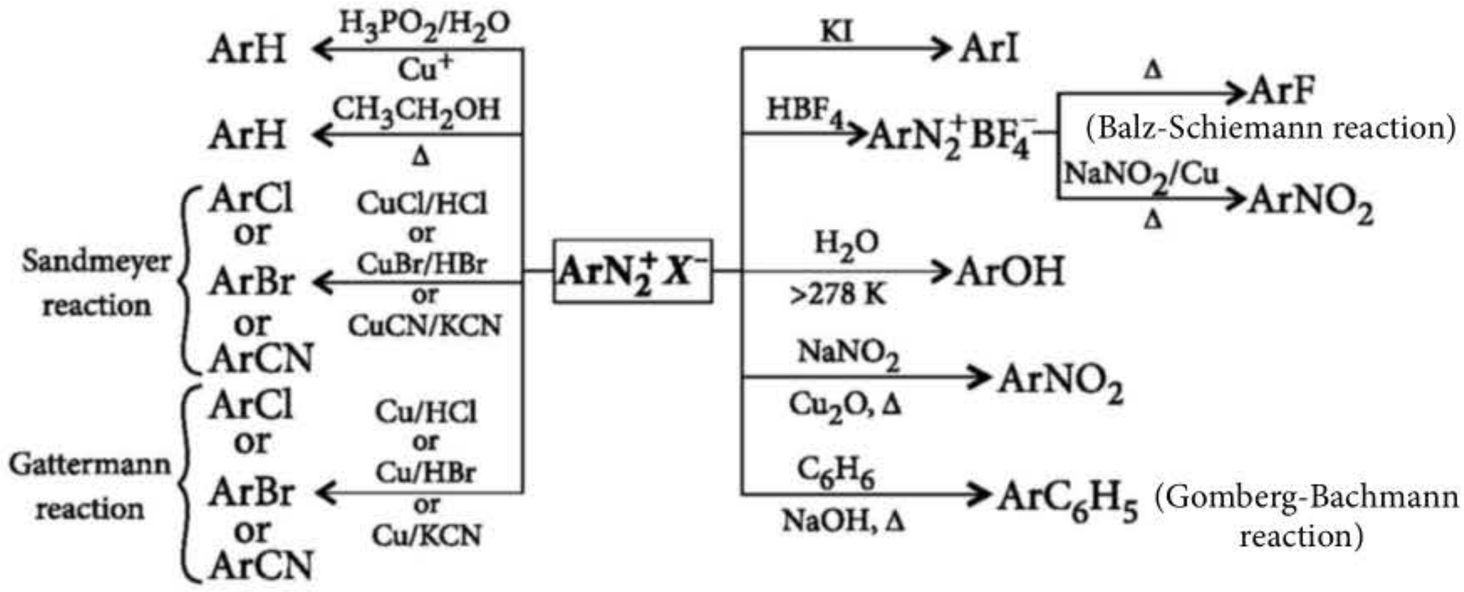
Chemical Properties

- **Reactions involving displacement of nitrogen (diazo group) :**



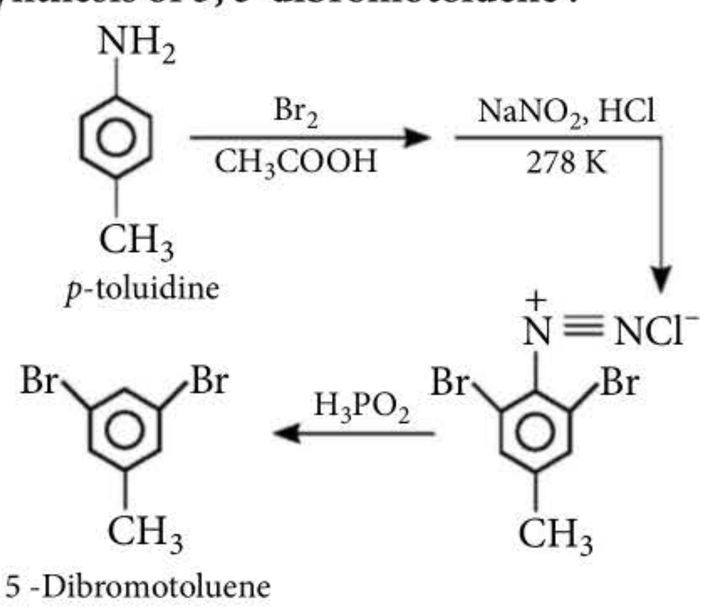
- **Reactions involving retention of diazo group (coupling reactions) :**

$$ArN{=}NC_6H_4NH_2 \xleftarrow[pH = 4\text{-}5,\ 0\text{-}5°C]{C_6H_5NH_2/H^+} \boxed{ArN_2^+X^-} \xrightarrow[pH = 9\text{-}10,\ 0\text{-}5°C]{C_6H_5OH/OH^-} ArN{=}NC_6H_4OH$$

Importance in Synthetic Organic Chemistry

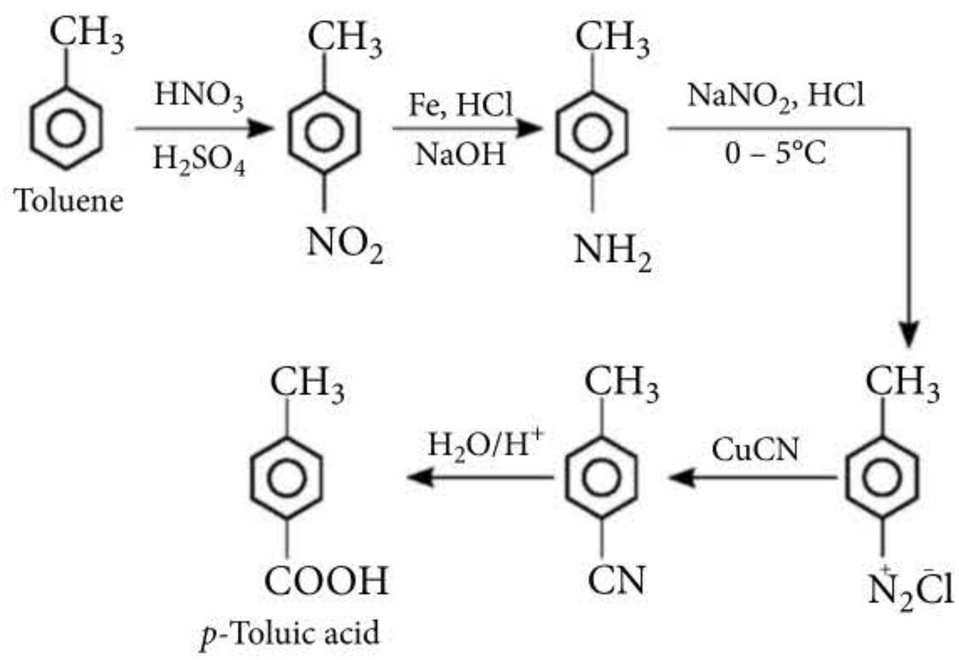
- Diazonium salts are highly useful intermediates in the synthesis of large variety of aromatic compounds. These are used for the preparation of many organic compounds especially aryl halides.

➢ **Synthesis of 3, 5-dibromotoluene :**



3, 5 -Dibromotoluene

➢ **Synthesis of *p*-toluic acid :**



p-Toluic acid

Similarly diazonium salts are used for the manufacture of azo dyes.

BIOMOLECULES

Carbohydrates

- Carbohydrates are defined as polyhydroxy aldehydes or ketones or substances that generally give these on hydrolysis and contain at least one chiral carbon, hence are optically active.
  Their general formula is $C_x(H_2O)_y$ where x and y can be 3, 4, 5, …, etc.

Classification of Carbohydrates

- Based on molecular size :

On the basis of the molecular size, carbohydrates have been classified into three types :

Monosaccharides

Oligosaccharides

Polysaccharides

- **Based on taste :**
  - Carbohydrates with sweet taste are called *sugars* while those without a sweet taste are called *non-sugars*.
  - All mono- and oligosaccharides are sugars while polysaccharides are non-sugars.
- **Based on reducing property :**

Reducing sugars
- Free aldehydic or ketonic group.
- Reduce Fehling's solution and Tollens' reagent
- *e.g.*, maltose and lactose.

Non-reducing sugars
- Do not have free aldehydic or ketonic group.
- Do not reduce Fehling's solution and Tollens' reagent.
- *e.g.*, Sucrose.

Glucose

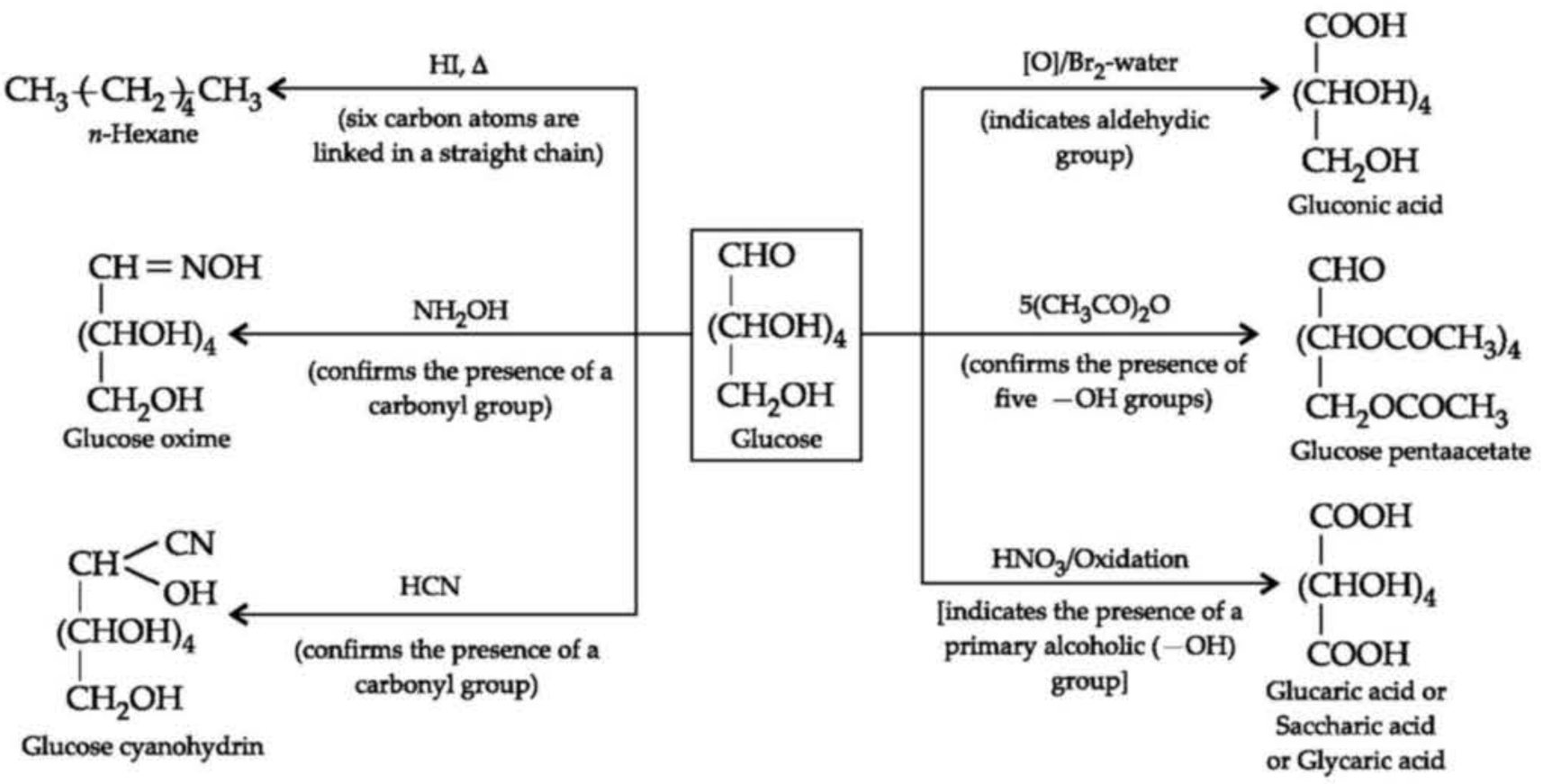
- Glucose ($C_6H_{12}O_6$) is an aldohexose as it has six carbon atoms and an aldehyde group.
- **Preparation**
  - Laboratory method :

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

  - **Commercial method :**

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

- **Structure**
  - Glucose was assigned open chain structure on the basis of following evidences :



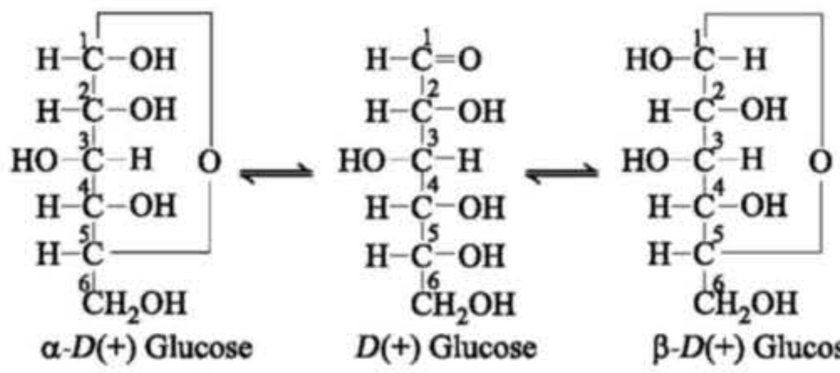
- The straight chain form of glucose explained most of its properties but could not explain a few reactions and observations like

(i) No reaction with 2,4-DNP and $NaHSO_3$.

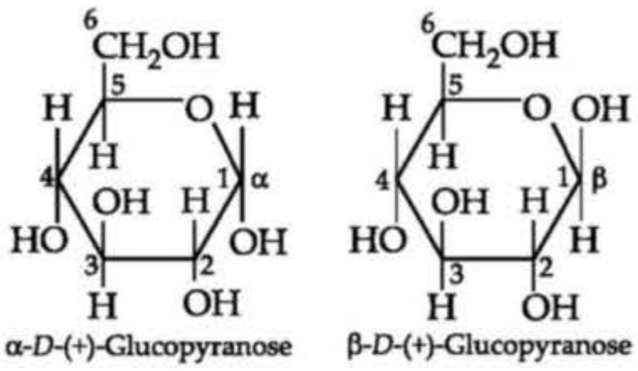
(ii) No reaction of its pentaacetate with NH_2OH.

(iii) Existence of α and β-forms of glucose.

These could however be explained by the cyclic structure of glucose which exists in equilibrium with the open chain form.



- The cyclic structure of glucose is represented by Haworth structure :


α-*D*-(+)-Glucopyranose

β-*D*-(+)-Glucopyranose

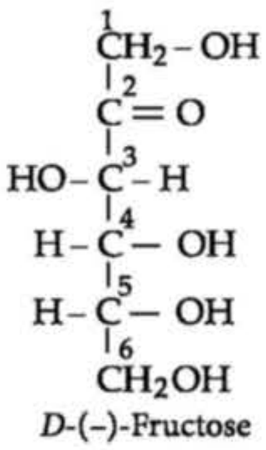
- **Mutarotation :** When these two anomeric forms are separately dissolved in water, they undergo a change in specific rotation till it becomes constant after some time. The change in specific rotation of isomers in aqueous solution is called mutarotation.

α-*D*-(+)-glucose $\rightleftharpoons$ Equilibrium $\rightleftharpoons$ β-*D*-(+)-glucose

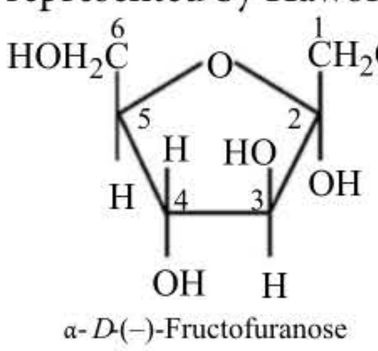
$[\alpha]^tD = 112°$ $[\alpha]^tD = +52.7°$ $[\alpha]^tD = +19°$

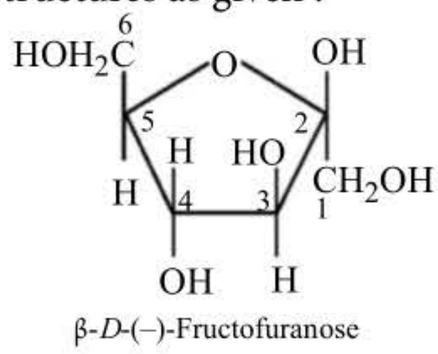
Fructose ($C_6H_{12}O_6$)

- It is present in abundance in fruits. Since naturally occurring fructose is laevorotatory, it is known as laevulose.


D-(–)-Fructose

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


α-*D*-(–)-Fructofuranose


β-*D*-(–)-Fructofuranose

Disaccharides and Polysaccharides

Carbohydrate	Hydrolysis products	Linkage	Reducing property
Sucrose (Disaccharide)	α-*D*-Glucose and β-*D*-Fructose	C-1 (Glucose) and C-2(Fructose)	Non-reducing
Maltose (Disaccharide)	α-*D*-Glucose	C-1 (Glucose) and C-4 (Glucose)	Reducing
Lactose (Disaccharide)	β-*D*-Galactose and β-*D*-Glucose	C-1 (Galactose) and C-4 (Glucose)	Reducing
Starch (Polysaccharide)	Amylose and Amylopectin	Amylose (C-1 and C-4 glycosidic linkage betweeen α-*D*-Glucose) Amylopectin (C-1 and C-4 linkage between α-*D*-Glucose and branching occurs by C-1 and C-6 linkage)	Non-reducing
Cellulose (Polysaccharide)	β-*D*-Glucose	C-1(Glucose) and C-4(Glucose)	Non-reducing
Glycogen (Polysaccharide)	α-*D*-Glucose	C-1 (Glucose) and C-4(Glucose)	Non-reducing

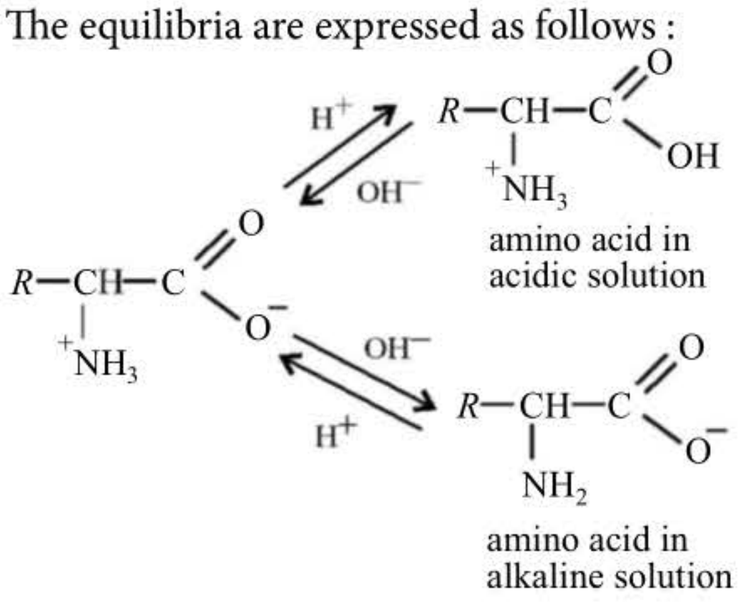
Proteins

Proteins are complex polyamides formed from amino acids. They are essential for proper growth and maintenance of body. They have many peptide (–CONH–) linkages. Therefore, proteins are long polymers of amino acids linked by peptide bonds (polypeptides).

Amino Acids

- Amino acids are colourless, non-volatile solids with high melting points, highly soluble in water yielding a neutral solution.

- Except glycine all amino acids have a chiral carbon and exist as optical isomers (*D* and *L* forms). All naturally occurring α-amino acids belong to the *L*-form.
- **Chemical properties of α-amino acids :**
  Since these form salt with acids as well as with bases, their chemical reactions are similar to primary amines and carboxylic acids.
  - The equilibria are expressed as follows :



  - **Isoelectric point :** The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, +ve and –ve charge is equal and it does not migrate to either electrode, is called isoelectric point. Amino acids have least solubility at isolelectric point which helps in their separation.

Classification of Proteins

Fibrous proteins

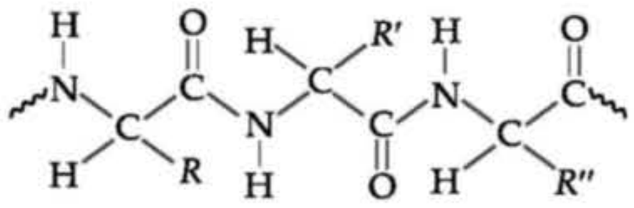
In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin and myosin.

Globular proteins

Globular proteins results when the polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, *e.g.*, insulin and albumins.

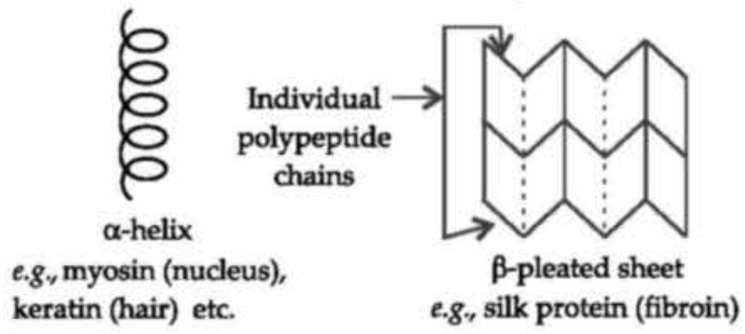
Structure

- **Primary structure :** It refers to the number and linear sequence of amino acids held together by peptide bonds.



Primary structure

- **Secondary structure:** It is due to folding or coiling of the peptide chain. It is mainly of two types :
  - **α-Helix :** These coils are stabilized by hydrogen bonds between carbonyl oxygen of first amino acid to amide nitrogen of fourth amino acid.
  - **β-Pleated sheet structure :** β-pleated sheet structure is formed when hydrogen bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains. The bonding in β-pleated sheet structure is intermolecular H-bonding. The structure is not planar but is slightly pleated. Silk fibroin is rich in β-pleated sheets.



- **Tertiary structure :** It represents overall folding of the polypeptide chains, *i.e.*, further folding of the secondary structure and the bonds responsible for such interaction are hydrophobic interactions, hydrogen bonds, ionic interactions, van der Waals' forces and disulphide bonds.
- **Quaternary structure :** The spatial arrangement of the subunits (two or more polypeptide chains) with respect to each other.

Denaturation of proteins

- When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix gets uncoiled and protein loses its biological activity. This is called denaturation of protein.
- The denaturation causes change in secondary and tertiary structures but primary structure remains intact.

Nucleic Acids

Nucleic acids are polynucleotides present in the nuclei of all living cells in the form of nucleoproteins.

- There are three basic components of each nucleotide monomeric unit, *viz*, pentose sugar, nitrogenous base and phosphate group.

Classification of Nucleic Acid

Components	Deoxyribonucleic Acid (DNA)	Ribonucleic Acid (RNA)
Sugar	2-deoxy-*D*-(–) ribose	*D*-(–)ribose
Pyrimidine base	Cytosine and thymine	Uracil and cytosine
Purine base	Adenine and guanine	Adenine and guanine
Phosphoric acid	H_3PO_4	H_3PO_4
Structure	Double stranded α-helix	Single stranded α-helix
Replication	Possible	Not possible

Chargaff's Rule

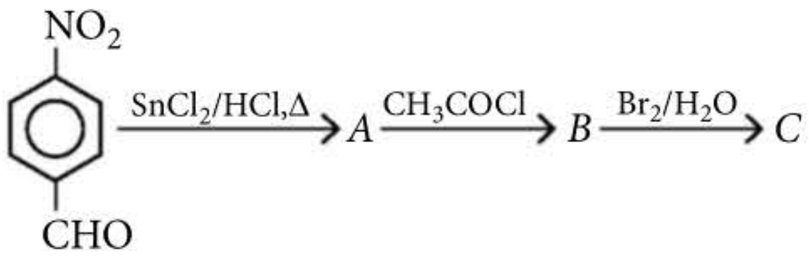
- The rule describes base composition of a DNA molecule.
  - ➢ It states that amount of purine bases is always equal to that of pyrimidine bases.
  - ➢ Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand.
  - ➢ Adenine (A) pairs with thymine (T) through two H-bonds (A ═ T) and guanine (G) pairs with cytosine (C) through three H-bonds (G ≡ C).
  - ➢ In case of RNA, adenine (A) pairs with uracil (U), (A ═ U).

Biological Functions of Nucleic Acids

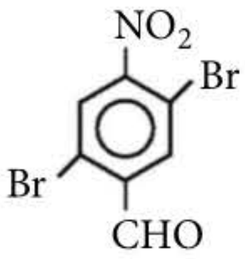
- **Replication :** It is the enzyme catalysed process by which a single DNA molecule produces two identical copies of itself.
- **Protein synthesis :** It is carried out by RNA molecules in two steps :
  - ➢ **Transcription :** It is the process of synthesis of RNA from DNA in the cytoplasm of the cell.
  - ➢ **Translation :** The *m*-RNA directs the protein synthesis by this process.
- **Genetic code :** Linear sequences of three nucleotides (triplets) in DNA or RNA that determines the specific amino acid sequence in the synthesis of proteins is called genetic code. It is the biochemical basis of heredity and nearly universal in all organisms.
- **Mutation :** It is a change in nitrogenous base sequence of DNA molecule which leads to the synthesis of proteins with an altered sequence of amino acids. Mutation may cause genetic disorders or diseases.

SPEED PRACTICE

1. In the given reaction,

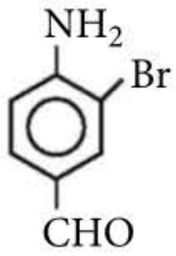


product *C* is

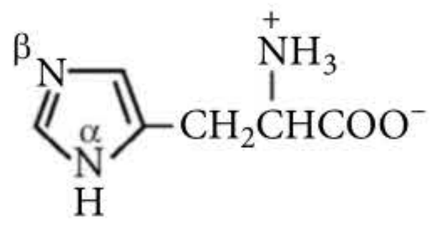
(a) 

(b) 

(c) Both (a) and (b)

(d) 

2. Which of the nitrogen of histidine is first protonated?



(a) α-N (b) β-N

(c) Both α-N and β-N (d) None of these

3. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give *P* (51 %), *Q* (47%) and *R* (2%). The major product(s) of the following reaction sequence is (are)