Chem Factsheet

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Polarimetry

Which of the following statements are true and which are false?

	Statement	True	False
1	Polarimetry determines the degree of polarity of a molecule		
2	A polarimeter can be used to follow the progress of some reactions		
3	A chiral molecule gives rise to optical isomers which are mirror images of each other		
4	Optical isomers result from the fact that carbon atoms on either side of a double bond cannot rotate freely		
5	Optical isomers have a chiral centre which can be a nitrogen atom		
6	A racemic mixture has equal amounts of two enantiomers		
7	A chiral centre is a carbon atom with two identical groups attached		
8	An enantiomer can be dextrorotatory (d) or laevorotatory (l) or a combination of both		
9	The polarised light from the polarimeter rotates the molecules		

If you answered true to questions 2, 3, 6 and false to all the others, then you are a star student! You may already have an excellent grasp of the fundamental knowledge needed to succeed in this area of your specification, so why not go straight to the sample questions at the end and try your knowledge further? Otherwise read on ……..

If you feel that this topic is a minefield of new terms and ideas which are difficult to express, then this Factsheet is structured to ensure that you can explain these in the way which examiners like and give marks for. It is designed to help you learn and understand:

(a) The fundamental principles of polarimetry and the use of a polarimeter.
(b) How to identify the molecular structure which results in optical isomerism.
(c) The terms chirality and chiral centre, racemate or racemic mixture and enantiomer.
(d) The importance of chiral molecules in living systems.
(e) The use of polarimetry in distinguishing between enantiomers and determining their relative concentrations, and its importance in relation to the synthesis of pharmaceuticals.

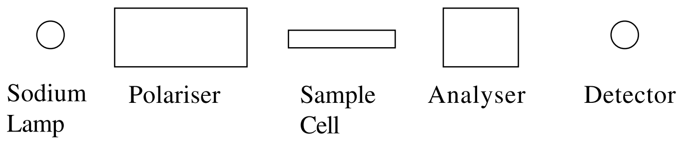
Key Fact 1

Polarimetry is the measurement of the angle of rotation of the plane of polarisation of plane-polarised light. This rotation of the plane of polarisation occurs when plane-polarised light passes through certain transparent materials.

Plane-polarised light results from the superposition of equal intensities of left- and right-circularly polarised light. When plane-polarised light travels through an optically active sample the left- and right- circularly polarised components travel at different velocities and, as it exits, the sum of the two components is still plane-polarised but at a different orientation from the light entering the sample. Even if you do not understand all of this, as it is somewhat outside the scope of the specification, do be careful to use correct terms: *"Some candidates used 'polarised light' as a synonym for plane-polarised light"* – critical extract from Examiners Report

Key Fact 2

A simple polarimeter consists of a monochromatic light source (e.g. sodium lamp), a polariser (e.g. Nicol prism of calcite) which sends a beam of plane-polarised light through the sample cell, a second polariser called the analyser, and a light detector.

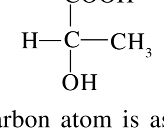


In the absence of the sample in the cell, the analyser is rotated until the light reaching the detector is a minimum. Then, with the sample in the cell the analyser is rotated to restore the light to minimum intensity. The direction and angle of rotation needed to restore the light to minimum intensity is recorded. This is the angle through which the sample has rotated the plane of polarisation of the plane-polarised light.

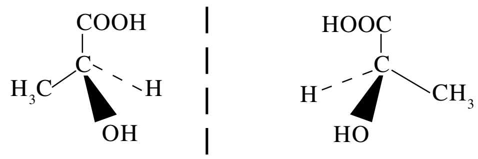
Key Fact 3

(a) A chiral centre may be identified or detected as a carbon atom with four different groups attached (also called an asymmetric carbon atom).

(b) The chiral centre results in the molecule being able to exist in two forms which are object and non-super imposable mirror image (rather like left and right hands).
e.g. Lactic acid (systematic name 2-hydroxypropanoic acid)



The central carbon atom is asymmetric. This means that the molecule can exist in two mirror image forms:



It is important to include the idea of non-super imposable mirror images when explaining the term 'chiral' – "*A large number of candidates gave a correct description of chiral, although there are still a few who just write that it is a carbon atom with four different atoms or groups attached"*. Detection involves looking for the four different groups - *"chirality is best defined in terms of non-super imposable mirror images, and many candidates used this idea and could say how chirality is detected"* – extracts from Examiners Reports.

Key Fact 4
The presence of a single asymmetric carbon atom (chiral centre) in a molecule results in the molecule being able to exist as two optical isomers which are called **enantiomers**.

Key Fact 5
The only difference between enantiomers is that one form rotates the plane of plane-polarised light clockwise and is called the (+) or dextrorotatory (d) isomer. The other rotates the plane of plane-polarised light anticlockwise and is called the (-) or laevorotatory (l) isomer.

Care is needed here when choosing words – *"Many candidates knew how to distinguish optical isomers, but some were still using words like reflect or deflect instead of rotate and there were some candidates who thought that the polarised light rotates the molecules"* – extract from Examiners Report

Key Fact 6
An equimolar mixture of the dextrorotatory (+) and laevorotatory (-) isomers is called a **racemic mixture or racemate**. A racemic mixture does not rotate the plane of plane-polarised light because the effect of the two isomers cancel one another out.

Key Fact 7
Many natural products are chiral (for example sugars, amino acids, proteins and nucleic acids). A polarimeter may be used to monitor reaction rates where these compounds are involved.

e.g. the hydrolysis of sucrose in acid solution using enzymes

$C_{12}H_{22}O_{11}$	+	H_2O	$\rightarrow$	$C_6H_{12}O_6$	+	$C_6H_{12}O_6$
Sucrose Dextrorotatory (+)				Glucose Dextrorotatory (+)		Fructose Laevorotatory (–)

Note that glucose and fructose are enantiomers. Although the reactants and products are all optically active, the extent and direction of rotation of the plane of plane-polarised light is different for each.

As the reaction proceeds, the formation of fructose with it's strongly (–) rotation dominates over the weaker (+) rotation of glucose, thus an inversion of rotation occurs. The progress of the hydrolysis can be determined by measuring changes in the optical rotation of the reaction solution.

Key Fact 8
Many of the molecules found in living organisms exist as enantiomers and usually only one of the enantiomers is biochemically active.

For example, nearly all of the amino acids which make up proteins are chiral molecules, but only one of the forms (the L-amino acids) is found in living systems.

Example: An enzymes is shaped selective. Thus only one enantiomer can act as its substrate.

Key Fact 9
The optical isomers of a pharmaceutical compound which is chiral must be isolated and tested separately as the isomers may have very different effects on living organisms. Medicines having chiral molecules often need to be administered as a pure enantiomer. Examples of this include:

(a) The Thalidomide molecule is chiral; one optical isomer acts as a non-addictive sedative but the other isomer has the potential to adversely affect foetal growth.

(b) Morphine is a chiral compound but only one isomer acts as an efficient (but addictive) painkiller.

(c) One optical isomer of DOPA, called L-DOPA, is effective in the treatment of Parkinson's disease but the other isomer is of no use.]

Key Fact 10
Synthetic organic reactions often result in a mixture containing both isomers in equal amounts (racemic mixture).

The isomers may be separated by crystallisation with a chiral acid or base or by chiral high performance liquid chromatography. Processes have also been developed which produce pure enantiomers, making separation unnecessary

The synthesis of pharmaceuticals often requires the production of chiral drugs containing a single optical isomer. The advantages are:
(a) Smaller doses (only half the drug is needed)

(b) Reduced side effects

(c) Improved pharmacological activity

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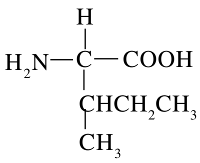
Practice Questions

1. There are four isomeric alcohols with the molecular formula C_4H_9OH. Only one of the isomers is optically active. Draw the structure of this isomer, and place an asterisk * next to the carbon which is a chiral centre.

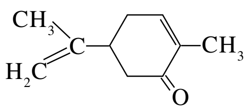
2. The amino acid isoleucine (structure shown below) has more than one chiral centre. Mark the chiral centres with asterisks.



3. Explain the meaning of the term chiral centre

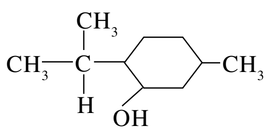
.

4. (a) Carvone is a chiral molecule, which exists in two forms in nature. One enantiomer gives the odour of spearmint and the other is the principal odour in caraway seed. Identify the chiral centre in the carvone molecule shown below:



(b) Explain the term enantiomer.

5. Menthol has more than one chiral centre. Mark the chiral centres with asterisks in the diagram below.



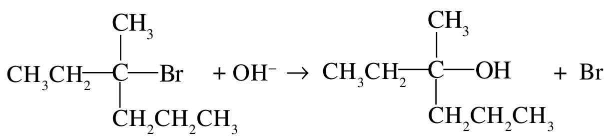
6. One isomer of $C_4H_9NH_2$ is optically active. Draw the full structural formula of this isomer and identify with an asterisk the feature which gives it its optical activity. Explain how this feature results in two enantiomers.

7. (a) How might you distinguish between two enantiomers.

(b) A chemical reaction produces two enantiomers. The mixture formed is not optically active. Explain this.

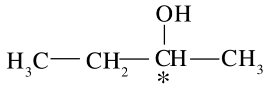
(c) What property of two enantiomers might be used as the basis for separation of a racemate?

8. When the following reaction was performed on a single enantiomer, the resulting mixture was found to be no longer optically active. Explain this by considering the mechanism involved.

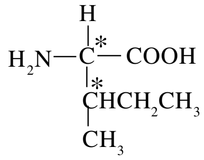


Answers

1.

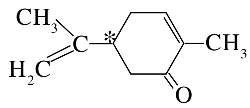


2.



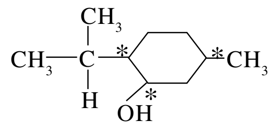
3. A carbon atom bonded to four different groups. This gives two possible optical isomers which are non-super imposable mirror images of each other.

4. (a)

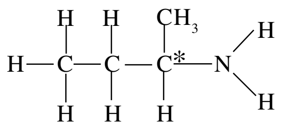


(b) Enantiomers have the same molecular formula but the molecule has an asymmetric carbon atom so can exist in two forms (enantiomers) which are non identical mirror images of each other. They rotate the plane of plane-polarised monochromatic light in opposite directions.

5.



6.



The asymmetric carbon atom has four different groups attached, which results in the two enantiomers (optical isomers) which are non identical mirror images of each other.

7. (a) By using a polarimeter, and measuring the rotation of the plane of plane-polarised monochromatic light. The light will be rotated anti-clockwise by one enantiomer and clockwise by the other.

(b) A racemic mixture is formed (which has equimolar amounts of each enantiomer). The plane of plane-polarised light is rotated anti-clockwise by one enantiomer and clockwise by the other enantiomer by an equal amount and so the two rotational effects cancel out.

(c) The two enantiomers react differently with other chiral molecules.

8. The single enantiomer contains an asymmetric carbon atom, which has four different groups attached and thus is optically active. The mechanism of the reaction is nucleophilic substitution.

The C-Br bond breaks to form a planar carbocation. The attack by the OH^- can occur from either above or below this plannar carbocation and is equally likely in any direction, and thus two enantiomers are formed in equal amounts. This gives a racemic mixture or racemate of (+) and (-) forms, which is optically inactive. (The effect of the (+) form on the plane of plane-polarised light is equal and opposite to the effect of the (-) form and thus the two effects cancel out.)

(This type of question is worth seven or eight marks so a careful, detailed explanation is needed.)

Note similar effects occur for planar alkenes and carbonyl compounds.