CHM 004 (ORGANIC CHEMISTRY)

LECTURE NOTE 3:

ISOMERISM

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LAGOS

Outline/Contents

- Prior knowledge
- Types of Isomerism
- Structural isomerism
- Stereoisomerism
  - Geometrical isomerism
  - Optical isomerism
- Check list

Learning outcome

- Understand the basic concept of isomerism and differentiate between the types.
- Identify the type of isomerism a given compound can exhibit.
- Draw and name isomers from a given molecular formula.

ISOMERISM

Prior knowledge

Before you start it would be helpful to...

- know the functional groups found in organic chemistry
- know the arrangement of bonds around carbon atoms
- know what affects the boiling point of organic molecules

Definition: phenomenon where different compounds have same molecular formula

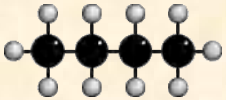
TYPES OF ISOMERISM

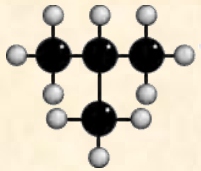
Phenomenon where different compounds have same molecular formula

STRUCTURAL ISOMERISM

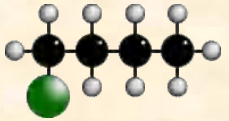
Same molecular formula but different structural formulae

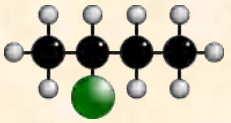
- CHAIN ISOMERISM



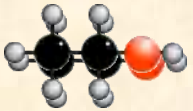


- POSITION ISOMERISM





- FUNCTIONAL GROUP ISOMERISM

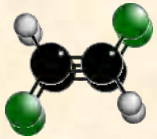


STEREOISOMERISM

Same molecular formula but atoms occupy different positions in space.

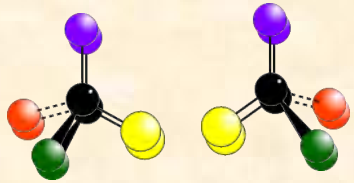
- GEOMETRICAL ISOMERISM

Occurs due to the restricted rotation of C=C double bonds... two forms... E and Z (CIS and TRANS)



- OPTICAL ISOMERISM

Occurs when molecules have a chiral centre. Get two non-superimposable mirror images.



STRUCTURAL ISOMERISM - INTRODUCTION

- Compounds have the same molecular formula but different structural formula

- Types are: chain, position, functional group isomerism, metamerism and tautomerism

Chain

different arrangements of the carbon skeleton
similar chemical properties
slightly different physical properties
more branching = lower boiling point

STRUCTURAL ISOMERISM - INTRODUCTION

❖ Compounds have the same molecular formula but different structural formula

Chain different arrangements of the carbon skeleton

similar chemical properties

slightly different physical properties

more branching = lower boiling point

Positional same carbon skeleton

same functional group

functional group is in a different position

similar chemical properties - slightly different physical properties

STRUCTURAL ISOMERISM - INTRODUCTION

❖ Compounds have the same molecular formula but different structural formula

Chain — different arrangements of the carbon skeleton
- similar chemical properties
- slightly different physical properties
- more branching = lower boiling point

Positional
- same carbon skeleton
- same functional group
- functional group is in a different position
- similar chemical properties - slightly different physical properties

Functional Group — different functional group
- different chemical properties
- different physical properties

- Sometimes more than one type of isomerism occurs in the same molecule.
- The more carbon atoms there are, the greater the number of possible isomers

STRUCTURAL ISOMERISM - INTRODUCTION

❖ Compounds have the same molecular formula but different structural formula

metamerism same functional group
difference in the size of alkyl groups on either side of the functional group.
similar chemical properties - slightly different physical properties

Tautomerism same carbon skeleton
differ in the location of double bond and hydrogen atom.
different compounds with interconvertible nature in equilibrium.
different chemical properties
different physical properties

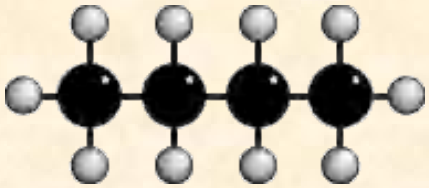
- Sometimes more than one type of isomerism occurs in the same molecule.
- The more carbon atoms there are, the greater the number of possible isomers

STRUCTURAL ISOMERISM - CHAIN

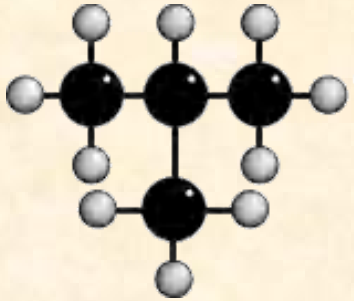
- caused by different arrangements of the carbon skeleton
- similar chemical properties
- slightly different physical properties
- more branching = lower boiling point

✔ There are two structural isomers of C_4H_{10}. One is a straight chain molecule where all the carbon atoms are in a single row. The other is a branched molecule where three carbon atoms are in a row and one carbon atom sticks out of the main chain.

BUTANE
straight chain



2-METHYLPROPANE
branched



C_4H_{10}

STRUCTURAL ISOMERISM - CHAIN

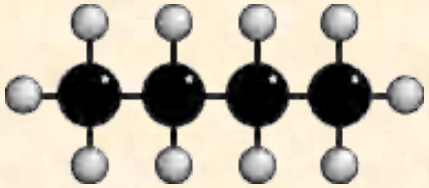
DIFFERENCES BETWEEN CHAIN ISOMERS

Chemical Isomers show similar chemical properties because the same functional group is present.

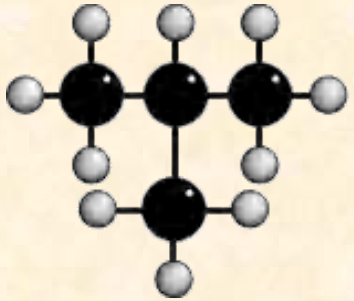
Physical Properties such as density and boiling point show trends according to the of the degree of branching

Boiling Point "straight" chain isomers have higher values than branched ones
the greater the degree of branching the lower the boiling point
branching decreases the effectiveness of intermolecular forces
less energy has to be put in to separate the molecules

- 0.5°C
straight chain



- 11.7°C
branched



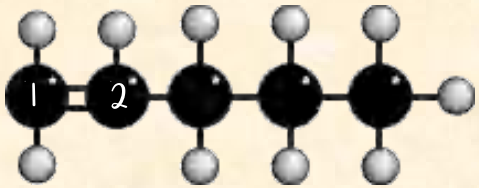
greater branching
= lower boiling point

STRUCTURAL ISOMERISM - POSITIONAL

- molecule has the same carbon skeleton
- molecule has the same functional group... BUT the functional group is in a different position
- have similar chemical properties / different physical properties

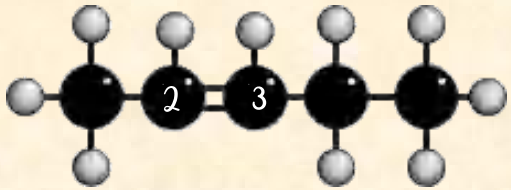
Example 1

POSITION OF A DOUBLE BOND IN ALKENES



PENT-1-ENE

double bond between carbons 1 and 2



PENT-2-ENE

double bond between carbons 2 and 3

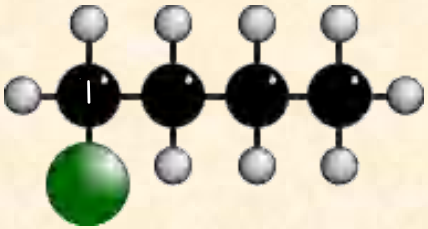
There are no other isomers with five C's in the longest chain but there are three other structural isomers with a chain of four carbons plus one in a branch.

STRUCTURAL ISOMERISM - POSITIONAL

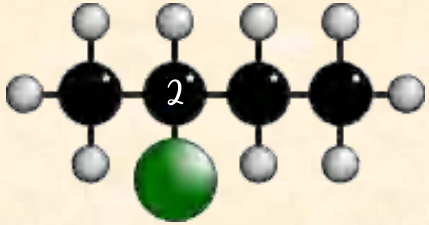
- molecule has the same carbon skeleton
- molecule has the same functional group... BUT the functional group is in a different position
- have similar chemical properties / different physical properties

Example 2

POSITION OF A HALOGEN IN A HALOALKANE

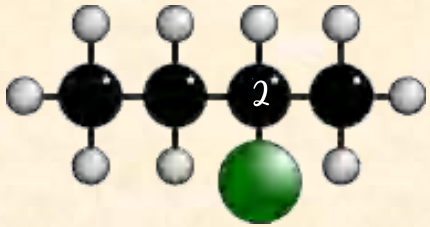


1-CHLOROBUTANE
halogen on carbon 1



2-CHLOROBUTANE
halogen on carbon 2

BUT



is NOT
3-CHLOROBUTANE

Moving the chlorine along the chain makes new isomers; the position is measured from the end nearest the functional group... the third example is 2- NOT 3-chlorobutane.

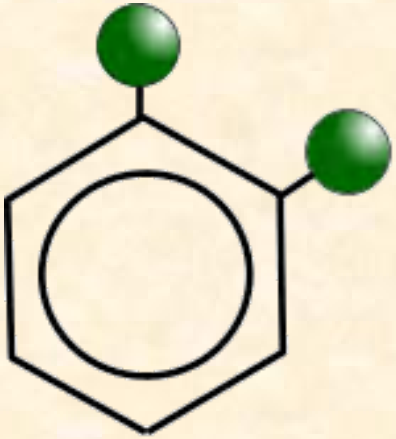
There are 2 more structural isomers of C_4H_9Cl but they have a longest chain of 3

STRUCTURAL ISOMERISM - POSITIONAL

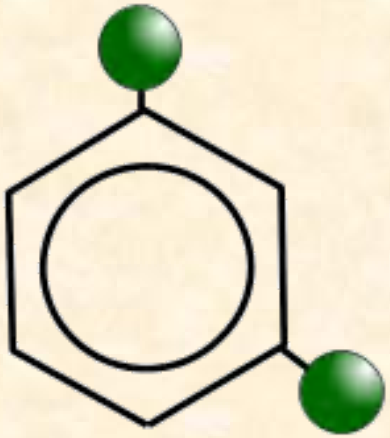
- molecule has the same carbon skeleton
- molecule has the same functional group... BUT the functional group is in a different position
- have similar chemical properties / different physical properties

Example 3

RELATIVE POSITIONS ON A BENZENE RING



1,2-DICHLOROBENZENE
ortho dichlorobenzene



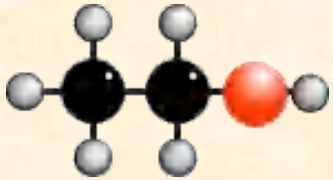
1,3-DICHLOROBENZENE
meta dichlorobenzene

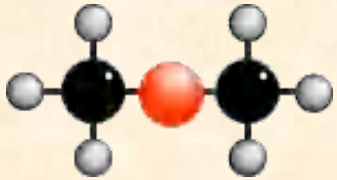
1,4-DICHLOROBENZENE
para dichlorobenzene

STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

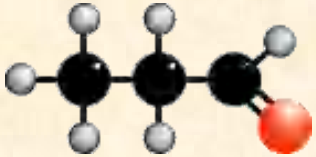
- molecules have same molecular formula
- molecules have different functional groups
- molecules have different chemical properties
- molecules have different physical properties

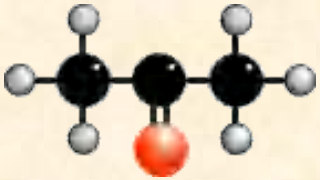
ALCOHOLS and ETHERS



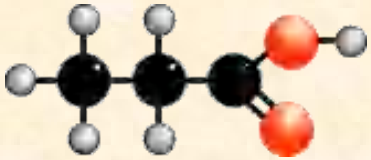


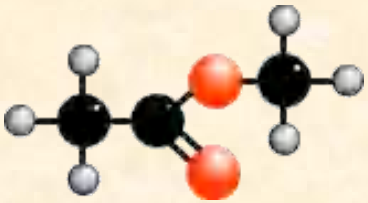
ALDEHYDES and KETONES





ACIDS and ESTERS

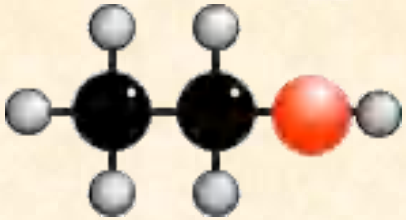


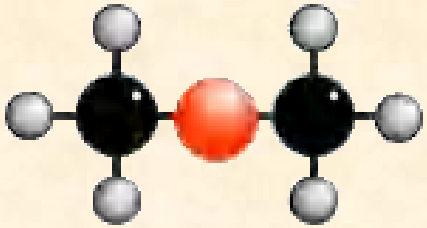


MORE DETAILS FOLLOW

STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

ALCOHOLS and ETHERS

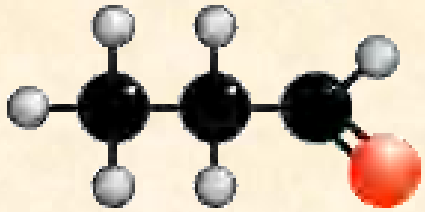


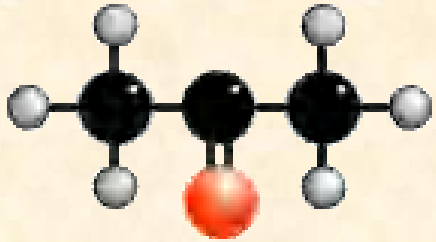


	ETHANOL	METHOXYMETHANE
Name		
Classification	ALCOHOL	ETHER
Functional Group	R-OH	R-O-R
Physical properties	polar O-H bond gives rise to hydrogen bonding. get higher boiling point and solubility in water	No hydrogen bonding low boiling point insoluble in water
Chemical properties	lewis base Wide range of reactions	Inert

STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

ALDEHYDES and KETONES

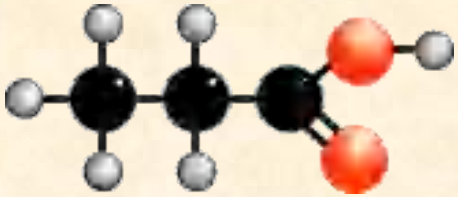


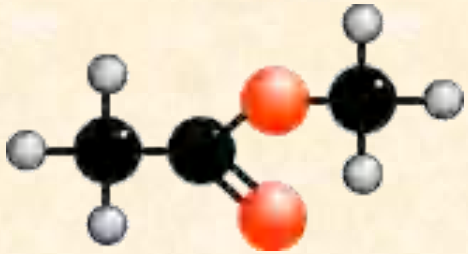


Name	PROPANAL	PROPANONE
Classification	ALDEHYDE	KETONE
Functional Group	R-CHO	R-CO-R
Physical properties	polar C=O bond gives dipole-dipole interaction	polar C=O bond gives dipole-dipole interaction
Chemical properties	easily oxidised to acids of same number of carbons	undergo oxidation under extreme conditions only
	reduced to 1° alcohols	reduced to 2° alcohols

STRUCTURAL ISOMERISM – FUNCTIONAL GROUP

CARBOXYLIC ACIDS and ESTERS

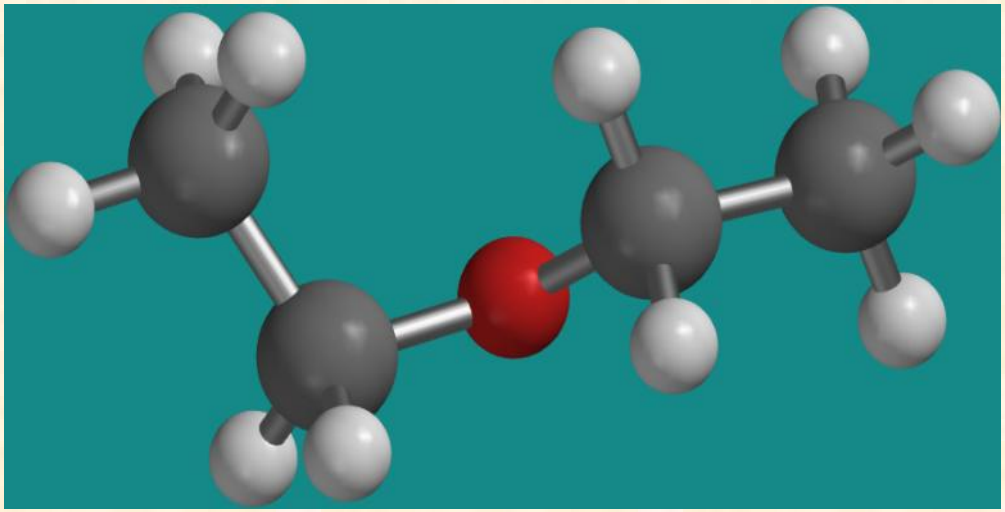




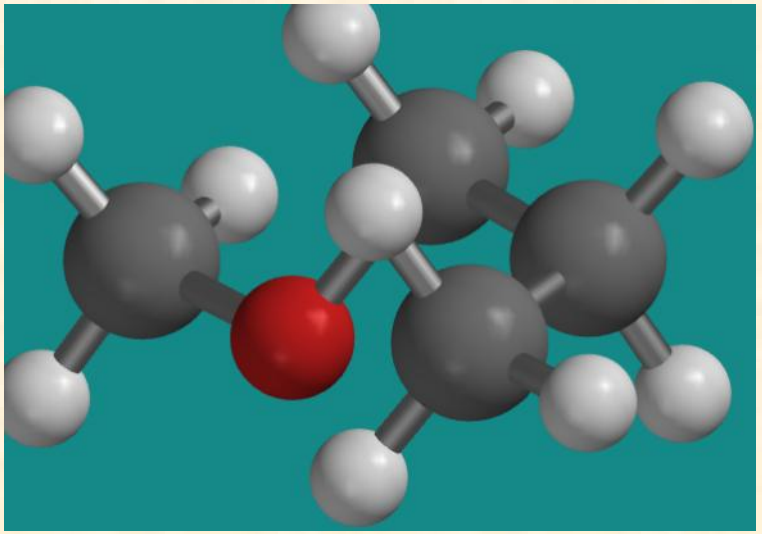
Name	PROPANOIC ACID	METHYL ETHANOATE
Classification	CARBOXYLIC ACID	ESTER
Functional Group	R-COOH	R-COOR
Physical properties	O-H bond gives rise to hydrogen bonding. get higher boiling point and solubility in water	No hydrogen bonding insoluble in water
Chemical properties	acidic react with alcohols	fairly unreactive hydrolysed to acids

STRUCTURAL ISOMERISM – METAMERISM

- same functional group
- difference in the size of alkyl groups on either side of the functional group.
- similar chemical properties
- slightly different physical properties



Ethoxyethane

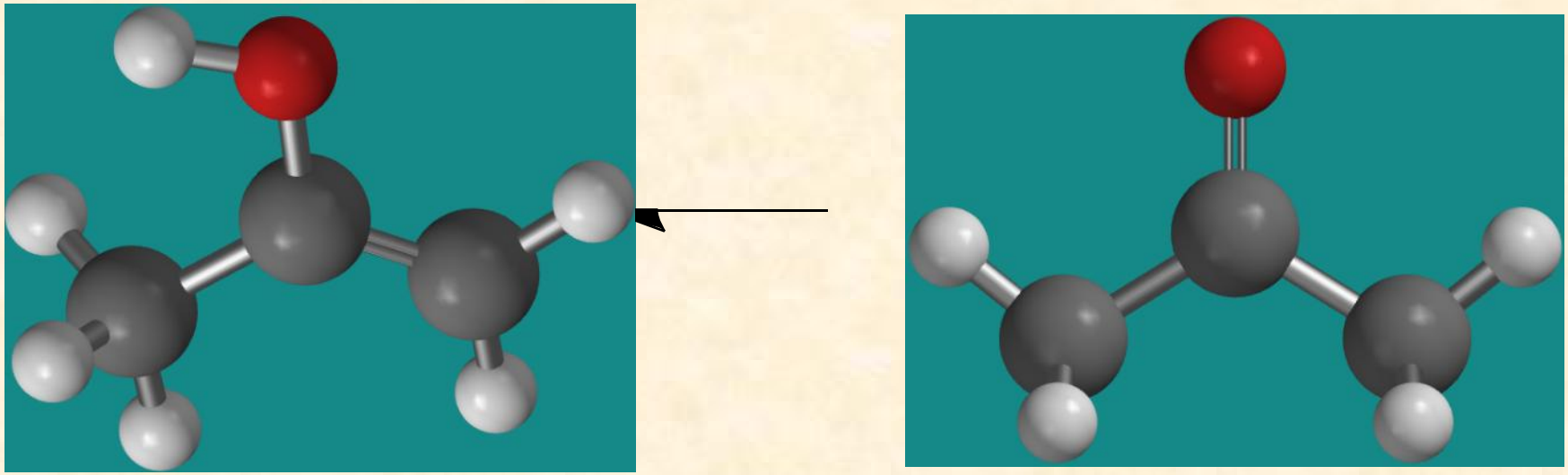


Methoxypropane

STRUCTURAL ISOMERISM – TAUTOMERISM

- differ in the location of double bond and hydrogen atom.
- different compounds with interconvertible nature in equilibrium
- different chemical properties
- different physical properties

ENOL and KETONE



1-Propen-2-ol

Propan-2-one

ACTIVITY 1

- Draw all possible isomers for a compound with the molecular formula of $C_4H_{10}O$
- Group the isomers into the different types

STEREOISOMERISM

Molecules have the **SAME MOLECULAR FORMULA** but the atoms are joined to each other in a **DIFFERENT SPACIAL ARRANGEMENT** - they occupy a different position in 3-dimensional space.

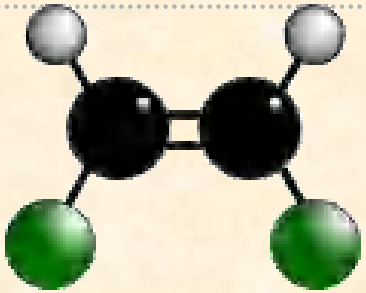
There are two types...

- GEOMETRICAL ISOMERISM
- OPTICAL ISOMERISM

GEOMETRICAL ISOMERISM IN ALKENES

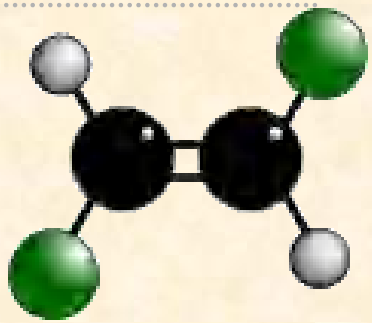
Introduction

- an example of stereoisomerism
- found in some, but not all, alkenes
- occurs due to the RESTRICTED ROTATION Of C=C bonds
- get two forms...



CIS (Z)

Groups/atoms are on the SAME SIDE of the double bond



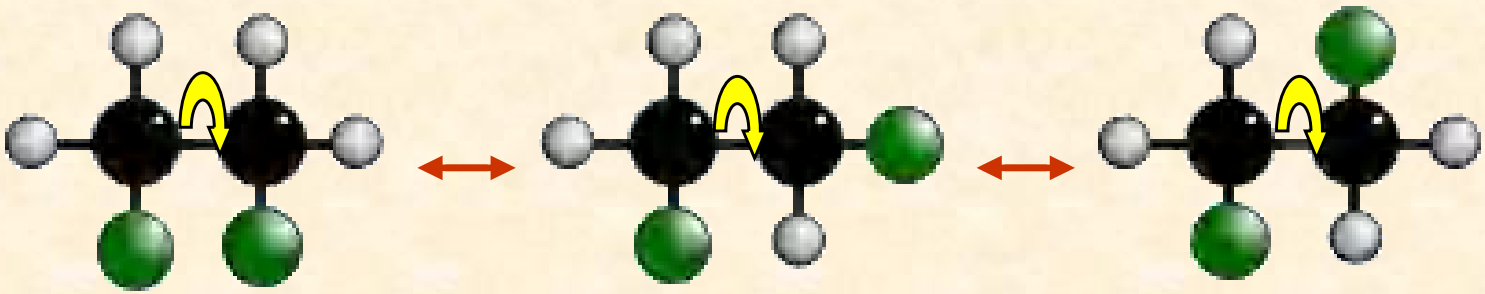
TRANS (E)

Groups/atoms are on OPPOSITE SIDES across the double bond

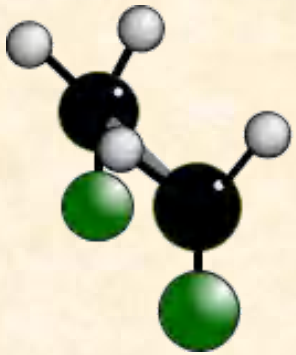
GEOMETRICAL ISOMERISM

RESTRICTED ROTATION OF C=C BONDS

Single covalent bonds can easily rotate. What appears to be a different structure is not. It looks like it but, due to the way structures are written out, they are the same.



ALL THESE STRUCTURES ARE THE SAME BECAUSE C-C BONDS HAVE 'FREE' ROTATION



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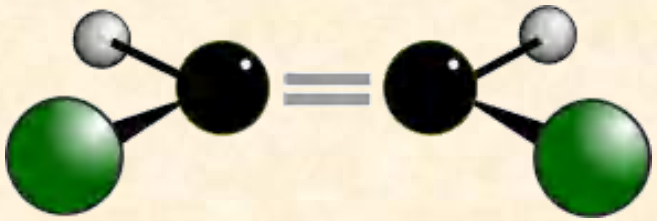
GEOMETRICAL ISOMERISM

RESTRICTED ROTATION OF C=C BONDS

C=C bonds have restricted rotation so the groups on either end of the bond are 'frozen' in one position; it isn't easy to flip between the two.



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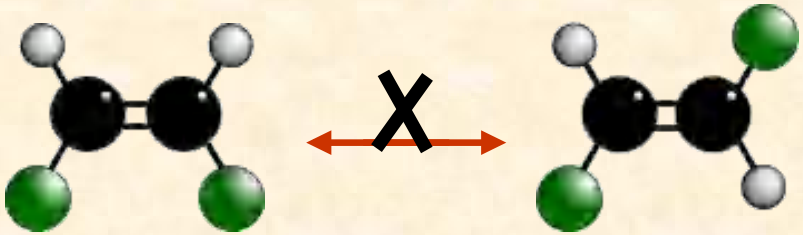
This produces two possibilities. The two structures cannot interchange easily so the atoms in the two molecules occupy different positions in space.



GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

E / Z

Z *(zusammen)* higher priority groups / atoms on the SAME side of C=C bond

E *(entgegen)* higher priority groups / atoms on OPPOSITE sides of C=C bond

GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

E / Z

Z *(zusammen)* higher priority groups / atoms on the SAME side of C=C bond

E *(entgegen)* higher priority groups / atoms on OPPOSITE sides of C=C bond

To determine priority, the Cahn, Ingold and Prelog convention is used.

eg $C_2H_5 > CH_3 > H$ and $I > Br > Cl > F > C > H$

GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

E / Z

Z *(zusammen)* higher priority groups / atoms on the SAME side of C=C bond

E *(entgegen)* higher priority groups / atoms on OPPOSITE sides of C=C bond

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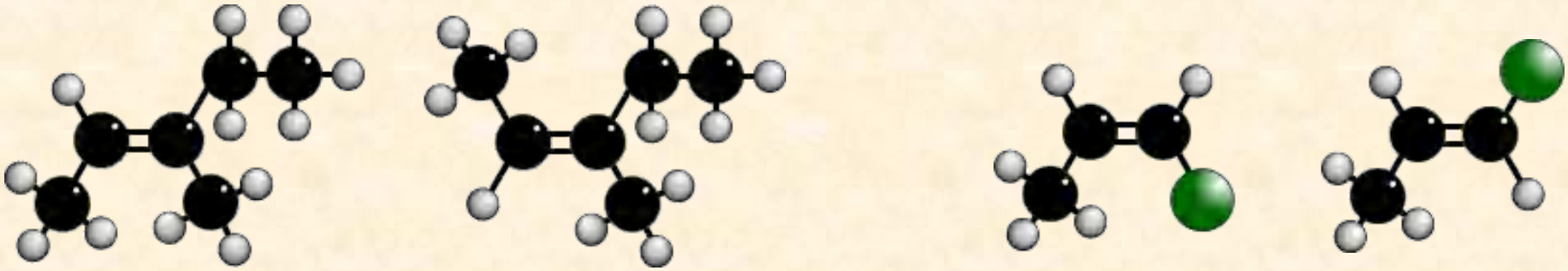


GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

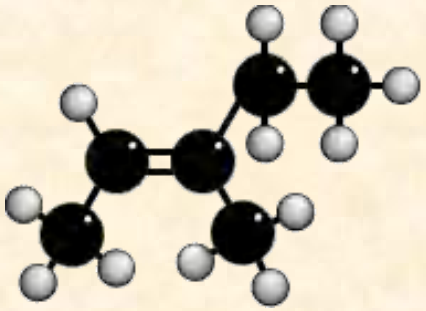
E / Z

Z *(zusammen)* higher priority groups / atoms on the SAME side of C=C bond

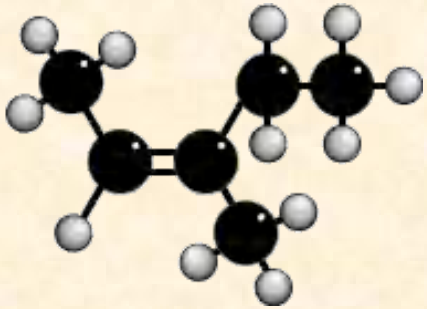
E *(entgegen)* higher priority groups / atoms on OPPOSITE sides of C=C bond

To determine priority, the Cahn, Ingold and Prelog convention is used.

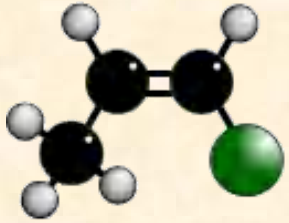
eg $C_2H_5 > CH_3 > H$ and $I > Br > Cl > F > C > H$



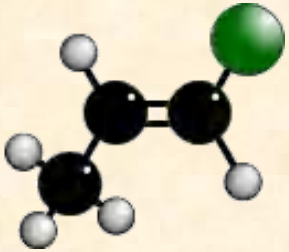
E



Z



Z



E

GEOMETRICAL ISOMERISM IN ALKENES

E/Z or CIS-TRANS

CIS / TRANS

Should only be used when there are two H's and two non-hydrogen groups attached to each carbon.

cis non-hydrogen groups / atoms on the SAME side of C=C bond

trans non-hydrogen groups / atoms on OPPOSITE sides of C=C bond

GEOMETRICAL ISOMERISM IN ALKENES

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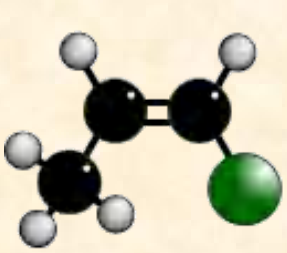
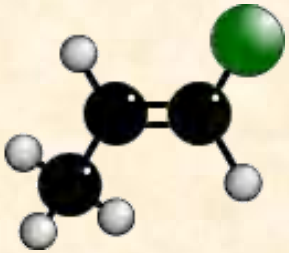
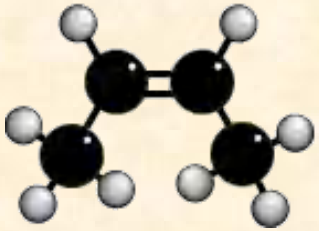


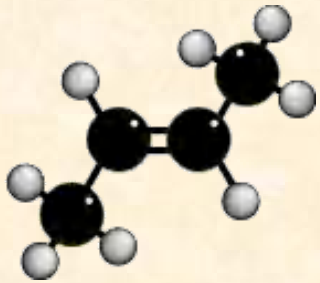
cis



trans



cis

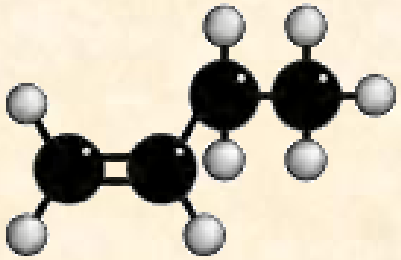


trans

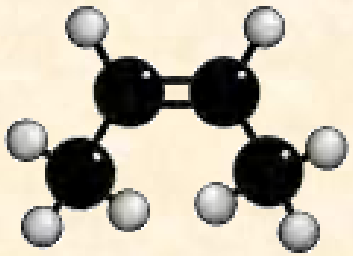
GEOMETRICAL ISOMERISM

Isomerism in butene

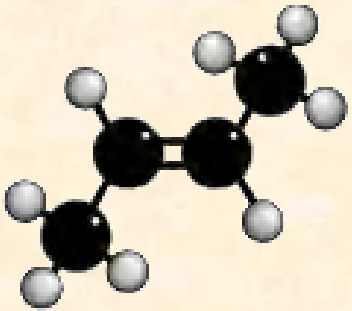
There are 3 structural isomers of C_4H_8 that are alkenes*. Of these ONLY ONE exhibits geometrical isomerism.



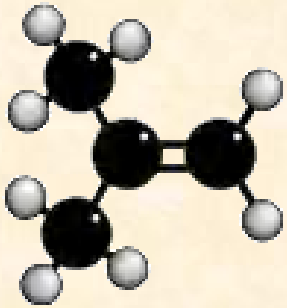
but-1-ene



cis but-2-ene
(*Z*) but-2-ene



trans but-2-ene
(*E*) but-2-ene

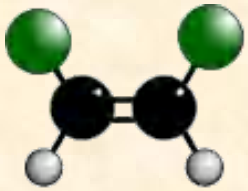


2-methylpropene

GEOMETRICAL ISOMERISM

How to tell if it exists

Two different atoms/groups attached

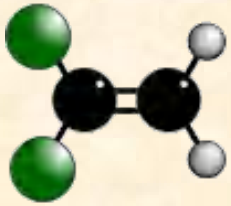


Two different atoms/groups attached

✔

GEOMETRICAL ISOMERISM

Two similar atoms/groups attached

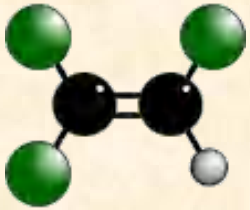


Two similar atoms/groups attached

☒

Once you get two similar atoms/groups attached to one end of a C=C, you cannot have geometrical isomerism

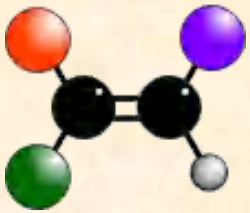
Two similar atoms/groups attached



Two different atoms/groups attached

☒

Two different atoms/groups attached



Two different atoms/groups attached

✔

GEOMETRICAL ISOMERISM

OPTICAL ISOMERISM

Occurrence another form of stereoisomerism

occurs when compounds have non-superimposable mirror images

Isomers the two different forms are known as optical isomers or enantiomers

they occur when molecules have a chiral centre

a chiral centre contains an asymmetric carbon atom

an asymmetric carbon has four different atoms (or groups)

arranged tetrahedrally around it.

ACTIVITY 2

❖ Which of the following compounds can exist as pairs of cis-trans isomers. Draw each pair of isomers and show the geometry.

a) $CH_3CH=CH_2$

(b) $(CH_3)_2C=CHCH_3$

(c) $CH_3CH_2CH=CHCH_3$

(d) $(CH_3)_2C=C(CH_3)CH_2CH_3$

(e) $ClCH=CHCl$

(f) $BrCH=CHCl$

OPTICAL ISOMERISM

Occurrence another form of **stereoisomerism**

occurs when compounds have **non-superimposable mirror images**

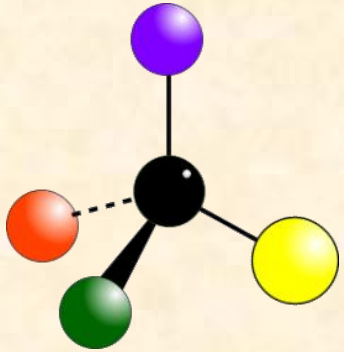
Isomers the two different forms are known as optical isomers or **enantiomers (Chiral molecules that are mirror images of one another)**

they occur when molecules have a **chiral centre**

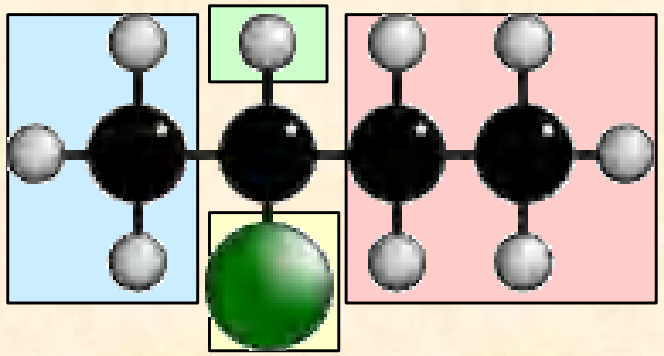
a chiral centre contains an **asymmetric carbon atom**

an asymmetric carbon has **four different atoms (or groups)** arranged in tetrahedral manner around it.

CHIRAL CENTRES



There are four different colours arranged tetrahedrally about the carbon atom



2-chlorobutane exhibits optical isomerism because the second carbon atom has four different atoms/groups attached

OPTICAL ISOMERISM

SPOTTING CHIRAL CENTRES

Look at each carbon atom in the chain and see what is attached to it. For a chiral centre you need an asymmetric carbon with four different atoms/groups) arranged tetrahedral manner around it.

IF A CARBON HAS MORE THAN ONE OF ANY ATOM/GROUP ATTACHED, IT CAN'T BE CHIRAL

$CH_3CH_2CH_2CH_2Cl$

1-chlorobutane

C	3 H's around it	NOT chiral
C	2 H's around it	NOT chiral
C	2 H's around it	NOT chiral
C	2 H's around it	NOT chiral

OPTICAL ISOMERISM

SPOTTING CHIRAL CENTRES

Look at each carbon atom in the chain and see what is attached to it. For a chiral centre you need an asymmetric carbon with four different atoms/groups) arranged tetrahedrally around it.

IF A CARBON HAS MORE THAN ONE OF ANY ATOM/GROUP ATTACHED, IT CAN'T BE CHIRAL

$CH_3CH_2CH_2CH_2Cl$

1-chlorobutane

C	3 H's around it		NOT chiral
C	2 H's around it		NOT chiral
C	2 H's around it		NOT chiral
C	2 H's around it		NOT chiral

$CH_3CH_2CHClCH_3$

2-chlorobutane

C	3 H's around it		NOT chiral
C	2 H's around it		NOT chiral
C	H, CH_3, Cl,C_2H_5 around it	CHIRAL	
C	3 H's around it		NOT chiral

OPTICAL ISOMERISM

SPOTTING CHIRAL CENTRES

Look at each carbon atom in the chain and see what is attached to it. For a chiral centre you need an asymmetric carbon with four different atoms/groups) arranged tetrahedrally around it.

IF A CARBON HAS MORE THAN ONE OF ANY ATOM/GROUP ATTACHED, IT CAN'T BE CHIRAL

$CH_3CH_2CH_2CH_2Cl$

1-chlorobutane

C	3 H's around it		NOT chiral
C	2 H's around it		NOT chiral
C	2 H's around it		NOT chiral
C	2 H's around it		NOT chiral

$CH_3CH_2CHClCH_3$

2-chlorobutane

C	3 H's around it		NOT chiral
C	2 H's around it		NOT chiral
C	H, CH_3, Cl,C_2H_5 around it	CHIRAL	
C	3 H's around it		NOT chiral

$(CH_3)_2CHCH_2Cl$

1-chloro-2-methylpropanane

C	3 H's around it		NOT chiral
C	2 CH_3's around it		NOT chiral
C	2 H's around it		NOT chiral

$(CH_3)_3CCl$

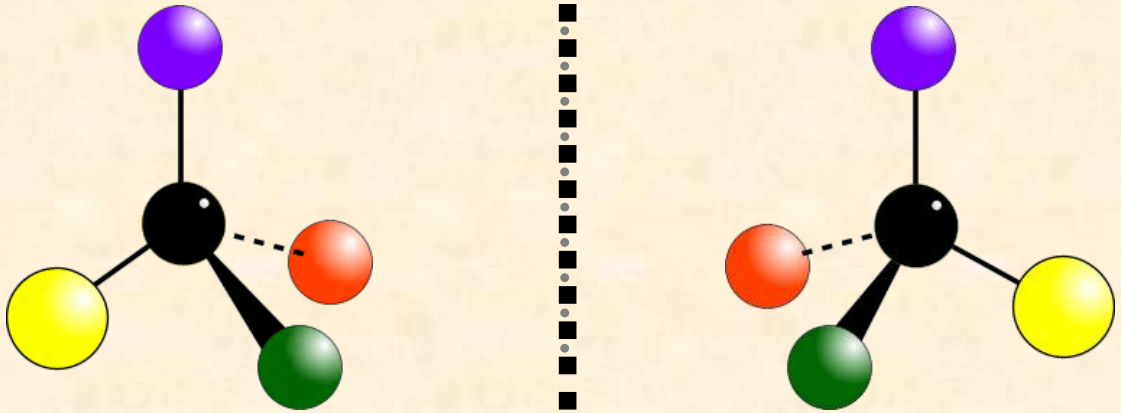
2-chloro-2-methylpropanane

C	3 H's around it		NOT chiral
C	3 CH_3's around it		NOT chiral

OPTICAL ISOMERISM

Spatial differences between isomers

- two forms exist which are NON-SUPERIMPOSABLE MIRROR IMAGES of each other
- non-superimposable means you can't stack one form exactly on top of the other



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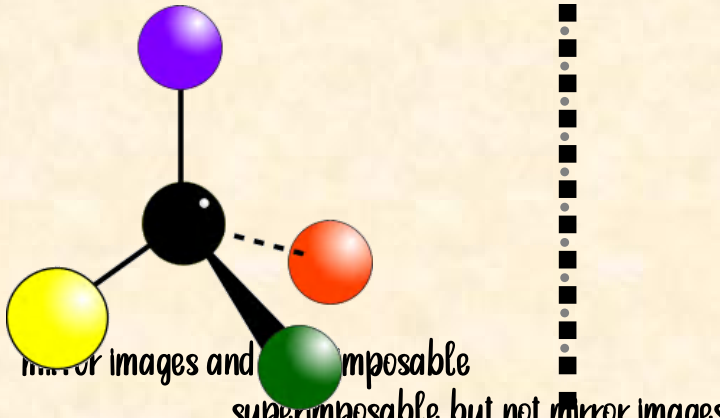


Some common objects are mirror images and superimposable

superimposable but not mirror images

non-superimposable mirror images

spoons

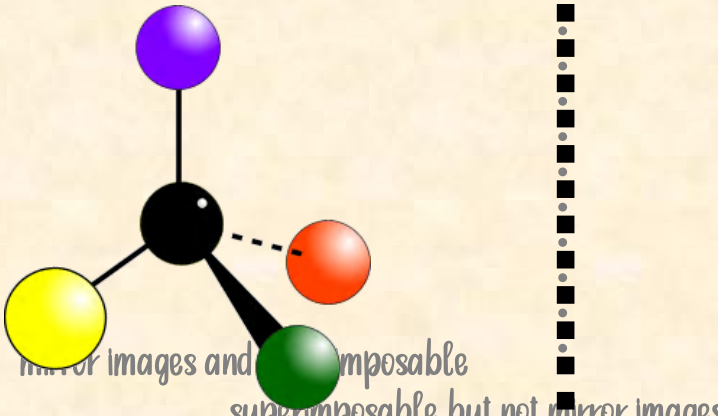
books

hands

OPTICAL ISOMERISM

Spatial differences between isomers

- two forms exist which are NON-SUPERIMPOSABLE MIRROR IMAGES of each other
- non-superimposable means you you can't stack one form exactly on top of the other



Some common objects are mirror images and superimposable

superimposable but not mirror images

non-superimposable mirror images

spoons

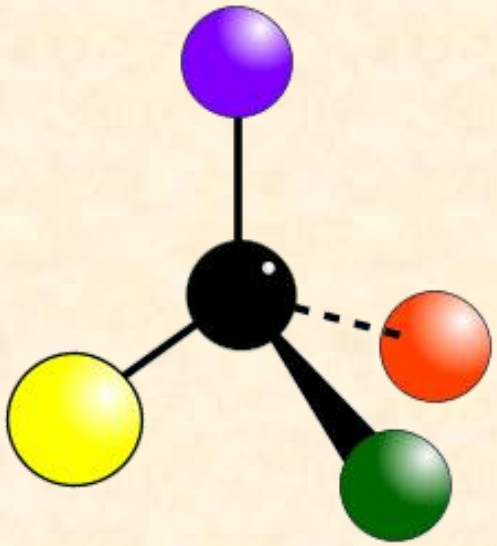
books

hands

NB for optical isomerism in molecules, both conditions must apply...
they must be mirror images AND be non-superimposable

OPTICAL ISOMERISM

What is a non-superimposable mirror image?



Animation doesn't work in old versions of Powerpoint

OPTICAL ISOMERS - DIFFERENCE

- isomers differ in their reaction to plane-polarised light
- plane polarised light vibrates in one direction only
- one isomer rotates light to the right, the other to the left
- rotation of light is measured using a polarimeter
- rotation is measured by observing the polarised light coming out towards the observer

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- If the light appears to have turned to the right turned to the left

DEXTROROTATORY	LAEVOROTATORY
d or + form	l or - form

OPTICAL ISOMERS - DIFFERENCE

- isomers differ in their reaction to plane-polarised light
- plane polarised light vibrates in one direction only
- one isomer rotates light to the right, the other to the left
- rotation of light is measured using a **Polarimeter**

- If the light appears to have turned to the right / turned to the left

DEXTROROTATORY	LAEVOROTATORY
d or + form	l or - form

Racemate a 50-50 mixture of the two enantiomers (dl) or (±) is a racemic mixture.
The opposite optical effects of each isomer cancel each other out

Benefit: in pharmaceutical industry in drug development

ACTIVITY 3

- ✔ Define the following:

a. chiral centre b. enantiomers

- ✔ The compound below is chiral. True or false? If true, identify the chiral centre (s) in the compound.