

ISOMERISM - A general survey

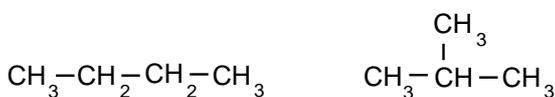
STRUCTURAL ISOMERS

have the **same molecular formula** but **different structural formulae**

They occur due to variations in . . .

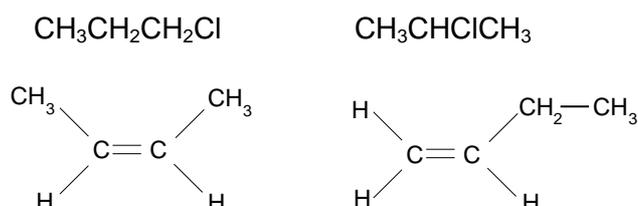
the carbon skeleton

CHAIN ISOMERISM

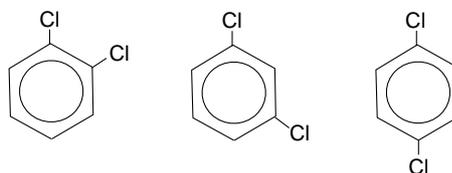


positions of a functional group on a chain

POSITION ISOMERISM

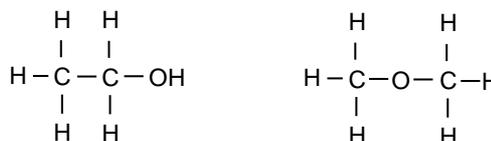


relative positions on a benzene ring



functional group

FUNCTIONAL GROUP ISOMERISM



Differences between isomers

Boiling Point

- “straight” chain isomers have higher boiling points than branched chain isomers
- the greater the degree of branching the lower the boiling point
- branching decreases the effectiveness of intermolecular attractive forces
- less energy has to be put in to separate the molecules
- boiling points can also vary between isomers containing different functional groups
e.g alcohols and ethers - due to dipole-dipole interaction and/or hydrogen bonding.

Chemical properties

Most isomers show similar chemical properties if the same functional group is present. However, it is best to have a look at each structure and apply any knowledge of the chemical reactions of the compounds in question.

Q.1 Draw all the structural isomers of C_4H_8 . How many are i) alkanes and ii) alkenes ?

Q.2 Draw all the structural isomers of formula $\text{C}_4\text{H}_{10}\text{O}$. How many are alcohols ?

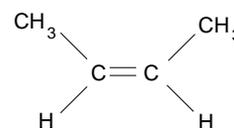
Q.3 Predict the isomer of pentane with the lowest boiling point.

GEOMETRICAL ISOMERISM

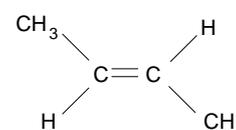
- Occurrence*
- a form of **stereoisomerism**.
 - found in alkenes, it occurs due to the **restricted rotation of C=C double bonds**
 - the two forms are known as **CIS** and **TRANS**

Q.4 *Make a model of but-2-ene and compare it with the examples shown below. What do you have to do to convert your structure to the other form?*

CIS groups on the same side of the double bond



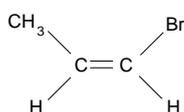
TRANS groups are across the double bond



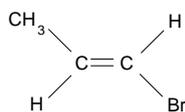
Both molecules have the double bond in the same position but the atoms occupy different positions within space.

Quick check

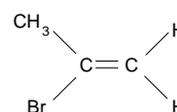
- are two similar atoms, or groups of atoms attached to the same end of the C=C ?
- if so you will not get geometrical isomers



A



B



C

A and B are geometrical isomers, C isn't. It is a structural isomer of the other two.

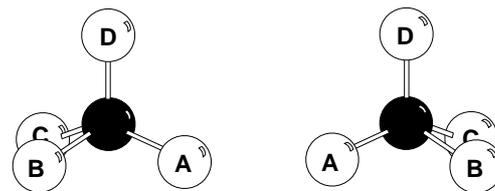
Q.5 *Work out all the possible structural isomers of pentene C_5H_{10} and hexene C_6H_{12} . How many exhibit geometrical isomerism?*

- Properties*
- Geometrical isomers have different physical properties (e.g. boiling point) and sometimes react differently in certain chemical reactions.

Q.6 *Using molecular models attach four different coloured balls to a central black one. Without looking at the model, repeat the procedure. Is it an exact copy of the first? Can it be stacked colour for colour on top of the first? If not, is there a relationship between the two? Swap any two colours. Is there any change?*

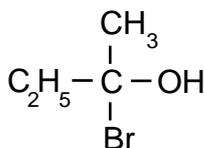
OPTICAL ISOMERISM

- Occurrence**
- another form of stereoisomerism
 - occurs when compounds have ... **non-superimposable mirror images**



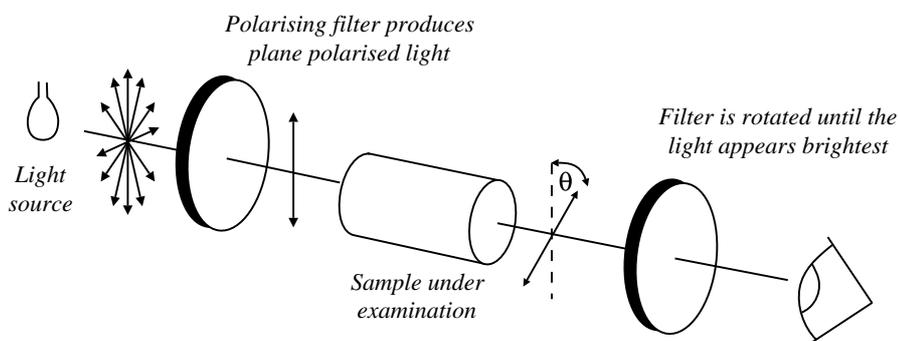
- Existence**
- the two different forms are known as **OPTICAL ISOMERS** or **ENANTIOMERS** and occur when molecules have a **CHIRAL centre**.
 - to find such a centre, look for an **ASYMMETRIC CARBON ATOM ... one with four different atoms, or groups of atoms arranged tetrahedrally around it.**

example



- two forms exist which are non-superimposable mirror images of each other; i.e. you can't stack one form exactly on top of the other.

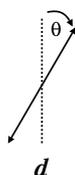
- Difference**
- isomers differ in their reaction to plane-polarised light (vibrates in one direction only)
 - one isomer rotates light to the right, the other to the left
 - rotation of light is measured using a polarimeter.



- rotation is measured by observing the polarised light **coming out** towards the observer
- If the light appears to have

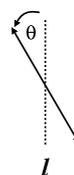
turned to the right
DEXTROROTATORY

d or + form



turned to the left
LAEVOROTATORY

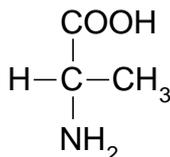
l or - form



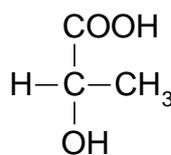
- Racemate**
- a 50-50 mixture of the two **enantiomers** (dl) or (\pm) is known as a **racemic mixture**
 - the opposite optical effects of each isomer cancel each other out

Examples Optical activity is widespread, especially in nature, biochemistry and pharmaceuticals.

e.g.



2-aminopropanoic acid
(Alanine)



2-hydroxypropanoic acid
(Lactic acid)

The drug **thalidomide** is optically active but only one of the optical isomers is effective. Many years ago women gave birth to babies with abnormalities caused by taking thalidomide tablets which contained some of the 'wrong' enantiomer.

Practical problems

- laboratory reactions are more likely to make mixtures than those occurring in the body
- a larger dose will be needed if a drug contains a mixture of enantiomers
- the non-reactive isomer may be dangerous (as in thalidomide)

Q.7 How many structural isomers of C_6H_{14} are optically active?
How many structural isomers of butanol, C_4H_9OH , are optically active?

Q.8 Which of the following can exist as enantiomers?

a) 2-bromopropane	b) 2-bromobutane
c) 2-bromopentane	d) 3-bromopentane
e) $CH_3CH(OH)C_2H_5$	f) $CH_3CH(OH)CH_3$

Q.9 Why is there the possibility of enantiomers being formed when butanone undergoes nucleophilic addition with HCN? Do all carbonyl compounds produce a mixture of products with HCN? If not, why not?

SUMMARY

