Constitutional or structural isomerism.

(1) **Chain, nuclear or skeleton isomerism:**This type of isomerism is arises due to the difference in the nature of the carbon chain (i.e., straight or branched) which forms the nucleus of the molecule.

Examples:

(i) **C_4H_{10}:** $\underset{n-\text{Butane}}{CH_3-CH_2-CH_2-CH_3}$, $\underset{\text{Isobutane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3}$

(ii) **C_5H_{12}:** (Three) $\underset{n-\text{Pentane}}{CH_3-CH_2-CH_2-CH_2-CH_3}$, $\underset{\text{Isopentane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3}$, $\underset{Neopentane}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3}$

(iii) **C_4H_8:** $\underset{\alpha-\text{butylene}}{CH_3-CH_2-CH=CH_2}$, $\underset{\text{Isobutylene}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2}$

(iv) **C_5H_8:** $\underset{\text{1-Pentyne}}{HC\equiv C-CH_2-CH_2-CH_3}$, $\underset{\text{2-Methyl-1-butyne}}{HC\equiv \underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-CH_3}$

(v) **C_4H_7N:** $\underset{\text{Butane nitrile}}{\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}N}$ $\underset{\text{2-Methyl propane nitrile}}{CH_3-\underset{\displaystyle {}_1CN}{\overset{2}{\underset{|}{C}}}H-\overset{3}{C}H_3}$

Note: Except alkynes chain isomerism is observed when the number of carbon atoms is four or more than four.

Chain isomers differ in the nature of carbon chain, i.e., in the length of carbon chain.

The isomers showing chain isomerism belong to the same homologous series, i.e., functional group, class of the compound (Cyclic or open) remains unchanged.

Chain and position isomerism cannot be possible together between two isomeric compounds. If two compounds are chain isomers then these two will not be positional isomers.

(2) **Position isomerism:**It is due to the difference in the position of the substituent atom or group or an unsaturated linkage in the same carbon chain.

Examples:

(i) **$C_4H_{10}O$:** $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$, $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

Isobutylal cohol — t–Butyl alcohol

(ii) **$C_3H_6Cl_2$:** $CH_3-CCl_2-CH_3$, $CH_3-CH_2-CH-Cl_2$, $CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$,

2,2–Dichloro propane, — 1,1–Dichloro propane — 1,2–Dichloro propane

$\underset{\underset{Cl}{|}}{CH_2}-CH_2-\underset{\underset{Cl}{|}}{CH_2}$

1,3–Dichloro propane

[Gem-two, vic-one and α,ω-one]

(iii) **C_4H_8:** $CH_3-CH_2-CH=CH_2$, $CH_3-CH=CH-CH_3$

1–Butene — 2–Butene

(iv) **C_4H_6:** $CH_3-CH_2-C\equiv CH$, $CH_3-C\equiv C-CH_3$, $CH_2=C=CH-CH_3$,

1–Butyne — 2–Butyne — 1,2–Butadiene

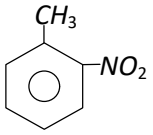
$CH_2=CH-CH=CH_2$

1,3–Butadiene

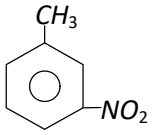
(v) **$C_3H_6O_2$:** $CH_3-\underset{\underset{OH}{|}}{CH}-CHO$, $\underset{\underset{OH}{|}}{CH_2}-CH_2-CHO$

2–Hydroxy propanal — 3–Hydroxy propanal

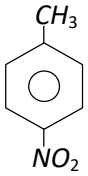
(vi) **$C_7H_7NO_2$ (Three aromatic):**



o - Nitrotoluene

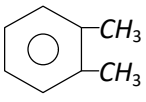


m - Nitrotoluene

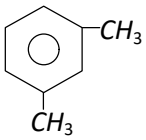


p - Nitrotoluene

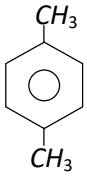
(vii) **C_8H_{10} (Three aromatic):**



o - Xylene

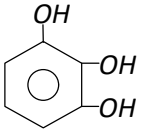


m - Xylene

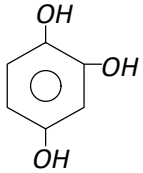


p - Xylene

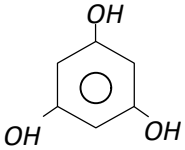
(viii) **$C_6H_3(OH)_3$ (Three aromatic):**



Paragallol

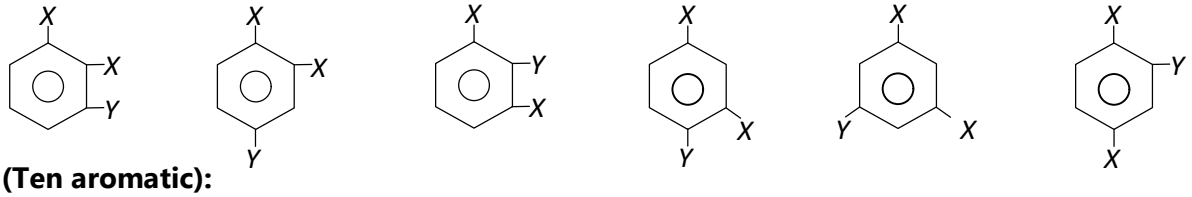


1,2,4 - Trihydroxybenzene

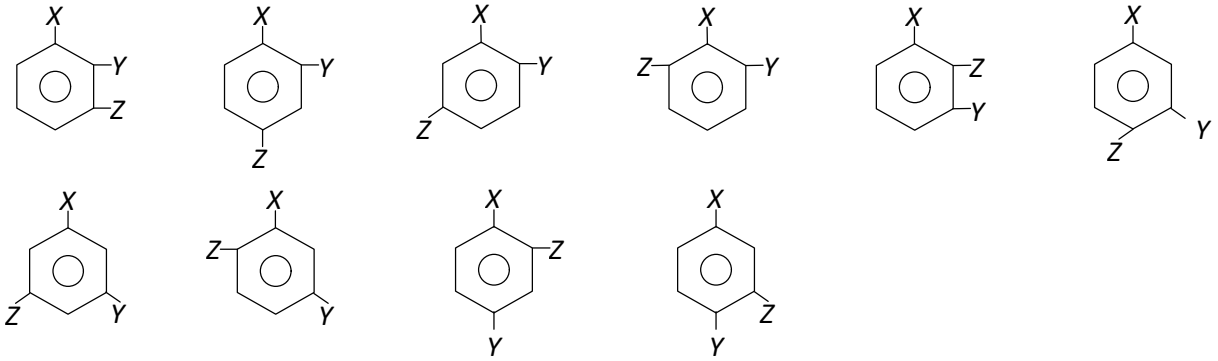


Phloroglucinol

(ix) **$C_6H_3X_2Y$ (Six aromatic):**



(x) **C_6H_3XYZ (Ten aromatic):**



(xi) **C_6H_{14}:** $CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_2-CH_3$, $CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_3$

2 – Methylpent ane 3 – Methylpent ane

(xii) **$C_4H_{11}N$:** $CH_3-NH-CH_2-CH_2-CH_3$ $CH_3-NH-\underset{\underset{CH_3}{|}}{C}H-CH_3$

N – Methyl-1-propaneami ne *N* – Methyl-2-propaneami ne

Note: Aldehydes, carboxylic acids (and their derivatives) and cyanides do not show position isomerism.

Monosubstituted alicylic compounds and aromatic compounds do not show position isomerism.

Structural isomers which differ in the position of the functional group are called regiomers. For example,

(i) $CH_3-CH_2-CH_2-OH$ (ii) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(3) **Functional isomerism:**This type of isomerism is due to difference in the nature of functional group present in the isomers. The following pairs of compounds always form functional isomers with each other.

Examples:

(i) **Alcohols and ethers ($C_n H_{2n+2}O$)**

C_2H_6O : $\underset{\text{Ethyle alcohol}}{CH_3-CH_2-OH}$; $\underset{\text{Dimethyl ether}}{H_3C-O-CH_3}$

C_3H_8O : $\underset{n-\text{propyl alcohol}}{CH_3-CH_2-CH_2-OH}$; $\underset{\text{Ethyl methyl ether}}{C_2H_5-O-CH_3}$

$C_4H_{10}O$: $\underset{n-\text{Butyl alcohol}}{CH_3-CH_2-CH_2-CH_2-OH}$; $\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}$

(ii) **Aldehydes, ketones and unsaturated alcohols …etc. ($C_n H_{2n}O$)**

C_3H_6O : $\underset{\text{Propionald ehyde}}{CH_3-CH_2-CHO}$; $\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$; $\underset{\text{1,2-Epoxy propane}}{CH_2-\underset{\diagdown\,\diagup}{CH}-CH_3}$; $\underset{\text{Allylalcohol}}{CH_2=CH-CH_2OH}$

(iii) **Acids, esters and hydroxy carbonyl compounds …etc.($C_n H_{2n}O_2$)**

$C_2H_4O_2$: $\underset{\text{Acetic acid}}{CH_3COOH}$; $\underset{\text{Methyl formate}}{HCOOCH_3}$

$C_3H_6O_2$: $\underset{\text{Propionic acid}}{CH_3-CH_2-COOH}$; $\underset{\text{Methyl acetate}}{CH_3COOCH_3}$; $\underset{\text{2-Hydroxy propanal}}{CH_3\underset{\underset{OH}{|}}{C}HCHO}$; $\underset{\text{1-Hydroxy propan-2-one}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-OH}$

(iv) **Alkynes and alkadienes($C_n H_{2n-2}$)**

C_4H_6 : $\underset{\text{1-Butyne}}{CH_3-CH_2-C\equiv CH}$; $\underset{\text{1,3-Butadiene}}{H_2C=CH-CH=CH_2}$; $\underset{\text{2-Butyne}}{CH_3-C\equiv C-CH_3}$;

$\underset{\text{1,2-Butadiene}}{H_2C=C=CH-CH_3}$

(v) **Cyanides and isocyanides** ($-CN$ and $-NC$)

C_2H_3N : CH_3CN ; CH_3NC

Methyl cyanide; Methyle isocyanide

(vi) **Nitro alkanes and alkyl nitrites(** $-NO_2$ **and** $-O-N=O$ **)**

$C_2H_5NO_2$: $C_2H_5-N\begin{matrix}O\\O\end{matrix}$; $C_2H_5-O-N=O$

Nitro ethane; Ethyl nitrite

(vii) **Amines** (Primary, secondary and tertiary)

C_3H_9N : $CH_3-CH_2-CH_2-NH_2$; $CH_3-CH_2-N\begin{matrix}H\\CH_3\end{matrix}$

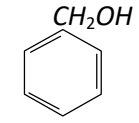
Propan -1- amine; N–Methyl ethanamine

$CH_3-\underset{\underset{NH_2}{|}}{C}H-CH_3$; $CH_3-N\begin{matrix}CH_3\\CH_3\end{matrix}$

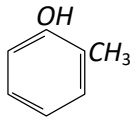
Propan -2- amine; N,N–Dimethyl methanamin e

(viii) **Alcohols and phenols**

C_7H_8O ;



Benzylalcohol



o-Cresol

(ix) **Oximes and amides**

C_2H_5NO : $CH_3-CH=NOH$; $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

Acetaldoxime; Acetamide

(x) **Thio alcohols and thio ethers**

C_2H_6S : C_2H_5SH ; CH_3-S-CH_3

Ethyl thioalcoho l; Dimethyl thioether

(4) **Ring-chain isomerism:**This type of isomerism is due to different modes of linking of carbon atoms, i.e., the isomers possess either open chain or closed chain structures.

Examples:

(i) **C_3H_6 :** $\underset{\text{Propene}}{CH_3-CH=CH_2}$; $\underset{\text{Cyclopropa ne}}{H_2C-CH_2}$ (with CH_2 above)

(ii) **C_4H_8 :** $\underset{1-\text{Butene}}{CH_3-CH_2-CH=CH_2}$; $\underset{\text{Cyclobutan e}}{H_2C(-CH_2)-CH_2-CH_2}$; $\underset{\text{Methyl cyclopropa ne}}{H_2C-CH(CH_3)}$ (with CH_2 above)

(iii) **C_6H_{12} :** $\underset{\text{Cyclohexan e}}{H_2C(-CH_2-CH_2-CH_2-CH_2-CH_2-)CH_2}$; $\underset{\text{Methyle cyclopenta ne}}{CH_2(-CH_2-CH_2-CH_2-CH_2-)CH(CH_3)}$; $\underset{1-\text{Hexene}}{CH_3CH_2CH_2CH_2CH=CH_2}$

Note: Ring – chain isomers are always functional isomers.

(5) **Metamerism :** This type of isomerism is due to the difference in the nature of alkyl groups attached to the polyvalent atoms or functional group. Metamers belong to the same homologous series. Compounds like ethers, thio-ethers ketones, secondary amines, etc. show metamerism.

Examples:

(i) **$C_4H_{10}O$:** $\underset{\text{Diethyl ether}}{C_2H_5-O-CH_3}$; $\underset{\text{Methyl propyl ethers}}{C_3H_7-O-CH_3}$

(ii) **$C_5H_{10}O$:** $\underset{\text{Diethyl ketone}}{C_2H_5-CO-C_2H_5}$; $\underset{\text{Methyl pro pyl ketone}}{C_3H_7-CO-CH_3}$

(iii) **$C_4H_{11}N$:** $\underset{\text{Diethyl amine}}{C_2H_5-NH-C_2H_5}$; $\underset{\text{Methyl pro pyl amine}}{C_3H_7-NH-CH_3}$

(iv) **$C_5H_{13}N$:** $\underset{\text{Dimethyl p ropyl amine}}{C_3H_7-N\begin{matrix}CH_3\\CH_3\end{matrix}}$; $\underset{\text{Diethyl methyl amine}}{C_2H_5-N\begin{matrix}C_2H_5\\CH_3\end{matrix}}$

(v) **$C_6H_{15}N$:** $\underset{\text{Dipropyl amine}}{C_3H_7-NH-C_3H_7}$; $\underset{\text{Ethyl buty l amine}}{C_2H_5-NH-C_4H_9}$

Note: If same polyvalent functional group is there in two or more organic compounds, then never write chain or position isomerism, it will be metamerism e.g.,

(a) $\underset{\text{(Pentan }-2-\text{one)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3}$; $\underset{\text{(Pentan }-3-\text{one)}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$ are metamers and not position isomers.

(b) $\underset{\text{(Pentan }-2-\text{one)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3}$; $\underset{\text{(3-Methylbuta n-2-one)}}{CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}H-CH_3}$ are metamers and not chain isomers.

Alkenes does not show metamerism.

(6) **Tautomerism**

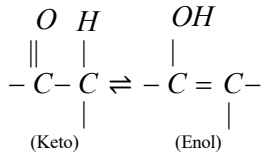
(i) The type of isomerism in which a substance exist in two readily interconvertible different structures leading to dynamic equilibrium is known as tautomerism and the different forms are called **tautomers** (or tautomerides).

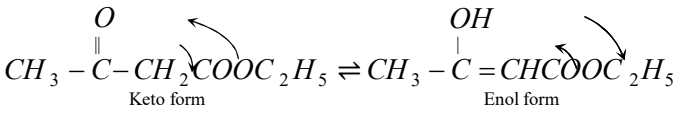
The term **tautomerism** (Greek: tauto = same; meros = parts) was used by **Laar** in 1885 to describe the phenomenon of a substance reacting chemically according to two possible structures.

(ii) It is caused by the wandering of hydrogen atom between two polyvalent atoms. It is also known as **Desmotropism** (Desmos = bond and tropos = turn). If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is a **dyad** and if the hydrogen atom travels from first to third in a chain, the system is a **triad**.

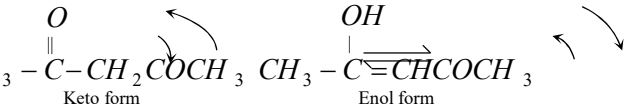
(a) Dyad system: Hydrocyanic acid is an example of dyad system in which hydrogen atom oscillates between carbon and nitrogen atoms. $H-C\equiv N \rightleftharpoons C \cong N-H$

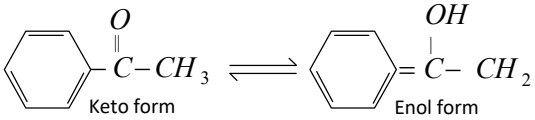
(b) Triad system Keto-enol system: Polyvalent atoms are oxygen and two carbon atoms.
Examples:

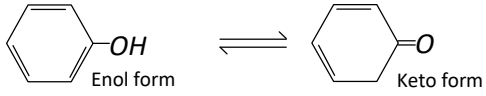


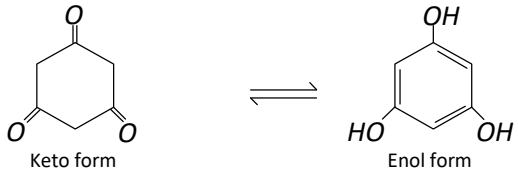
Acetoacetic ester (Ethyl acetoacetate): 

Acetoacetic ester gives certain reactions showing the presence of keto group (Reactions with HCN, H_2NOH, $H_2NNHC_6H_5$, etc.) and certain reactions showing the presence of enolic group (Reactions with $Na, CH_3COCl, NH_3, PCl_5, Br_2$ water and color with neutral $FeCl_3$, etc.).

Acetyl acetone: 

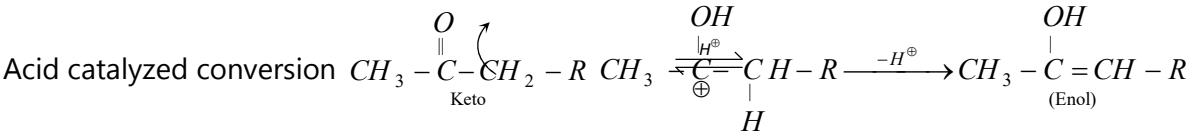




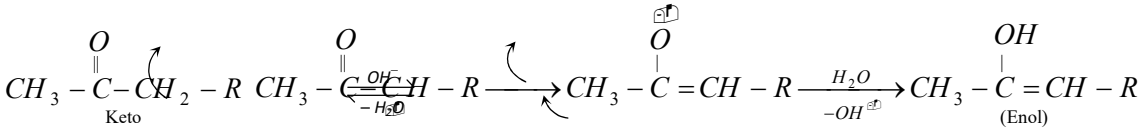


Enolisation is in order

$$CH_3COCH_3 < CH_3COCH_2COOC_2H_5 < C_6H_5COCH_2COOC_2H_5 < CH_3COCH_2COCH_3 < CH_3COCH_2CHO$$

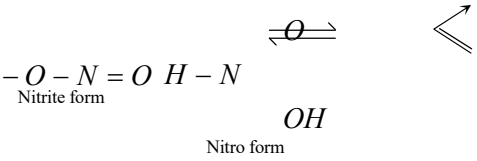
Acid catalyzed conversion 

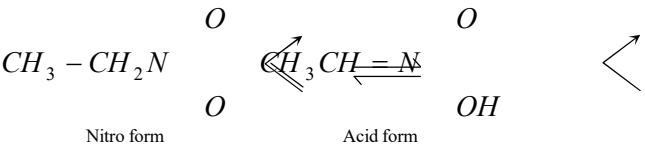
Base catalyzed conversion



Triad system containing nitrogen

Examples:

Nitrous acid: 

Nitroethane: 

(iii) **Characteristics of tautomerism**

(a) Tautomerism (cationotropy) is caused by the oscillation of hydrogen atom between two polyvalent atoms present in the molecule. The change is accompanied by the necessary rearrangement of single and double bonds.

(b) It is a reversible intramolecular change.

(c) The tautomeric forms remain in dynamic equilibrium. Hence, their separation is a bit difficult. Although their separation can be done by special methods, yet they form a separate series of stable derivatives.

(d) The two tautomeric forms differ in their stability. The less stable form is called the labile form. The relative proportion of two forms varies from compound to compound and also with temperature, solvent etc. The change of one form into another is also catalyzed by acids and bases.

(e) Tautomers are in dynamic equilibrium with each other and interconvertible (⇌).

(f) Two tautomers have different functional groups.

(g) Tautomerism has no effect on bond length.

(h) Tautomerism has no contribution in stabilizing the molecule and does not lower its energy.

(i) Tautomerism may occur in planar or nonplanar molecules.

Note: Keto=enol tautomerism is exhibited only by such aldehydes and ketones which contain at least one α -hydrogen. For example $CH_3CHO, CH_3CH_2CHO, CH_3COCH_2COCH_3$.

Tautomerism is not possible in benzaldehyde (C_6H_5CHO), benzophenone $(C_6H_5COC_6H_5)$, tri methyl acetaldehyde, $(CH_3)_3C-CHO$ and chloral CCl_3-CHO as they do not carry $\alpha-H$.

Number of structural isomers

Molecular formula	**Number of isomers**
Alkanes	
C_4H_{10}	Two
C_5H_{12}	Three
C_6H_{14}	Five
C_7H_{16}	Nine
C_8H_{18}	Eighteen
C_9H_{20}	Thirty five
$C_{10}H_{22}$	Seventy five
Alkenes and cycloalkanes	
C_3H_6	Two (One alkene + one cycloalkane)
C_4H_8	Six (Four alkene + 2 - cycloalkane)
C_5H_{10}	Nine (Five alkenes + 4 – cycloalkanes)
Alkynes	
C_3H_4	Two
C_4H_6	Six
Monohalides	
C_3H_7X	Two

C_4H_9X	Four
$C_5H_{11}X$	Eight
Dihalides	
$C_2H_4X_2$	Two
$C_3H_6X_2$	Four
$C_4H_8X_2$	Nine
$C_5H_{10}X_2$	Twenty one
Alcohols and ethers	
C_2H_6O	Two (One alcohol and one ether)
C_3H_8O	Three (Tow alcohols and one ether)
$C_4H_{10}O$	Seven (Four alcohols and three ethers)
$C_5H_{12}O$	Fourteen (Eight alcohols and six ethers)
Aldehydes and ketones	
C_3H_6O	Two (One aldehyde and one ketone)
C_4H_8O	Three (Two aldehydes and one ketone)
$C_5H_{10}O$	Three (Four aldehydes and three ketone)
Monocarboxylic acids and esters	
$C_2H_4O_2$	Two (One acid and one ester)
$C_3H_6O_2$	Three (One acid and two esters)
$C_4H_8O_2$	Six (Two acids and four esters)
$C_5H_{10}O_2$	Thirteen (Four acids and nine esters)
Aliphatic amines	
C_2H_7N	Two (One 1°-amine and one 2°-amine)
C_3H_9N	Four (Two 1°-amines, one 2°-amine and one 3°-amine)
$C_4H_{11}N$	Eight (Four 1°-amines, three 2°-amines and one 3°-amines)
Aromatic compounds	
C_8H_{10}	Four
C_9H_{12}	Nine
C_7H_8O	Five