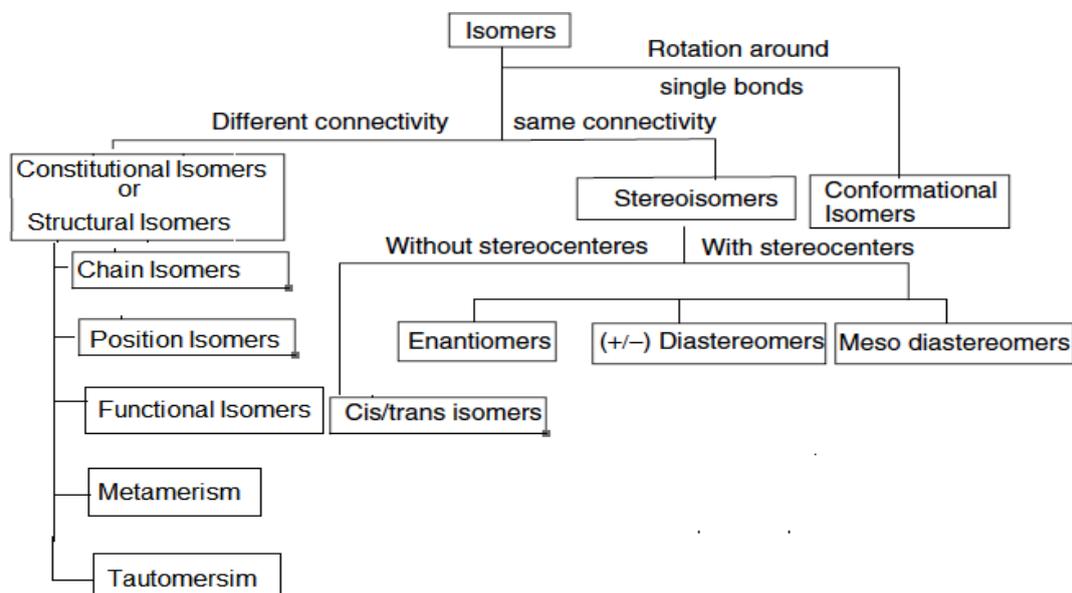


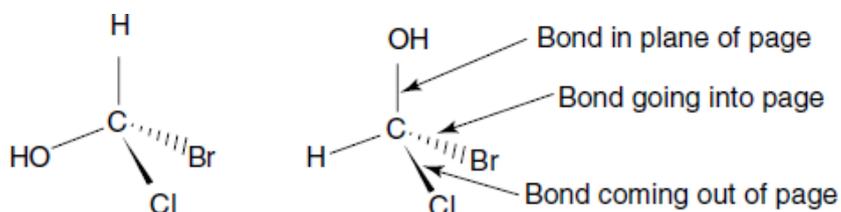
## UNIT –I: Structural isomerisms in organic compounds

- *Isomers* are compounds that have the same formula but different structures.
- The three main types of isomers are constitutional isomers, conformational isomers and stereoisomers.
- Stereoisomers have the same connectivity but a different spatial orientation. Stereoisomers do not differ from each other as a result of rotation around single (sigma) bonds. They are different compounds.



### ❖ CONNECTIVITY

- The term connectivity means all the atoms in a molecule are connected in the same sequence.
- For a molecule containing atoms A, B, and C; one connectivity is A-B-C while A-C-B is a different connectivity. Both have the same connectivity but the atoms have a different orientation in space.



- The same atoms or groups are connected to the central carbon atom. The connectivity is the same, but OH and H are oriented differently in space. To change the positions of H and OH, one would have to break the H-C and HO-C bonds and connect them in the reverse order.
- The two compounds differ in their connectivity: **C-O-C** and **C-C-O**





## UNIT –I: Structural isomerisms in organic compounds

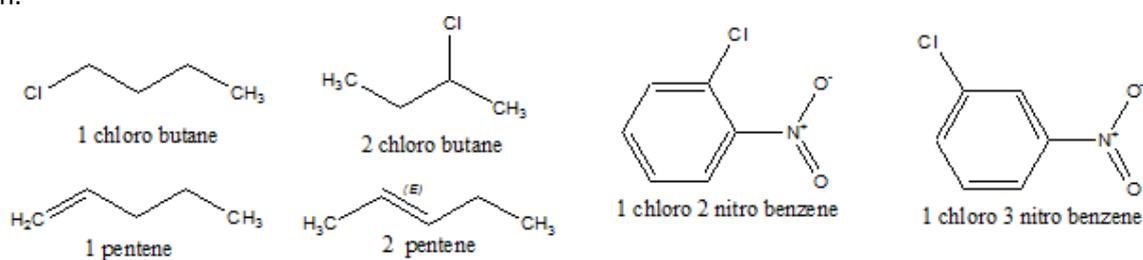
- ✓ Number of possible chain-isomers for Alkane

Molecular Formula	Possible Number of Constitutional Isomers
C <sub>4</sub> H <sub>10</sub>	2
C <sub>5</sub> H <sub>12</sub>	3
C <sub>6</sub> H <sub>14</sub>	5
C <sub>7</sub> H <sub>16</sub>	9
C <sub>8</sub> H <sub>18</sub>	18
C <sub>9</sub> H <sub>20</sub>	35
C <sub>10</sub> H <sub>22</sub>	75

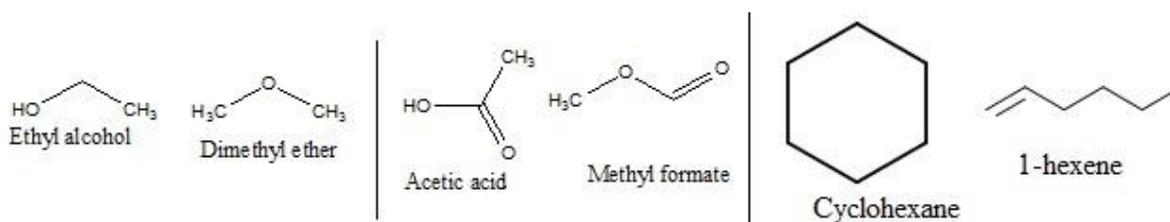
- ✓ Physical Constants of the Hexane Isomers

Physical Constants of the Hexane Isomers Molecular Formula	Structural Formula	mp (°C)	bp (°C) (1 atm)	Index of Refraction ( <i>n<sub>D</sub></i> 20°C)
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-95	68.7	1.3748
C <sub>6</sub> H <sub>14</sub>	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	-153.7	60.3	1.3714
C <sub>6</sub> H <sub>14</sub>	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	-118	63.3	1.3765
C <sub>6</sub> H <sub>14</sub>	$\begin{array}{c} \text{CH}_3\text{CH} - \text{CHCH}_3 \\   \quad \quad   \\ \text{H}_3\text{C} \quad \quad \text{CH}_3 \end{array}$	-128.8	58	1.3750
C <sub>6</sub> H <sub>14</sub>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C} - \text{C} - \text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	-98	49.7	1.3688

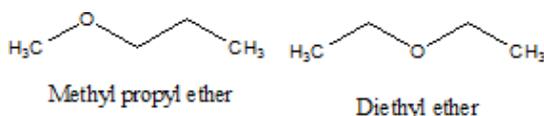
- ii. **Position isomerism:** It has the same molecular formula but differ in the position of a functional group on the carbon chain.



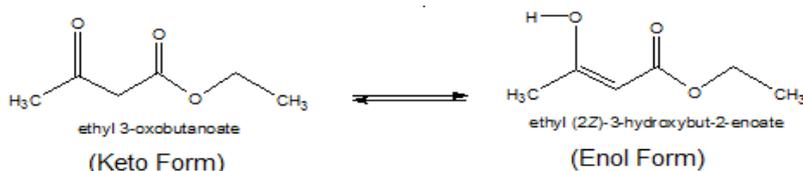
- iii. **Functional isomerism:** It has the same molecular formula but different functional groups.



- iv. **Metamerism:** This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group. Member belongs in the same homologous series.

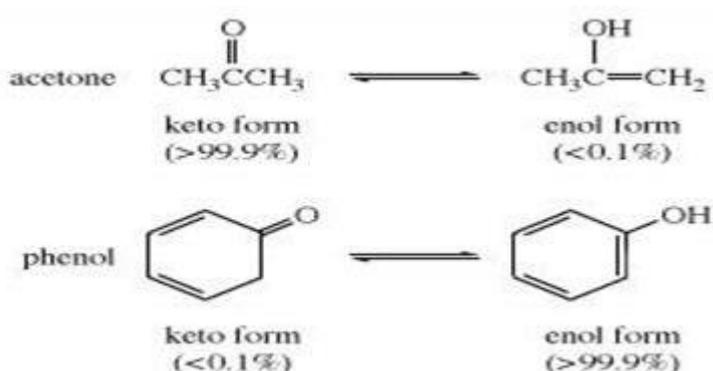


- v. **Tautomerism:** This is special type of functional isomerism in which the isomers are dynamic equilibrium with each other.



### ❖ Tautomerism

- Tautomers are isomers of a compound which differ only in the position of the protons and electrons. The carbon skeleton of the compound is unchanged. A reaction which involves simple proton transfer in an intramolecular fashion is called a tautomerism.
- Sometimes the term tautomerism is also called as desmotropism (In Greek desmos-bond; tropos-turn), since the interconversion of the two forms involves a change of bonds or dynamic isomerism as the two forms are in dynamic equilibrium with each other.
- Other names for tautomerism are kryptomerism, allelotropism or merotropy; however, tautomerism is the most widely accepted term.
- There are several types of tautomerism of which keto-enol tautomerism is the most important. In this type, one form (tautomer) exists as a ketone while the other exists as an enol. The two simplest examples are of acetone and phenol. The conversion of a keto form into enol form is known as enolisation.



- The most widely studied example of keto-enol tautomerism is that of **acetoacetic ester** (ethyl acetoacetate).



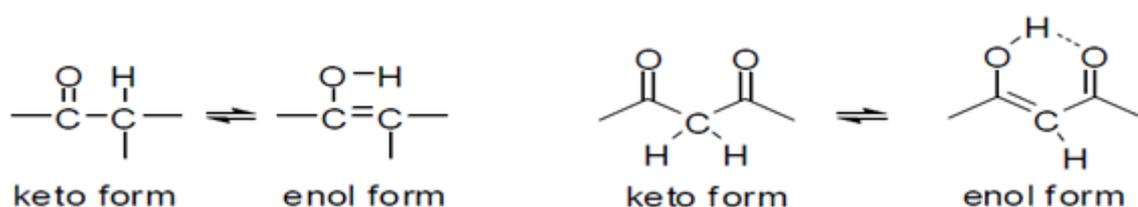
- **Why the KETO form is more stable than ENOL:** In most keto-enol tautomerisms, the equilibrium lies by far toward the keto form, indicating that the keto form is usually much more stable than the enol form, which can be attributed to the fact that a carbon-oxygen double bond is significantly stronger than a carbon-carbon double bond.

## UNIT –I: Structural isomerisms in organic compounds

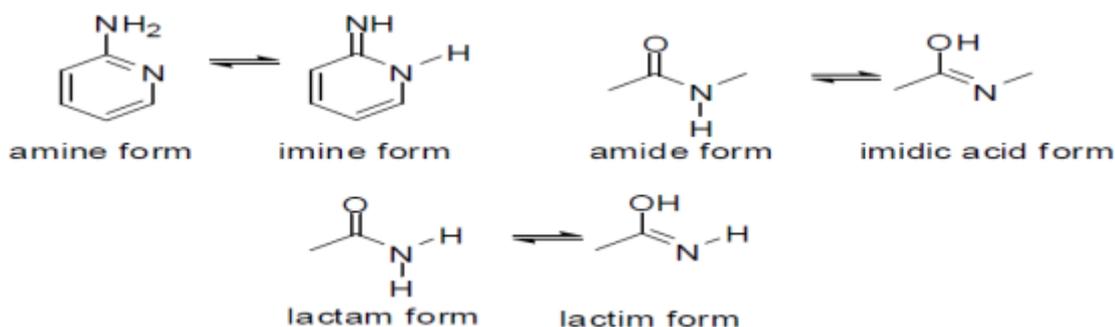
- **Are Tautomers stereoisomers:** No, Tautomers are Structural Isomerism or Constitutional Isomers. Tautomers are two molecules with the same molecular formula but different connectivity - constitutional isomers, in other words - which can interconvert in a rapid equilibrium. The most common tautomeric relationship in organic chemistry is the keto-enol pair.
- Types of tautomerism:
  1. Prototropic tautomerism
  2. Annular tautomerism
  3. Non-prototropic tautomerism
  4. Ring-chain tautomerism
  5. Valence tautomerism

### 1) Prototropic Tautomerism

- **Prototropic tautomerism** involves the relocation of an **H atom** and a **double bond**.
- One example of prototropic tautomerism is that between **keto** and **enol** forms.
- The **keto tautomer** possesses a **C=O** group, while the **enol form** has a **vinyl alcohol structure**. Increasing acidity of the **α-H** affects this tautomerism, favoring the **enol form**.
- **Conjugated double bonds** and intramolecular **H-bonds** can also stabilize the **enol form**.

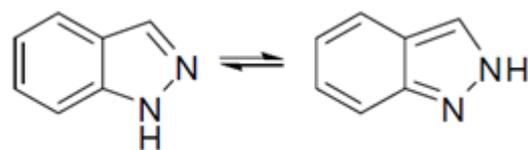
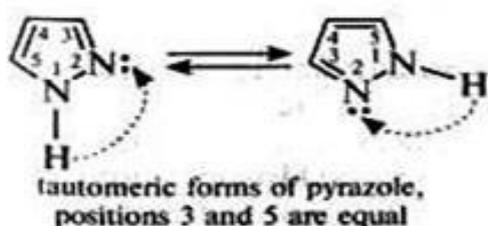


- Other types of **prototropic tautomerism** are **amine-imine tautomerism** (e.g. in adenines), **amide-imidic acid tautomerism** (related to asparagine-linked glycosylation) and, as a special case, **lactam-lactim tautomerism** (present in uracil and thymine).



### 2) Annular Tautomerism

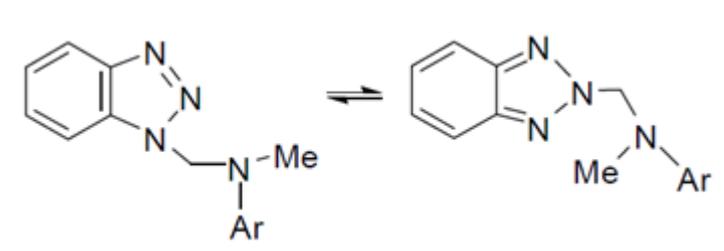
- This is a special case of prototropic tautomerism, where an H can occupy two or more possible locations in a heterocyclic system, e.g. imidazole, which can have **1H** and **2H** tautomers.



1H and 2H tautomers of imidazole

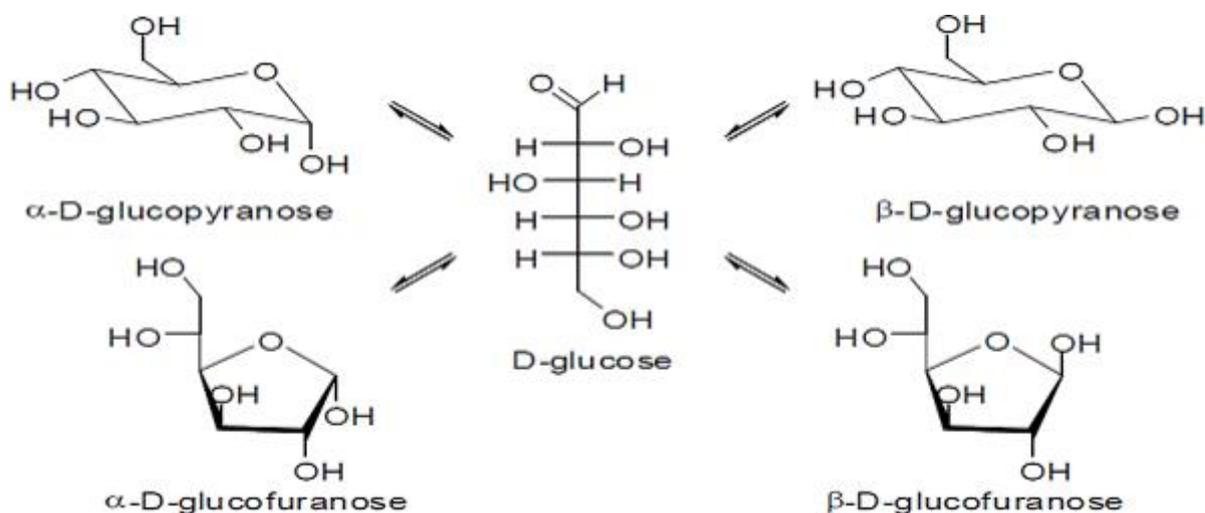
### 3) Non-Prototropic Tautomerism

- Non-prototropic tautomerism involves the relocation of a substituent other than H, e.g. the tautomerism of 1- and 2-(N,N-disubstituted aminomethyl)benzotriazoles.



#### 4) Ring-Chain Tautomerism

- In ring-chain tautomerism, a structural change occurs between an **open-chain** form and a **ring form** through an **H-transfer**.
- This is an important process for monosaccharides such as sugars. Glucose is a well-known example, which can exist in five different tautomeric forms in solution. Ring-chain tautomerism was first discovered by Sir Emil Fischer in the 1890.



#### 5) Valence Tautomerism

- Valence tautomerism involves the reorganization of bonding electrons, which results in changes in molecular geometry.



*1,3,5-cyclo-octatriene*

*bicyclo[4.2.0]octa-2,4-diene*

#### • Difference of Tautomerism from Resonance

1. **Tautomerism** involves a change in the position of atom (generally hydrogen), while **Resonance** involves a change in the position of the unshared or  $\pi$  electron.
2. **Tautomers** are definite compounds and may be separated and isolated. **Resonating structures** are only imaginary and can't be isolated.
3. The two tautomeric forms have different structures (i.e. functional groups). The various resonating structures have the same functional group.
4. **Tautomers** are in dynamic equilibrium with each other, resonating structures are not in dynamic equilibrium.
5. **Tautomerism** has no effect on bond length, while **Resonance** affects the bond length.
6. **Tautomerism** does not lower the energy of the molecule and hence does not play any role in stabilising the molecule, while **Resonance** decreases the energy and hence increases the stability of the molecule.
7. **Tautomerism** can occur in planar as well as non-planar molecules, while **Resonance** occurs only in planar molecules.
8. **Tautomerism** is indicated by ( $\rightleftharpoons$ ) whereas **Resonance** by ( $\longleftrightarrow$ )