

ISOMERISM - A general survey

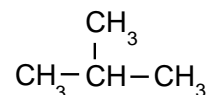
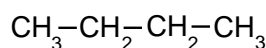
STRUCTURAL ISOMERS

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

They occur due to variations in . . .

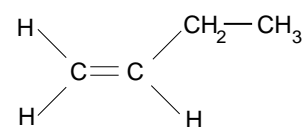
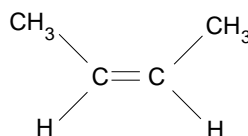
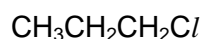
the carbon skeleton

CHAIN ISOMERISM

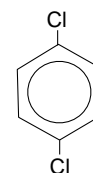
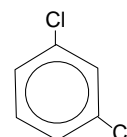
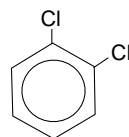


positions of a functional group on a chain

POSITION ISOMERISM

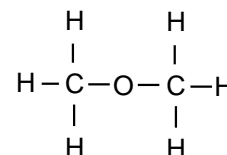
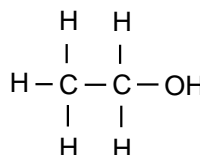


relative positions on a benzene ring



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 also vary between isomers containing different functional groups
e.g alcohols and ethers - due to permanent dipole-dipole interactions or hydrogen bonding.

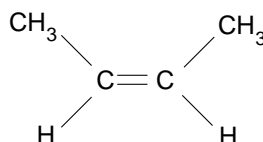
Chemical properties

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.

E/Z ISOMERISM

- Occurrence**
- a form of **stereoisomerism**.
 - found in alkenes, it occurs due to the **restricted rotation of C=C double bonds**
 - certain forms are known as **CIS** and **TRANS**
 - to occur, there must be two different groups/atoms on one end of the C=C and two different groups/atoms on the other end

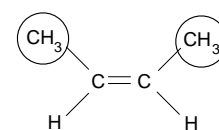
2 different groups on this end



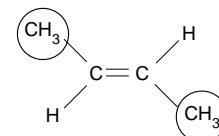
2 different groups on this end

- Cis-trans**
- if there are two H's and two non-hydrogen groups attached to each carbon

CIS groups on the same side of the double bond



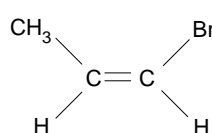
TRANS groups are across the double bond



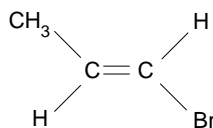
Both molecules have the double bond in the same position but the atoms occupy different positions within space.

Quick check

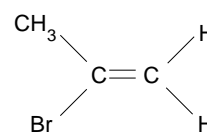
- are two similar atoms, or groups of atoms attached to the same end of the C=C ?
- if so you will not get E/Z isomers



A



B

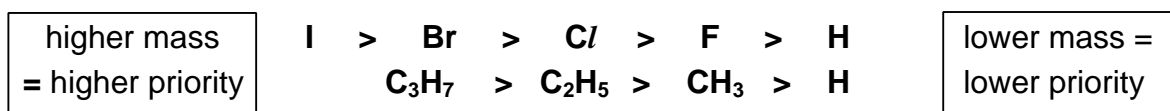


C

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

E/Z

- a newer system based on the masses of groups/atoms attached to the C=C
- CIP rules are used to allocate priority
- the heavier the atom / group attached to the C=C bond, the higher its priority...



Z ZUSAMMEN

Higher priority groups are on the same **side** of C=C

E ENTGEGEN

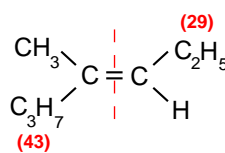
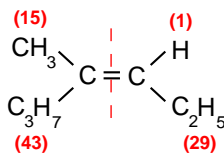
Higher priority groups are on opposite **sides** of C=C

- CIP RULES**
- they **work out if a geometrical isomer is E or Z**
 - named after the people who developed the system... Cahn-Ingold-Prelog
 - groups/atoms either side of the C=C are prioritised according to their mass
 - **higher mass number = higher priority**

4-methylheptane

higher priorities are on the same side of the C=C

(Z) isomer



higher priorities are on the same side of the C=C

(E) isomer

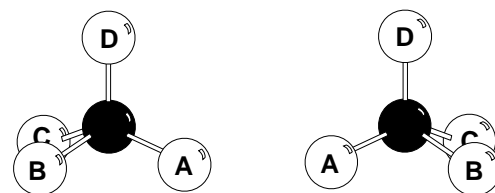
Properties E/Z isomers have different physical properties (e.g. boiling point) and sometimes react differently in certain chemical reactions.

Q.1

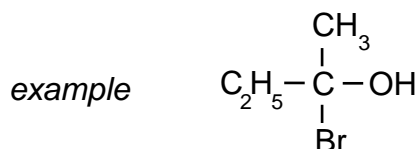
Work out all the possible structural isomers of pentene C_5H_{10} and hexene C_6H_{12} . How many exhibit E/Z isomerism?

OPTICAL ISOMERISM

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



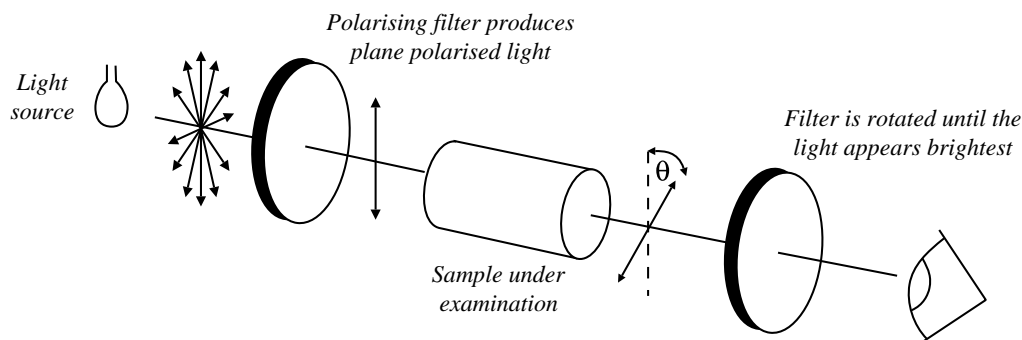
- Existence**
- the two different forms are known as **OPTICAL ISOMERS** or **ENANTIOMERS** and occur when molecules have a **CHIRAL centre**.
 - to find such a centre, look for an **ASYMMETRIC CARBON ATOM** ... one with four different atoms or arranged tetrahedrally around it.



- 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
 - one isomer rotates light to the right, the other to the left
 - rotation of light is measured using a polarimeter

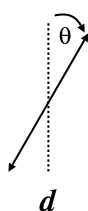
A POLARIMETER



- rotation is measured by observing the polarised light as it **emerges towards** the observer. If the light appears to have...

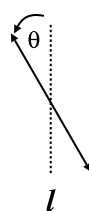
turned to the right
DEXTROROTATORY

d or + form



turned to the left
LAEVOROTATORY

l or - form

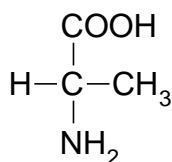
**Racemate**

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

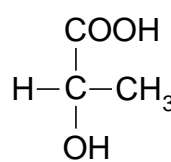
Examples

Optical activity is widespread 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 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.2 How many structural isomers of C_6H_{14} are optically active?

How many structural isomers of butanol, C_4H_9OH , are optically active?

Q.3 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.4 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?

