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

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

Priorities The heavier the atom / group attached to the C=C bond, the higher its priority...

I > Br > Cl > F > O > C > H
C₃H₇ > C₂H₅ > CH₃ > H

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

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 C₅H₁₀ and hexene C₆H₁₂. 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.

Example

\[
\begin{align*}
  \text{CH}_3 \\
  \text{C}_2\text{H}_5 \\
  \text{Br}
\end{align*}
\]

• 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.

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
Optical activity is widespread in nature, biochemistry and pharmaceuticals. 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 C₆H₁₄ are optically active?
How many structural isomers of butanol, C₄H₉OH, 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) CH₃CH(OH)C₂H₅  f) CH₃CH(OH)CH₃

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?