

FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY

Learning outcomes

The learners will be able to:

- Define and classify isomerism in organic compounds (structure isomerism, types of structure isomerism: chain isomerism, position isomerism, functional isomerism, metamerism and tautomerism).
- State and explain the concept of geometrical isomerism (cis&trans) & optical isomerism (d & l form).

13.3 Isomerism in Organic Compounds

Isomers are different types of compounds possessing the same molecular formula, and the phenomenon by which **different compounds are represented by the same molecular formula** is called isomerism.

13.4 Definition and classification of isomerism

Isomers are different types of compounds possessing the same molecular formula, and the phenomenon by which different compounds are represented by the same molecular formula is called isomerism.

Types of isomerism:

Isomerism is of two different types:

1. Structural isomerism
2. Stereoisomerism

72/67) Define isomerism.

13.5 Structural isomerism and its types: chain isomerism, position isomerism, functional isomerism, metamerism and tautomerism

Structural isomerism

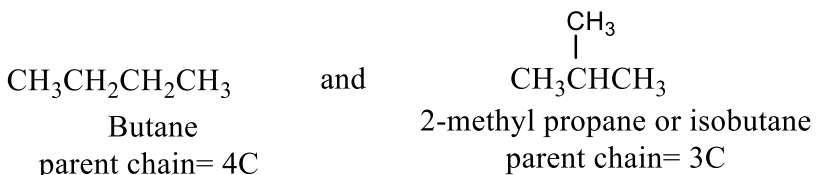
The compounds with the **same molecular formula but different structure** are termed as structural isomers, and the phenomenon is called structural isomerism. There are 5 types of structural isomers:

1. Chain or nuclear, or skeletal isomerism
2. Position isomerism
3. Functional isomerism
4. Tautomerism
5. Metamerism

1. Chain or nuclear, or skeletal isomerism

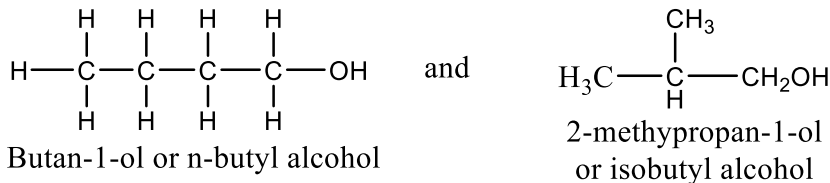
If two or more compounds have the **same molecular formula but have different carbon chains** or skeletons, then they are called chain isomers and the phenomenon is called structural isomerism

For example: C_4H_{10} . The two isomers of C_4H_{10} differ only in the length of the carbon chain.



Molecular formula for both: C_4H_{10}

Similarly, butyl alcohol and isobutyl alcohol are two chain isomers

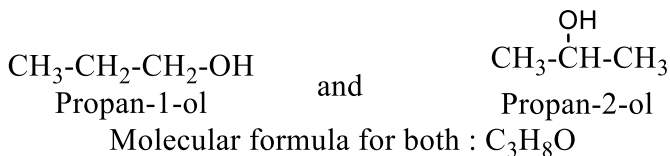


Molecular formula for both: $C_4H_{10}O$

2. Position isomerism

The compounds having the same molecular formula but **different positions of functional groups** are termed as position isomers, and the phenomenon is known as positional isomerism.

For example, the two isomers of the compound having molecular formula C_3H_8O are as follows:

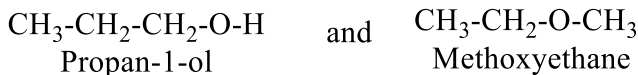


3. Functional isomerism

The compounds with the same molecular formula but **different functional groups** are termed as functional isomers, and the phenomenon is known as functional isomerism.

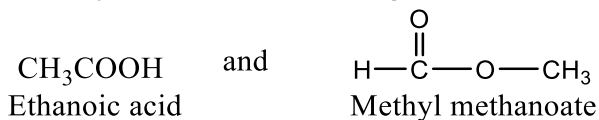
For example,

1. Aldehydes and ketones, e.g. CH_3CH_2CHO and CH_3COCH_3
2. Alcohol and ether, e.g. CH_3CH_2OH and CH_3OCH_3



Molecular formula for both: C_3H_8O

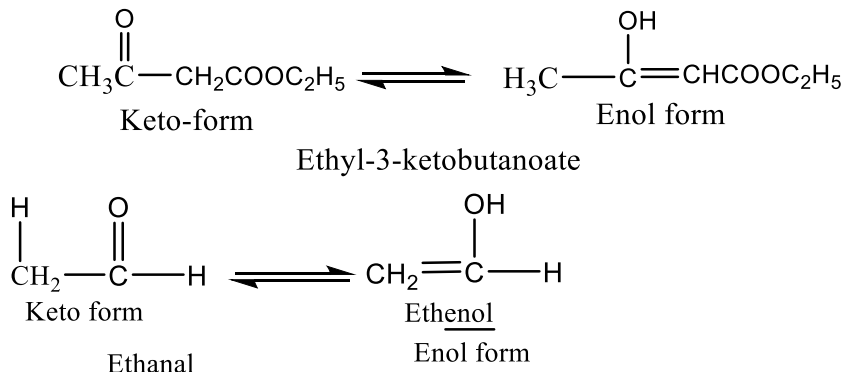
3. Carboxylic acid and esters, e.g.



1. Chain and position isomers of alcohol of formula $C_4H_{10}O$ are
 - a. 2
 - b. 3
 - c. 4
 - d. 1

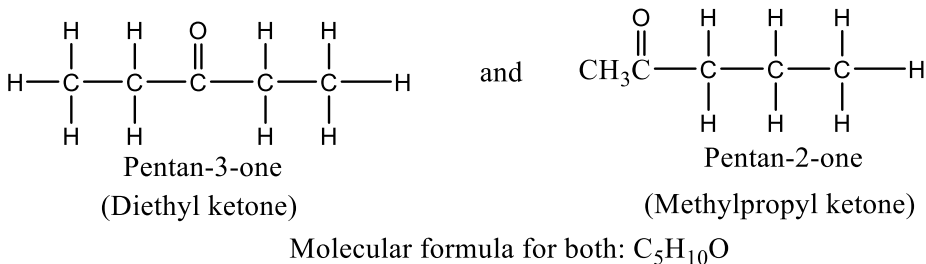
4. Tautomerism

It is a **special** type in which the isomers are interconvertible due to the **change in the position of the hydrogen** atom within the molecule. For example:



5. Metamerism

The compounds of the same family having the same molecular formula, which **differ in the arrangement of carbon atoms on either side of the functional group**, are termed metamers, and the phenomenon is called metamerism. *Ketones, Ethers, Esters*, etc., can exhibit metamerism.



1. 1-chloropropane and 2-chloropropane have same molecular formula ($\text{C}_3\text{H}_7\text{Cl}$) but are different compounds. The pair of compounds represent;

- Functional isomers
- Positional isomers
- Metamers
- Optical isomers

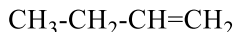
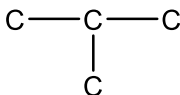
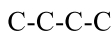
70/69/65) Write short note on: Structural isomerism in organic compounds.

5

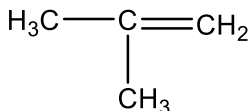
62) Write short note on: Structural isomerism in organic compounds. 2

69/56) Write the isomers of C_4H_{10} and give their IUPAC names. 2

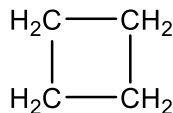
67) Write down two structure isomers and their IUPAC names of C_4H_8 . 2



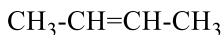
But-1-ene



2-methylprop-1-ene
Methylpropene



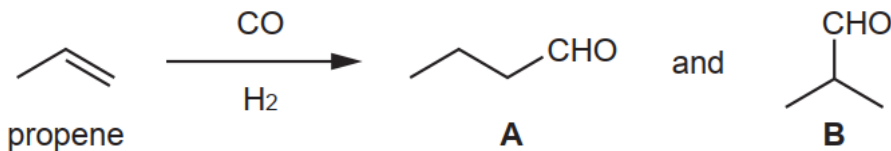
Cyclobutane



But-2-ene

1. Alkenes undergo an addition reaction with a 1:1 mixture of CO and H₂ to form aldehydes.

Fig. 3.1 shows the reaction of propene with a 1:1 mixture of CO and H₂.

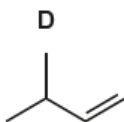
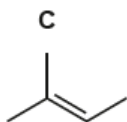


Aldehydes **A** and **B** are structural isomers.

(i) State the type of structural isomerism shown by **A** and **B**.

(ii) Name **A**.

2. Draw the structure of a molecule that is a positional isomer of **C** and **D**.



63/58/57) Write short notes on the isomers of C₆H₁₀.

5

71) Give a functional isomer of C₃H₇OH and write its IUPAC name

2

72) Write down the functional isomers of CH₃-CH₂-CH₂-OH and give the IUPAC name.

2

74) Write down the functional isomer of Propanol and give its IUPAC name.

1

68) Write down the functional isomers of CH₃-CH₂-OH and give IUPAC name.

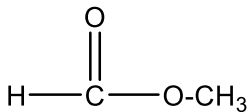
2

71/60) Give a functional isomer of C₂H₄O₂ and write its IUPAC name.

2

$\text{CH}_3\text{-COOH}$
Ethanoic acid

HCOOCH_3
Methylmethanoate



prefix -methyl
word root-meth
pri suffix -ane
sec suffix -oate

74) Give the functional isomer of Ethanoic acid with the structural formula.
1

75) Write down the functional isomer of Propanoic acid and give its IUPAC name.
2

74) Write down the functional isomer of Methyl methanoate and give its IUPAC name.
1

72) Write down the functional isomers of $\text{CH}_3\text{-CH}_2\text{-COOH}$ and give the IUPAC name.
1

72) Give possible isomers of $\text{C}_3\text{H}_6\text{O}_2$ and write their IUPAC names. 2

67) Write down two structure isomers and their IUPAC names of $\text{C}_3\text{H}_6\text{O}$.
2

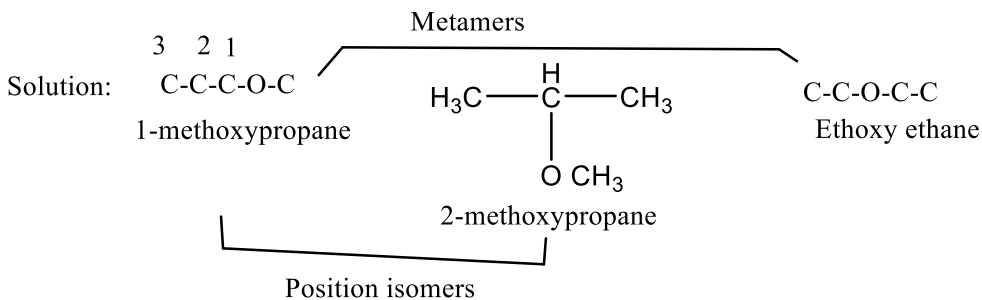
74) Give the functional isomer of Propanone with the structural formula.
1

59) Write the isomers of $\text{C}_2\text{H}_6\text{O}$ and give their IUPAC names. 2

75) Write down the functional isomer of Methoxymethane and give its IUPAC name.
1

66) Give possible isomers of $\text{C}_3\text{H}_6\text{O}$ and write their IUPAC names. 2

Write possible isomeric ethers for the molecular formula $\text{C}_4\text{H}_{10}\text{O}$.



67) Write the IUPAC name and structure for the possible compound with formula $\text{C}_3\text{H}_6\text{O}$. 1

2. Compounds which have the same molecular formula but possess different properties are called
 - a. isotopes
 - b. isomers
 - c. isobars
 - d. isochors
 - e. isotherms
3. Compounds having the same molecular formula but different structural formulas are called
 - a. Isotopes
 - b. Structural isomers
 - c. Isobars
 - d. polymers
4. Isomers must have
 - a. Same chemical properties
 - b. Same structural formula
 - c. Same molecular formula
 - d. Same functional group
5. Structural isomers have the same molecular formula but different
 - a. Structure
 - b. Functional group
 - c. Physical properties
 - d. Chemical properties

6. Two isomeric forms of saturated hydrocarbons have
- Same structure
 - Same molecular formula
 - Same properties
 - Different composition of elements
7. $\text{CH}_3\text{-O-CH}_3$ and $\text{C}_2\text{H}_5\text{OH}$ are
- Isomers
 - Allotropes
 - Isobars
 - Isomorphs
8. Which of the following compounds is a functional isomer of $\text{C}_2\text{H}_5\text{OH}$?
- CH_3CHO
 - CH_3COOH
 - $(\text{CH}_3)_2\text{O}$
 - $(\text{C}_2\text{H}_5)_2\text{O}$
9. How many structural isomers does pentane have?
- 1
 - 2
 - 3
 - 4
10. Chain isomers differ in
- Molecular formula
 - Empirical formula
 - Molecular weight
 - Length of the carbon chain
11. Which compound is not an isomer of the other three?
- Pentane
 - 2-methylbutane
 - 2,2-dimethylpropane
 - 2,3-dimethylbutane
12. But-1-yne and But-2-yne are
- Chain isomers
 - Metamers

- c. Functional isomers
- d. Positional isomers

13. Which two formulae correctly represent a pair of structural isomers?

A	$\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$ and $(\text{CH}_3)_2\text{CHCOOH}$
B	$\text{CH}_3\text{CH}(\text{COOH})\text{CH}_3$ and $(\text{CH}_3)_2\text{CHCOOH}$
C	CH_3CHCOOH and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
D	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ and $(\text{CH}_3)_2\text{CHCOOH}$

14. Which pair of alcohols are isomers of each other?

- A** butan-1-ol and 2,2-dimethylpropan-1-ol
- B** butan-2-ol and 2-methylpropan-2-ol
- C** pentan-1-ol and 2-methylpropan-2-ol
- D** propan-2-ol and 2-methylpropan-2-ol

15. Metamerism is shown by

- a. Ketones
- b. Alkanes
- c. Aldehydes
- d. Alcohols

16. The number of possible alcoholic isomers of $\text{C}_4\text{H}_{10}\text{O}$ is

- a. 2
- b. 3
- c. 4
- d. 8

17. How many isomeric ethers can be formed from $\text{C}_4\text{H}_{10}\text{O}$?

- a. 2
- b. 3
- c. 4
- d. 5

18. Maximum number of isomeric alkenes with molecular formula C_4H_8 is

- a. 2
- b. 3
- c. 4

d. 5

19. Which of the following are isomers?
- Propanone and Ethanal
 - Ethanol and Methoxymethane
 - Propanone and Propanoic acid
 - Methanol and Methoxymethane
20. Isomerism in which a single compound exists in two or more readily interconvertible structures is called
- Chain isomerism
 - Metamerism
 - Tautomerism
 - Stereoisomerism

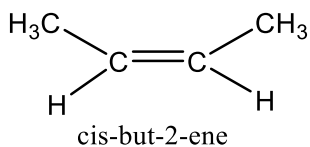
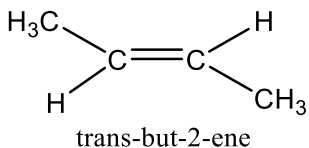
13.6 Concept of geometrical isomerism (cis & trans) & optical isomerism (d & l form)

Compounds having same molecular formula and structural formula but different spatial arrangements of the atoms or groups of atoms in a molecule are called stereo isomers. The phenomenon of existence of such compounds is called **stereoisomerism**.

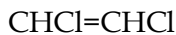
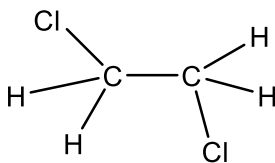
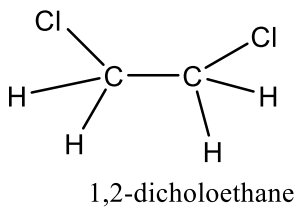
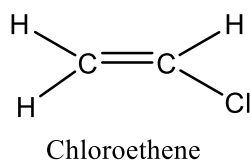
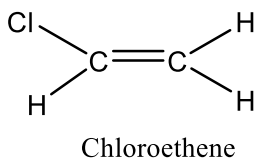
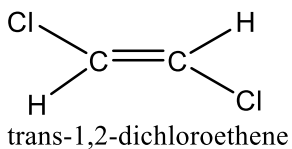
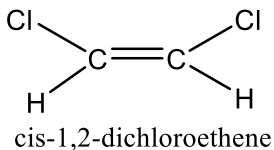
Stereoisomerism can be further subdivided into geometrical and optical isomerism.

Geometrical Isomerism (cis, trans isomerism)

When the same molecular formula represents two compounds which differ in the spatial arrangement of atoms or groups around carbon carbon-carbon double bond, these are geometrical isomers. Such isomerism arises due to the inability to rotate around a double bond. e.g, But-2-ene has two geometrical isomers, i.e, cis-but-2-ene and trans-but-2-ene

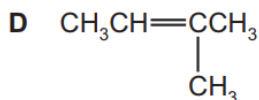
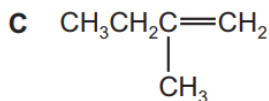
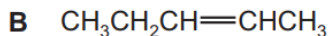
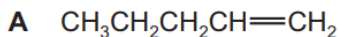


1,2-dichloroethene can be taken as another example of such isomerism.



3. Draw the two stereoisomers of but-2-ene.

1. Which alkene shows geometric isomerism?



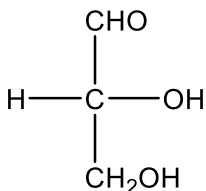
21. Geometrical isomerism is generally found in

- alkanes
- alkenes
- alcohols
- alkynes

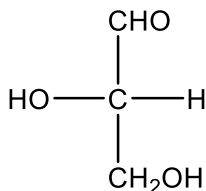
Optical isomerism

- Optical isomerism can be defined as the phenomenon by which isomers are obtained due to different arrangement of atoms or groups in the three-dimensional space.
- Such compounds resemble in their chemical and most physical properties but differ in **optical rotation**.
- Optical rotation is a phenomenon where a plane of the **plane polarized light** is rotated either in a clockwise or anticlockwise direction.
- The optical rotation is measured by an instrument called a polarimeter.
- The optical isomers which are mirror images to each other are called **enantiomers**.
- The enantiomer which rotates the plane of the polarized light to clockwise direction (right) and the anti-clockwise direction are

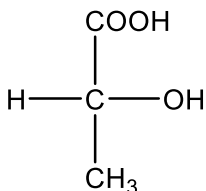
called dextrorotatory and laevorotatory, respectively and designated as + or *d* and - or *l*, respectively.



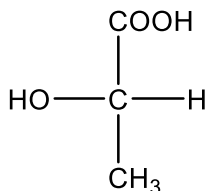
(+)- Glyceraldehyde
or *d*-Glyceraldehyde



(-)- Glyceraldehyde
or *l*-Glyceraldehyde



(+)- Lactic acid
or *d*-Lactic acid

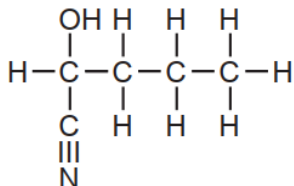


(-)- Lactic acid
or *l*-Lactic acid

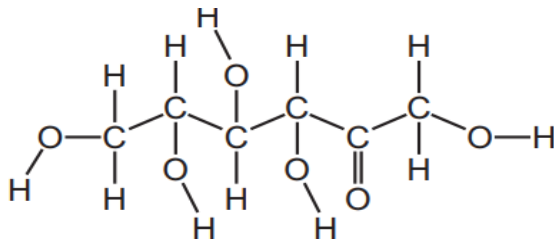
For a compound to exhibit enantiomerism there should be presence of chiral carbon atom. A carbon atom that is bonded with 4 different groups is called a chiral carbon. In above four examples it can be seen that the central atom is chiral.

4. C is a chiral molecule.

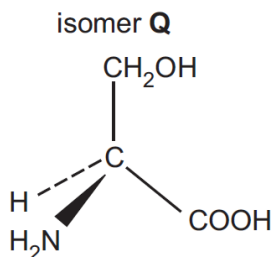
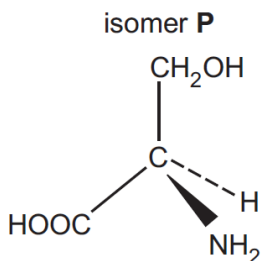
Circle any chiral centres in the structure of C shown in Fig. 3.2.



5. On the diagram of the fructose molecule, label all the chiral centres with an asterisk (*).



6. The amino acid serine, $\text{HOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$, exists in two optically active forms. These optical isomers, isomer P and isomer Q, are shown in Fig. 8.1.



Isomer P and isomer Q have identical physical and chemical properties, except for two specific properties. One of these two properties is their differing effect on plane-polarised light.

- (i) A solution of pure isomer P of a particular concentration rotates plane-polarised light by 5.0° in a clockwise direction.

Describe how a solution of pure isomer Q of the same concentration affects plane-polarised light. [1]

- (ii) State another term, in addition to stereoisomers, optical isomers and non-superimposable mirror images, which can be used to describe this pair of chiral compounds, isomer P and isomer Q.

7. Alanine exists as a pair of optical isomers. The structure of one optical isomer is shown in Fig.

Draw the three-dimensional structure of the other optical isomer of alanine.

optical isomer 1	optical isomer 2

8. The structure of compound **P** is shown in Fig. 7.1.

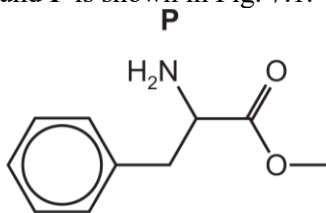


Fig. 7.1

(i) **P** is optically active.

Use an asterisk (*) to identify all chiral carbon atoms on the structure of **P** in Fig. 7.1.

(ii) Plane polarised light is passed through a pure sample of one enantiomer of **P**. This is then repeated with a pure sample of the other enantiomer of **P**.

Describe the results of these two experiments, stating the similarities and differences of the results.

9. Cortisone is an optically active molecule.

Explain what is meant by optically active.

10. Explain what is meant by the term chiral centre.

11. Define enantiomers.

22. cis-but-2-ene and trans-but-2-ene are

- position isomers
- optical isomers
- conformational isomers
- geometrical isomers

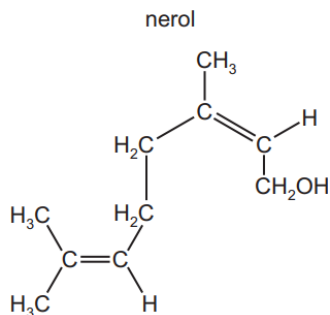
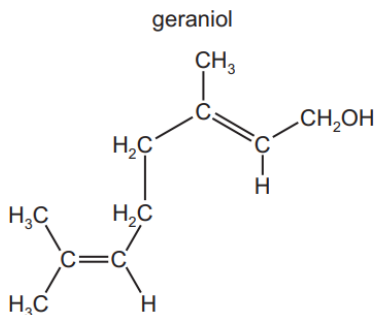
23. Optical activity is measured by

- Nicol prism
- Analyzer
- Polarimeter
- Polaroid

24. Which of the following compound is chiral?

- 2-chloropropane
- 2-methoxybutane
- Propan-2-ol
- Methanal

25. Which can exist in optically active form
 a. Butan-1-ol b. butan-2-ol c. pentan-3-ol d. heptan-4-ol
26. But-1-ene exhibits
 a. Geometrical isomerism c. optical isomerism
 b. Position isomerism d. none of these
27. Geraniol and nerol are isomers of each other.



Which type of isomerism is shown here?

- A chain B geometrical (cis /trans) C optical D positional
28. Which compound shows stereoisomerism?
 A 2-methylbut-2-ene
 B 2-chloropropan-1-ol
 C difluorochlorobromomethane
 D pent-1-ene

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****