Chem Factsheet

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How to Answer Questions on Isomerism

To succeed in this topic you need to:-
- Be able to interpret molecular, structural and displayed formulas
- Be familiar with organic functional groups

After working through this Factsheet you will:-
- Recognise the differences between different types of isomerism
- Have had the opportunity to see some worked examples of typical exam questions on this topic.

This Factsheet will present an overview of the key definitions associated with the topic of isomerism, illustrate the different types of isomerism with examples and, finally, give some worked examples of typical questions on this topic.

Isomerism

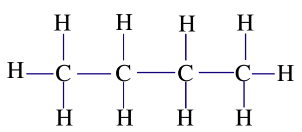
Isomerism
The existence of different molecules with the same molecular formula

- **Structural Isomerism**
  The different molecules have different structural formulas
  - **Chain**
    The different structural formulas are due to branching of the main carbon chain
  - **Positional**
    The different structural formulas are due to different positions of a functional group on the main carbon chain
  - **Functional Group**
    The different structural formulas are due to the presence of different functional groups
- **Stereoisomerism**
  The different molecules have the same structural formula but a different arrangement of their atoms in space
  - **E-Z (cis-trans)**
    The different spatial arrangements are due to restricted rotation about (usually) a C=C double bond
  - **Optical**
    The different spatial arrangements are due to the presence of a chiral carbon atom in the molecules

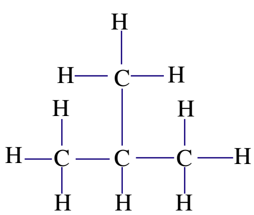
Examples

Chain Isomerism

The molecular formula C_4H_{10} represents two possible alkanes. $CH_3CH_2CH_2CH_3$ (butane) or $CH_3CH(CH_3)CH_3$ (methylpropane) (alternatively, $(CH_3)_3CH$). The butane molecule has a four-carbon 'backbone' while the methylpropane has a three-carbon 'backbone' with a one-carbon side-chain from the second carbon along in the chain. This can be seen more clearly using displayed formulae, but the difference is evident in the basic structural formulae as shown above, which is why this is an example of structural isomerism.



butane

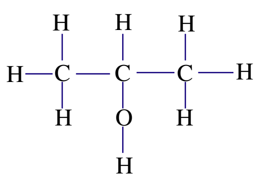


2-methylpropane

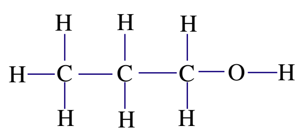
Positional Isomerism

The molecular formula C_3H_8O could refer to an alcohol, C_3H_7OH. It could also refer to an ether (C-O-C) but this would not be an example of positional isomerism – see below.

There are however two different alcohols with the formula C_3H_7OH; $CH_3CH_2CH_2OH$ (propan-1-ol) or $CH_3CH(OH)CH_3$ (propan-2-ol). This is an example of positional isomerism as both molecules contain the same functional group (–OH) but in different positions (C1 or C2) on the carbon 'backbone'



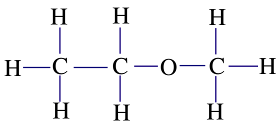
propan-2-ol



propan-1-ol

Functional Group Isomerism

As well as the two alcohols shown above, the molecular formula C_3H_8O could also refer to the molecule $CH_3CH_2OCH_3$ (methoxyethane). The difference between this molecule and either propan-1-ol or propan-2-ol is functional group isomerism as the nature of the difference in structural formula is a difference in the functional group present, an ether vs an alchol.



ethoxymethane

E-Z (cis-trans) Isomerism

Note : also previously called geometric isomerism.

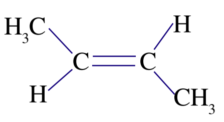
This type of isomerism is most commonly encountered in the context of alkenes, in the organic chemistry section of the syllabus, and this is what will be covered here. However you will also need to check if your syllabus requires you to recognise this type of isomerism with reference to transition metal complex ions.

The formula C_4H_8 could indicate one of several different structures:
1. $CH_3CH_2CH{=}CH_2$ (but-1-ene)
2. $CH_3CH{=}CHCH_3$ (but-2-ene)
3. $(CH_3)_2C{=}CH_2$ (2-methylpropene)
4. There are also two cyclic alkanes with this formula; cyclobutane and methylcyclopropane.

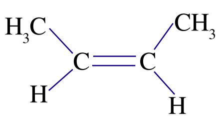
The differences between all of these are example of structural isomerism as the different molecules have different structural formulae (and, therefore, different names).

1 vs 2 is an example of positional isomerism; 3 vs 1 or 2 are example of chain isomerism; 4 vs 1 or 2 or 3 are examples of functional group isomerism and the two different cyclic alkanes represent chain isomerism.

However, if we look more closely at the structure of $CH_3CH{=}CHCH_3$ we can see that there are two different compounds with this molecular AND structural formula. The difference is only evident if we look at the displayed formulae of the compounds.



(trans)-but-2-ene



(cis)-but-2-ene

These are two different compounds as the nature of a double bond prevents free rotation, unlike a single bond. This means that the relative positions of the groups on each carbon are fixed in space; giving rise to the two arrangements shown.

As both of these compounds have the same structural formula and hence the same name, prefixes are needed to indicate the different arrangements of the atoms. In this case, the 'trans' prefix is used to indicate that the methyl groups are on opposite 'sides' of the double bond while the 'cis' prefix indicates that they are both on the same 'side' of the double bond.

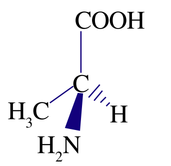
In some syllabuses the use of the 'trans' and 'cis' prefixes has been replaced with the more versatile '*E*/*Z*' system, which is based on the relative priorities of each group attached to a double bonded carbon, where the priorities are decided on the basis of atomic number. In this example *cis*-but-2-ene becomes *Z*-but-2-ene and *trans*-but-2-ene becomes *E*-but-2-ene.

Optical Isomerism

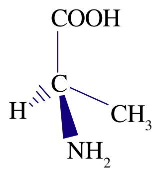
This possibility is also most commonly encountered in organic compounds but can again also apply to some transition metal complexes so you will need to check your syllabus for this possibility.

Optical isomers (also called *enantiomers*) are defined as *non-superimposable mirror images*. This occurs when a molecule is asymmetric i.e. when it contains a chiral carbon atom, which is a carbon atom attached to four different atoms or groups of atoms. Common examples are amino acids such as alanine (2-aminopropanoic acid), $CH_3CH(NH_2)COOH$.

The presence of the chiral carbon atom means that there is no plane or line of symmetry in the molecule, which means that the mirror images of the structure are non-superimposable.



(S)-2-aminopropanoic acid



(R)-2-aminopropanoic acid

Again prefixes have to be used to represent the two alternative arrangements of atoms and '*S*' and '*R*' are now usually used in place of '*L*' and '*D*'. However, most syllabuses do not expect you to be able to decide which isomer is which in terms of the use of these prefixes. (An exception is the Pre-U syllabus where you are expected to be able to apply the Cahn-Ingold-Prelog rules to assign '*S*' or '*R*' prefixes as appropriate).

The only difference in the properties of a pair of such enantiomers is the effect that they have on the plane of vibration of plane polarised light with one of the isomers rotating the plane of vibration clockwise while the other (all other conditions such as concentration and temperature being kept constant) rotates the plane of vibration through the same angle, but anti-clockwise. The 'clockwise-rotator' is referred to as '+' (or '*d*') while the 'anti-clockwise-rotator' is referred to as '–' (or '*l*') – but there is no correlation between '*S*' ('*L*') or '*R*' ('*D*') and the direction of rotation. An equimolar mixture of the two enantiomers, called a *racemate* or *racemic mixture*, can be considered to be a third form of the same structure and has no optical activity since the opposite rotations cancel out.

Question-Answering Advice

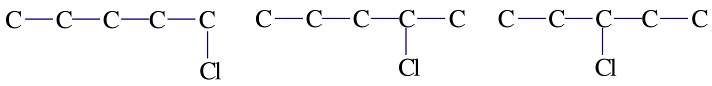
Many isomerism questions require candidates to identify isomers corresponding to a particular formula. There are two key ideas that must be applied for success in such questions.

Take a logical approach when suggesting possible structures as it is very easy to end up drawing different 'versions' of the same structure instead of actually drawing different structures. e.g. You may be asked to draw all the structural isomers corresponding to the formula $C_5H_{11}Cl$. (The diagrams below have been simplified by leaving out the hydrogen atoms).

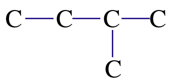
(a) start with a five-carbon chain – best drawn straight for clarity.

C—C—C—C—C

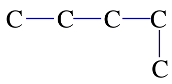
(b) Then identify how many different positions are possible for the Cl.



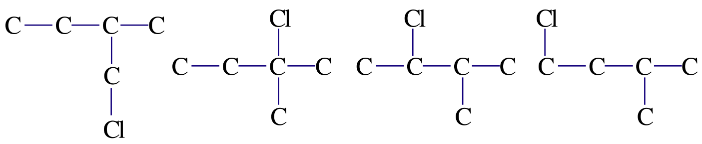
(c) Having exhausted all the possibilities based on a five-carbon chain the next thing to try is a four-carbon chain with branches.



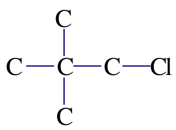
remember that any 'branch' on the end of the chain simply extends the chain such that

 is the same as C—C—C—C—C

(d) Then, again, identify all possible positions for the C*l*.



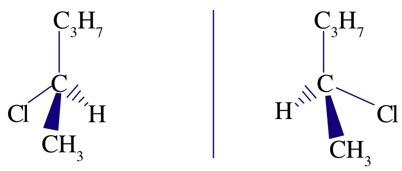
(e) Having exhausted all the four-carbon chain possibilities try three. In this case any attempt to add 'branches' to either end carbon simply recreates a four-carbon chain so the only option is to put both the other carbons on the middle carbon of the three-carbon chain and there is then only one possible position for the Cl as all four methyl groups are equivalent.



(f) In this example it has been assumed that the question asked for all the *structural* isomers. If it wanted *all* isomers then you also need to check for the possibility of stereoisomerism. Three of the eight structural isomers above are chiral. Can you see which?

Answer:
2-chloropentane (in (b)), 1-chloro-2-methylbutane and 2-chloro-3-methylbutane (in (d)).

For 2-chloropentane:

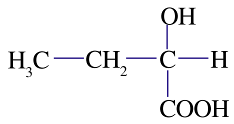


Try drawing 3D representations of the other enantiomers!

Practice Questions

1. 2-iodobutane can be converted into butan-2-ol by treatment with aqueous sodium hydroxide.
   (a) Give the structural formula of 2-iodobutane.
   (b) State the conditions under which the same reagent could be used to convert the 2-iodobutane to an alkene instead of an alcohol.
   (c) Give the structures of the alkenes produced by the reaction in part b.

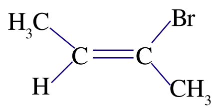
2. Two stereoisomers are formed by the dehydration of compound **Q**.



Q

Give the structures of these two stereoisomers and name the type of stereoisomerism.

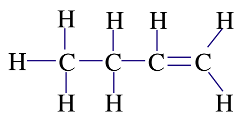
2. Select A-D as the correct name for the molecule shown below



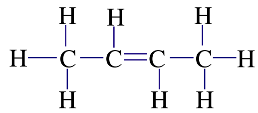
A *Z*-2-bromobut-2-ene
B *E*-2-bromobut-2-ene
C *E*-3-bromobut-2-ene
D *Z*-3-bromobut-2-ene

Answers

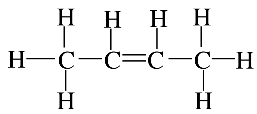
1. (a) $CH_3CH_2CHICH_3$ (the full displayed formula would be accepted as an alternative).
   (b) Ethanolic solution (the use of ethanol instead of water as the solvent favours the elimination reaction instead of the nucleophilic substitution reaction to form an alcohol).
   (c) This is the section of the question that involves isomerism as simple familiarity with the production of alkenes from halogenoalkanes will lead to the suggestion of two possibilities – namely but-1-ene and but-2-ene. However, candidates also need to recognise the possibility of geometric isomerism in but-2-ene so that they show both the cis (or Z) and trans (or E) isomers.



but-1-ene

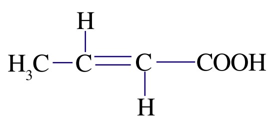


trans-but-2-ene

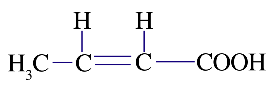


cis-but-2-ene

2. This involves recognising the dehydration of an alcohol to an alkene and then recognising that the alkene formed can exhibit geometric / EZ / cis-trans isomerism as there are two different groups attached to each of the double-bonded carbon atoms.



cis-but-2-enoic acid



trans-but-2-enoic acid

3. A is the correct answer as, on the left-hand carbon, 'C' has a higher priority than 'H' and on the right-hand carbon 'Br' has a higher priority than 'C' because the increasing order of atomic number is H < C < Br. The two higher priority groups are both 'above' the double bond so this is the 'Z' isomer.

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