

Section 7

Organic Chemistry

Organic Chemistry

Nomenclature - IUPAC system

- Prefixes and suffixes

Isomerism

- Recognition of the different physical and chemical properties of structural, geometric and optical isomers.

Chemical reactions on functional groups

- alkanes, alkenes, alkynes, alcohols, haloalkanes, amines, aldehydes, ketones, carboxylic acids, acid chlorides, esters and amides
- Amino acids, zwitterions and dipeptides

Types of reactions

- (Free radical) Substitution
- Nucleophilic Substitution
- Substitution (with chlorinating/brominating agents)
- Combustion
- Reduction and Oxidation
- Addition
- Condensation
- Elimination
- Hydrolysis
- Acid-Base Reaction
- Salt Formation
- Complex Ion Formation
- Thermal Decomposition

Polymers

- Addition and Condensation polymers
- Preparation of polyamides and polyesters.

Some words to learn before we start:

Organic compound

A compound consisting of carbon and any other elements. Note that compounds and ions containing carbon and oxygen only are inorganic not organic (e.g. CO, CO₂ and CO₃²⁻).

Functional group

A site on an organic molecule with the characteristic arrangement of atoms and bonds where we would expect reactions to take place (e.g. -OH, C=C, etc.).

Homologous series

This is a family of organic compounds having the same functional group and represented by the same general formula, such as Alkanes, Alkenes, Alcohols, etc..

Saturated compound

An organic compound that contains only C-C single bonds between any carbon atoms present. It is incapable of undergoing addition reactions. E.g. Alkanes, Haloalkanes, etc..

Unsaturated compound

An organic compound that contains one or more C=C double bonds or C≡C triple bond. It is capable of undergoing addition reactions.

Alkyl group

A group obtained by removing a hydrogen atom from an alkane or other non-cyclic hydrocarbons. This is often abbreviated in formulae to R, R' or R".

Branched carbon chain

A carbon chain branched with one or more alkyl groups.

Straight carbon chain

Unbranched carbon chain, not linear though, zigzagged with bond angles of 109°.

Writing Organic Compounds

In general, there are six types of formula used to describe organic molecules.

A displayed **structural formula (SF)** is a two dimensional arrangement of atoms in the molecule and displays all the bonds between atoms.

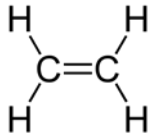
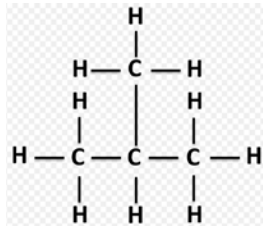

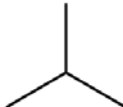
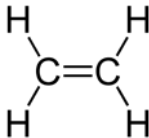
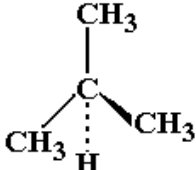
A **constitutional formula** or **condensed structural formula (CF)** is also a 2-D arrangement of atoms in the molecule but only displays C=C and C≡C bonds, other bonds like C–C, C–H, C=O, etc. are not necessary to be shown.

A **molecular formula (MF)** shows the actual number of each type of atom in the molecule.

An **empirical formula (EF)** shows the simplest ratio between different types of atoms.

A **general formula (GF)** is a type of empirical formula that represents the composition of any member of an entire family of organic compounds.

A **three-dimensional formula (3-D Formula)** shows the spatial arrangements of atoms, groups of atoms and covalent bonds in the molecule in three dimensions.

Formula	Ethene	2-Methylpropane
SF		
Skeletal Formula SKF		
CF	CH ₂ =CH ₂	CH ₃ CH(CH ₃)CH ₃
MF	C ₂ H ₄	C ₄ H ₁₀
EF	CH ₂	C ₂ H ₅
GF	C _n H _{2n}	C _n H _{2n+2}
3-D Formula		

Finding Empirical Formulae

It is possible to determine an empirical formula of a compound given its percentage composition by mass or the ratio of the masses of the elements that make it. This is particularly useful for organic compounds which can be converted to carbon dioxide and water by combustion.

Example 1:

Calculate the empirical formula of a compound of carbon and hydrogen containing 81.8% carbon and 18.2% hydrogen.

	C	H
Relative numbers of moles	81.8/12	18.2/1
	= 6.82	: 18.2
(Divide by smallest number)	= 6.82/6.82	: 18.2/6.82
	= 1	: 2.67
Change to whole number ratio by multiplying by 3	= 3	: 8

Therefore, the EF is C₃H₈.

To find the molecular formula, the molar mass of the compound must be given. Then use the following formula to find the number of empirical formulae involved.

$$n = \frac{M(MF)}{M(EF)}$$

Example 2:

Both compounds A and B have the EF of CH₂. The molar mass of compound A, M(A), is found to be 28 g mol⁻¹ and M(B) is 56 g mol⁻¹. Find the MF for A and B.

$$n(A) = \frac{M(MF)}{M(EF)} = \frac{28}{12+2} = 2 \quad \text{and} \quad n(B) = \frac{M(MF)}{M(EF)} = \frac{56}{12+2} = 4$$

Therefore, the molecular formula for compound A is C₂H₄ and for B is C₄H₈

Questions 1

Naming Organic Compounds

In the simplest terms the name of an organic compound consists of:

A **prefix**, which indicates how many carbon atoms are present.

A **suffix**, which indicates the functional group present in the molecule.

1. The same prefixes are used in naming all members of a homologous series.

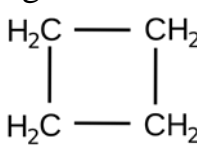
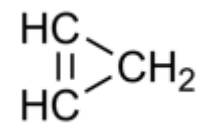
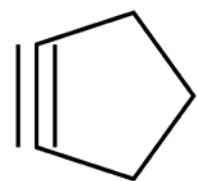
Number of carbon atoms in chain	Prefix	Number of carbon atoms in chain	Prefix
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

2. When an alkane molecule loses a hydrogen atom it becomes an **alkyl group**. Alkyl groups are used to name the branches/side groups in branched-chain compounds.

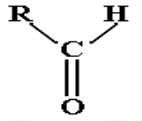
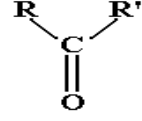
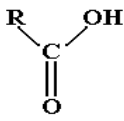
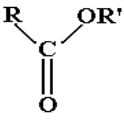
Number of carbon atoms in chain	Formula of alkyl group	Name of alkyl group
1	CH ₃ —	methyl
2	CH ₃ CH ₂ —	ethyl
3	CH ₃ CH ₂ CH ₂ —	propyl
4	CH ₃ (CH ₂) ₂ CH ₂ —	butyl
5	CH ₃ (CH ₂) ₃ CH ₂ —	pentyl

3. Two tables below show the suffixes for the main functional groups.

(a) Table One: **Hydrocarbons** (organic compounds containing H and C atoms only)

Name & Formula of functional group	Suffix for naming	Homologous series	General formula	Constitutional formula
Carbon-carbon single bond (Not a functional group.) $C-C$ Tetrahedral, 109°	-ane	Alkane	C_nH_{2n+2}	e.g. $CH_3CH_2CH_3$ propane
		Cyclic alkane	C_nH_{2n}	e.g.  cyclobutane
Carbon-carbon double bond $C=C$ Trigonal planar $\approx 120^\circ$	-ene	Alkene	C_nH_{2n}	e.g. $H_2C=CHCH_3$ propene
		Cyclic alkene	C_nH_{2n-2}	e.g.  cyclopropene
Carbon-carbon triple bond $C\equiv C$ Linear, 180°	-yne	Alkyne	C_nH_{2n-2}	e.g. $HC\equiv CCH_3$ propyne
		Cyclic alkyne	C_nH_{2n-4}	e.g.  cyclopentyne

(b) Table two (Note: R or R' represents an alkyl group.)

Name & Formula of functional group		Suffix for naming	Homologous series	General formula	Constitutional formula
Hydroxyl group —OH		-ol <i>side group:</i> hydroxy	#* Alcohol	$C_nH_{2n+2}O$	ROH e.g. CH_3CH_2OH
Ether oxygen group —O—		ether <i>side group:</i> oxy	Ether	$C_nH_{2n+2}O$	ROR' e.g. CH_3OCH_3
Halo group —X		<i>side group:</i> fluoro, chloro bromo, iodo	#Haloalkane	$C_nH_{2n+1}X$	RX e.g. CH_3Br CH_3CH_2Cl
Amino group (1°) —NH ₂		-amine <i>side group:</i> amino	#* Amine	$C_nH_{2n+3}N$	RNH₂ e.g. CH_3NH_2
Aldehyde group		-al	Aldehyde	$C_nH_{2n}O$	RCHO e.g. CH_3CHO
Ketone group		-one <i>side group:</i> oxo	Ketone	$C_nH_{2n}O$	RCOR' e.g. CH_3COCH_3
Carboxyl group, —COOH 		-oic acid	*Carboxylic acid	$C_nH_{2n}O_2$	RCOOH e.g. CH_3COOH $HCOOH$
Ester group, —COOR' 		-yl -oate	Ester	$C_nH_{2n}O_2$	RCOOR' e.g. CH_3COOCH_3 $HCOOCH_2CH_3$
Acid chloride group —COCl		-oyl chloride	Acid chloride	$C_nH_{2n-1}OCl$	RCOCl e.g. CH_3COCl
Amide group (1°) —CONH ₂		-amide	#* Amide	$C_nH_{2n+1}ON$	RCONH₂ e.g. CH_3CONH_2

Note: (i) Compounds in Families with a “#” can be classified as primary, secondary or tertiary.

(ii) Compounds in Families with a “*” can form H-bonding between their molecules except for tertiary amines and amides.

4. Names are obtained by combining prefix and suffix according to the **IUPAC** system. **IUPAC** stands for International Union of Pure and Applied Chemists. Some examples of the application of the IUPAC system of naming are given:



This compound contains a chain of five carbon atoms and it is an alkane (all C—C single bonds), so its name is **pentane**.

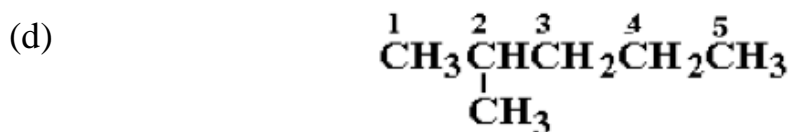


This compound contains a chain of four carbon atoms and is a carboxylic acid, so its name is **butanoic acid**.

In many compounds the carbon skeleton is branched. The names give to the side chains also depend on the number of carbon atoms they contain. Methyl, ethyl and propyl indicate one, two and three carbon atoms in a side chain, respectively. The position of the side chains is indicated by numbering the carbon atoms in the longest carbon chain of the molecule.



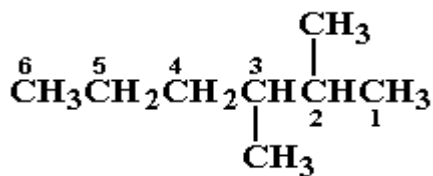
The longest carbon chain in this molecule is four atoms long, so its name is based on butane. There is a side-chain containing one carbon atom so it is methylbutane. Since there is only one place for the methyl group to attach (position 2 and 3 are the same and attaching to position 1 will just elongate the chain) there is no need to indicate the position of the carbon atom in this case. However, 2-methylbutane is also acceptable.



The longest carbon chain in this molecule is five atoms long, so its name is based on pentane. In this case, the side-chain could be attached to carbon atom 2 or 3 to giving two different possible arrangement of the atoms. The position of the methyl group must be given. This is 2-methylpentane.

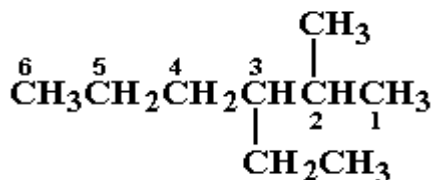
Notice that the longest chain is numbered so that the side chain is on the lowest numbered carbon atom of the longest chain. Numbering the longest chain in this example from the opposite end would have given 4-methylpentane, which is not correct.

(e)



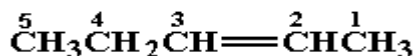
When side chains of equal length are present the prefix ‘**di**’, ‘**tri**’ or ‘**tetra**’ etc. is used. This compound is **2,3-dimethylhexane**.

(f)



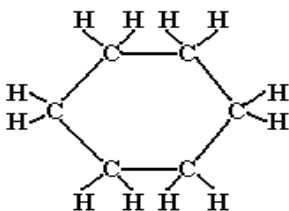
When side-chains of an unequal length are present they are given in alphabetical order. This compound is **3-ethyl-2-methylhexane**.

(g)



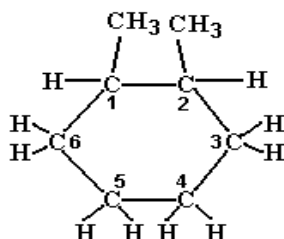
In alkenes the C=C double bond is assigned to the lower numbered carbon atom. This compound is **pent-2-ene** and NOT pent-3-ene.

(h)



The prefix ‘**cyclo**’ is used to indicate a cyclic compound. The name is determined by the number of carbon atoms in the ring. This compound is **cyclohexane** as it has 6 carbon atoms in the ring.

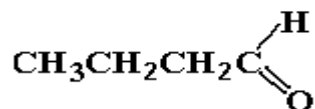
(i)



The carbon atoms in a ring are always numbered in such a way that the side chains are on the lowest numbered carbon atom. This compound should be named as

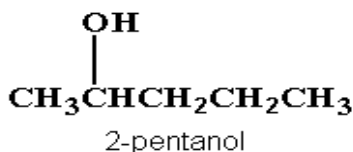
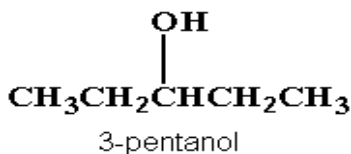
1,2-dimethylcyclohexane.

(j)



In aldehydes and carboxylic acids the functional group can only be at the end of a carbon chain. The end carbon atom is therefore numbered 1, although the number is not included in the name. This compound is **butanal**.

(k)



In alcohols the functional group can be anywhere on the carbon chain and so the carbon atom that carries the function group needs to be identified. In the alcohols derived from pentane the functional group may be on the first, second or third carbon atom, giving three possible compounds **pentan-1-ol**, **pentan-2-ol** and **pentan-3-ol**.

(l)



In ketones the functional group cannot be at the end of the chain. In the ketones derived from pentane the functional group may be on the second or third carbon (but not on the first carbon atom since this would be an aldehyde), giving two possible compounds **pentan-2-one** and **pentan-3-one**.

(m) CH_3NH_2

The IUPAC name of the above compound is **methylamine** or **aminomethane**.

(n) CH_3CONH_2

The IUPAC name of this compound is **ethanamide**.

(o) $\text{CH}_3\text{CH}_2\text{COCl}$

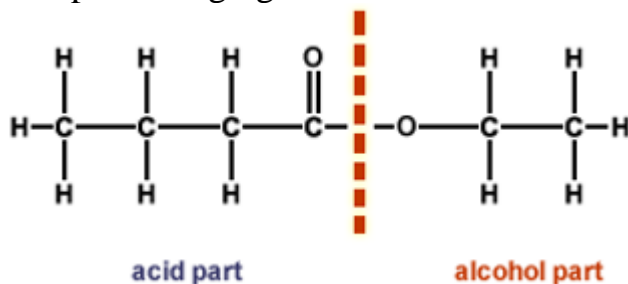
The IUPAC name of this compound is **propanoyl chloride**.



The IUPAC name of this compound is **dimethyl ether** or **methoxymethane**.

(q) Esters are named after the alcohol and carboxylic acid from which they were formed. To name esters:

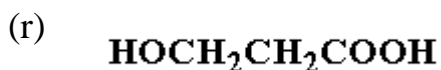
- 1) Divide the ester group into two parts by drawing a line crossing the C—O single bond as shown in the diagram below;
- 2) The part with the C=O bond is the acid part and the other is the alcohol part;
- 3) Name the alcohol part first as an alkyl group;
- 4) Name the acid part changing the -oic of the acid to its conjugate base -oate.



Therefore, the ester shown above is called **ethyl butanoate**.

When two functional groups are present in a molecule, the order of precedence of being a suffix for naming is:

Halo < Amino < Alcohol < Ketone < Aldehydes/Amide/Acid chloride/Ester/Carboxylic acid



The above compound is therefore **3-hydroxypropanoic acid**.



The systematic name for this compound is **4-iodopentan-1-ol**.

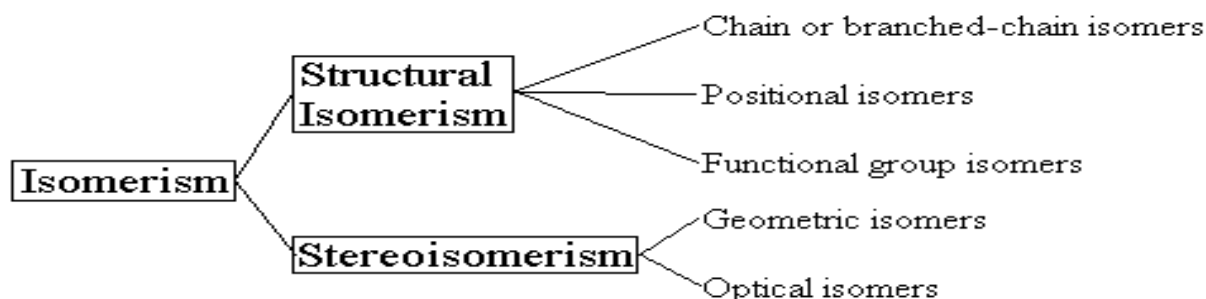


The systematic name for this compound is **aminoethanoic acid**. It is also known as **glycine**.

Questions 2

Isomerism

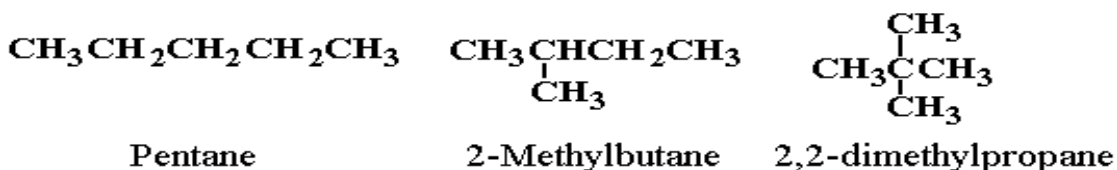
Isomerism occurs when organic compounds have the **same molecular formula (MF)** but **different structural formulae (SF)**. The types of isomerism can be summarised in the following diagram.



Structural isomerism

This arises where compounds have different structural formulae – the same number and type of atoms arranged in a different way. It can arise in 3 different ways.

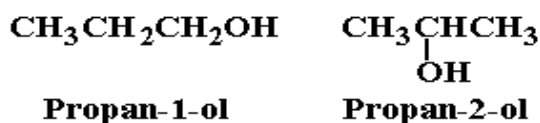
- (a) **Chain and branched-chain isomers:** These are compounds with different carbon skeletons. For example the following three isomers share the same MF C_5H_{12} .



Branched chain compounds tend to have lower melting points and boiling points than the straight chain isomers. This is because branched chain molecules occupy more space when they pack together in solid and liquid states, resulting in a weaker intermolecular forces. For example the two isomers of C_4H_{10} .

Isomer	Chain type	Melting point	Boiling point
butane	straight	-138.4°C	-0.5°C
2-methylpropane	branched	-159.6°C	-11.7°C

- (b) **Positional isomers:** These have the same carbon skeleton and the same functional group. What makes them different is that the functional group is attached to different positions on the carbon skeleton.



Positional isomers have similar chemistry, since they have the same functional group, however, the positioning of the function group sometimes results in differences in physical properties.

(c) **Functional group isomers:** These arise when isomeric molecules belong to different homologous series and hence have different physical and chemical properties.

(i) **Aldehydes and Ketones** (with same number of C atoms)

e.g. Two compounds with the MF C_3H_6O (**GF: $C_nH_{2n}O$**)



(ii) **Alcohols and Ethers** (with same number of C atoms)

e.g. Two compounds with the MF C_2H_6O (**GF: $C_nH_{2n+2}O$**)



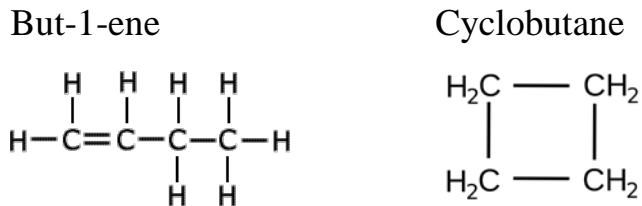
(iii) **Carboxylic Acids and Esters** (with same number of C atoms)

e.g. Two compounds with the MF $C_2H_4O_2$ (**GF: $C_nH_{2n}O_2$**)



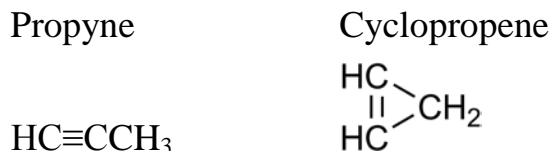
(iv) **Alkenes and Cyclic Alkanes** (with same number of C atoms)

e.g. Two compounds with the MF C_4H_8 (**GF: C_nH_{2n}**)



(v) **Alkynes and Cyclic Alkenes** (with same number of C atoms)

e.g. Two compounds with the MF C_3H_4 (**GF: C_nH_{2n-2}**)



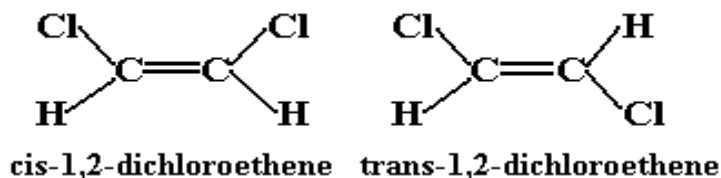
Stereoisomerism

This type of isomerism arises because of the different spatial arrangements of atoms in a molecule.

Geometric isomerism: This occurs in compounds in which free rotation (about a bond) is prevented by the presence of C=C double bond or a C—C ring structure. Geometric isomers also are called *cis*- and *trans*- isomers. They have atoms or groups of atoms in a different spatial arrangement on the two carbon atoms with the double bond between them.

(a) Alkenes

Example One:



These isomers, which are both liquids, have different boiling points as shown below:

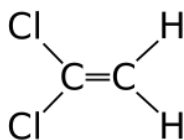
	<i>cis</i> -1,2-dichloroethene	<i>trans</i> -1,2-dichloroethene
Boiling point	60°C	48°C

In the *cis*- isomer the two polar bonds $\text{C}^{\delta+}\text{—Cl}^{\delta-}$ form an angle of 60° so these two dipoles do not cancel each other, therefore it is polar; while in the *trans*- isomer the two polar bonds $\text{C}^{\delta+}\text{—Cl}^{\delta-}$ are parallel with opposite directions, so these two dipoles cancel out, therefore it is non-polar.

Both isomers (having the same MF) have the same temporary dipole-dipole attraction but the polar *cis*- isomer has extra permanent dipole-dipole attraction. So overall, the *cis*- isomer has stronger intermolecular forces which require more energy to break down.

In general, *cis*- isomers tend to be more polar and thus have higher boiling points than their corresponding *trans*- isomers.

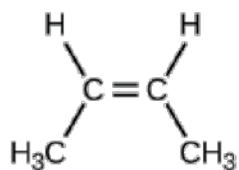
Not all the alkenes have geometric isomers. For example, 1,1-dichloroethene does not exist as *cis*-/*trans*- isomers because each C atom has two identical atoms attached to it.



Example Two:

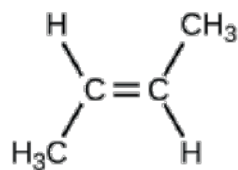
Geometric isomers

cis-2-butene



methyl groups on
same side of double bond

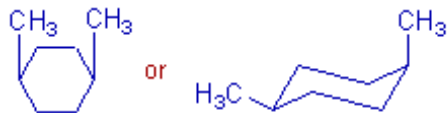
trans-2-butene



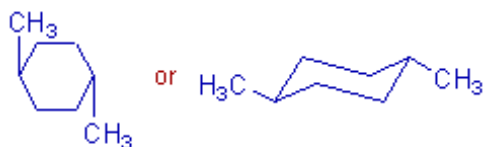
methyl groups on opposite
sides of double bond

(b) Cyclic alkanes

Example One:

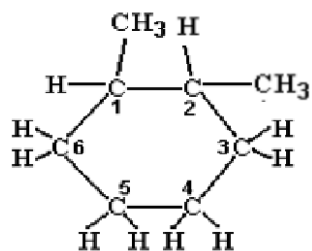


cis-1,4-dimethylcyclohexane

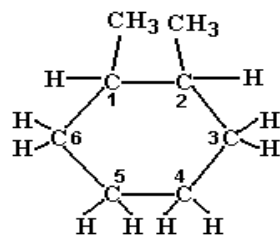


trans-1,4-dimethylcyclohexane

Example Two:



trans-1,2-dimethylcyclohexane

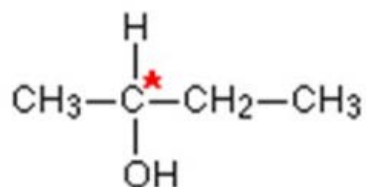


cis-1,2-dimethylcyclohexane

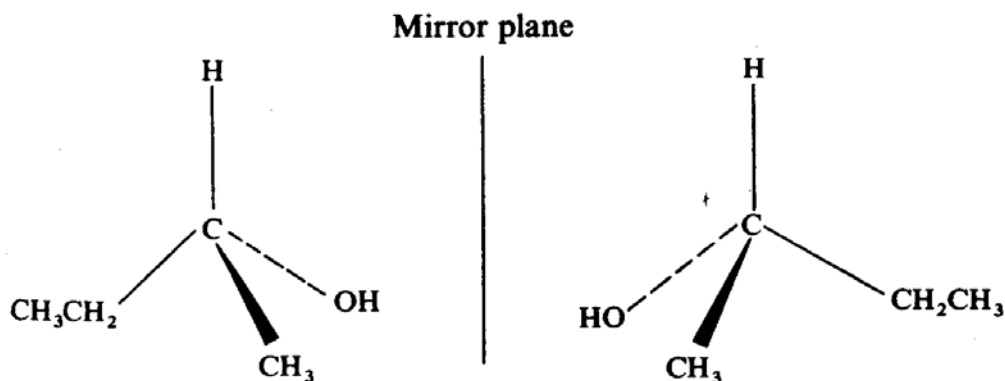
Optical isomerism: This occurs when four different atoms or groups of atoms are attached to the same carbon. The isomers produced are called a pair of enantiomers or optical isomers.

The central carbon atom, to which the four different atoms or groups are attached, is called **an asymmetric carbon atom** or a **chiral centre**, often labelled with an asterisk “*”.

e.g. Butan-2-ol has a chiral C* in its structure as shown below. The four different attachments are a hydrogen atom, a methyl group, an ethyl group and a hydroxyl group.

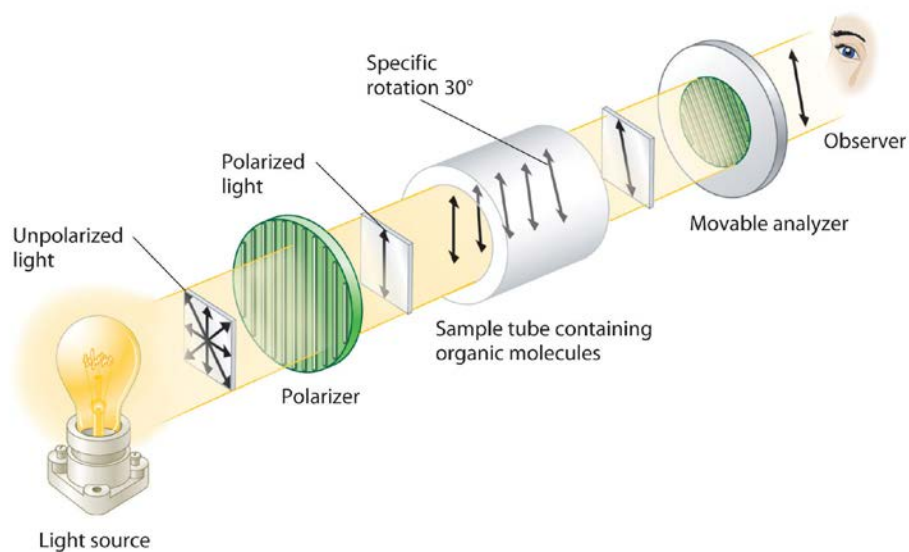


Consider the two optical isomers of butan-2-ol in three dimensions:



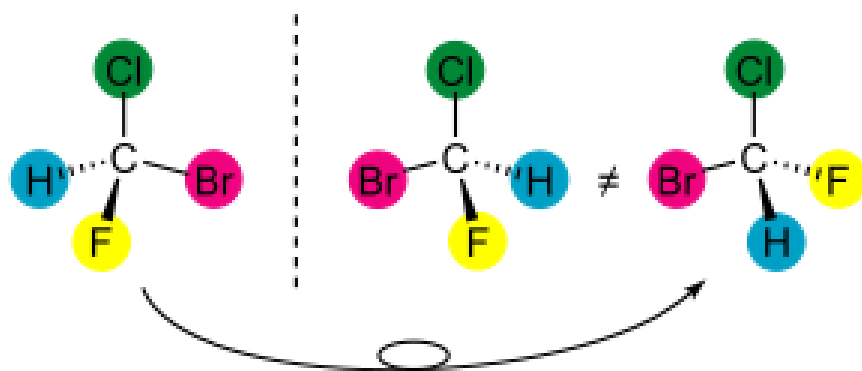
Both enantiomers have the same physical and chemical properties. Compounds that show optical isomerism often act as enzymes in biological processes. In this case, only one of the isomers has the catalytic property.

A pair of enantiomers may be distinguished from each other by their ability to **rotate the plane of polarised light in opposite directions**. It is because of this property that such isomers are said to be optically active. One enantiomer will rotate the plane of polarisation to the right and is called the **dextrorotatory** or '**D**' enantiomer while the other enantiomer will rotate the plane of polarisation to the left and is called the **laevorotatory** or '**L**' enantiomer.

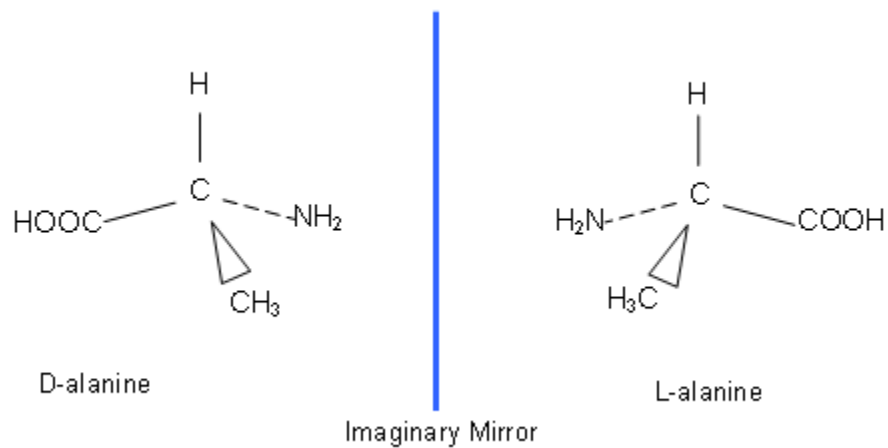


Other examples of optical isomers:

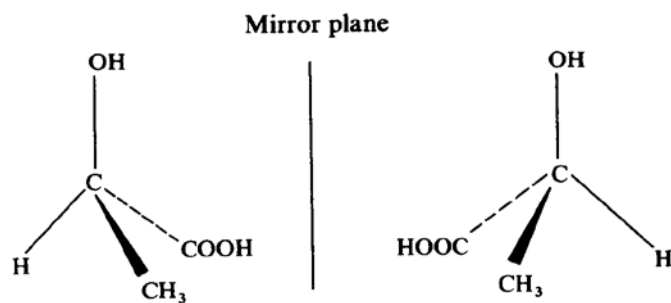
(i) bromochlorofluoromethane



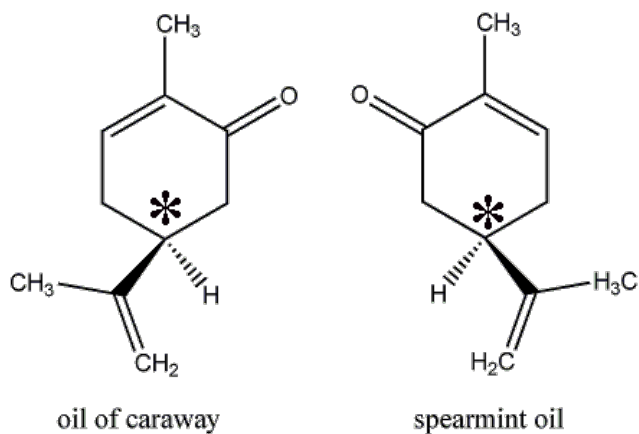
(ii) 2-aminopropanoic acid (alanine)



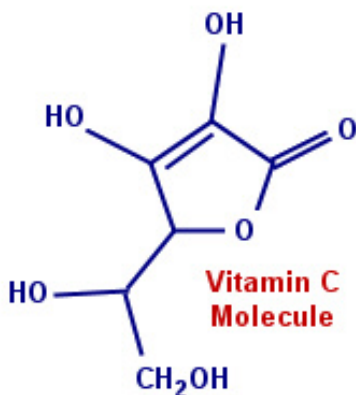
(iii) 2-hydroxypropanoic acid (lactic acid)



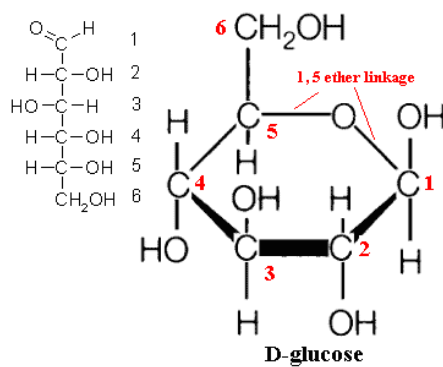
(iv) D-/L-carvone



(v) Ascorbic acid (vitamin C)



(vi) D-glucose



Questions 3