

# CLASSIFICATION OF ORGANIC ISOMERS

If two different substances with *different chemical and/or physical properties* have the *same molecular formula* they are said to exhibit *isomerism* and to be *isomers* of one another.

This phenomenon is of interest because one can easily write the formula of one compound without realizing that it can also represent others. Isomerism is frequently encountered in organic compounds, although there are some inorganic compounds which exhibit isomerism. There are *two general types of isomers*:

(1) *constitutional isomers* and (2) *stereoisomers*.

Each general isomer class can be further subdivided into different types.

## Constitutional Isomers

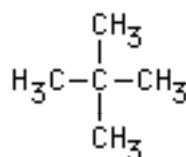
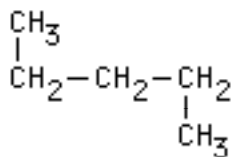
Constitutional isomerism arises when a formula represents compounds in which the atoms are attached to one another in different ways-i.e. bonding is different. *Constitutional isomers are molecules that have the same molecular formula but different spatial arrangements of the atoms*. A structural formula shows the order in which atoms are bonded together. There are three main kinds of constitutional isomers:

- 1) skeletal isomers
- 2) positional isomers
- 3) functional group isomers.

### 1. Skeletal isomerism:

The hydrocarbon chain may be arranged in different ways i.e. the carbon 'skeletons' differ, i.e. different structural 'backbones'. The isomers possess the same functional group, and belong to the same homologous series.

Examples:



i) Pentane

ii.  $\text{C}_6\text{H}_{12}$     cyclohexane                      Methylcyclopentane    1,1-dimethylcyclobutane

*Only the physical properties differ in these cases.* Compounds of branched chain molecules always have lower boiling point than that of the related straight chain compound. The straight chain molecule can have greater areas in contact with one another, therefore, increase in intermolecular forces (LDF) than the branched chain molecules (in the same way as pieces of rope in contact with one another would have more area touching than would footballs placed together). As branching increases, boiling point decreases : van-der-Waal's forces are weaker due to smaller effective surface area.

### 2. Positional isomers There are two types of position isomerism:

(i) Positional isomers are compounds with the same structural 'backbone' but different positions of substituents or functional groups.

Example:  $\text{C}_5\text{H}_{11}\text{Cl}$

1-chloropentane

2-chloropentane

3-chloropentane

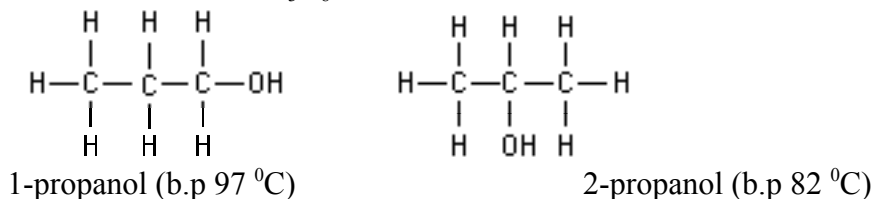
Example:  $\text{C}_8\text{H}_{10}$

1,2-dimethylbenzene (o-xylene)

1,3-dimethylbenzene (m-xylene)

1,4-dimethylbenzene

There are two alcohol isomers  $C_3H_8O$



Example:

1,2-dichlorobenzene

1,3-dichlorobenzene

1,4-dichlorobenzene

(ii) Functional group forms part of the chain, and the hydrocarbon radicals on each side are different.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$   
1-methoxypropane

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$   
ethoxyethane

$\text{CH}_3\text{CH}_2\text{COOCH}_3$   
methylpropanoate

$\text{CH}_3\text{COOCH}_2\text{CH}_3$   
ethylethanoate

*The isomers are chemically similar because they possess the same functional group.*

### 3. Functional Group Isomers

These are compounds with the same molecular formula but the atoms are arranged so as to give different functional groups, thus belonging to different homologous series.

Examples:

$C_2H_6O$

$\text{CH}_3\text{CH}_2\text{OH}$   
ethanol

$\text{CH}_3-\text{O}-\text{CH}_3$   
methoxymethane

$C_3H_6O$

$\text{CH}_3\text{CH}_2\text{CHO}$   
propanal

$\text{CH}_3-\text{CO}-\text{CH}_3$   
propanone

$\text{H}_2\text{C}=\text{CH}-\text{CH}_2(\text{OH})$   
prop-2-en-1-ol

$C_3H_6O_2$

$\text{CH}_3\text{CH}_2-\text{COOH}$   
propanoic acid

$\text{CH}_3-\text{COOCH}_3$   
methyl ethanoate

Note that every ether has alcohols as isomer, every ketone has aldehydes, every acid has an ester.

*Both physical and chemical properties are quite different in these cases.*

## STEREO-ISOMERS

Isomers that possess the same molecular formula and also identical atoms in the same arrangement with respect to one another, (i.e. identical connectivity), but still differ because of the spatial arrangement of their atoms. These are **stereo-isomers**. The atoms are arranged differently in space, i.e. they have different configurations.

There are *two types of stereo-isomers*: (1) **diastereoisomers** (2) **optical** (See Later Notes)

### 1. diastereoisomers

If one bond of a molecule is not free to rotate, as in the case of a double bond, then two spatial arrangements are possible.

The compounds differ only in the relative spatial position of the groups and are called diastereomers.

The  $\text{C}=\text{C}$  bond of an alkene is a rigid structure that produces diastereomers. The substituents attached are 'locked' in place and cannot be interchanged without breaking and making bonds.

There is normally free rotation about a C - C single bond, but there is no free rotation about a C = C bond.

Since such a rotation would require the breaking of the weaker  $\pi$ - bond to allow free rotation without breaking the  $\sigma$  - bond and thus rotate from time to time.

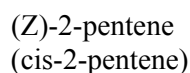
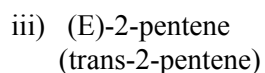
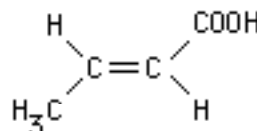
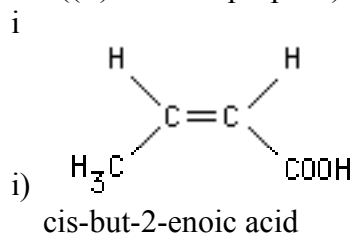
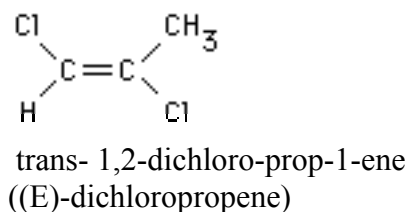
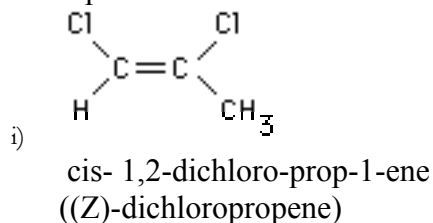
This would require more energy than is available at ordinary temperatures, there is therefore a temperature above which diastereomers can change from one form into another.

[The two forms are known as the *cis* and *trans* isomer. (Cis: if like groups are on one side of the double bond and trans: if same groups are on the opposite side) ]

The two diastereomers have the same molecular formula, same skeleton, same organization of atoms and bonds but differ in the directions taken by the groups attached to the bonds, i.e. different spatial arrangement of the atoms.

The two isomers have *different physical properties and many of their chemical properties also differ.*

Example :



iv) cis- and trans- butenedioic acid (maleic acid and fumaric acid).

The physical and chemical properties of cis-trans isomers differ.

In general the cis-isomer is generally more reactive, has lower melting point, i.e. lower stability and greater solubility than the trans isomer ( because the large substituent groups have a greater separation from one another in the trans form, therefore are less likely to interfere with one another than in the cis form.)

***Because of differing physical properties, geometrical isomers may be separated by fractional distillation or by fractional crystallization.***

Geometrical isomerism depends not only on the existence of a double bond but also on the groups attached to the C -atoms joined by the C = C bond ( ex. 1,1-dichloroethene : no isomers!)

The key feature for geometrical isomerism is the presence of two different groups on each end of the double bond.

Thus there can be *no cis-trans* diastereomers *if either of the C -atom supports two identical groups*. Each carbon atom of the double bond must have two different substituent groups (one of which is a hydrogen atom). (Example: 1,1- dichloroethene)

The existence of **geometrical isomerism applies to any class of compounds which contains a double bond:** - C = N ex.

**Ring structures also lock out free rotation, geometric isomers of ring compounds are also possible:**

Carbon rings containing fewer than five carbon atoms are strained because the C—C—C bond angle in the smaller rings must be less than the  $109.5^\circ$  tetrahedral angle. The amount of strain increases as the rings get smaller. In cyclopropane, which has the shape of an equilateral triangle, the angle is only  $60^\circ$ ; this molecule is therefore much more reactive than either propane, or cyclohexane, which has no ring strain.

Example:

cis- and trans- 1,2-dimethylcyclopropane

cis- and trans-1,2-dimethylcyclohexane

[Note that compounds with **triple bond do not exhibit isomerism:** a - C  $\equiv$  C - b

*Flat molecule*, a and b have *free rotation*, therefore *no geometrical isomers possible*, only skeletal isomerism exhibited, ex. 1- butyne or 2- butyne. ]

### Assignment

- Write structural formulae for three compounds of formula  $C_5H_{12}$ .
- Write the structural formulae of the three structural isomers of the formula  $C_3H_8O$ .
- The molecular formula  $C_5H_{10}O$  corresponds to a number of carbonyl compounds, which contain the carbonyl group: — C = O. Write their structural formulae.
- (a) Explain why cis-trans isomerism:
  - does exist for 1,2-dibromoethene
  - does not exist for 1,2-dibromoethane
  - does not exist for 1,1-dibromoethene

b) (i) draw displayed formulae for the following compounds: hex-3-ene, butenedioic acid  
(ii) State and explain which, if either, of hex-3-ene and butenedioic acid can display cis-trans isomerism.  
(iii) Suggest how these isomers might be distinguished.
- Explain how the nature of the C = C bond gives rise to cis-trans isomerism.
- There are both cyclic and non-cyclic isomers of hydrocarbons with a given molecular formula.
  - (i) Draw full structural formulae for cyclopropane, **A**, and cyclopropene, **B**.
  - (ii) Draw two non-cyclic structural isomers of A and B: state the class of compound to which each belongs.
  - (iii) A common polymer has the same empirical formula as A. Give the empirical formula, and name of the polymer.

(b) 0.54 g of a hydrocarbon, C, were burnt in excess oxygen. The water produced was absorbed by passing through calcium chloride tubes, which gained 0.54 g in mass. The carbon dioxide was absorbed by potassium hydroxide, which gained 1.76 g.

  - Show that the empirical formula of C is  $C_2H_3$ .
  - Given that 0.01 mol of C was used, derive the molecular formula of C.
  - Draw the structural formula of one possible isomer of C and comment on the shape around any multiple bond(s), or on other points of interest in its structure.