2 Isomerism Tutorial

Properties of isomers

1 Two organic isomers are known to contain the **same** functional group. Assess the following statements about the two molecules.

(a) They have the same empirical formula. **true ~~/ may be true / false~~**

(b) They have the same boiling point. **~~true /~~ may be true ~~/ false~~**

Enantiomers have same boiling point, however structural isomers & cis-trans isomers have different boiling point.

(c) They have the same chemical properties. **true ~~/ may be true / false~~**

Isomers with same functional group same the same chemical properties.

(d) They have the same solubility in water. **~~true /~~ may be true ~~/ false~~**

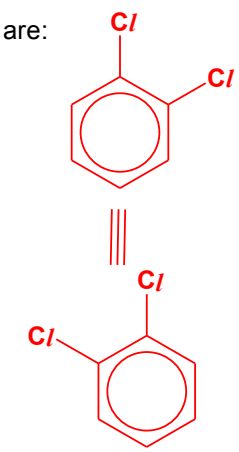
E.g. cis-trans isomers with polar groups may have different polarity (e.g. trans 1,2-chloroethene is non-polar while cis 1,2-dichloroehthene is polar) and could have different solubility in polar solvent.

Constitutional Isomerism (Structural Isomerism)

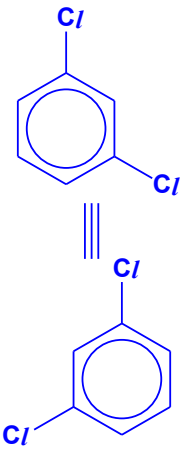
2 How many isomers of dichlorobenzene are there? (benzene: )

A 2 **B** 3 **C** 4 **D** 5

The 3 isomers are:



1,2-dichlorobenzene



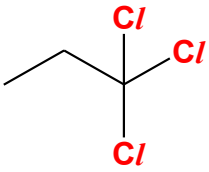
1,3-dichlorobenzene

1,4-dichlorobenzene

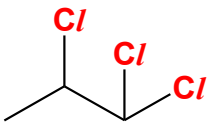
3 A halogenoalkane has the molecular formula $C_3H_5Cl_3$.
Which are the possible names of the isomers of this compound?

1 1,1,1-trichloropropane
2 1,2,2-trichloropropane
3 2,2,3-trichloropropane

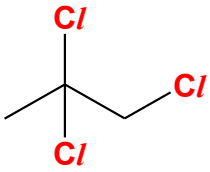
A **1, 2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct



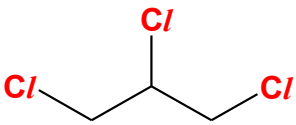
1,1,1-trichloropropane



1,1,2-trichloropropane



1,2,2-trichloropropane

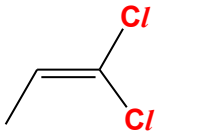


1,2,3-trichloropropane

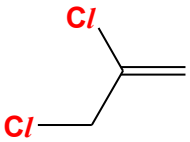
Cis-Trans Isomerism

4 How many structural and *cis-trans* isomers are there in dichloropropene, $C_3H_4Cl_2$?

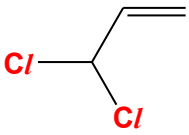
A 3 **B** 5 **C** 6 **D** 7



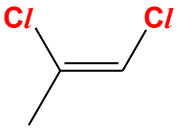
1,1-dichloropropene



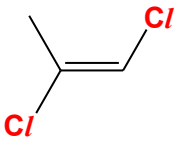
2,3-dichloropropene



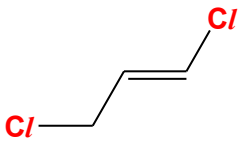
3,3-dichloropropene



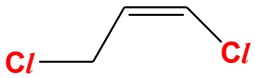
***cis*-1,2-dichloropropene**



***trans*-1,2-dichloropropene**

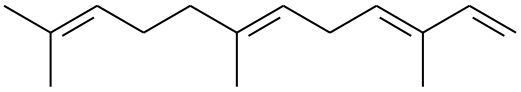


***trans*-1,3-dichloropropene**



***cis*-1,3-dichloropropene**

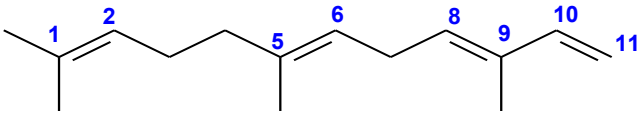
5 α–*Farnesene* is a constituent of the natural wax found on apples. It is also responsible for the characteristic odour of green apples.



α–*Farnesene*

How many *cis-trans* isomers does this molecule have?

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



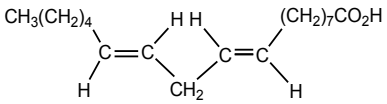
each C of C=C (C_3, C_4 and C_5, C_6) has 2 different groups attached
no of *cis-trans* isomers = 2^2 = 4

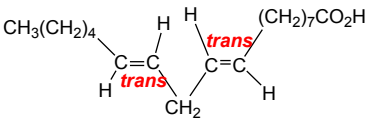
6 Low fat sunflower spreads which are high in polyunsaturated contain esters of linoleic acid.

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$$

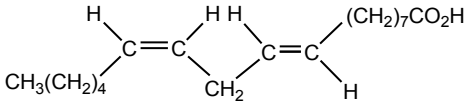
On the lid of a brand of spread, it is claimed that the spread contains virtually no *trans* fatty acid. Which isomer does **not** contain a *trans* linkage that could be present in the spread?

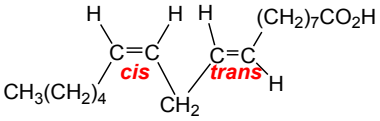
A



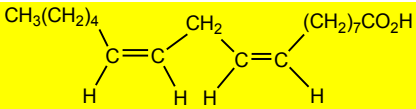


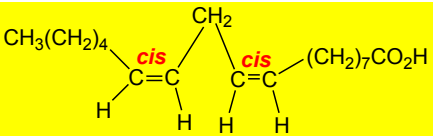
B



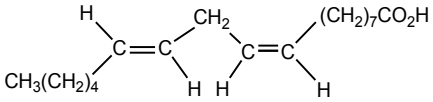


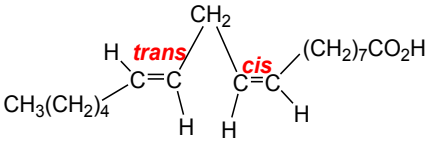
C





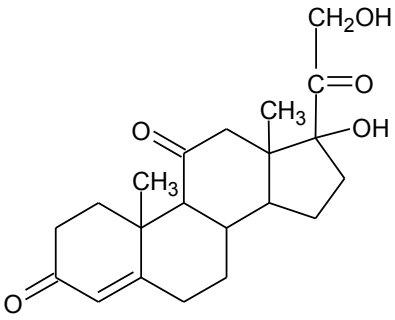
D

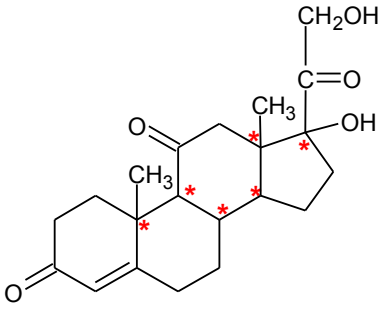




Optical Isomerism (Enantiomerism)

7 The drug cortisone has the formula shown.



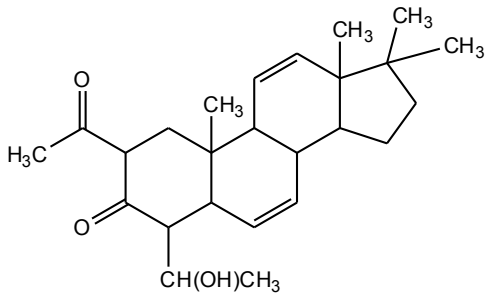


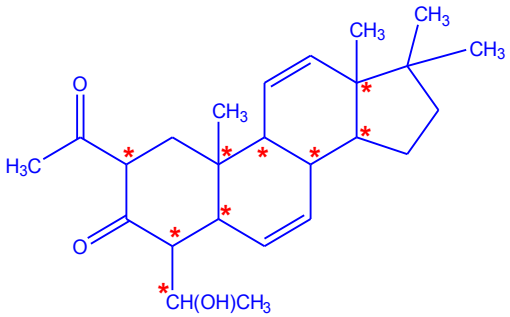
cortisone

How many chiral centers are present in each cortisone molecule?

A 3 **B** 4 **C** 5 **D** 6

8 What is the maximum number of stereoisomers for the molecule shown below?





(*: chiral C)

A 2^8 **B** 2^9 **C** 2^{10} **D**. 2^{11}

Note : C=C in a ring cannot exhibit cis-trans isomerism

[Ans Q2 – 8: **BBDBCDB**]

[N22/1/18]

The drug ibuprofen has two enantiomers. One enantiomer has the desired pharmacological activity while the other is inactive.

9 Which statement gives correct reasons for this difference?

1 The biological receptors that the drugs bond with are chiral
2 The enantiomers are structural isomers with different chemical properties.
3 The enantiomers have many different physical properties.

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

1. As the receptors are chiral and specific in shape, they can only bind to the drug which can fit the receptors. Hence, only one of the two enantiomers of ibuprofen that fits the receptors is able to bind successfully to it.

2. Enantiomers are stereoisomers, not structural isomers.

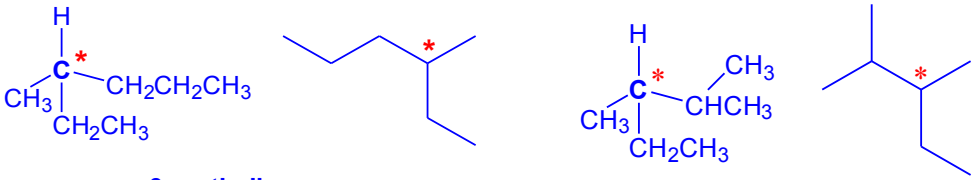
3. Enantiomers have similar physical properties and chemical properties (except for interactions with another chiral molecule)

10(a) What is meant by the term 'optical isomerism'?

Optical isomers (**enantiomers**) are molecules with the **same structural** formula which are **not superimposable** mirror images of each other. These molecules lack both a point and plane symmetries.

(b) What conditions must be fulfilled for a compound to exhibit optical activity?
- has at least 1 chiral C (C with 4 different atoms / groups of atoms attached)
- is not a racemic mixture (mixture containing equal amount of the non-superimposable mirror images (enantiomers) or molecule does not have an internal mirror plane / a plane of symmetry

(c) Draw the structural formula of the alkane with the lowest M_r that can exhibit optical isomerism.



3-methylhexane or **2,3-dimethylpentane**

Application Questions

11 A hydrocarbon **Q** consists of 86% carbon by mass.

(a) Calculate the empirical formula of **Q**.

	C	H
Mass in 100g /g	86	14
Amount /mol	7.17	14
simplest ratio	1	1.95 ≈ 2

The empirical formula is CH_2

(b) 5.0 g of **Q** was found to occupy 2.0 dm^3 at 0 °C and 1 atm. Deduce the molecular formula of **Q**.

$$\mathbf{M_r} = \frac{mRT}{PV} = \mathbf{56.0}$$

Let MF of Q be $(CH_2)_n$

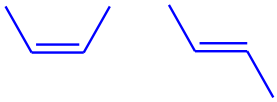
$14n = 56.0$

$n = 4$

Molecular Formula of **Q** is **C_4H_8.**

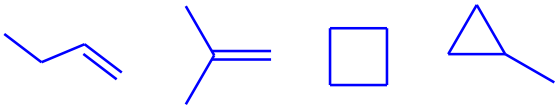
(c) **Q** exists as a pair of *cis-trans* isomers. Draw the structural formulae for the isomers.

Q is **but-2-ene** (each C of C=C bond has 2 different groups attached)

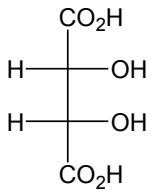


(d) **P** is a structural isomer of **Q** and does **not** show *cis-trans* isomerism. Suggest a structure for **P**.

P: alkene or cycloalkane



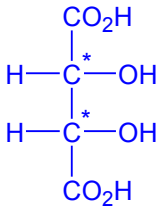
12 The effect of plane-polarised light on tartaric acid, $HO_2CCH(OH)CH(OH)CO_2H$, was investigated by Louis Pasteur.



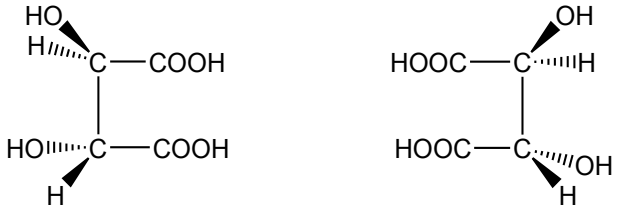
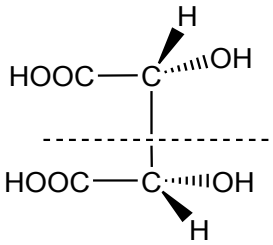
tartaric acid

Pasteur identified three different 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** has no effect on plane-polarised light.

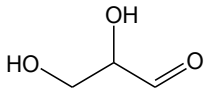
(a) Label each chiral centre in tartaric acid with an asterisk (*).



(b) Suggest an explanation for the observations that Pasteur made.

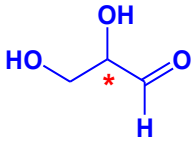
Molecule	Explanation
A	 **A & B**
B	**Both chiral centres in Molecule A rotate plane of polarised light in the same direction. The rotation effect does not cancel out.** **Molecule B is the enantiomer of Molecule A. It rotates plane of polarized light in the opposite direction as Molecule A.** (Note: It is impossible to tell from the structure the direction in which plane-polarised light is rotated. We can only do this by direct measurement using a polarimeter.)
C	**There is a plane of symmetry in Molecule C. The 2 chiral centers in Molecule C have opposite chirality. The rotation of plane-polarised light by each half cancels each other out; Molecule C does not rotate plane polarised light and is known as a meso compound.** 

13 Glyceraldehyde as shown below is chiral and exists as two enantiomers, *D*-glyceraldehyde, and *L*-glyceraldehyde.



glyceraldehyde

(a) Identify the chiral centre using *.



glyceraldehyde

(b) Given that sample **I** contains only the *D*-isomer which rotates the plane of plane-polarised light in the clockwise direction. Complete the table below using the given information.

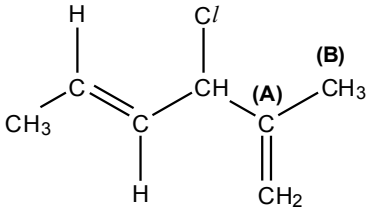
sample number	relative amount of *D*-isomer in sample	relative amount of *L*-isomer in sample	about the sample	Is sample optically active?	direction of rotation of plane-polarised light
I	100	0	pure *D*-isomer	yes	clockwise
II	75	25	excess *D*-isomer	yes	clockwise
III	**50**	**50**	racemic mixture	no	-
IV	25	75	excess *L* isomer	yes	anticlockwise
V	0	100	pure *L* isomer	yes	anticlockwise

(c) The samples of glyceraldehyde were analysed for optical activity. Only one sample was found to be optically inactive.

Identify the optically inactive sample and account for its optical activity.

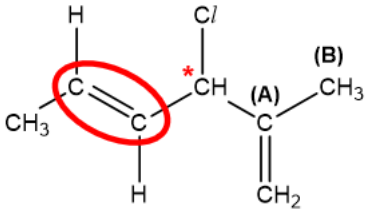
Samples III is optically **inactive** as it is a racemic mixture (50% of each isomer). The equal but opposite rotation of plane-polarized light by each enantiomer cancels out completely. The racemic mixture is optically inactive.

14 Compound **X** can exhibit stereoisomerism.



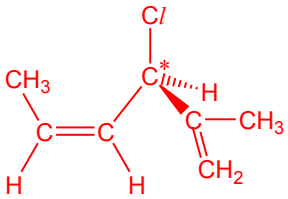
Compound **X**

(a) What is the maximum number of stereoisomers that **X** can have? Explain your answer.

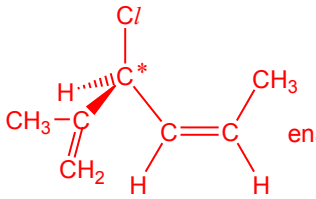


No. of cis-trans C=C = 1
No. of chiral carbon = 1
Total number of stereoisomers = $2^2 = 4$

(b) Draw all the stereoisomers of **X**. [4]

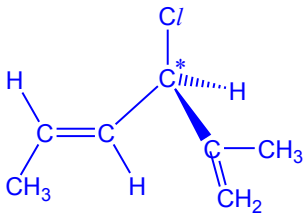


cis isomer

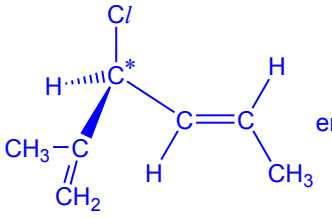


cis isomer

enantiomers of *cis* isomers



trans isomer



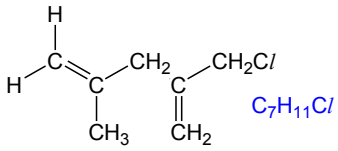
trans isomer

enantiomers of *trans* isomers

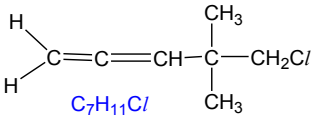
[1 – each; correct relationships]

(c) Draw a structural isomer of **X** which does not exhibit any form of stereoisomerism. [1]

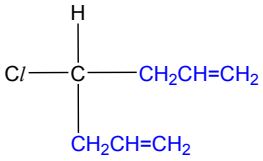
- any structure that does not contain chiral C, or does not have any C in the C=C that is bonded to 2 different atoms/groups of atoms. e.g.,



$C_7H_{11}Cl$;

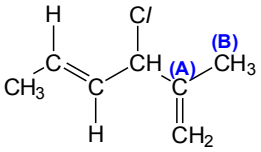


$C_7H_{11}Cl$;



- $(CH_2{=}CHCH_2)_2CHCl$

(d) Explain why the C−C single bond between carbons (A) and (B) is stronger than a typical C−C single bond in an alkane such as ethane. [2]



X

C_A -> sp^2 hybridised

C_B -> sp^3 hybridised

C-C single bond between carbons (A) and (B) is formed via **sp^2–sp^3** overlap of hybrid orbitals,

which is **more effective** than sp^3–sp^3 overlap of hybrid orbitals between 2 carbon atoms in ethane; bond is **shorter** and hence **stronger.**

***Hybrid orbitals of higher % of s character overlap to form a stronger bond.**

[1 – correct types of hybridisation; 1 – correct comparison]