VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT

ISOMERISM

Scan here for to ask question related to the lecture

LECTURE OUTLINE

ASSESSMENT OBJECTIVES

Candidates should be able to:

(a) describe constitutional (structural) isomerism

(b) describe *cis-trans* isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds
[use of *E*, *Z* nomenclature is **not** required]

(c) explain what is meant by a chiral centre

(d) deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry

(e) recognise that an optically active sample rotates plane-polarised light and contains chiral molecules

(f) recognise that enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light
[usage of the term diastereomers is **not** required]

(g) recognise that enantiomers have identical chemical properties except in their interactions with another chiral molecule

(h) recognise that different stereoisomers exhibit different biological properties, for example in drug action

(i) deduce the possible isomers for an organic molecule of known molecular formula

(j) identify chiral centres and/or *cis-trans* isomerism in a molecule of given structural formula

ISOMERISM

Isomerism is the occurrence of two or more compounds with the same molecular formula but having different structures or spatial orientation. There are two main types of isomerism.

Firstly, constitutional (structural) isomerism, which is further divided into chain isomerism, positional isomerism and functional group isomerism. Secondly, stereoisomerism, which is further divided into *cis-trans* isomerism and enantiomerism.

1 Constitutional (Structural) Isomerism

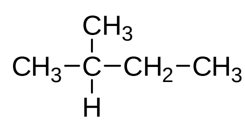
Candidates should be able to:
(a) describe constitutional (structural) isomerism

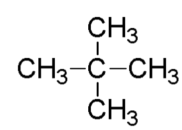
It refers to isomers containing the same number of each kind of atom but differing in regard to how the atoms are linked to one another, i.e. they have the **same molecular formula** but **different structural formula**. There are three types: chain, positional and functional group isomerism.

- **Chain isomerism**
  The isomers differ in the way **carbon** atoms are linked together. They possess the same functional group or homologous series.

  E.g. C_5H_{12}

  $CH_3–CH_2–CH_2–CH_2–CH_3$

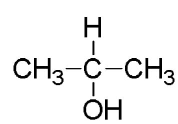




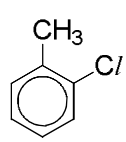
- **Positional isomerism**
  The isomers have the **same functional group but differ in its position along the same carbon chain length**.

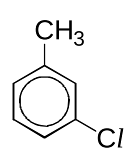
  E.g. C_3H_8O

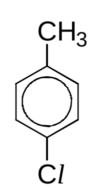
  $CH_3–CH_2–CH_2–OH$

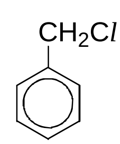


  E.g. C_7H_7Cl (contains benzene ring)









  Exercise
  Draw all possible positional isomers for a six-carbon chain alkene with molecular formula C_6H_{12}.

- **Functional group isomerism**
  The isomers have **different functional groups**.

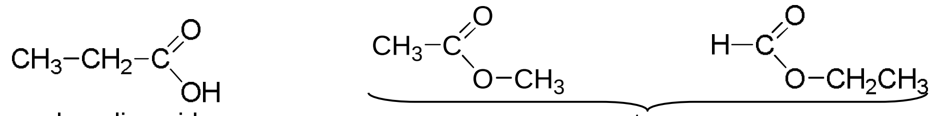
  E.g. C_2H_6O

$CH_3–CH_2–OH$	$CH_3–O–CH_3$
alcohol	ether

E.g. C_3H_6O

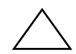
aldehyde ketone

E.g. $C_3H_6O_2$



carboxylic acid esters

Exception: Alkene and cycloalkane share the same molecular formula, C_nH_{2n}. They are constitutional isomers but are not classified as functional group isomers as alkane is not regarded as a functional group.

E.g. C_3H_6: $CH_3–CH=CH_2$ 

propene cyclopropane

- **Determination of constitutional isomers from given molecular formula**

Candidates should be able to: (i) deduce the possible isomers for an organic molecule of known molecular formula

Step 1: arrangement of carbon atoms

Consider the longest possible carbon chain followed by subsequent removal of one C atom from the chain and re-attach it to any C atom **except an end carbon** (as this will restore the original chain length).

Step 2: possible functional groups

For example, the presence of **one oxygen atom** indicates that alcohol, ether, aldehyde or ketone could be present. If the compound is **saturated with C_nH_{2n+2} ratio**, alcohol or ether could be present. For each arrangement of carbon atoms in step 1, attach the functional group to all possible positions that give rise to a **different** structure.

Note:

(i) The greater the number of atoms in a molecule, the greater the number of isomers.

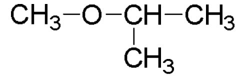
(ii) Isomers with the **same functional groups** (i.e. they belong to the same homologous series) have **similar chemical properties but different physical properties**.

(iii) Isomers with **different functional groups** (i.e. they belong to different homologous series) have **different physical and chemical properties**.

E.g. $C_4H_{10}O$ (alcohol or ether)

Alcohols:

Ethers:

$CH_3-O-CH_2-CH_2-CH_3$  $CH_3-CH_2-O-CH_2-CH_3$

Exercise

Draw the skeletal formulae of all the possible constitutional isomers with one functional group with the molecular formula $C_4H_8O_2$.

Exercise

Determine all the possible constitutional isomers for a compound with molecular formula C_3H_5Br.

2 Stereoisomerism

It refers to isomers having the **same molecular and constitutional (structural) formulae** but **differs** in the way the atoms are **arranged in 3-dimensional space**.

There are two types of stereoisomerism: *cis-trans* isomerism and enantiomerism.

2.1 *Cis-trans* isomersim

Candidates should be able to: (b) describe *cis-trans* isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds [use of *E*, *Z* nomenclature is **not** required]

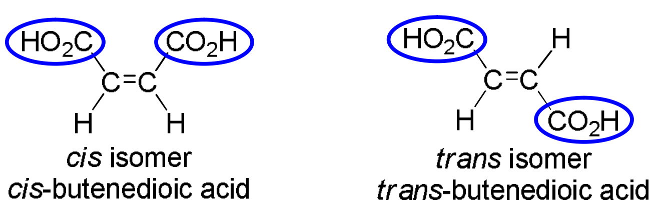
- *Cis–trans* isomerism occurs in compounds in which **free rotation is prevented by the presence of double bonds, a ring structure or steric factors**.

  A single bond can be easily rotated but not a double bond as rotation reduces the extent of lateral overlap of p orbitals. If a multiple bond is rotated through 90°, p orbital overlap will be reduced to zero which implies the non-existence of the pi bond.

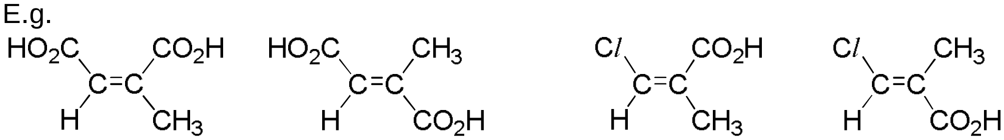
- In alkenes, *cis–trans* isomerism arises from the **restricted rotation about the C=C bond due to the presence of π bond**. Each carbon atom of the C=C bond is bonded to **two different atoms / groups**.

  cis isomer: same atoms / groups are on the same side of the C=C bond
  trans isomer: same atoms / groups are on opposite sides of the C=C bond

  E.g.



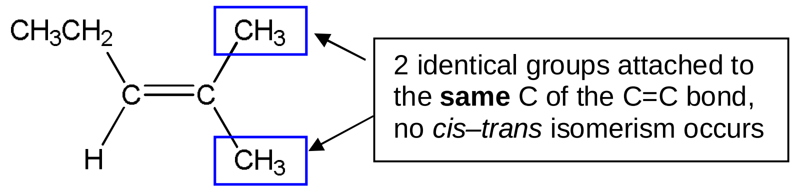
E.g.



For above molecules with four different atoms / groups, the isomers are designated using the *E, Z* nomenclature (**not in H2 syllabus**) instead of *cis* and *trans*.

- *Cis-trans* isomerism **cannot** exist if either carbon of the C=C bond is bonded to **two identical groups**.

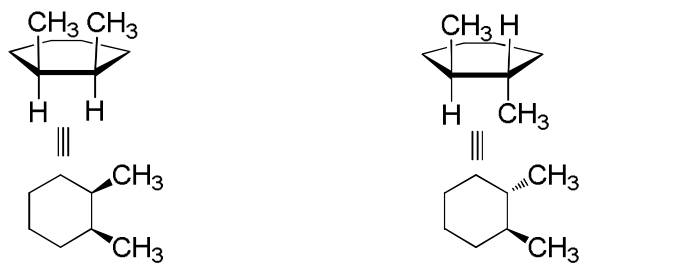
E.g.



- Cyclic alkenes with 3 to 7 carbon atoms are fixed in the *cis* structure. A *trans* structure for a double bond can exist in cyclic compounds only when a large ring is present, otherwise the ring strain in the compound is very high. Hence, **C=C bond in a ring** does **not** show *cis-trans* isomerism due to **ring strain** in the *trans* isomer.

- For a given structure which exhibits only *cis-trans* isomerism,
no. of *cis-trans* isomers = $\mathbf{2^n}$, where n = no. of C=C bond with *cis-trans* isomerism

- **Cyclic compounds** can also exhibit *cis-trans* isomerism due to restricted rotation about the **single bonds** in cyclic systems. The substituents of the *cis* isomer are on the **same side** of the ring while the substituents of the *trans* isomer are on **opposite sides** of the ring.

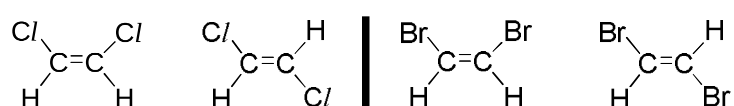


cis-1,2-dimethylcyclohexane *trans*-1,2-dimethylcyclohexane

- **Restricted rotation** about C=C bond **prevents spontaneous inter–conversion** of *cis* isomer into *trans* isomer, i.e. they can be isolated as two different compounds.

- *Cis-trans* isomers contain the same functional groups and hence show **similar chemical properties**. However, chemical properties are **not identical** as the structures are neither identical nor mirror images. They react with the same reagents but perhaps at different rates.

- *Cis-trans* isomers have **different physical properties**. Generally, the ***cis* isomer** has a **higher boiling point** than the *trans* isomer as it has higher dipole moment but it has a **lower melting point** as *cis* isomers pack less closely together.



	cis	*trans*	*cis*	*trans*
dipole moment / D	1.85	0	1.35	0
boiling point / °C	60	48	112	108
melting point / °C	–80	–50	–53	–6

Making Thinking Visible

Question: Why is a single bond easily rotated?
Answer: A single bond is a sigma bond in which two orbitals overlap head-on. The rotation about the bond does not reduce the extent of orbital overlap.

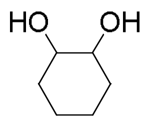
Question: Does 'restricted rotation' mean the C=C bond cannot be rotated at all?
Answer: No. The C=C bond needs more energy to be rotated than a single bond. This does not mean it cannot be rotated at all. The rotation of the C=C bond will cause the pi bond to break only.

Exercise
Indicate whether *cis-trans* isomerism occurs in the following. If yes, draw the stereoisomers.

(a) $CH_3CH{=}CHCH_2Cl$

(b) $(CH_3)_2C{=}CHCH_3$

(c)



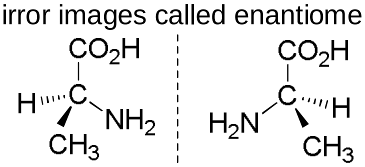
2.2 Chirality and Enantiomerism

- A molecule that does not have an internal plane of symmetry cannot be superimposed on its mirror image. Such a molecule is said to be a **chiral molecule**. The chiral molecule and its non–superimposable mirror image form a pair of **enantiomers**.

Candidates should be able to:
(c) explain what is meant by a chiral centre
(d) deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry

- A carbon atom with **four different atoms or groups of atoms** attached to it is known as a **chiral carbon atom** or **chiral centre**. Molecules with chiral carbon atoms are usually (but not always) chiral.

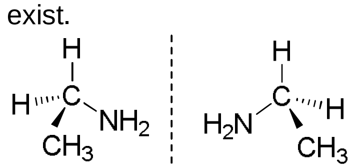
  E.g. $HO_2C\overset{*}{C}H(CH_3)NH_2$ has a chiral centre (marked with *) and hence exists as two non-superimposable mirror images called enantiomers.



mirror

non-superimposable mirror images, enantiomerism exists

  E.g. $CH_3CH_2NH_2$ has **no** chiral centre. Mirror images are superimposable and hence enantiomerism does **not** exist.



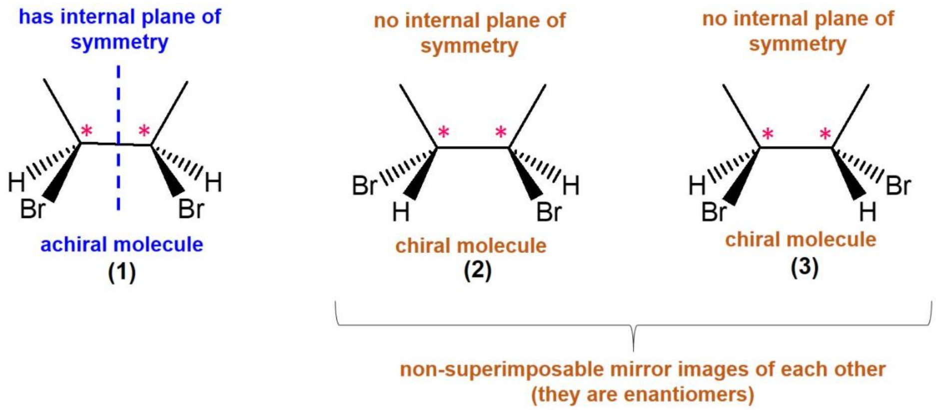
mirror

superimposable mirror images, no enantiomerism

- For a given structure which exhibits only enantiomerism,
  no. of enantiomers = $\mathbf{2^n}$, where n = no. of chiral centres

- A molecule with **only one** chiral carbon atom will not have an internal plane of symmetry and it has a non-superimposable mirror image of itself. Hence, it is chiral. However, the presence of chiral centres is not a sufficient condition for a molecule to be chiral.

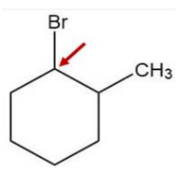
Consider 2,3-dibromobutane as shown below. It has two chiral centres and three stereoisomers only (instead of 2^2 = 4 stereoisomers). Stereoisomer (1) is achiral (i.e. non-chiral) as it has an internal plane of symmetry. Its mirror image is identical to itself and hence it does not have a non-superimposable mirror image.

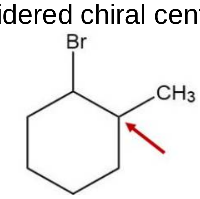


- To determine if a given molecule is chiral, check for presence of chiral centre(s) and presence of internal plane of symmetry. If the molecule has chiral centres and an internal plane of symmetry, then it is achiral.

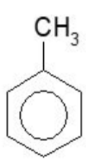
- A carbon atom in a cyclic aliphatic structure can also be chiral as long as it is attached to four different atoms or groups of atoms.

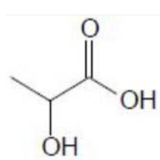
  Are the carbon atoms shown below considered chiral centres?

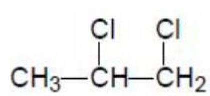


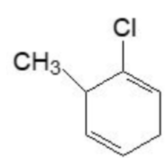


Exercise
Which of the following compound(s) contain chiral centre(s)? Identify the chiral centres (if any) by an asterisk in the molecules below.

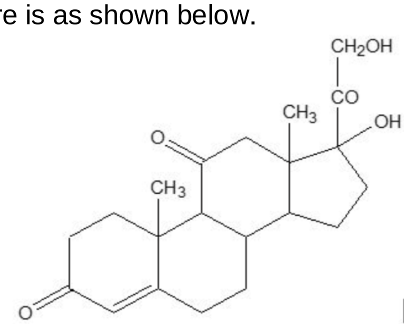

methylbenzene


2-hydroxypropanoic acid


1,2-dichloropropane


2-chloro-3-methylcyclohexa-1,4-diene

Exercise
Cortisone is a drug used to treat many different conditions such as allergic disorders and skin conditions. Its molecular structure is as shown below.



How many chiral centres are present in the molecule?

Exercise

Draw the two enantiomers of $CH_3CH_2CH(OH)CH_3$.

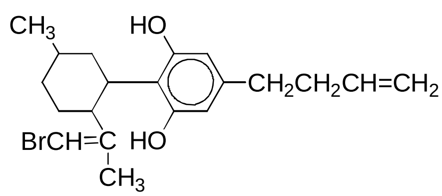
> **Making Thinking Visible**
>
> Question: Can a molecule without any chiral carbon atom still be chiral?
>
> Answer: Yes. At A-Level, we are **only** concern with a chiral carbon atom which is bonded to four different atoms / groups of atoms. **Note:** A molecule may contain chiral carbon atoms but overall the molecule may not be chiral.

3 Molecules Exhibiting Multiple Isomerism

- In general, total number of stereoisomers = $\mathbf{2^n}$, where n = no. of chiral centres + no. of C=C bond or C–C bond (part of a ring structure) with *cis-trans* isomerism.

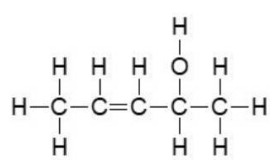
> Candidates should be able to:
>
> (j) identify chiral centres and/or *cis-trans* isomerism in a molecule of given structural formula

E.g. How many stereoisomers does the following molecule have?

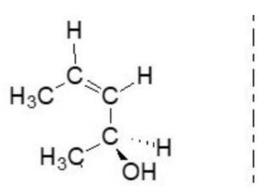


The molecule has three chiral centres and one C=C bond with *cis-trans* isomerism. Hence, the total number of stereoisomers = 2^{3+1} = 16

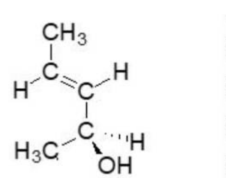
E.g. What is the total number of possible stereoisomers for this molecule below?



Draw the mirror images of the structures of the stereoisomers of the above compound, consisting of a chiral centre and a C=C bond exhibiting both enantiomerism and *cis-trans* isomerism.

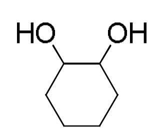


cis mirror



trans mirror

E.g. Draw all the possible stereoisomers of the molecule shown and state the isomeric relationship between these stereoisomers.

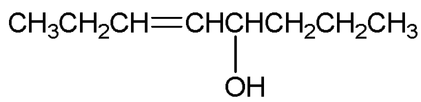


- Both structural isomerism and stereoisomerism could be present in a molecule.

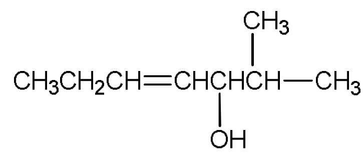
  Step 1: Determine all possible **structural** isomers.
  Step 2: For each structure, determine the number of **stereoisomers**.

  E.g. How many isomers are possible for the formula $CH_3CH_2CH{=}CHCH(OH)\mathbf{C_3H_7}$?

  As there are two ways to arrange $–C_3H_7$, there are 2 constitutional (chain) isomers **(I)** and **(II)** as shown below.



(I)



(II)

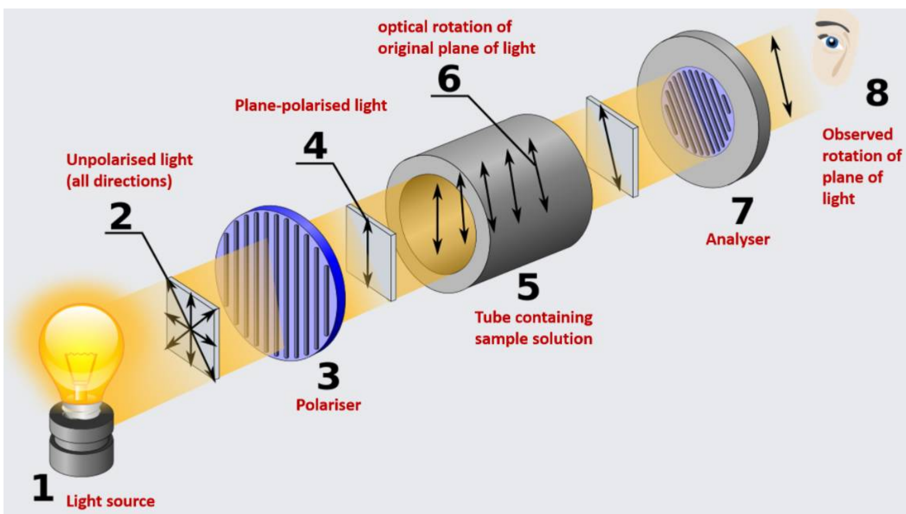
  Either constitutional isomers **(I)** or **(II)** has $2^{1+1} = 4$ stereoisomers.
  Total number of stereoisomers = $4 \times 2 = 8$

4 Differences between Properties of Enantiomers

- Difference in physical properties

Candidates should be able to:
(e) recognise that an optically active sample rotates plane-polarised light and contains chiral molecules
(f) recognise that enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light [usage of the term diastereomers is **not** required]

Enantiomers have **identical physical properties** except for the **direction** of rotation of plane of polarised light. Both enantiomers rotate the plane-polarised light by **an equal angle but in opposite directions**.



A ray of normal light has waves which vibrate in many directions (label 2) at right angles to the direction of travel of the ray. Some materials (called the 'polarisers') have the ability to remove from normal light all waves except those vibrating in a single plane. The light is said to be plane-polarised (label 4) after it passes through the polariser. Compounds that are optically active have the ability to rotate plane-polarised light (label 6) in either a clockwise or counter-clockwise direction, and to different extents. The direction and extent of rotation can be measured using an analyser (label 7). The rotation of plane-polarised light is the result of interactions between light and the individual molecules in the sample that the light passes through.

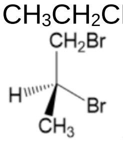
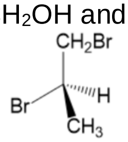
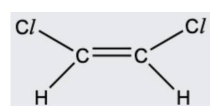
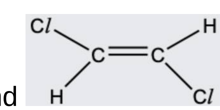
Certain substances have the ability to rotate the plane of polarised light. Such substances are said to be **optically active**. **Chiral molecules are optically active** while non–chiral molecules are not.

Optically active substances that rotate the plane of polarised light to the right, that is clockwise as viewed through the analyser are said to be dextro-rotatory and the rotation is designated (+). If rotation of plane is to the left, that is, anti-clockwise, substance is said to be laevo-rotatory and the rotation is designated (–).

Optically pure samples contain either (+) or (–) enantiomer only. Thus, for two optically pure samples, each containing the same concentration of either the (+) or (–) enantiomer, the observed rotation of plane-polarised light for the two samples will be of the **same extent but in opposite directions**.

Racemic mixture is a sample containing a 50:50 mixture (i.e. equal amounts) of the (+) and (–) enantiomers. The clockwise rotation caused by one enantiomer is exactly cancelled by the anti-clockwise rotation of the other enantiomer as the pair of equal amounts of enantiomers will rotate the plane of polarised light by the same extent but in opposite directions. Thus, there is no net effect on the passage of plane-polarised light and the sample is **optically inactive**. A racemic mixture has the same chemical properties as the single enantiomers but differs in physical properties that depend on the packing of molecules in the solid, e.g. melting points and solubilities.

Exercise
Which of the following sample(s) are optically active? [You can choose more than one answer.]
A A sample containing equal amounts of (+)-lactic acid and (–)-lactic acid
B A sample containing (+)-lactic acid
C A sample containing (–)-lactic acid
D A sample containing 70% of (+)-lactic acid and 30% of (–)-lactic acid

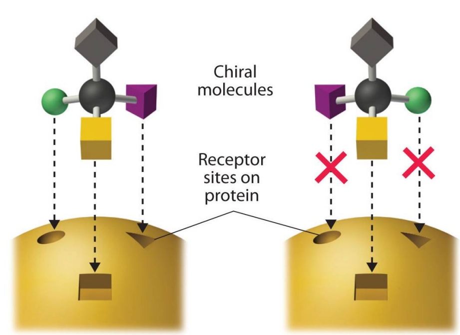
Exercise
Which one of the following pairs of compounds have identical boiling points?
A $CH_3CH_2CH_2CH_2OH$ and $(CH_3)_2CHCH_2OH$
B $CH_3(CH_2)_2CH_3$ and $(CH_3)_2CHCH(CH_3)_2$
C  and 
D  and 

- Difference in chemical properties

Candidates should be able to: (g) recognise that enantiomers have identical chemical properties except in their interactions with another chiral molecule (h) recognise that different stereoisomers exhibit different biological properties, for example in drug action

Enantiomers have **identical chemical properties** except towards **chiral reagents**, i.e. they differ in their interactions with another chiral molecule.

Enantiomers have different biological properties, e.g. in drug action. Drug molecules work by binding to targets like enzymes and receptors in the human body via a lock–and–key mechanism. As these **targets are chiral** in nature, only the drug molecule with the right spatial configuration, i.e. **only one** of the two enantiomers, **can bind to the target** and hence be effective.



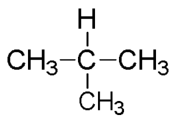
(a) Molecule fits receptor site, leading to a response
(b) Molecule does not fit receptor site; no response

Summary

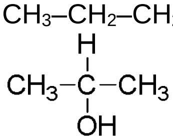
Isomerism
(compounds with ***same*** molecular formula)

Constitutional (structural) isomerism
(**same** molecular formula, **different** structural formula)

(i) **Chain** isomers have the same functional group but different carbon chains.
E.g. C_4H_{10}:
$CH_3–CH_2–CH_2–CH_3$,



(ii) **Positional** isomers have the same functional group but differ in its position along the same carbon chain.
E.g. C_3H_8O
$CH_3–CH_2–CH_2–OH$,



(iii) **Functional group** isomers have different functional groups.
Examples:
- alcohol vs ether
- aldehyde vs ketone
- carboxylic acid vs ester

Exception:
Alkene vs cycloalkane (strictly not functional group isomers as alkane is not regarded as a functional group)

Stereoisomerism
(**same** molecular and structural formula, **different** arrangement in space)

Enantiomerism
Presence of chiral centre(s) and non-superimposable mirror images

Properties
Enantiomers have:
(i) identical physical properties except that they rotate plane–polarised light in opposite directions.

(ii) identical chemical properties except towards chiral reagents.

(iii) different biological properties. Only one enantiomer with the correct spatial arrangement can bind to chiral targets in human body and be effective as a drug.

***Cis-trans* isomerism**
Presence of C=C bond with restricted rotation and two different atoms / groups attached to each C atom of C=C bond

Note: C=C bond in a ring does not show *cis-trans* isomerism due to ring strain in the *trans* isomer.

Properties
Generally, *cis* isomer has higher boiling point than *trans* isomer as it has higher dipole moment but has a lower melting point as *cis* isomers pack less closely together.

Note:
For a given structure, no. of stereoisomers = $\mathbf{2^n}$,
where n = no. of chiral centres + no. of C=C bond with *cis-trans* isomerism

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Isomerism Tutorial

Constitutional (structural) isomerism

1 Write down all the possible constitutional isomers with the molecular formula below.

(a) C_6H_{14}

(b) C_5H_{10} (alkene, indicate if *cis-trans* isomerism exists)

(c) C_9H_{12} (contains a benzene ring)

2 **N2020 / P1 / Q17**
Which statement is correct to describe constitutional isomers?

A C_4H_{10} has three constitutional isomers.
B But-1-ene and pent-1-ene are examples of constitutional isomers.
C Constitutional isomers may differ in their chemical properties.
D Constitutional isomers may have different molecular formulae.

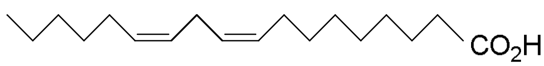
Cis-trans isomerism

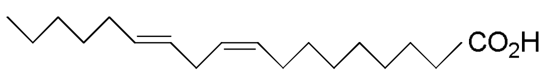
3 Which formula could represent a compound which has *cis-trans* isomers?

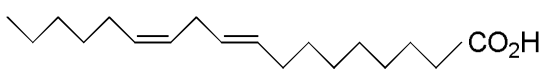
A $C_2H_6O_2$ **B** $C_2H_2O_4$ **C** C_2H_3Cl **D** $C_2H_2Cl_2$

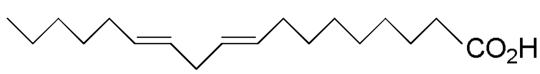
4 It is claimed that many polyunsaturated margarines contain esters derived from *cis-cis*-linoleic acid, $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$.

Which simplified formula of linoleic acid contains the *cis-cis* arrangement?

A 

B 

C 

D 

Enantiomerism and chiral centres

5 **N2019 / P1 / Q17**
Ethers have the general structure R_1–O–R_2 where R_1 and R_2 are hydrocarbon groups.

What is the lowest number of carbon atoms an ether molecule must contain to have a chiral carbon atom?

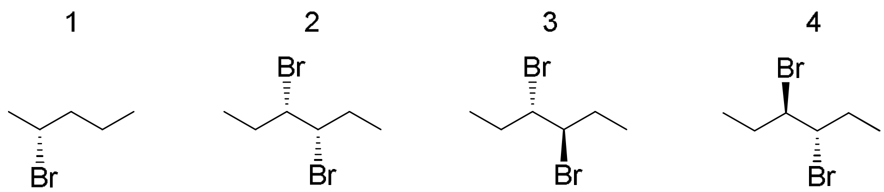
A 4 **B** 5 **C** 6 **D** 7

6 **N2019 / P2 / Q4(b)**
A mixture contains equal quantities of two isomers, **G** and **H**. These isomers have the molecular formula C_3H_5ClO.

(i) When plane-polarised light is passed through this mixture there is no effect, but pure **G** rotates plane-polarised light. Explain these observations. [3]

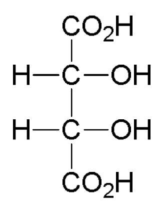
(ii) Draw the three-dimensional structures of **G** and **H**. [2]

7 **N2018 / P1 / Q23**
Which molecules rotate plane polarised light?



A 1, 2, 3 and 4 **B** 1 and 2 only **C** 3 and 4 only **D** none

8 **N2012 / P2 / Q5(c)**
The effect of plane polarised light on tartaric acid (2,3-dihydroxybutanedioic acid) $HO_2CCH(OH)CH(OH)CO_2H$ was investigated by Louis Pasteur.



Tartaric acid

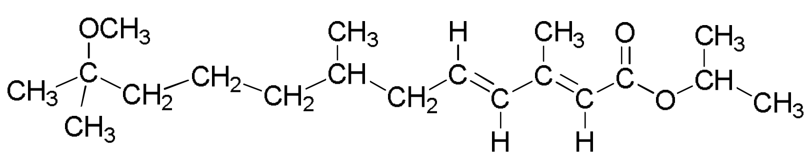
Pasteur identified three types of tartaric acid molecule.

Molecule **A** rotated plane polarised light to the right.
Molecule **B** rotated plane polarised light to the left.
Molecule **C** had no effect on plane polarised light.

Suggest an explanation for these observations.

Miscellaneous types of isomerism

9 **J1993 / P4 / Q22 (modified)**
The diagram shows the structure of the insect attractant *methoprene*.



What is the total number of stereoisomers in this molecule?

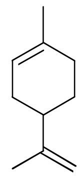
A 2 **B** 4 **C** 8 **D** 16

10 Determine whether each of the following molecules exhibits enantiomerism and/or *cis-trans* isomerism. If so, draw the stereoisomers.

(a) $CH_3CH=CHCH_2CH(OH)CH_3$

(b) $(CH_3)_2C=CHCH_2CH(OH)CH_2CH=C(CH_3)_2$

11 The structure of limonene is shown below.



(a) Despite the presence of two C=C bonds in limonene, limonene does **not** exhibit *cis-trans* isomerism. Explain why.

(b) Limonene, however, exists as two enantiomers. One enantiomer smells like lemon while the other smells like orange.

Smells are detected when the molecule responsible for the smell binds to a particular receptor in our nose, sending a response to the brain.

Do you think the receptors in our nose which detect smell are chiral? Why?

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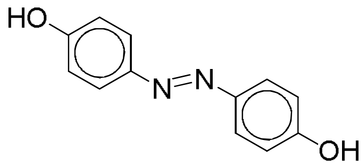
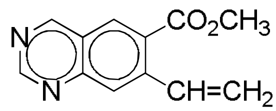
Isomerism Tutorial Supplementary Questions

Constitutional (structural) isomerism

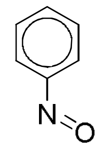
1 **N2011 / P1 / Q33**
The three compounds, **X**, **Y** and **Z** have the following structures.



X



Y



Z

Which statements about **X**, **Y** and **Z** are correct?

1 **X** and **Z** have the same empirical formula.
2 **X** and **Y** are isomers.
3 The M_r of **Y** is exactly twice that of **Z**.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

2 **J2002 / P1 / Q2**
What is the total number of different chloroethanes (formula $C_2H_{6-n}Cl_n$, where n can be any integer from 1 to 6)?

A 6 **B** 8 **C** 9 **D** 10

Cis-trans isomerism

3 How many structural and *cis–trans* isomers are there for dichloropropene, $C_3H_4Cl_2$?

A 3 **B** 5 **C** 6 **D** 7

4 Which molecules have isomers that exhibit *cis-trans* isomerism?

I	**II**	**III**	**IV**
C_3H_6BrI	C_3H_5I	$C_3H_4I_2$	C_3H_4BrI

A **I**, **II** and **III** only
B **II**, **III** and **IV** only
C **II** and **IV** only
D **III** and **IV** only

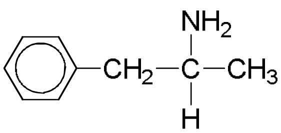
Enantiomerism and chiral centres

5 What is the smallest number of carbon atoms needed in a molecule containing only carbon, hydrogen and a single oxygen atom for it to be both chiral and a ketone?

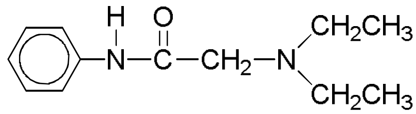
A 4 **B** 5 **C** 6 **D** 9

6 N2003 / P1 / Q20

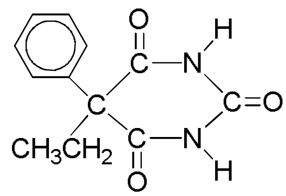
Many drugs show enantiomerism. The diagrams show the structure of three drugs.



amphetamine



lidocaine



phenobarbital

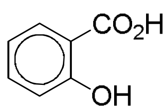
What is the total number of chiral carbon centres in these three structures?

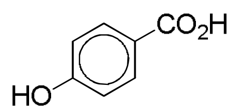
A 1 **B** 2 **C** 3 **D** 4

Miscellaneous

7 VJC 2013 H1 Prelim / P1 / Q8 (modified)

In which one of the following pairs of compounds does the first member have a higher boiling point than the second member?

A 



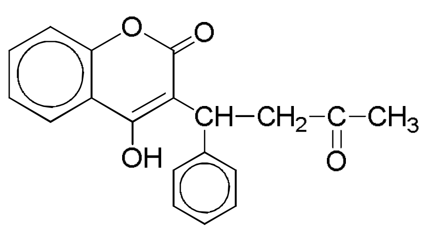
B CH_3CH_2OH H_2O

C *trans* $CH_3CCl{=}CClCH_3$ *cis* $CH_3CCl{=}CClCH_3$

D $CH_3CH_2CH_2CH_3$ $(CH_3)_3CH$

8 N1992 / P4 / Q21 (modified)

Warfarin is used as a rat poison.



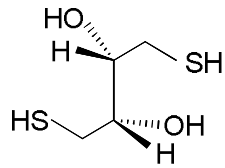
State the number of chiral centres in the Warfarin molecule.

9 Ethanoic acid reacts with butan-2-ol in the presence of concentrated sulfuric acid to form the ester $CH_3CO_2CH(CH_3)CH_2CH_3$.

State the type of stereoisomerism shown by the ester and draw the stereoisomers.

10 Dithiothreitol (DTT) is used in biochemical laboratories to maintain proteins in their reduced form. DTT has the structure $CH_2SH–CH(OH)–CH(OH)–CH_2SH$ and exists as three stereoisomers.

One of the stereosiomers, **A**, is shown below.



stereoisomer **A**

(a) Draw the enantiomer of **A** above.

(b) Draw the structure of another stereoisomer that is **not** a mirror image of **A**.

(c) A molecule with *n* chiral centres can have a maximum of 2^n stereoisomers. DTT has two chiral centres but it exists as only three different stereoisomers instead of four. Explain why.

(d) State whether the stereoisomer you have drawn in **(b)** rotates the plane of polarised light.

11 **(a)** Compound **X** has the structure $CH_2(OH)CH(OH)CHO$. Draw its displayed formula.

(b) Lactic acid, $CH_3CH(OH)CO_2H$, is a constitutional isomer of compound **X** and plays a role in several biochemical processes.

The table below lists some properties of three samples of lactic acid prepared from different natural sources.

sample	source	effect on plane-polarised light	melting point / °C
A	meat extract	rotate clockwise	26
B	fermentation of sucrose	rotate anti–clockwise	26
C	sour milk	no effect	18

(i) With the aid of relevant structures, explain why samples **A** and **B** behave differently towards plane-polarised light.

(ii) Explain why sample **C** has no effect on plane-polarised light and suggest why it has a different melting point from **A**.

Answers for Supplementary Questions

1	**A**	**5**	**C**
2	**C**	**6**	**A**
3	**D**	**7**	**D**
4	**B**	**8**	1