives of ammonia having a pyramidal structure;
- classify amines as primary, secondary and tertiary;
- name amines by common names and IUPAC system;
- describe some of the important methods of preparation of amines;
- explain the properties of amines;
- distinguish between primary, secondary and tertiary amines;
- describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.

"The chief commercial use of amines is as intermediates in the synthesis of medicines and fibres" .

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dyestuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes. In this Unit, you will learn about amines and diazonium salts.

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:

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

13.1 Structure of Amines

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.

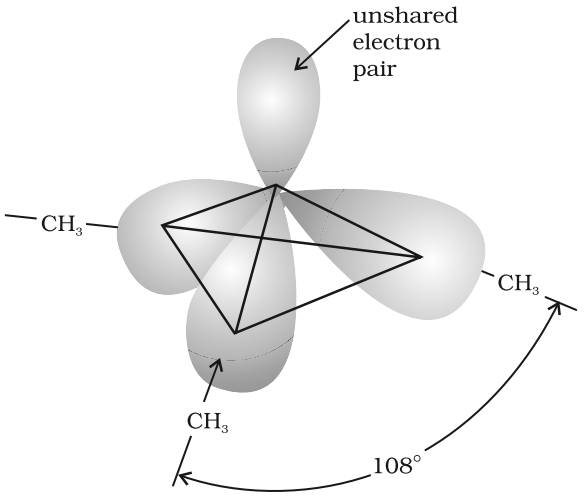
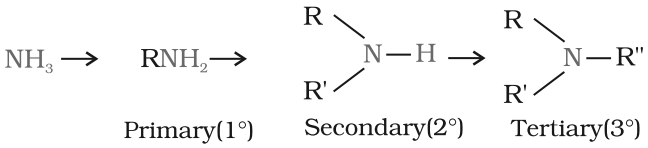


Fig. 13.1 *Pyramidal shape of trimethylamine*

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.

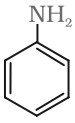
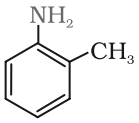
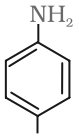
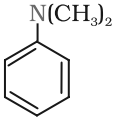


13.3 Nomenclature

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.

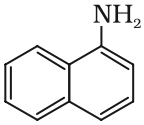
In arylamines, $-NH_2$ group is directly attached to the benzene ring. $C_6H_5NH_2$ is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name. While naming arylamines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'. Thus in 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.

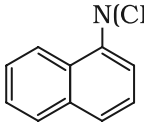
Table 13.1: Nomenclature of Some Alkylamines and Arylamines

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
$CH_3-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-\underset{\displaystyle H}{\underset{\vert}{N}}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
$C_2H_5-\underset{\displaystyle C_2H_5}{\underset{\vert}{N}}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	*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

Intext Questions

13.1 Classify the following amines as primary, secondary or tertiary:

(i) 

(ii) 

(iii) $(C_2H_5)_2CHNH_2$ (iv) $(C_2H_5)_2NH$

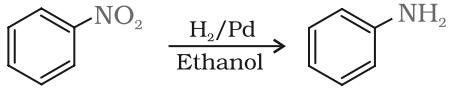
13.2 (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.
(ii) Write IUPAC names of all the isomers.
(iii) What type of isomerism is exhibited by different pairs of amines?

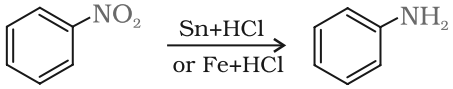
13.4 Preparation of Amines

Amines are prepared by the following methods:

1. Reduction of nitro compounds

Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

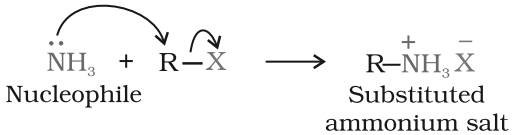
(i) 

(ii) 

Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

2. Ammonolysis of alkyl halides

You have read (Unit 10, Class XII) that the carbon - halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile. Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($–NH_2$) group. This process of cleavage of the C–X bond by ammonia molecule is known as **ammonolysis**. The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.



$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}X^-}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base:

$$R\text{–}\overset{+}{N}H_3X^- + NaOH \longrightarrow R\text{–}NH_2 + H_2O + \overset{+}{N}aX^-$$

Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of ammonia.

The order of reactivity of halides with amines is RI > RBr >RCl.

Example 13.1

Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl.

Solution

(i) $C_2H_5\text{–}Cl \xrightarrow{NH_3} C_2H_5\text{–}NH_2 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5\text{–}\underset{H}{\underset{|}{N}}\text{–}C_2H_5 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5\text{–}\underset{C_2H_5}{\underset{|}{N}}\text{–}C_2H_5$

Chloroethane — Ethanamine — N-Ethylethanamine — N,N-Diethylethanamine

(ii) $C_6H_5\text{–}CH_2\text{–}Cl \xrightarrow{NH_3} C_6H_5\text{–}CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5\text{–}CH_2\text{–}\underset{CH_3}{\underset{|}{N}}\text{–}CH_3$

Benzylchloride — Benzylamine — N,N-Dimethylphenylmethanamine

3. *Reduction of nitriles*

Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines. This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.

$$R\text{–}C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R\text{–}CH_2\text{–}NH_2$$

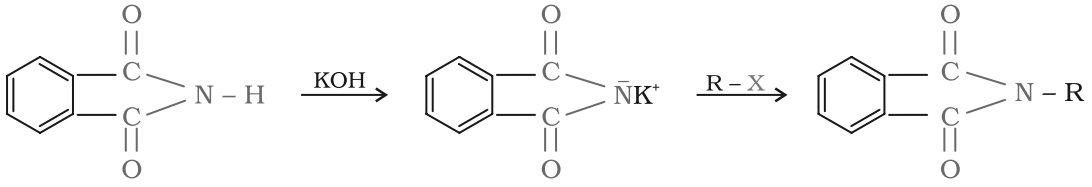
4. *Reduction of amides*

The amides on reduction with lithium aluminium hydride yield amines.

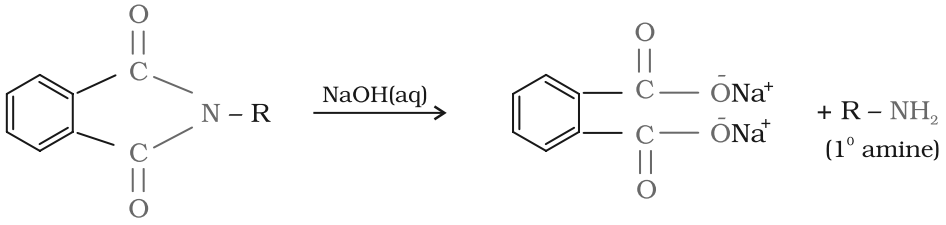
$$R\text{–}\underset{\|}{\overset{O}{C}}\text{–}NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R\text{–}CH_2\text{–}NH_2$$

5. *Gabriel phthalimide synthesis*

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

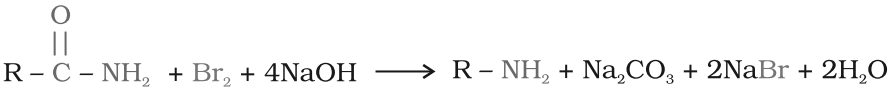


Phthalimide N-Alkylphthalimide



6. *Hoffmann bromamide degradation reaction*

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.



Example 13.2 Write chemical equations for the following conversions:

(i) $CH_3–CH_2–Cl$ into $CH_3–CH_2–CH_2–NH_2$

(ii) $C_6H_5–CH_2–Cl$ into $C_6H_5–CH_2–CH_2–NH_2$

Solution

(i) $CH_3–CH_2–Cl$ (Chloroethane) $\xrightarrow{\text{Ethanolic NaCN}}$ $CH_3–CH_2–C\equiv N$ (Propanenitrile) $\xrightarrow{\text{reduction}}$ $CH_3–CH_2–CH_2–NH_2$ (Propan-1-amine)

(ii) $C_6H_5–CH_2–Cl$ (Chlorophenylmethane (Benzyl chloride)) $\xrightarrow{\text{Ethanolic NaCN}}$ $C_6H_5–CH_2–C\equiv N$ (Phenylethanenitrile (Benzyl cyanide)) $\xrightarrow{H_2/Ni}$ $C_6H_5–CH_2–CH_2–NH_2$ (2-Phenylethanamine)

Example 13.3

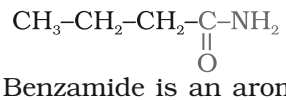
Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

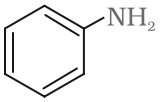
Solution

(i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



Butanamide

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Aniline or benzenamine

Intext Question

13.3 How will you convert

(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline

(iii) $Cl–(CH_2)_4–Cl$ into hexan-1,6-diamine?

13.5 Physical Properties

The lower aliphatic amines are gases with fishy odour. Primary amines with three or more carbon atoms are liquid and still higher ones are solid. Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. Considering the electronegativity of nitrogen of amine and oxygen of alcohol as 3.0 and 3.5 respectively, you can predict the pattern of solubility of amines and alcohols in water. Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why? Amines are soluble in organic solvents like alcohol, ether and benzene. You may remember that alcohols are more polar than amines and form stronger intermolecular hydrogen bonds than amines.

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

Intermolecular hydrogen bonding in primary amines is shown in Fig. 13.2.

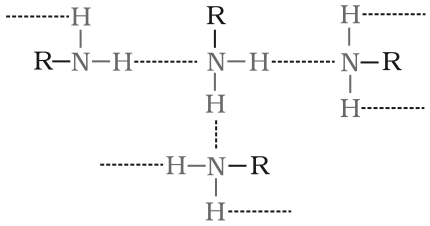


Fig. 13.2 *Intermolecular hydrogen bonding in primary amines*

Boiling points of amines, alcohols and alkanes of almost the same molar mass are shown in Table 13.2.

Table 13.2: Comparison of Boiling Points of Amines, Alcohols and Alkanes of Similar Molecular Masses

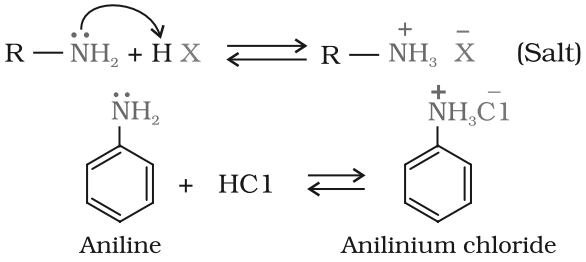
Sl. No.	Compound	Molar mass	b.p./K
1.	n-$C_4H_9NH_2$	73	350.8
2.	$(C_2H_5)_2NH$	73	329.3
3.	$C_2H_5N(CH_3)_2$	73	310.5
4.	$C_2H_5CH(CH_3)_2$	72	300.8
5.	n-C_4H_9OH	74	390.3

13.6 Chemical Reactions

Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive. The number of hydrogen atoms attached to nitrogen atom also decides the course of reaction of amines; that is why primary ($-NH_2$), secondary $\left(\begin{array}{l}\\ \end{array}\!\!>\!\!N-H\right)$ and tertiary amines $\left(\begin{array}{l}\\ \end{array}\!\!>\!\!N-\right)$ differ in many reactions. Moreover, amines behave as nucleophiles due to the presence of unshared electron pair. Some of the reactions of amines are described below:

1. Basic character of amines

Amines, being basic in nature, react with acids to form salts.



Amine salts on treatment with a base like NaOH, regenerate the parent amine.

$$R\overset{+}{N}H_3\ \overset{-}{X} + \overset{-}{O}H \longrightarrow R\ddot{N}H_2 + H_2O + \overset{-}{X}$$

Amine salts are soluble in water but insoluble in organic solvents like ether. This reaction is the basis for the separation of amines from the non basic organic compounds insoluble in water.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as **Lewis base.** Basic character of amines can be better understood in terms of their K_b and pK_b values as explained below:

$$R - NH_2 + H_2O \rightleftharpoons R - \overset{+}{N}H_3 + \overset{-}{O}H$$

$$K = \frac{\left[R - \overset{+}{N}H_3\right]\left[\overset{-}{O}H\right]}{[R - NH_2][H_2O]}$$

$$\text{or } K[H_2O] = \frac{\left[R - \overset{+}{N}H_3\right]\left[\overset{-}{O}H\right]}{[R - NH_2]}$$

$$\text{or } K_b = \frac{\left[R - \overset{+}{N}H_3\right]\left[\overset{-}{O}H\right]}{[R - NH_2]}$$

$$pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b, stronger is the base. The pK_b values of few amines are given in Table 13.3.

pK_b value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom. Their pK_b values lie in the range of 3 to 4.22. On the other hand, aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group.

Table 13.3: pK_b Values of Amines in Aqueous Phase

Name of amine	pK_b
Methanamine	3.38
N-Methylmethanamine	3.27
N,*N*-Dimethylmethanamine	4.22
Ethanamine	3.29
N-Ethylethanamine	3.00
N,*N*-Diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
N-Methylaniline	9.30
N,*N*-Dimethylaniline	8.92

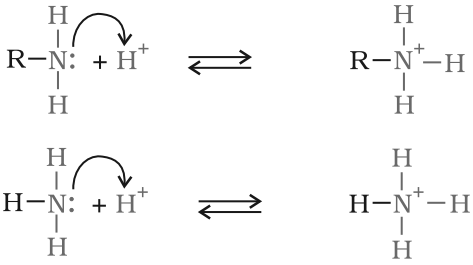
You may find some discrepancies while trying to interpret the K_b values of amines on the basis of +I or –I effect of the substituents present in amines. Besides inductive effect, there are other effects like solvation effect, steric hinderance, etc., which affect the basic strength of amines. Just ponder over. You may get the answer in the following paragraphs.

Structure-basicity relationship of amines

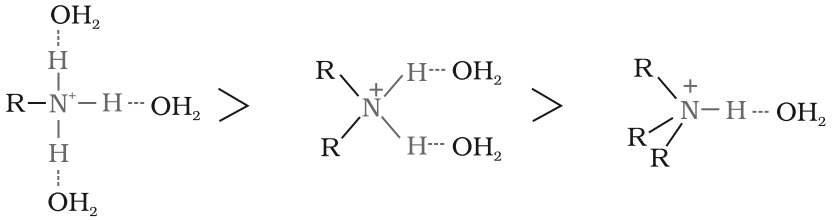
Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

(a) Alkanamines versus ammonia

Let us consider the reaction of an alkanamine and ammonia with a proton to compare their basicity.



Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups. This trend is followed in the gaseous phase. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3. The trend is not regular in the aqueous state as evident by their pK_b values given in Table 13.3. In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. The order of stability of ions are as follows:



1° 2° 3°

Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.

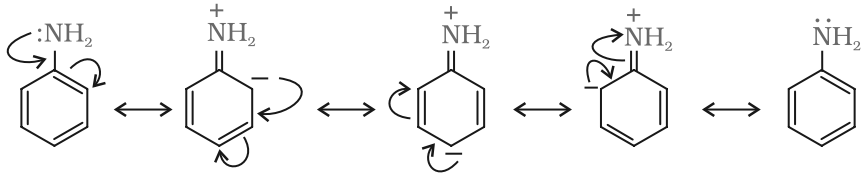
Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order. Secondly, when the alkyl group is small, like $-CH_3$ group, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH_3 group, there will be steric hinderance to H-bonding. Therefore, the change of nature of the alkyl group, e.g., from $-CH_3$ to $-C_2H_5$ results in change of the order of basic strength. Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

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

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

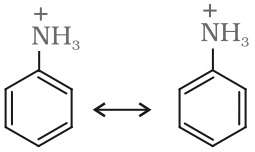
(b) Arylamines versus ammonia

pK_b value of aniline is quite high. Why is it so? It is because in aniline or other arylamines, the $-NH_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. If you write different resonating structures of aniline, you will find that aniline is a resonance hybrid of the following five structures.



I II III IV V

On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).



I II

We know that greater the number of resonating structures, greater is the stability. Thus you can infer that aniline (five resonating structures) is more stable than anilinium ion. Hence, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like $-OCH_3$, $-CH_3$ increase basic strength whereas electron withdrawing groups like $-NO_2$, $-SO_3$, –COOH, –X decrease it.

Example 13.4 Arrange the following in decreasing order of their basic strength:
$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

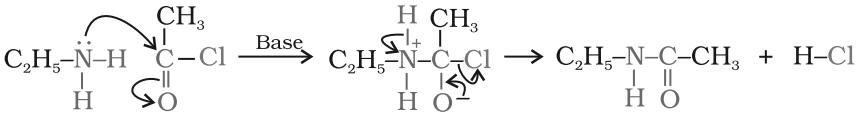
Solution The decreasing order of basic strength of the above amines and ammonia follows the following order:
$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

2. Alkylation

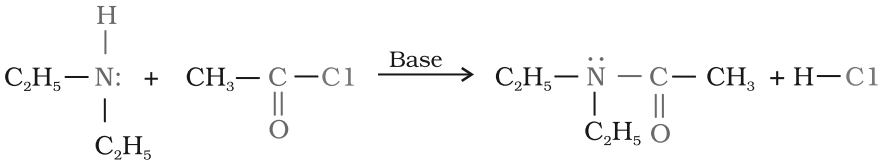
Amines undergo alkylation on reaction with alkyl halides (refer Unit 10, Class XII).

3. Acylation

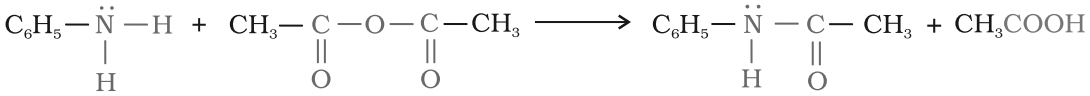
Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. You can consider this reaction as the replacement of hydrogen atom of $-NH_2$ or >N–H group by the acyl group. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.



Ethanamine N-Ethylethanamide



N-Ethylethanamine N,N-Diethylethanamide



Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

Amines also react with benzoyl chloride (C_6H_5COCl). This reaction is known as benzoylation.

Methanamine Benzoyl chloride N – Methylbenzamide

What do you think is the product of the reaction of amines with carboxylic acids ? They form salts with amines at room temperature.

4. *Carbylamine reaction*

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R{-}NC + 3KCl + 3H_2O$$

5. *Reaction with nitrous acid*

Three classes of amines react differently with nitrous acid which is prepared *in situ* from a mineral acid and sodium nitrite.

(a) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

$$R{-}NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R{-}\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

(b) Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds discussed in Section 13.7.

$$C_6H_5{-}NH_2 \xrightarrow[273-278\ K]{NaNO_2 + 2HCl} C_6H_5{-}\overset{+}{N}_2\overset{-}{Cl} + NaCl + 2H_2O$$

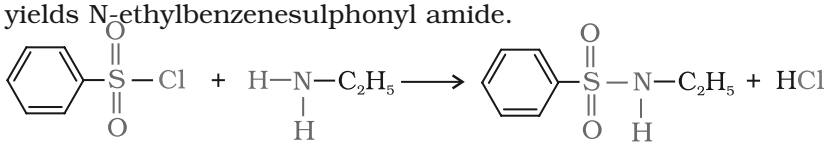
Aniline — Benzenediazonium chloride

Secondary and tertiary amines react with nitrous acid in a different manner.

6. *Reaction with arylsulphonyl chloride*

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

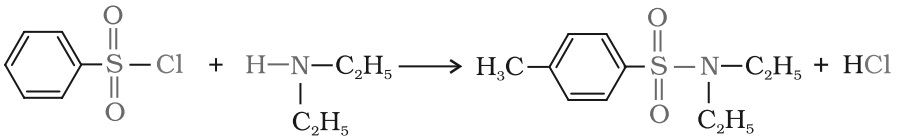
(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethyl-benzenesulphonamide is formed.



N,N-Diethylbenzenesulphonamide

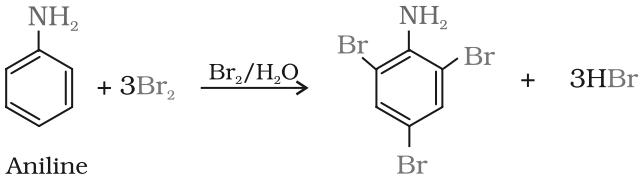
Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzenesulphonyl chloride is replaced by *p*-toluenesulphonyl chloride.

7. Electrophilic substitution

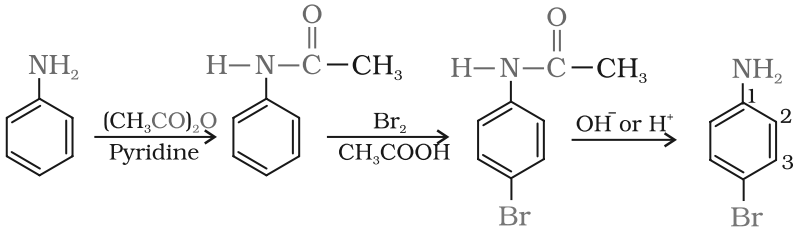
You have read earlier that aniline is a resonance hybrid of five structures. Where do you find the maximum electron density in these structures? *Ortho*- and *para*-positions to the $-NH_2$ group become centres of high electron density. Thus $-NH_2$ group is *ortho* and *para* directing and a powerful activating group.

(a) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



Aniline — 2,4,6-Tribromoaniline

The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their very high reactivity. Substitution tends to occur at *ortho*- and *para*-positions. If we have to prepare monosubstituted aniline derivative, how can the activating effect of $-NH_2$ group be controlled ? This can be done by protecting the $-NH_2$ group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

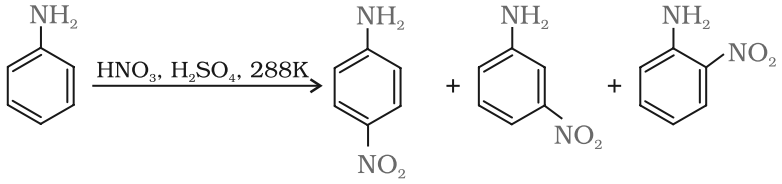


Aniline — *N*-Phenylethanamide (Acetanilide) — (Major) — 4-Bromoaniline

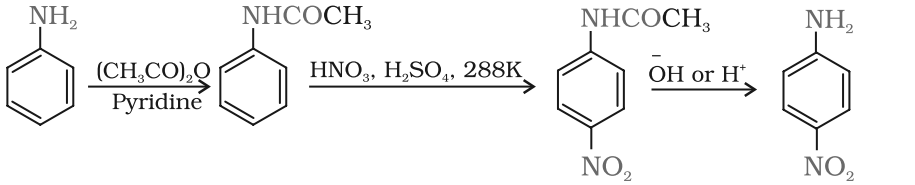
The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of $-NHCOCH_3$ group is less than that of amino group.

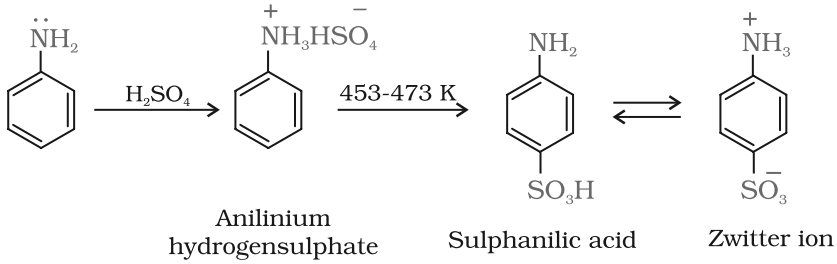
(b) *Nitration:* Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



However, by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.



(c) *Sulphonation*: Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.



Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

Intext Questions

13.4 Arrange the following in increasing order of their basic strength:
(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$
(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$
(iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

13.5 Complete the following acid-base reactions and name the products:
(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$ (ii) $(C_2H_5)_3N + HCl \rightarrow$

13.6 Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

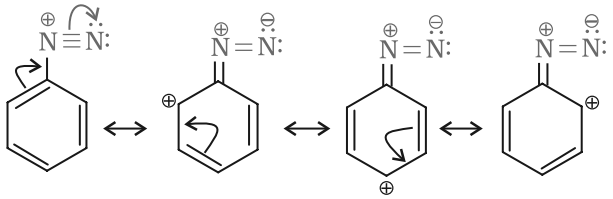
13.7 Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

13.8 Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

II. DIAZONIUM SALTS

The diazonium salts have the general formula $R\overset{+}{N}_2\,\overset{-}{X}$ where R stands for an aryl group and $\overset{-}{X}$ ion may be Cl^- Br^-, HSO_4^-, BF_4^-, etc. They are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc. The $\overset{+}{N}_2$ group is called diazonium group. For example, $C_6H_5\overset{+}{N}_2\,\overset{-}{Cl}$ is named as benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as benzenediazonium hydrogensulphate.

Primary aliphatic amines form highly unstable alkyldiazonium salts (refer to Section 13.6). Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



13.7 Method of Preparation of Diazonium Salts

Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as **diazotisation**. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2Cl + NaCl + 2H_2O$$

13.8 Physical Properties

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state. Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

13.9 Chemical Reactions

The reactions of diazonium salts can be broadly divided into two categories, namely (A) reactions involving displacement of nitrogen and (B) reactions involving retention of diazo group.

A. Reactions involving displacement of nitrogen

Diazonium group being a very good leaving group, is substituted by other groups such as Cl^-, Br^-, I^-, CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

1. *Replacement by halide or cyanide ion*: The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called **Sandmeyer reaction**.

$$ArN_2^+X^- \xrightarrow{CuCl/HCl} ArCl + N_2$$
$$ArN_2^+X^- \xrightarrow{CuBr/HBr} ArBr + N_2$$
$$ArN_2^+X^- \xrightarrow{CuCN/KCN} ArCN + N_2$$

Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as **Gatterman reaction**.

$$ArN_2^+X^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$ArN_2^+X^- \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

2. *Replacement by iodide ion*: Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

$$ArN_2^+Cl^- + KI \longrightarrow ArI + KCl + N_2$$

3. *Replacement by fluoride ion*: When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

$$ArN_2^+Cl^- + HBF_4 \longrightarrow Ar-N_2^+BF_4^- \xrightarrow{\Delta} Ar-F + BF_3 + N_2$$

4. *Replacement by H*: Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal, respectively.

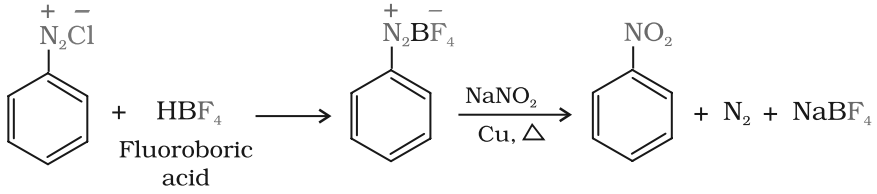
$$ArN_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$ArN_2^+Cl^- + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$$

5. *Replacement by hydroxyl group*: If the temperature of the diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to phenol.

$$ArN_2^+Cl^- + H_2O \longrightarrow ArOH + N_2 + HCl$$

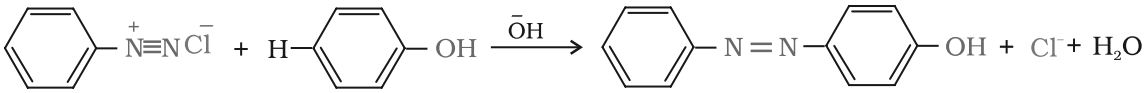
6. *Replacement by –NO_2 group*: When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by –NO_2 group.



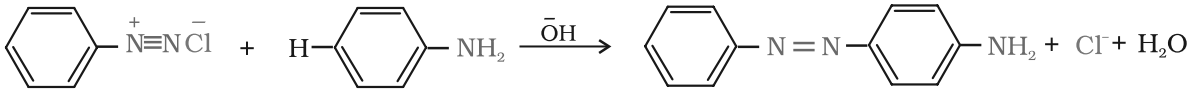
B. Reactions involving retention of diazo group

coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-aminoazobenzene. This is an example of electrophilic substitution reaction.



p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene
(yellow dye)

13.10 Importance of Diazonium Salts in Synthesis of Aromatic Compounds

From the above reactions, it is clear that the diazonium salts are very good intermediates for the introduction of –F, –Cl, –Br, –I, –CN, –OH, –NO_2 groups into the aromatic ring.

Aryl fluorides and iodides cannot be prepared by direct halogenation. The cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt.

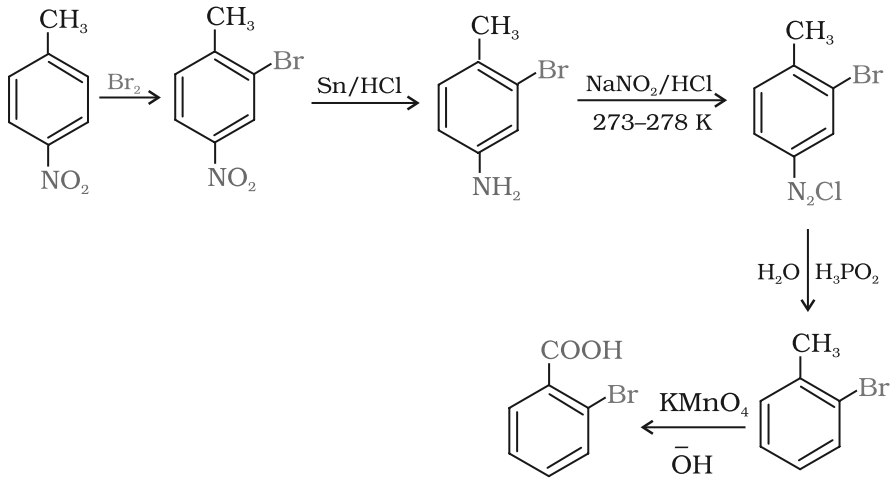
Thus, the replacement of diazo group by other groups is helpful in

preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.

Example 13.5

How will you convert 4-nitrotoluene to 2-bromobenzoic acid ?

Solution



Intext Question

13.9 Convert

(i) 3-Methylaniline into 3-nitrotoluene.

(ii) Aniline into 1,3,5 - tribromobenzene.

Summary

Amines can be considered as derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups. Replacement of one hydrogen atom of ammonia gives rise to structure of the type **R-NH$_2$**, known as **primary amine**. **Secondary amines** are characterised by the structure **R$_2$NH** or **R-NHR′** and **tertiary amines** by **R$_3$N, RNR′R″** or **R$_2$NR′**. Secondary and tertiary amines are known as simple amines if the alkyl or aryl groups are the same and mixed amines if the groups are different. Like ammonia, all the three types of amines have one unshared electron pair on nitrogen atom due to which they behave as **Lewis bases**.

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influence their physical properties. In **alkylamines**, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. In **aromatic amines**, electron releasing and withdrawing groups, respectively increase and decrease their basic character. **Aniline** is a weaker base

than ammonia. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. *p*-Toluenesulphonyl chloride is used for the identification of primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Reactivity of aromatic amines can be controlled by **acylation** process, i.e., by treating with acetyl chloride or acetic anhydride. Tertiary amines like **trimethylamine** are used as insect attractants.

Aryldiazonium salts, usually obtained from arylamines, undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group. Coupling reaction of aryldiazonium salts with phenols or arylamines give rise to the formation of **azo dyes**.

Exercises

13.1 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$ (iii) $CH_3NHCH(CH_3)_2$

(iv) $(CH_3)_3CNH_2$ (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$

(vii) *m*–$BrC_6H_4NH_2$

13.2 Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine (ii) Secondary and tertiary amines

(iii) Ethylamine and aniline (iv) Aniline and benzylamine

(v) Aniline and N-methylaniline.

13.3 Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

13.4 Arrange the following:

(i) In decreasing order of the pK_b values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:
(a) Aniline, *p*-nitroaniline and *p*-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

(iv) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

13.5 How will you convert:

(i) Ethanoic acid into methanamine

(ii) Hexanenitrile into 1-aminopentane

(iii) Methanol to ethanoic acid

(iv) Ethanamine into methanamine

(v) Ethanoic acid into propanoic acid

(vi) Methanamine into ethanamine

(vii) Nitromethane into dimethylamine

(viii) Propanoic acid into ethanoic acid?

13.6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

13.7 Write short notes on the following:

(i) Carbylamine reaction

(ii) Diazotisation

(iii) Hofmann's bromamide reaction

(iv) Coupling reaction

(v) Ammonolysis

(vi) Acetylation

(vii) Gabriel phthalimide synthesis.

13.8 Accomplish the following conversions:

(i) Nitrobenzene to benzoic acid

(ii) Benzene to *m*-bromophenol

(iii) Benzoic acid to aniline

(iv) Aniline to 2,4,6-tribromofluorobenzene

(v) Benzyl chloride to 2-phenylethanamine

(vi) Chlorobenzene to *p*-chloroaniline

(vii) Aniline to *p*-bromoaniline

(viii) Benzamide to toluene

(ix) Aniline to benzyl alcohol.

13.9 Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

13.10 An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

13.11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc.KOH} \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4\ (\text{conc.}) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2\ (aq) \rightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

(vii) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2\ /\ Cu,\ \Delta]{(i)\ HBF_4}$

13.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

13.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

13.14 Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

Answers to Some Intext Questions

13.4 (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

Unit

14

Biomolecules

Objectives

After studying this Unit, you will be able to

- define the biomolecules like carbohydrates, proteins and nucleic acids;
- classify carbohydrates, proteins, nucleic acids and vitamins on the basis of their structures;
- explain the difference between DNA and RNA;
- appreciate the role of biomolecules in biosystem.

"It is the harmonious and synchronous progress of chemical reactions in body which leads to life".

A living system grows, sustains and reproduces itself. The most amazing thing about a living system is that it is composed of non-living atoms and molecules. The pursuit of knowledge of what goes on chemically within a living system falls in the domain of ***biochemistry***. Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. These biomolecules interact with each other and constitute the molecular logic of life processes. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms. Structures and functions of some of these biomolecules are discussed in this Unit.

14.1 Carbohydrates

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. Some common examples are cane sugar, glucose, starch, etc. Most of them have a general formula, $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived. For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6(H_2O)_6$. But all the compounds which fit into this formula may not be classified as carbohydrates. Acetic acid (CH_3COOH) fits into this general formula, $C_2(H_2O)_2$ but is not a carbohydrate. Similarly, rhamnose, $C_6H_{12}O_5$ is a carbohydrate but does not fit in this definition. A large number of their reactions have shown that they contain specific functional groups. Chemically, *the carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis*. Some of the carbohydrates,

which are sweet in taste, are also called sugars. The most common sugar, used in our homes is named as sucrose whereas the sugar present in milk is known as lactose. Carbohydrates are also called saccharides (Greek: *sakcharon* means sugar).

14.1.1 Classification of Carbohydrates

Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups.

(i) *Monosaccharides*: A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. About 20 monosaccharides are known to occur in nature. Some common examples are glucose, fructose, ribose, etc.

(ii) *Oligosaccharides*: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. For example, sucrose on hydrolysis gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose only.

(iii) *Polysaccharides*: Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc. Polysaccharides are not sweet in taste, hence they are also called non-sugars.

The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are *reducing sugars.*

In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are non-reducing sugars e.g. sucrose. On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

14.1.2 Monosaccharides

Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose. Number of carbon atoms constituting the monosaccharide is also introduced in the name as is evident from the examples given in Table 14.1

Table 14.1: Different Types of Monosaccharides

Carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

I Glucose

Glucose occurs freely in nature as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts. It is prepared as follows:

14.1.3 Preparation of Glucose

1. *From sucrose (Cane sugar)*: If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

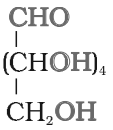
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

2. *From starch*: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

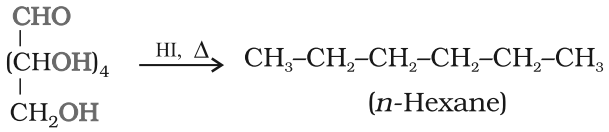
$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

14.1.4 Structure of Glucose

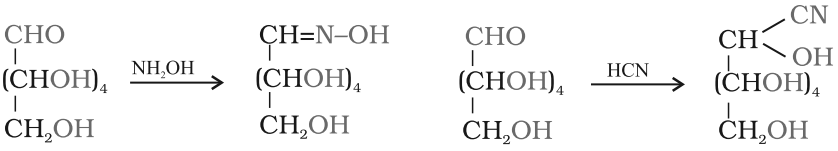
Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. It is probably the most abundant organic compound on earth. It was assigned the structure given below on the basis of the following evidences:



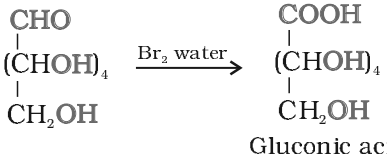
1. Its molecular formula was found to be $C_6H_{12}O_6$.
2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



3. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = 0) in glucose.

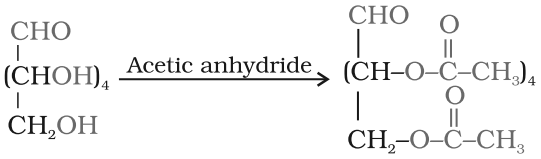


4. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.

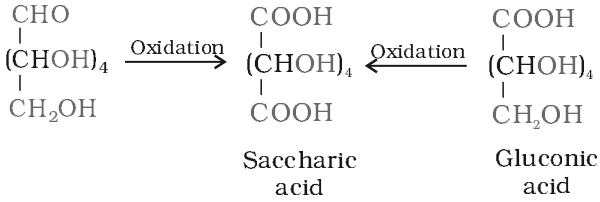


Gluconic acid

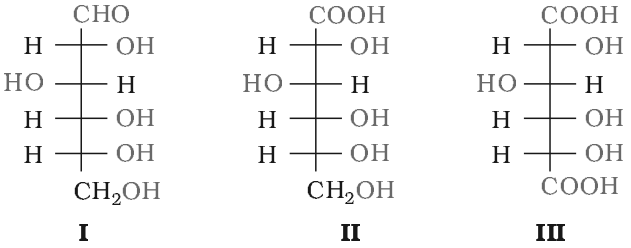
5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups. Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms.



6. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.

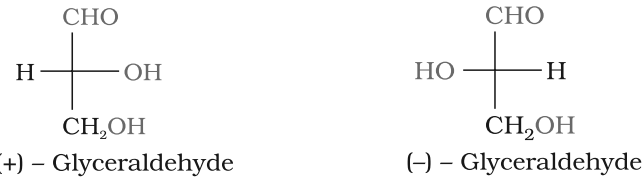


The exact spatial arrangement of different —OH groups was given by Fischer after studying many other properties. Its configuration is correctly represented as **I**. So gluconic acid is represented as **II** and saccharic acid as **III**.

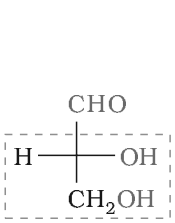


Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. It may be remembered that 'D' and 'L' have no relation with the optical activity of the compound. The meaning of D– and L– notations is given as follows.

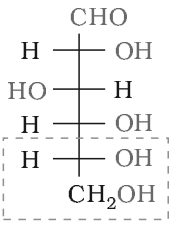
The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer. This refers to their relation with a particular isomer of glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below.



All those compounds which can be chemically correlated to (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to (–) isomer of glyceraldehyde are said to have L—configuration. For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so it is assigned D-configuration. For this comparison, the structure is written in a way that most oxidised carbon is at the top.



D– (+) – Glyceraldehyde



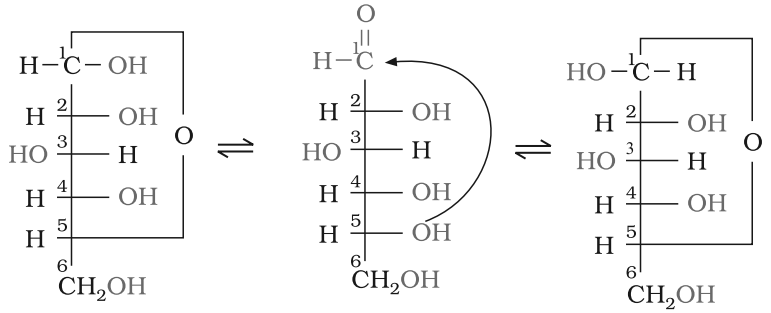
D–(+) – Glucose

14.1.5 Cyclic Structure of Glucose

The structure **(I)** of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

1. Despite having the aldehyde group, glucose does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.
2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.
3. Glucose is found to exist in two different crystalline forms which are named as α and β. The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

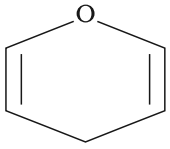
   This behaviour could not be explained by the open chain structure **(I)** for glucose. It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure. It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation. This explains the absence of —CHO group and also existence of glucose in two forms as shown below. These two cyclic forms exist in equilibrium with open chain structure.



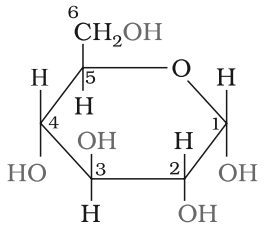
α – D – (+) – Glucose

β – D– (+) – Glucose

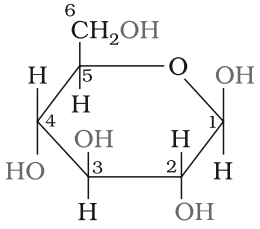
The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* (the aldehyde carbon before cyclisation). Such isomers, i.e., α-form and β-form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** (α– or β–), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.



Pyran



α – D – (+) – Glucopyranose



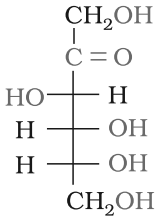
β – D – (+) – Glucopyranose

II. Fructose

Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose.

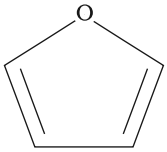
14.1.6 Structure of Fructose

Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(–)-fructose. Its open chain structure is as shown.

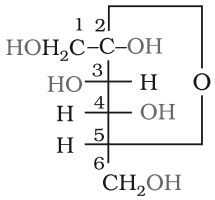


D – (–) – Fructose

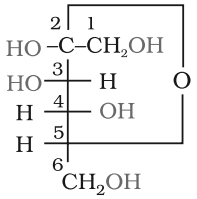
It also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the (>C=O) group. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.



Furan

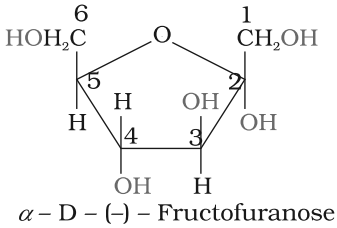


α – D – (–) – Fructofuranose

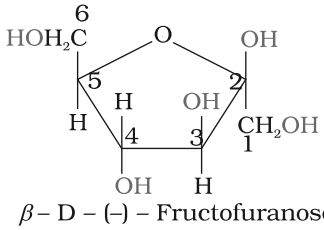


β – D – (–) – Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given.



α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose

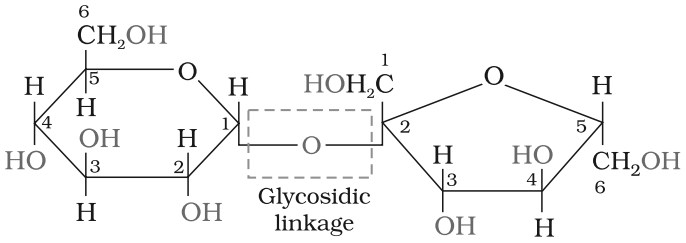
14.1.7 Disaccharides

You have already read that disaccharides on hydrolysis with dilute acids or enzymes yield two molecules of either the same or different monosaccharides. The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called *glycosidic linkage.*

(i) Sucrose: One of the common disaccharides is **sucrose** which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

These two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.

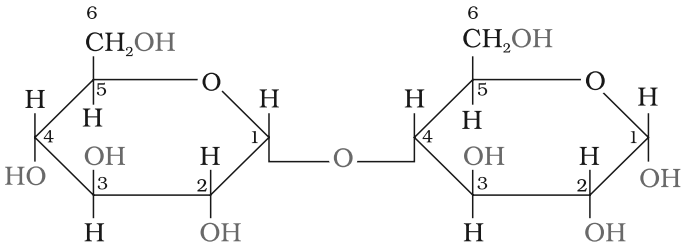


α – D – Glucose β – D – Fructose

Sucrose

Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4) is more than dextrorotation of glucose (+ 52.5), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as **invert sugar**.

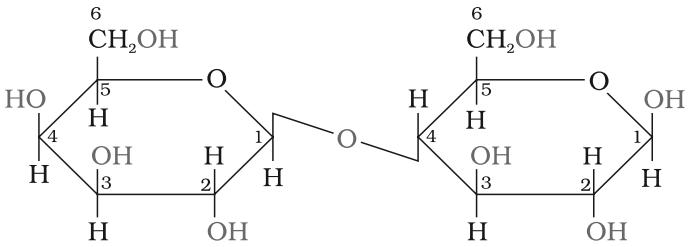
(ii) Maltose: Another disaccharide, maltose is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.



(I) α – D – Glucose (II) α – D – Glucose

Maltose

(iii) *Lactose*: It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of β-D-galactose and β-D-glucose. The linkage is between C1 of galactose and C4 of glucose. Hence it is also a reducing sugar.



β– D – Galactose β– D – Glucose

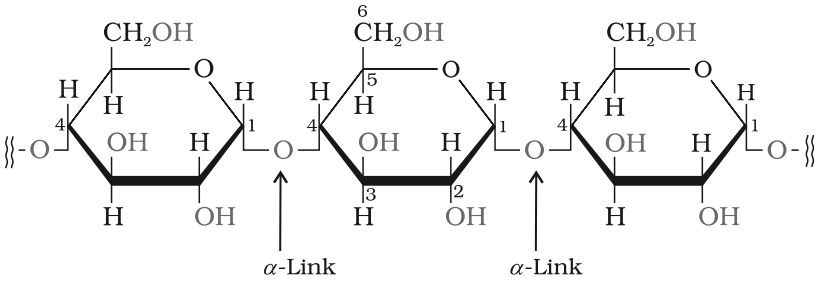
Lactose

14.1.8 Polysaccharides

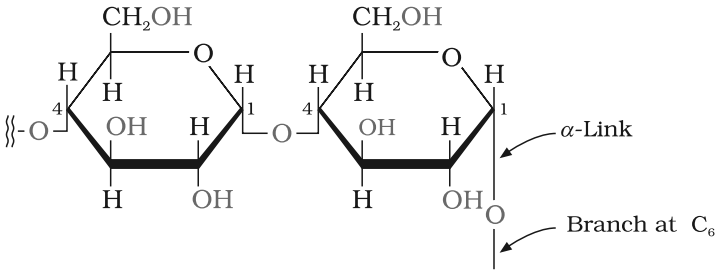
Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. These are the most commonly encountered carbohydrates in nature. They mainly act as the food storage or structural materials.

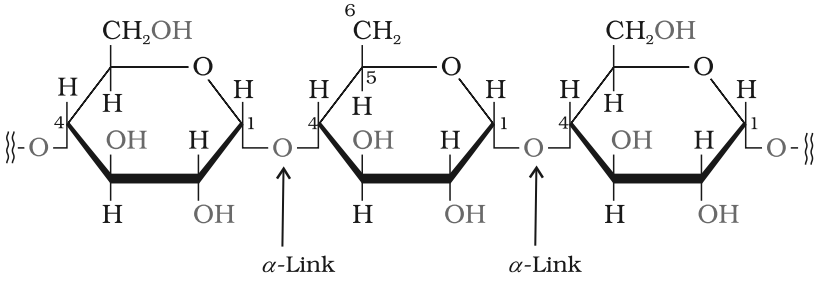
(i) *Starch*: Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α-glucose and consists of two components— **Amylose** and **Amylopectin**. Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units held by C1– C4 glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α-D-glucose



Amylose

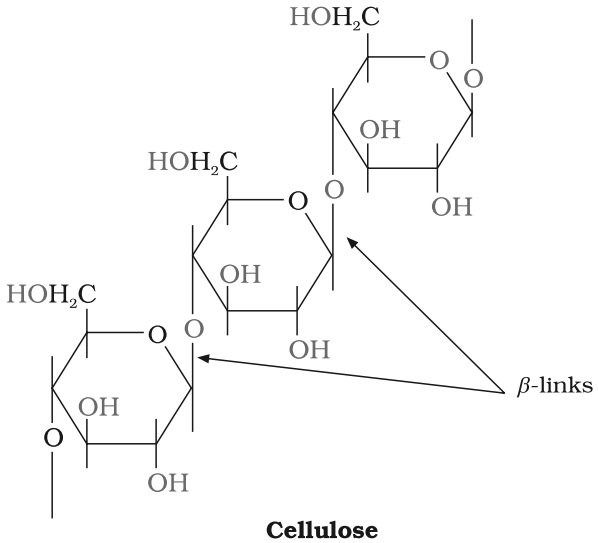




Amylopectin

units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.

(ii) *Cellulose*: Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain



Cellulose

polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

(iii) *Glycogen*: The carbohydrates are stored in animal body as glycogen. It is also known as *animal starch* because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

14.1.9 Importance of Carbohydrates

Carbohydrates are essential for life in both plants and animals. They form a major portion of our food. Honey has been used for a long time as an instant source of energy by '**Vaids**' in ayurvedic system of medicine. Carbohydrates are used as storage molecules as starch in plants and **glycogen** in animals. Cell wall of bacteria and plants is made up of cellulose. We build furniture, etc. from cellulose in the form of wood

and clothe ourselves with cellulose in the form of cotton fibre. They provide raw materials for many important industries like textiles, paper, lacquers and breweries.

Two aldopentoses viz. D-ribose and 2-deoxy-D-ribose (Section 14.5.1, Class XII) are present in nucleic acids. Carbohydrates are found in biosystem in combination with many proteins and lipids.

Intext Questions

14.1 Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.

14.2 What are the expected products of hydrolysis of lactose?

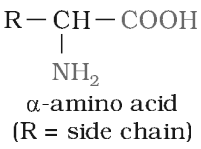
14.3 How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

14.2 Proteins

Proteins are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc. They occur in every part of the body and form the fundamental basis of structure and functions of life. They are also required for growth and maintenance of body. The word protein is derived from Greek word, "**proteios**" which means primary or of prime importance. All proteins are polymers of α-amino acids.

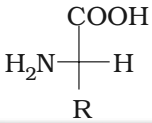
14.2.1 Amino Acids

Amino acids contain amino ($-NH_2$) and carboxyl (–COOH) functional groups. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α, β, γ, δ and so on. Only α-amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.

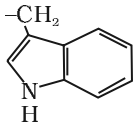
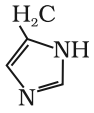
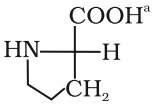

α-amino acid
(R = side chain)

All α-amino acids have trivial names, which usually reflect the property of that compound or its source. Glycine is so named since it has sweet taste (in Greek *glykos* means sweet) and tyrosine was first obtained from cheese (in Greek, *tyros* means cheese.) Amino acids are generally represented by a three letter symbol, sometimes one letter symbol is also used. Structures of some commonly occurring amino acids along with their 3-letter and 1-letter symbols are given in Table 14.2.

Table 14.2: Natural Amino Acids



Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine	H	Gly	G
2. Alanine	$-CH_3$	Ala	A
3. Valine*	$(H_3C)_2CH-$	Val	V
4. Leucine*	$(H_3C)_2CH-CH_2-$	Leu	L

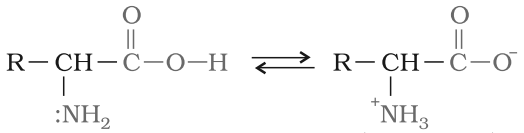
5. Isoleucine*	$H_3C\text{-}CH_2\text{-}CH(CH_3)\text{-}$	Ile	I
6. Arginine*	$HN{=}C(NH_2)\text{-}NH\text{-}(CH_2)_3\text{-}$	Arg	R
7. Lysine*	$H_2N\text{-}(CH_2)_4\text{-}$	Lys	K
8. Glutamic acid	$HOOC\text{-}CH_2\text{-}CH_2\text{-}$	Glu	E
9. Aspartic acid	$HOOC\text{-}CH_2\text{-}$	Asp	D
10. Glutamine	$H_2N\text{-}C(=O)\text{-}CH_2\text{-}CH_2\text{-}$	Gln	Q
11. Asparagine	$H_2N\text{-}C(=O)\text{-}CH_2\text{-}$	Asn	N
12. Threonine*	$H_3C\text{-}CHOH\text{-}$	Thr	T
13. Serine	$HO\text{-}CH_2\text{-}$	Ser	S
14. Cysteine	$HS\text{-}CH_2\text{-}$	Cys	C
15. Methionine*	$H_3C\text{-}S\text{-}CH_2\text{-}CH_2\text{-}$	Met	M
16. Phenylalanine*	$C_6H_5\text{-}CH_2\text{-}$	Phe	F
17. Tyrosine	$(p)HO\text{-}C_6H_4\text{-}CH_2\text{-}$	Tyr	Y
18. Tryptophan*		Trp	W
19. Histidine*		His	H
20. Proline		Pro	P

** essential amino acid, a = entire structure*

14.2.2 Classification of Amino Acids

Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Equal number of amino and carboxyl groups makes it neutral; more number of amino than carboxyl groups makes it basic and more carboxyl groups as compared to amino groups makes it acidic. The amino acids, which can be synthesised in the body, are known as **non-essential amino acids.** On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as **essential amino acids** (marked with asterisk in Table 14.2).

Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as *zwitter ion*. This is neutral but contains both positive and negative charges.

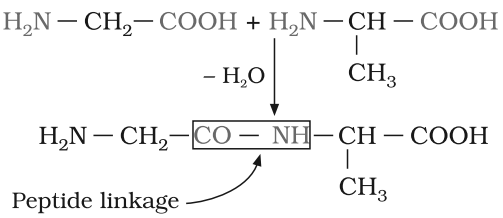

(Zwitter ion)

In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

Except glycine, all other naturally occurring α-amino acids are optically active, since the α-carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. L-Aminoacids are represented by writing the $-NH_2$ group on left hand side.

14.2.3 Structure of Proteins

You have already read that proteins are the polymers of α-amino acids and they are connected to each other by **peptide bond** or **peptide linkage.** Chemically, peptide linkage is an amide formed between –COOH group and $-NH_2$ group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond –CO–NH–. The product of the reaction is called a dipeptide because it is made up of two amino acids. For example, when carboxyl group of glycine combines with the amino group of alanine we get a **dipeptide**, glycylalanine.


Glycylalanine (Gly-Ala)

If a third amino acid combines to a dipeptide, the product is called a **tripeptide**. A tripeptide contains three amino acids linked by two peptide linkages. Similarly when four, five or six amino acids are linked, the respective products are known as **tetrapeptide, pentapeptide or hexapeptide**, respectively. When the number of such amino acids is more than ten, then the products are called **polypeptides**. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein. However, the distinction between a polypeptide and a protein is not very sharp. Polypeptides with fewer amino acids are likely to be called proteins if they ordinarily have a well defined conformation of a protein such as insulin which contains 51 amino acids.

Proteins can be classified into two types on the basis of their molecular shape.

(a) Fibrous proteins

When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre– like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

(b) Globular proteins

This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

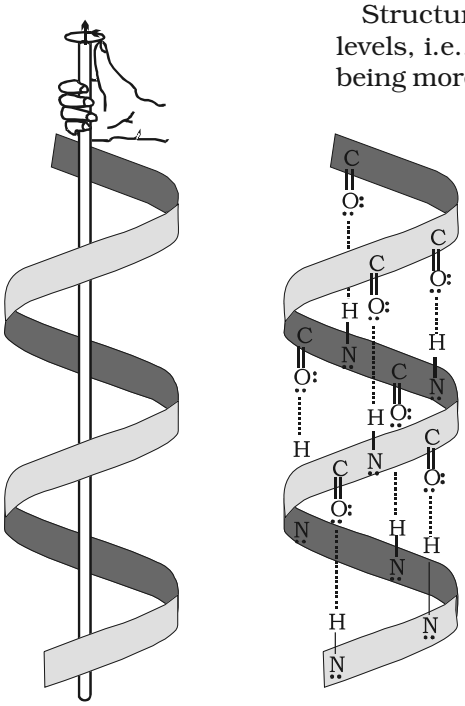


Fig. 14.1: *α-Helix structure of proteins*

(i) Primary structure of proteins: Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.

*(ii) Secondary structure of proteins***:** The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz. α-helix and β-pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between $-\overset{\overset{O}{\|}}{C}-$ and –NH– groups of the peptide bond.

α-Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the $\diagdown C{=}O$ of an adjacent turn of the helix as shown in Fig.14.1.

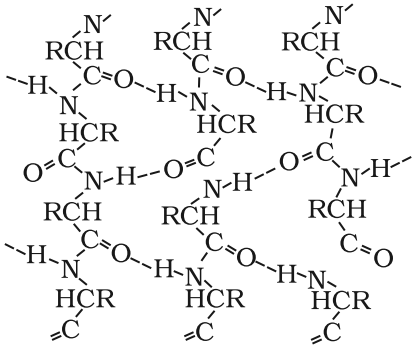


Fig. 14.2: *β-Pleated sheet structure of proteins*

In β-structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β-pleated sheet.

*(iii) Tertiary structure of proteins***:** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the 2 and 3 structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

*(iv) Quaternary structure of proteins***:** Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

A diagrammatic representation of all these four structures is given in Figure 14.3 where each coloured ball represents an amino acid.

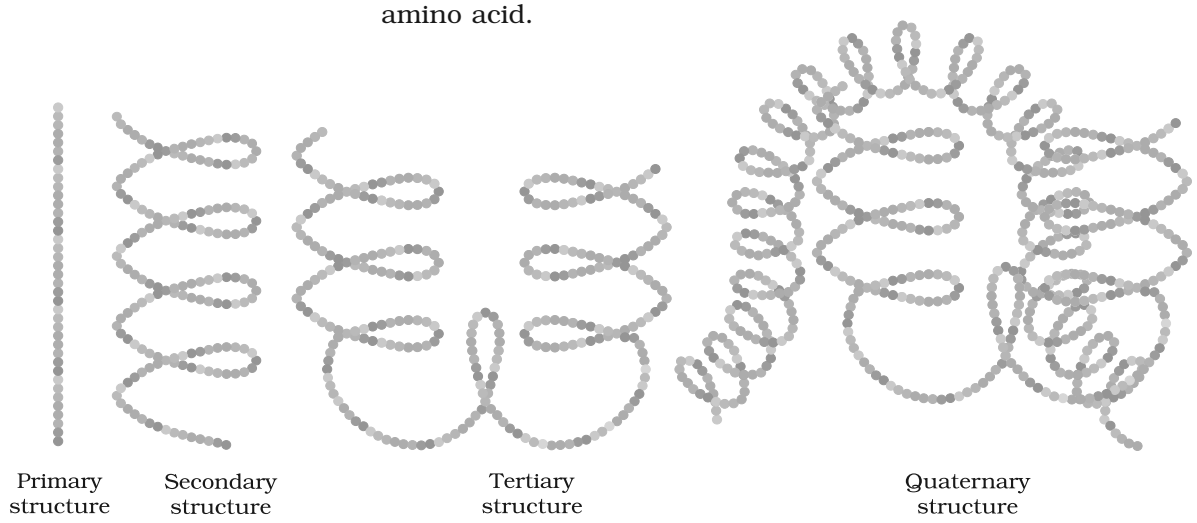


Fig. 14.3: *Diagrammatic representation of protein structure (two sub-units of two types in quaternary structure)*

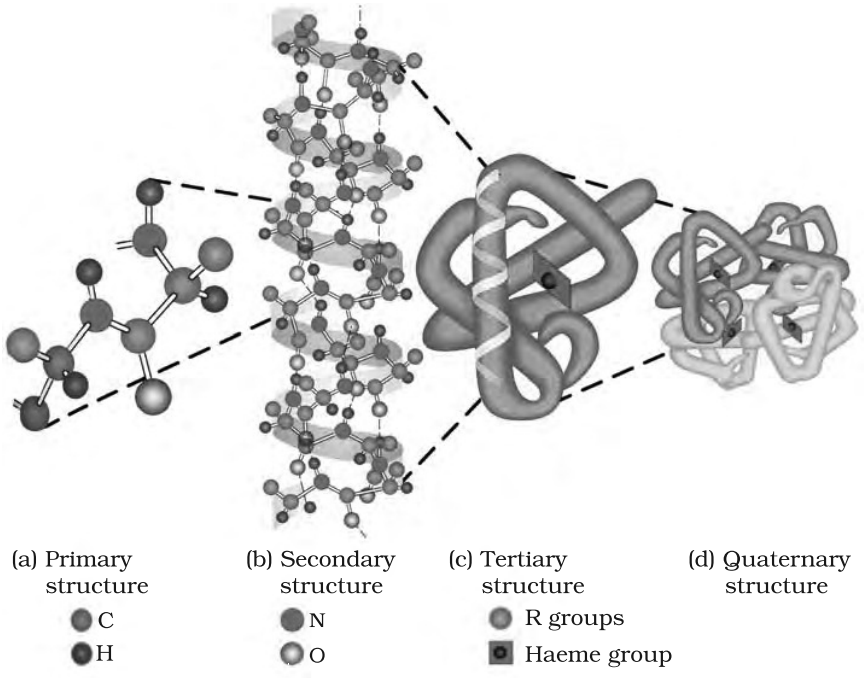


Fig. 14.4: *Primary, secondary, tertiary and quaternary structures of haemoglobin*

14.2.4 Denaturation of Proteins

Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of

protein. During denaturation 2 and 3 structures are destroyed but 1º structure remains intact. The coagulation of egg white on boiling is a common example of denaturation. Another example is curdling of milk which is caused due to the formation of lactic acid by the bacteria present in milk.

Intext Questions

14.4 The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

14.5 Where does the water present in the egg go after boiling the egg?

14.3 Enzymes

Life is possible due to the coordination of various chemical reactions in living organisms. An example is the digestion of food, absorption of appropriate molecules and ultimately production of energy. This process involves a sequence of reactions and all these reactions occur in the body under very mild conditions. This occurs with the help of certain biocatalysts called **enzymes.** Almost all the enzymes are globular proteins. Enzymes are very specific for a particular reaction and for a particular substrate. They are generally named after the compound or class of compounds upon which they work. For example, the enzyme that catalyses hydrolysis of maltose into glucose is named as *maltase*.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Maltase}} 2\,\underset{\text{Glucose}}{C_6H_{12}O_6}$$

Sometimes enzymes are also named after the reaction, where they are used. For example, the enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate are named as **oxidoreductase** enzymes. The ending of the name of an enzyme is **-ase**.

14.3.1 Mechanism of Enzyme Action

Enzymes are needed only in small quantities for the progress of a reaction. Similar to the action of chemical catalysts, enzymes are said to reduce the magnitude of activation energy. For example, activation energy for acid hydrolysis of sucrose is 6.22 kJ mol^{-1}, while the activation energy is only 2.15 kJ mol^{-1} when hydrolysed by the enzyme, sucrase. Mechanism for the enzyme action has been discussed in Unit 5.

14.4 Vitamins

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called **vitamins.** Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them, so they are considered as essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us. All the vitamins are generally available in our diet. Different vitamins belong to various chemical classes and it is difficult to define them on the basis of structure. They are generally regarded as **organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth**

and health of the organism. Vitamins are designated by alphabets A, B, C, D, etc. Some of them are further named as sub-groups e.g. B_1, B_2, B_6, B_{12}, etc. Excess of vitamins is also harmful and vitamin pills should not be taken without the advice of doctor.

The term "**Vitamine**" was coined from the word vital + amine since the earlier identified compounds had amino groups. Later work showed that most of them did not contain amino groups, so the letter 'e' was dropped and the term **vitamin** is used these days.

14.4.1 Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) *Fat soluble vitamins*: Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) *Water soluble vitamins*: B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Some important vitamins, their sources and diseases caused by their deficiency are listed in Table 14.3.

Table 14.3: Some important Vitamins, their Sources and their Deficiency Diseases

Sl. No.	Name of Vitamins	Sources	Deficiency diseases
1.	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2.	Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
3.	Vitamin B_2 (Riboflavin)	Milk, eggwhite, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5.	Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6.	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
7.	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)

8. Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
9. Vitamin K	Green leafy vegetables	Increased blood clotting time

14.5: Nucleic Acids

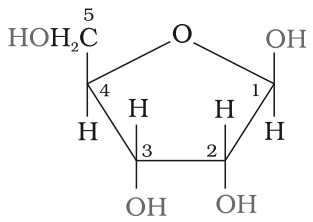
Every generation of each and every species resembles its ancestors in many ways. How are these characteristics transmitted from one generation to the next? It has been observed that nucleus of a living cell is responsible for this transmission of inherent characters, also called **heredity**. The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids.** These are mainly of two types, the **deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).** Since nucleic acids are long chain polymers of **nucleotides,** so they are also called polynucleotides.

James Dewey Watson

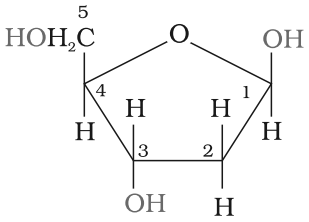
Born in Chicago, Illinois, in 1928, Dr Watson received his Ph.D. (1950) from Indiana University in Zoology. He is best known for his discovery of the structure of DNA for which he shared with Francis Crick and Maurice Wilkins the 1962 Nobel prize in Physiology and Medicine. They proposed that DNA molecule takes the shape of a double helix, an elegantly simple structure that resembles a gently twisted ladder. The rails of the ladder are made of alternating units of phosphate and the sugar deoxyribose; the rungs are each composed of a pair of purine/ pyrimidine bases. This research laid the foundation for the emerging field of **molecular biology**. The complementary pairing of nucleotide bases explains how identical copies of parental DNA pass on to two daughter cells. This research launched a revolution in biology that led to modern recombinant DNA techniques.

14.5.1 Chemical Composition of Nucleic Acids

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecule, it is β-D-ribose.

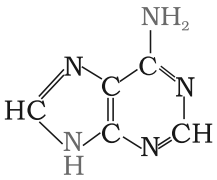


β–D–ribose

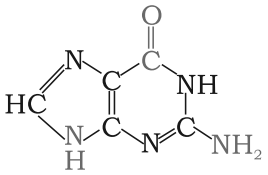


β–D–2–deoxyribose

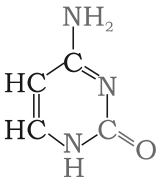
DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



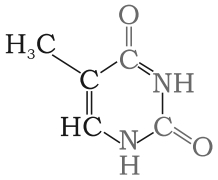
Adenine (A)



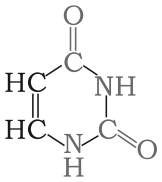
Guanine (G)



Cytosine (C)



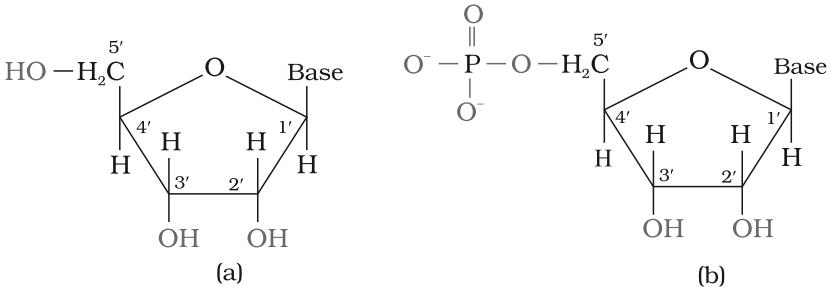
Thymine (T)



Uracil (U)

14.5.2 Structure of Nucleic Acids

A unit formed by the attachment of a base to 1′ position of sugar is known as **nucleoside.** In nucleosides, the sugar carbons are numbered as 1′, 2′, 3′, etc. in order to distinguish these from the bases (Fig. 14.5a). When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, we get a nucleotide (Fig. 14.5).



(a) (b)

Fig. 14.5: *Structure of (a) a nucleoside and (b) a nucleotide*

Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig. 14.6.

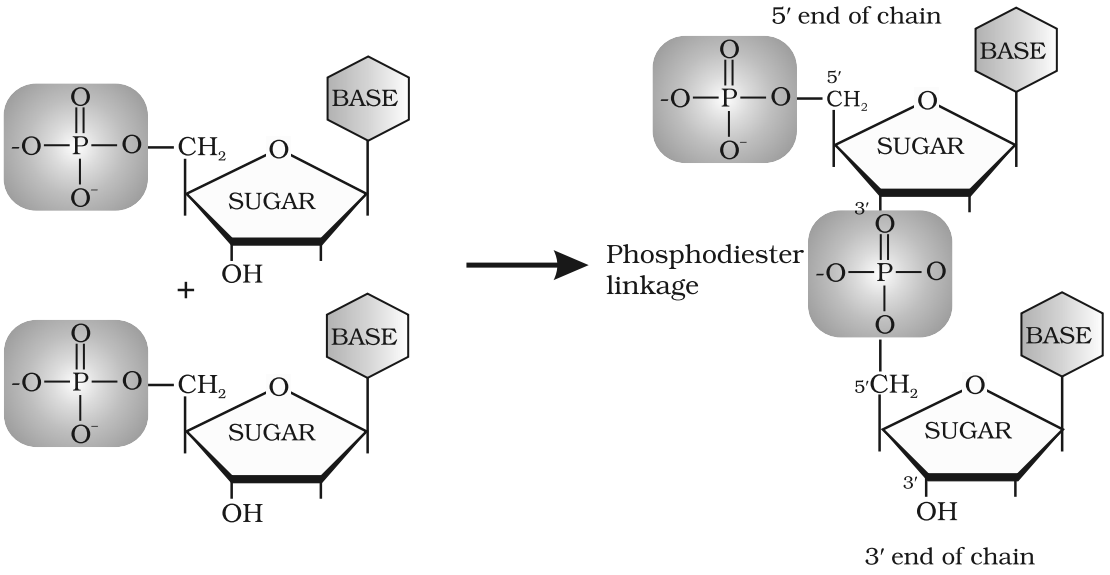
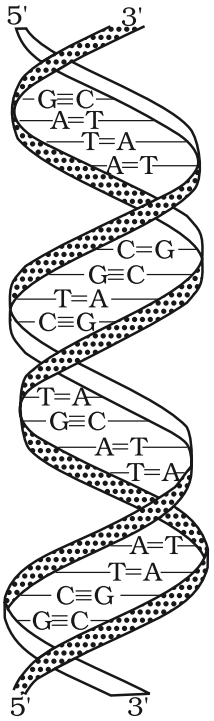
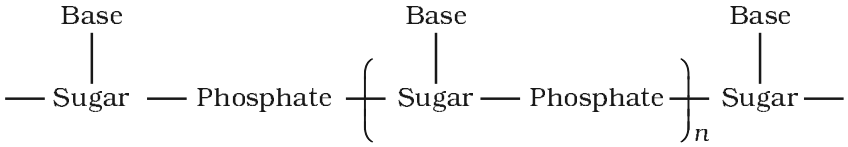


Fig. 14.6: *Formation of a dinucleotide*



A simplified version of nucleic acid chain is as shown below.



Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA (Fig. 14.7). Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure. RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA).**

Fig. 14.7: *Double strand helix structure for DNA*

Har Gobind Khorana

Har Gobind Khorana, was born in 1922. He obtained his M.Sc. degree from Punjab University in Lahore. He worked with Professor Vladimir Prelog, who moulded Khorana's thought and philosophy towards science, work and effort. After a brief stay in India in 1949, Khorana went back to England and worked with Professor G.W. Kenner and Professor A.R.Todd. It was at Cambridge, U.K. that he got interested in both proteins and nucleic acids. Dr Khorana shared the Nobel Prize for Medicine and Physiology in 1968 with Marshall Nirenberg and Robert Holley for cracking the genetic code.

DNA Fingerprinting

It is known that every individual has unique fingerprints. These occur at the tips of the fingers and have been used for identification for a long time but these can be altered by surgery. A sequence of bases on DNA is also unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment. DNA fingerprinting is now used

(i) in forensic laboratories for identification of criminals.

(ii) to determine paternity of an individual.

(iii) to identify the dead bodies in any accident by comparing the DNA's of parents or children.

(iv) to identify racial groups to rewrite biological evolution.

14.5.3 Biological Functions of Nucleic Acids

DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. DNA is exclusively responsible for maintaining the identity of different species of organisms over millions of years. A DNA molecule is capable of self duplication during cell division and identical DNA strands are transferred to daughter cells. Another important function of nucleic acids is the protein synthesis in the cell. Actually, the proteins are synthesised by various RNA molecules in the cell but the message for the synthesis of a particular protein is present in DNA.

Intext Questions

14.6 Why cannot vitamin C be stored in our body?

14.7 What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?

14.8 When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA?

Summary

Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis. They are broadly classified into three groups — **monosaccharides**, **disaccharides** and **polysaccharides**. Glucose, the most important source of energy for mammals, is obtained by the digestion of starch. Monosaccharides are held together by glycosidic linkages to form disaccharides or polysaccharides.

Proteins are the **polymers** of about twenty different **α-amino acids** which are linked by peptide bonds. Ten amino acids are called essential amino acids because they cannot be synthesised by our body, hence must be provided through diet. Proteins perform various structural and dynamic functions in the organisms. Proteins which contain only α-amino acids are called simple proteins. The **secondary** or **tertiary structure of proteins** get disturbed on change of pH or temperature and they are not able to perform their functions. This is called **denaturation of proteins**. Enzymes are **biocatalysts** which speed up the reactions in biosystems. They are very specific and selective in their action and chemically all **enzymes** are proteins.

Vitamins are accessory food factors required in the diet. They are classified as fat soluble (A, D, E and K) and water soluble (B group and C). Deficiency of vitamins leads to many diseases.

Nucleic acids are the polymers of nucleotides which in turn consist of a base, a pentose sugar and phosphate moiety. Nucleic acids are responsible for the transfer of characters from parents to offsprings. There are two types of nucleic acids — **DNA** and **RNA**. DNA contains a five carbon sugar molecule called **2-deoxyribose** whereas RNA contains ribose. Both DNA and RNA contain adenine, guanine and cytosine. The fourth base is thymine in DNA and uracil in RNA. The structure of DNA is a double strand whereas RNA is a single strand molecule. DNA is the chemical basis of heredity and have the coded message for proteins to be synthesised in the cell. There are three types of RNA — mRNA, rRNA and tRNA which actually carry out the protein synthesis in the cell.

Exercises

14.1 What are monosaccharides?

14.2 What are reducing sugars?

14.3 Write two main functions of carbohydrates in plants.

14.4 Classify the following into monosaccharides and disaccharides.
Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.

14.5 What do you understand by the term glycosidic linkage?

14.6 What is glycogen? How is it different from starch?

14.7 What are the hydrolysis products of
(i) sucrose and (ii) lactose?

14.8 What is the basic structural difference between starch and cellulose?

14.9 What happens when D-glucose is treated with the following reagents?
(i) HI (ii) Bromine water (iii) HNO_3

14.10 Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.

14.11 What are essential and non-essential amino acids? Give two examples of each type.

14.12 Define the following as related to proteins
(i) Peptide linkage (ii) Primary structure (iii) Denaturation.

14.13 What are the common types of secondary structure of proteins?

14.14 What type of bonding helps in stabilising the α-helix structure of proteins?

14.15 Differentiate between globular and fibrous proteins.

14.16 How do you explain the amphoteric behaviour of amino acids?

14.17 What are enzymes?

14.18 What is the effect of denaturation on the structure of proteins?

14.19 How are vitamins classified? Name the vitamin responsible for the coagulation of blood.

14.20 Why are vitamin A and vitamin C essential to us? Give their important sources.

14.21 What are nucleic acids? Mention their two important functions.

14.22 What is the difference between a nucleoside and a nucleotide?

14.23 The two strands in DNA are not identical but are complementary. Explain.

14.24 Write the important structural and functional differences between DNA and RNA.

14.25 What are the different types of RNA found in the cell?