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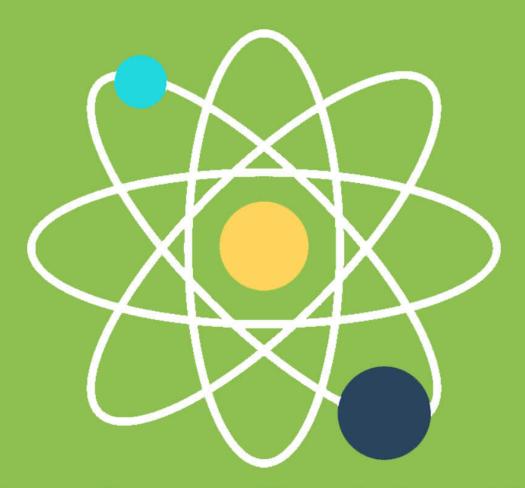
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20.3 Stereoisomerism



IB Chemistry - Revision Notes

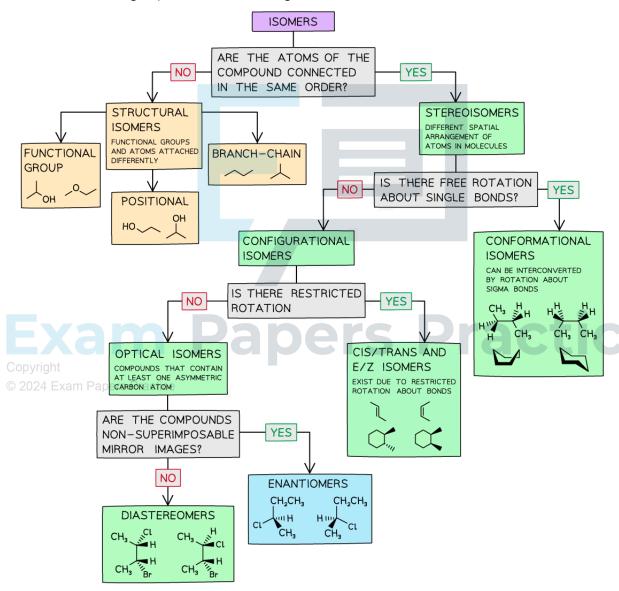
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20.3.1 Stereoisomers

Conformational & Configurational Isomers

- Isomers are compounds that have the same molecular formula but a different arrangement of atoms
- Isomers can be grouped into various categories, as shown:



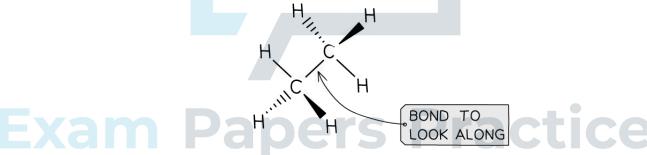
Flow chart of the various isomers with points to help identify them



- At Standard Level, we encountered three types of structural isomers:
 - Functional group isomers, e.g. propanal and propanone
 - Position isomers, e.g. propan-1-ol and propan-2-ol
 - Branch-chain isomers, e.g. butane and methylpropane
- If the atoms within an isomer are arranged in the same order then we are dealing with stereoisomers
 - Stereoisomers can be **conformational** or **configurational**

ConformationalIsomers

- Conformational isomers, or conformers, occur due to free rotation about a single σ-bond and can be described as:
 - Staggered
 - Eclipsed
- One of the simplest examples of conformational isomerism is ethane, CH₃CH₃

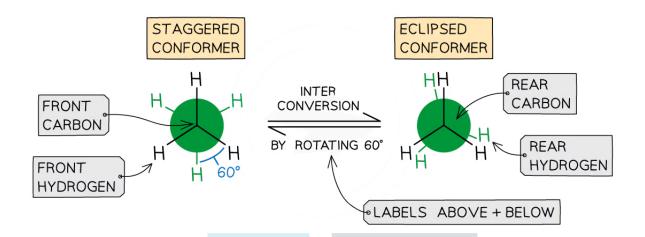


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© 2024 ExaThree-dimensional structure of ethane identifying the bond for conformational isomerism

 By looking along the C-C bond highlighted in the diagram we can draw the two Newman projections, staggered and eclipsed



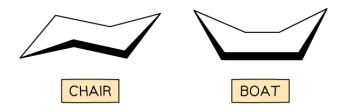


The staggered and eclipsed conformers of ethane

- The staggered conformer has angles between hydrogen atoms on adjacent carbons of 60°, as shown
 - It is also more stable / lower energy than the eclipsed conformer because the C-H bonds are as far apart as possible to minimise the repulsion between the electrons in the C-H bonds
- The eclipsed conformer has angles between hydrogen atoms on adjacent carbons of 0°, this is not shown in the diagrams so that the conformation can be seen
 - The eclipsed conformer is less stable / higher energy due to the repulsion between the electrons in the C-H bonds that are closer to gether
- The free rotation that causes these conformers means that it is easy to interconvert from one conformer to the other and back
 - This is also the reason that it is almost impossible to isolate a single conformer

Conformational Isomerism in Cyclic Structures

- Conformational isomerism can also be seen in cyclic structures
- A common example of this is cyclohexane, C₆H₁₂
 - Cyclohexane isomers exist in boat and chair forms:



Skeletal structures showing the boat and chair forms of cyclohexane



- The boat form is less stable / higher energy as there are four eclipsed bonds causing strain on the overall structure
 - There is also repulsion of the hydrogen atoms on the end of the boat structure
- It is possible to "flip" between the boat and chair forms which explains the difficulty in isolating just one of the forms
 - During the interconversions, it also possible to get other structures commonly called the half chair and the twisted boat

ConfigurationalIsomers

- Interconversion of configurational isomers can only occur by breaking bonds or rearranging stereocentres
- Configurational isomers can be divided into:
 - *cis/trans* isomers and *E/Z* isomers
 - optical isomers



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20.3.2 Cis-Trans & E/Z Isomers

Cis-Trans & E/Z Isomers

- Configurational isomerism can be seen in unsaturated compounds, cyclic structures or compounds that contain at least one asymmetric carbon (sometimes called a chiral centre)
 - These structures have the same molecular formula and order of atoms (the atoms are connected similarly to each other) but different shapes
- As previously discussed, these can be grouped into further types of isomers:
 - Cis / trans
 - E/Z
 - Optical



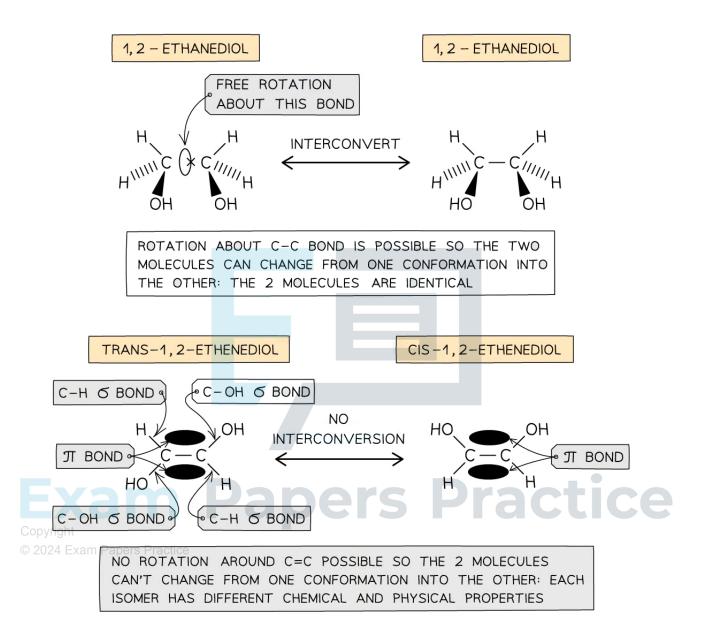
Exam Tip

You may still see the term geometric isomers being used when talking about some configurational isomers This was recommended by IUPAC but it is now obsolete and being replaced with cis-trans iso mers and E/Z iso mers

Cis/transisomers

- In saturated compounds, the atoms / functional groups attached to the single, σ-bonded carbons are not fixed in their position due to the free rotation about the C-C σ -bond
 - This causes **conformational isomers**, as previously discussed
- In unsaturated compounds, the groups attached to the C=C carbons remain fixed in their Copyright
- © 2024 Exam Papers Practice presence of a π bond
 - Cis/trans nomenclature can be used to distinguish between the isomers
 - Cis isomers have two functional groups on the same side of the double bond / carbon ring, i.e. both above the C=C bond or both below the C=C bond
 - Trans isomers have two functional groups on opposite sides of the double bond / carbon ring, i.e. one above and one below the C=C bond





The presence of $a\pi$ bond in unsaturated compounds restricts rotation about the C=C bond forcing the groups to remain fixed in their position and giving rise to the formation of certain configurational isomers

Naming cis/transisomers

• For cis / trans isomers to exist, we need two different atoms or groups of atoms on either side of the C=C bond



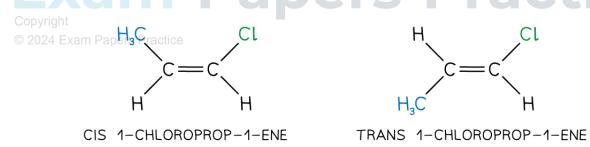
■ This means that 2-methylpropene cannot have cis / trans isomers as the methyl groups are both on the same side of the C=C bond:

2-methylpropene molecules do not have cis / trans isomers

 However, moving one of the methyl groups to the other side of the C=C bond causes cis / trans isomerism:

But-2-ene does have cis / trans isomers

The atoms or groups of atoms on either side of the C=C bond do not have to be the same for cis /trans isomers:

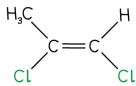


1-chloroprop-1-ene also shows cis / trans isomerism

- However, the cis / trans naming system starts to fail once we have more than one atom or group of atoms on either side of the C=C bond
 - The cis / trans naming system can still be used with three atoms / groups of atoms but only if:



- Two of the three atoms or groups of atoms are the same
- These two atoms or groups of atoms are on opposite sides of the double bond

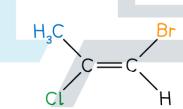


CIS 1,2-DICHLOROPROPENE HAS BOTH CL ATOMS ON THE SAME SIDE

TRANS 1,2-DICHLOROPROPENE HAS BOTH CL ATOMS ON THE OPPOSITE SIDES

1,2-dichloropropene can be named using cis / trans

- The cis / trans naming system cannot be used with three atoms / groups of atoms when they are all different
 - This requires the use of the E/Znaming system



1-BROMO-2CHLOROPROPENE

1-bromo-2-chloropropene cannot be named using cis / trans



Exam Tip Practice

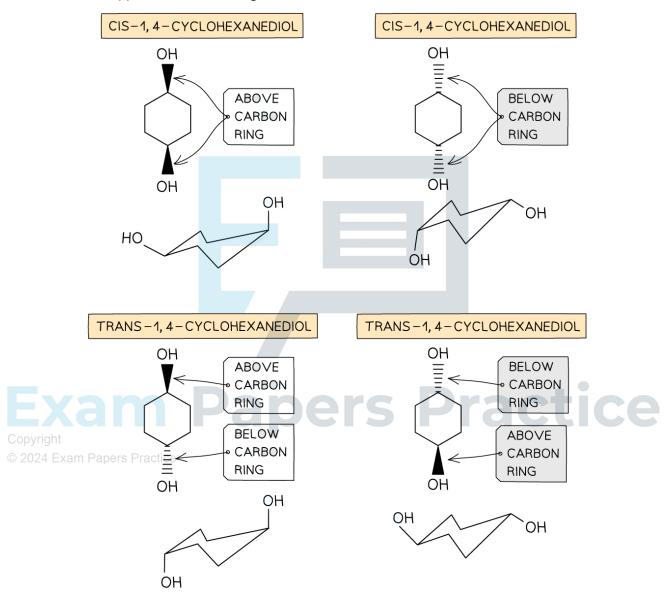
Although not part of this topic, the relationship between cis/trans isomers, their packing and melting points is applicable to the Option B: Biochemistry topic Cis / trans isomerism affects the intermolecular forces by introducing a dipole moment between molecules, not just London dispersion forces. This will affect the packing of the molecules as well as physical properties such as melting and boiling point

Cyclic cis / transisomers

- Cis/trans isomerism can also occur in cyclic structures
 - Even though cyclic alkanes contain single carbon-carbon bonds, the rigid structure of the ring system does not allow for free rotation



- Therefore, cis isomers can occur when the atoms (or groups of atoms) are on the same side of the ring, i.e. both above or both below
- While trans isomers can occur when the atoms (or groups of atoms) are on the opposite side of the ring, i.e. one above and one below



Cis / trans isomerism in cyclic compounds

E/Zisomers

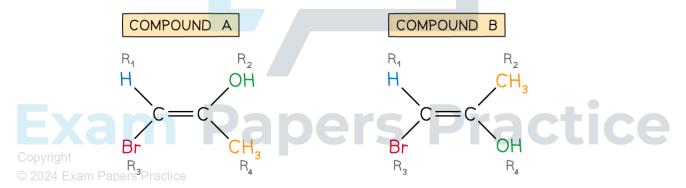
• To discuss E/Z isomers, we will use an alkene of the general formula C_2R_4 :



$$R_1$$
 $C = C$ R_2 R_3

The general alkene, C₂R₄

- When the groups R_1 , R_2 , R_3 and R_4 are all different (i.e. $R_1 \neq R_2 \neq R_3 \neq R_4$), we have to use the E/Z naming system
 - This is based on Cahn-Ingold-Prelog (CIP) priority rules
- To do this, we look at the atomic number of the first atom attached to the carbon in question
 - The higher the atomic number; the higher the priority
- For example, 2-bromo-1-propen-1-ol has four different atoms or groups of atoms attached to the C=C bond
 - This means that it can have two different displayed formulae:



2-Bromo-1-propen-1-ol (compounds A and B)

Compound A

- Step 1: Apply the CIP priority rules
 - Look at R₁ and R₃:
 - Bromine has a higher atomic number than hydrogen so bromine has priority
 - Look at R_2 and R_4 :
 - Oxygen has a higher atomic number than carbon so oxygen has priority
- Step 2: Deduce For Z



- Eisomers have the highest priority groups on opposite sides of the C=C bond, i.e. one above and one below
 - The Ecomes from the German word "entgegen" meaning opposite
- Zisomers have the highest priority groups on the same side of the C=C bond, i.e. both above or both below
 - The Zcomes from the German word "zusammen" meaning together
- In compound A, the two highest priority groups are on opposite sides (above and below) the C=C bond
 - Therefore, compound A is *E*-2-bromo-1-propen-1-ol

Compound B

- Step 1: Apply the CIP priority rules
 - Look at R₁ and R₃:
 - Bromine has a higher atomic number than hydrogen so bromine has priority
 - Look at R_2 and R_4 :
 - Oxygen has a higher atomic number than carbon so oxygen has priority
- Step 2: Deduce Eor Z
 - In compound B, the two highest priority groups are on the same side (both below) the C=C
 bond
 - Therefore, compound B is Z-2-bromo-1-propen-1-ol

More complicated E/Zisomers

Compound X exhibits E/Zisomerism

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$$H_3CH_2C$$
 $C = C$
 CH_2OH
 R_3

Compound X

- Step 1: Apply the CIP priority rules
 - Look at R₁ and R₃:
 - Carbon is the first atom attached to the C=C bond, on the left hand side



- Look at R_2 and R_4 :
 - Carbon is the first atom attached to the C=C bond, on the right hand side
- This means that we cannot deduce if compound X is an Eor Z isomer by applying the CIP priority rules to the first atom attached to the C=C bond
 - Therefore, we now have to look at the second atoms attached
- Look again at R₁ and R₃:
 - The second atoms attached to R₁ are hydrogens and another carbon
 - The second atoms attached to R₃ are hydrogens and bromine
 - We can ignore the hydrogens as both R groups have hydrogens
 - Bromine has a higher atomic number than carbon, so bromine is the higher priority
 - Therefore, the CH₂Br group has priority over the CH₃CH₂ group
- Look again at R₂ and R₄:
 - The second atoms attached to R₂ are hydrogens
 - The second atoms attached to R₃ are hydrogens and an oxygen
 - Oxygen has a higher atomic number than hydrogen, so oxygen is the higher priority
 - Therefore, the CH₂OH group has priority over the CH₃ group
- Step 2: Deduce For Z
 - In compound X, the two highest priority groups are on the same side (both below) the C=C
 bond
 - Therefore, compound X is the Z isomer

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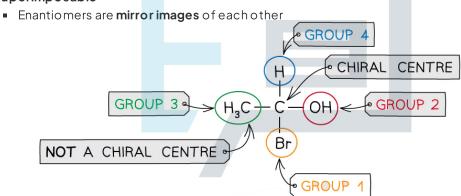


20.3.3 Optical Isomers

Optical Isomers

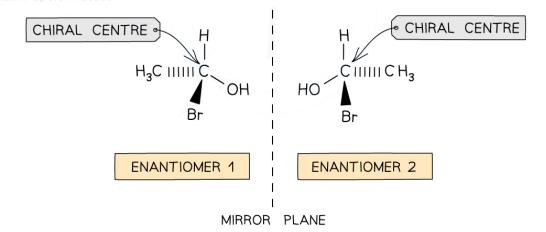
Optical isomers

- A carbon atom that has four different atoms or groups of atoms attached to it is called a chiral carbon or chiral centre
 - Chira comes from a Greek word meaning hand, so we talk about these molecules having a handedness
- The carbon atom is described as being asymmetric, i.e. there is no plane of symmetry in the
- Compounds with one chiral centre (chiral molecules) exist as two optical isomers, also known as enantiomers
- Just like the left hand cannot be superimposed on the right hand, enantiomers are nonsuperimposable



THIS CHIRAL CENTRE GIVES RISE TO TWO ENANTIOMERS

(MIRROR IMAGES WHICH ARE NON-SUPERIMPOSABLE)

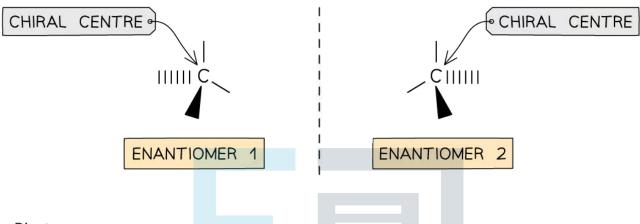


A molecule has a chiral centre when the carbon atom is bonded to four different atoms or group of atoms; this gives rises to enantiomers



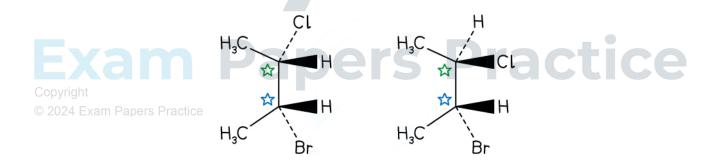
Exam Tip

When drawing optical isomers, always draw mirror images including wedge and dashed bonds



Diastereomers

- Diastereomers are compounds that contain more than one chiral centre
 - Diastereomers are not mirror images of each other because each chiral carbon has two isomers
 - This also means that they have different physical and chemical properties



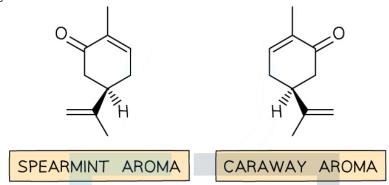
2-bromo-3-chlorobutane exists as a diastereomer due to 2 chiral centres



Polarimetry

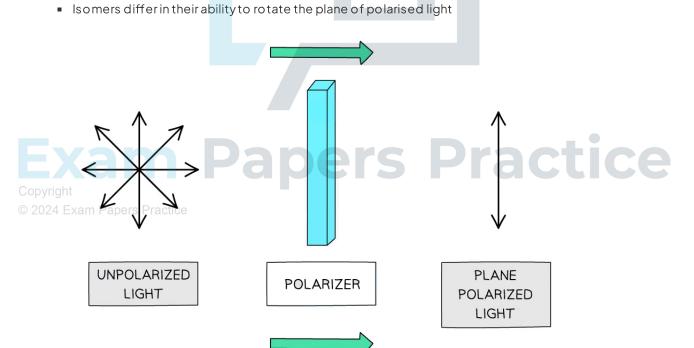
Properties of optical isomers

- The chemical properties of optical isomers are generally identical, with one exception
 - Optical isomers interact with biological sensors in different ways
 - For example, one enantiomer of carvone smells of spearmint, while the other smells of caraway



Carvone optical isomers have distinctive smells

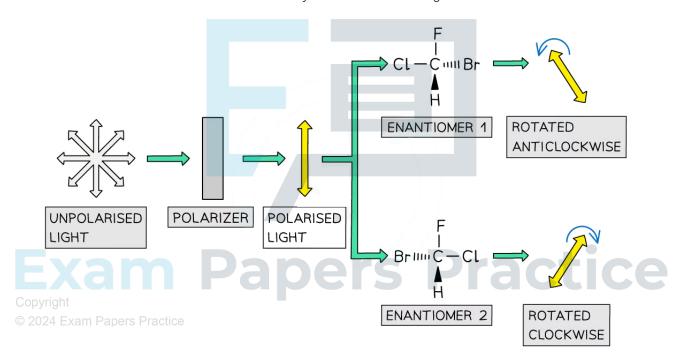
• Optical isomers have identical physical properties, with one exception



When unpolarised light is passed through a polariser, the light becomes polarised as the waves will vibrate in one plane only



- The major difference between the two enantiomers is:
 - One enantiomerrotates plane polarised light in a **clockwise** manner and the other in an **anticlockwise** fashion
 - A common way to differentiate the isomers is to use (+) and (-), but there are other systems using d and I, D and L, or R and S
- The rotation of plane polarised light can be used to determine the identity of an optical isomer of a single substance
 - For example, pass plane polarised light through a sample containing one of the two optical isomers of a single substance
 - Depending on which isomer the sample contains, the plane of polarised light will be rotated either clockwise or anti-clockwise by a fixed number of degrees

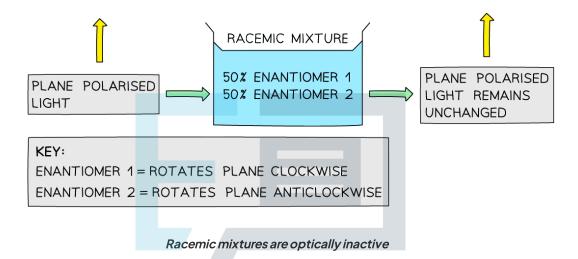


Each enantiomer rotates the plane of polarised light in a different direction



Racemic Mixtures

- A racemic mixture (or racemate) is a mixture containing equal amounts of each enantiomer
 - One enantiomer rotates light clockwise, the other rotates light anticlockwise
- A racemic mixture is **optically inactive** as the enantiomers will cancel out each others effect
 - This means that the plane of polarised light will **not change**



Racemic mixtures and drugs

- In the pharmaceutical industry, it is much easier to produce synthetic drugs that are racemic mixtures than producing one enantiomer of the drug
- Around 56% of all drugs in use are chiral and of those 88% are sold as racemic mixtures
- Separating the enantiomers gives a compound that is described as enantiopure, it contains only
 Copyrigione enantiomer
- © 20.44 This separation process is very expensive and time consuming, so for many drugs it is not worthwhile, even though only half the of the drug is pharmacologically active
 - For example, the pain reliever ibuprofen is sold as a racemic mixture



The structure of ibuprofen showing the chiral carbon that is responsible for the racemic mixture produced in the synthesis of the drug

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