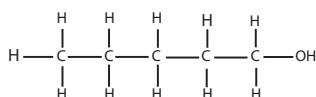


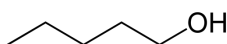
## Chapter 2 : Some Basic Concepts in Organic Chemistry

*This Chapter consists mainly of definitions and concepts that have already been introduced in Chapter 1 which you have just read, and much of this Chapter is therefore in note form.*

- The word “**Nomenclature**” refers to the naming of different things.
- An **Empirical** formula is the *smallest whole number ratio of atoms of the elements in a compound* e.g. the Molecular Formula of Butane is  $C_4H_{10}$ , but its Empirical Formula is  $C_2H_5$ . [Atoms do not exist in fractions, therefore “ $C_1H_{2.5}$ ” is not a permissible formula.]
- A **Molecular** formula is the *actual whole number ratio of atoms of the elements in a compound but it does not attempt to show how the molecule is constructed* e.g. the Molecular Formula of Butane ( $C_4H_{10}$ ) does not attempt to show how the atoms have been linked together.
- A **Structural** formula is the *minimum amount of detail that will define the simplest combination of atoms that form that molecule* e.g. “ $CH_3CH_2CH_2CH_2CH_2OH$ ” is “ $CH_3(CH_2)_3CH_2OH$ ” is “Pentan-1-ol”.
- A **Displayed** formula sets out the *interrelationship between the different atoms and the associated functional groups in an Organic molecule* e.g. this is a displayed formula for Pentan-1-ol.



- A **Skeletal** formula sets out to describe the *interrelationship between all the Carbon atoms (and their associated functional groups) in an Organic molecule* – but it does not show any of the Carbon nor any of the Hydrogen atoms in the molecule, and therefore none of the C–H bonds therein e.g. the molecule below is the skeletal representation of pentan-1-ol



- A **Functional** Group identifies that *part of a compound that is responsible for its characteristic reactions* e.g. the “ $-OH$ ” in Alcohols.
- Homologous Series** in Organic Chemistry are groups of Organic compounds that
  - contain the same functional group
  - have the same general formula, and
  - differ in composition by a multiple of  $CH_2$ .

*All three conditions must be fulfilled* e.g. ethanol ( $C_2H_5OH$ ) and cyclohexanol ( $C_6H_{11}OH$ ) are both alcohols, but they are NOT members of the same homologous series *because they do not differ from each other by a function of  $CH_2$ .*
- In your exams, if you ever see the phrase “a general formula for the Homologous series.....”, then the examiner wants you to quote a general formula such as the ones below

Homologous Series	General (or generic) formula
Alkanes	$C_nH_{2n+2}$
Alkyl Additions	$C_nH_{2n+1}$
Cycloalkanes	$C_nH_{2n}$
Alkenes	$C_nH_{2n}$
Alkynes	$C_nH_n$
Aliphatic <sup>1</sup> alcohols	$C_nH_{(2n+1)}OH$ [NB $(2n+1)$ because an “ $-OH$ ” has replaced an “ $-H$ ”.]

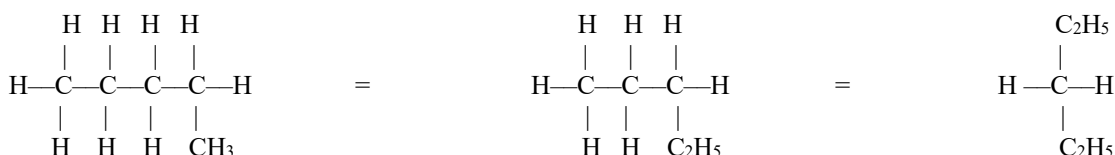
<sup>1</sup> The words “Aliphatic”/“Alicyclic”/and “Aromatic” are defined on page 6.

NB You DO need to know these general formulae; but, until you are much more familiar with Organic Chemistry, you should **NOT** use ANY general formula other than that for Alkanes ( $C_nH_{2n+2}$ ) – and even with Alkanes, you should physically count every single bond and every single Carbon atom in order to check that you have not made a mistake! At this stage, the careless use of general (or generic) formulae can get you into trouble if you do not know what you are doing e.g. **look at the general formulae for Cycloalkanes and Alkenes!**

## ISOMERS

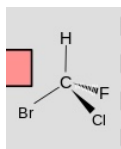
- Substances that possess the same **molecular formula** but possess some identifying difference that gives them **different chemical and or different physical properties** are called **Isomers**. The essence of isomerism therefore is that substances that appear to be the same, nevertheless have something that differentiates them (and we then need to investigate what the difference is and see how it arises).
- Let me start with what isomers are NOT! **The different-looking substances below are not isomers because they are all the same substance!** I have just drawn the same substance in three different ways. The surest way to tell whether or not two different-looking substance are isomers is to name the substances (and always start by finding the longest C atom chain). **If they have the same name then they ARE the same substance.** The three different looking substances below are all bog-standard pentane.

**THESE ARE NOT ISOMERS! They are all the same substance viz. pentane.**

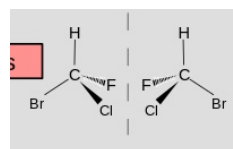


- However, **CH<sub>3</sub>-CH(OH)-CH<sub>3</sub>** and **CH<sub>3</sub>-O-CH<sub>2</sub>CH<sub>3</sub>** both have the same molecular formula (i.e. C<sub>3</sub>H<sub>8</sub>O) but they are NOT the same substance: they are functional group isomers of each other. The one on the left is propan-2-ol (which US NIST calls 2-propanol), and the one on the right is *what*? If you do not know what it is, then please go back and read Chapter 1 again and you will find an answer on page 17 (and please remember the alphabetic rule).
- The substance could be thought of as an ether (ethyl methyl ether) or it could be regarded as an ethane (methoxyethane) – and there you have three possible isomers for the formula C<sub>3</sub>H<sub>8</sub>O.
- It is easily possible to get confused about different sorts of isomers, and please could you note that in this subject the terminology seeks to distinguish extremely subtle differences between almost identical substances, but that at 'A' Level you are required to be aware only of *broad* distinctions.
- The examiners love to set a question to see whether or not you really understand what an isomer is – therefore it is sensible to examine in some detail how isomerism arises. However, the only sorts of isomers that you need to know about at 'A' Level (and you DO need to know about them **in detail**) are
  - Structural** isomers (as with propan-2-ol/ethyl methyl ether/and methoxyethane above), and
  - Stereoisomers** of which you are required to know about the two subdivisions “**Cis-trans**” or “**E/Z**” isomers and **Enantiomers** (or **Optical isomers**). However, in order to know about Enantiomers you need to know about Chirality.<sup>2</sup>

<sup>2</sup> Chirality has to do with symmetry, and in this Chapter we will need to do no more than mention **Chirality** – and an atom that is attached to **four DIFFERENT species** is said to be chiral and it has a "chiral centre". For example, in the diagram from Wikipedia on the next page, the bromochlorofluoromethane molecule is chiral. Please forget the pink bit (and if you type in “stereoisomer” into Wikipedia, you will see why I cannot get rid of it).

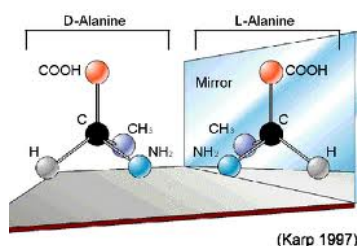


Bromochlorofluoromethane



Bromochlorofluoromethane with its mirror image

- Anything that is chiral can have two forms/two isomers that will exhibit **optical isomerism**. In other words, if you put a mirror up against one of these two isomers, then the reflection in the mirror will give you the second isomer (cf. above) – and as with all mirror images, the two substances cannot be superimposed on each other in three-dimensional space i.e. if you were able to pluck the mirror image isomer out of the mirror and try to overlay it on the original isomer, then **you would NOT be able to do so**.
- Please try to do this with your hands and you will see what I am talking about. If you put your right hand next to a mirror, the image that you get will be the image of your **right hand**, and if you take that **right hand** out of the mirror and try to super-impose it on your actual right hand (which it originally was) then you will not be able to do so. It will in fact be the same as your LEFT hand, and your right and your left hand are *not* the same as each other because they are (so to speak) “back-to-front” of each other. **In a mirror your right hand may look like your right hand, but in reality it is not exactly the same as your right hand!** What you see in the mirror is actually a replica of your **left** hand.
- Quite a few of you are doing Biology, therefore the enantiomers below are real life examples from Biology. “L” and “D” stand for “Left” and “Right”. (“Dexter; is the Latin word for “Right”.) Left and Right-handed enantiomers<sup>3</sup> are of extraordinary importance in Biology and in Medicine. Can you see how the diagram above and the one below are *almost* replicas of each other? <sup>4</sup>



Source : Memorial University, Newfoundland

- Let us now consider the main divisions between differing sorts of isomers.**
- Structural isomers** have the same molecular formula but different **structural** formulae.
- Stereoisomers/Geometric isomers** have the same structural formulae but are **arranged differently** in space. If stereoisomers are
  - mirror images of each other, then they are called **optical isomers** or enantiomers, or
  - if they are not mirror images of each other they are called **diastereoisomers**.<sup>5</sup>

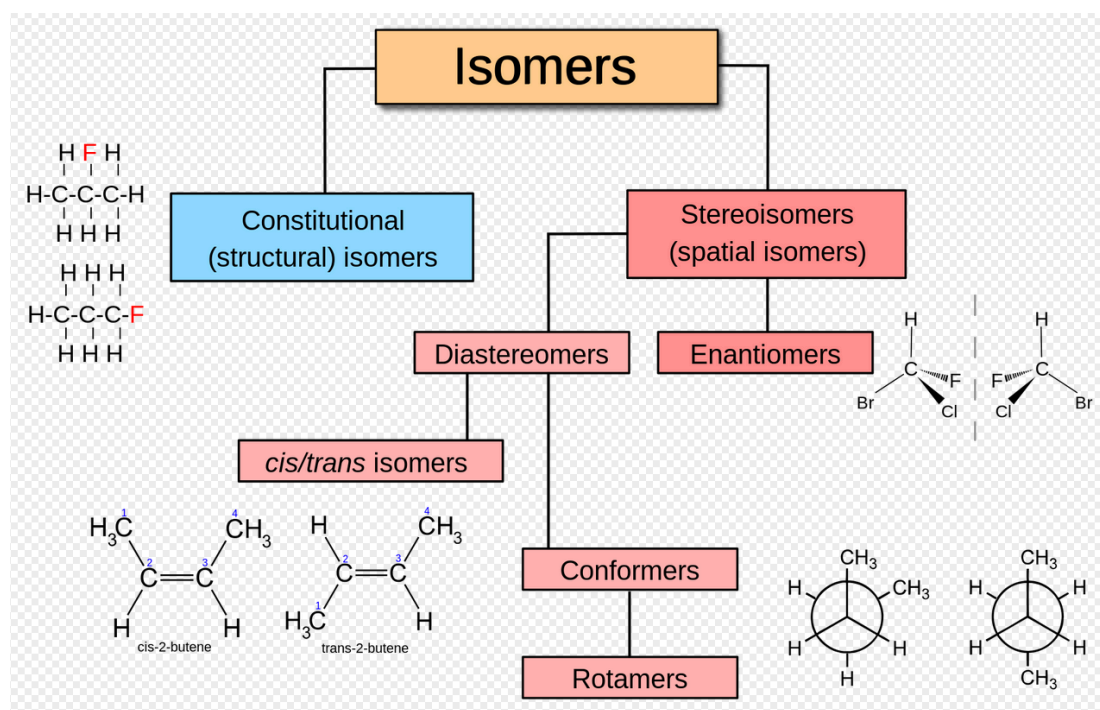
<sup>3</sup> Sometimes you will see it written as “S” and “R” (where “S” stands for “Sinister” which is the Latin word for “Left”). “Dexter” is the word for “Right” in Latin.

<sup>4</sup> This has nothing whatsoever to do with ‘A’ Level Chemistry, but I am now going to introduce you to something important that you will come across when you get to University. When someone wants to cite a reference source and its authors, then this is how they can write it. Author(s), Date, Title, Journal as in: Chhabra, N., Aseri, M. L. & Padmanabhan, D. (2013). A review of drug isomerism and its significance. *International Journal of Applied Basic Medical Resources*, 3(1), pp16–18, and that now tells the reader exactly where to find the article that has been referenced. The citing methodology that I have used is that of the American Psychological Association, but there are other citing methodologies (such as the Harvard methodology).

<sup>5</sup> The Greek prefix “dia” here has the function of conveying the impression that there is an invisible line drawn through the molecule, and that the isomerism occurs around this invisible line.

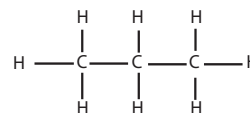
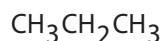
- There are two forms of diastereoisomers that you need to be aware of viz. (i) **cis** and (ii) **trans isomers**. Both the descriptions “Stereoisomer” and “Geometric isomer” mean that you are considering a molecule *in all its three dimensions*.
- Cis/trans isomerism** arises from the fact that it is not possible to rotate two  $\pi$  bonded Carbon atoms around each other *without breaking the  $\pi$  bond and destroying the overlap of the two unhybridised ‘p’ orbitals and thus changing the substance* (cf. page 6), therefore atoms or groups of atoms that are attached to each of the two C atoms on the **same** side of the double bond may form a different configuration from the same attachments when they are on **opposite** sides of the double bond – **and a different configuration would then form a different substance from the original substance**.
- Optical Isomers** : In exactly the same way that a right hand glove and a left hand glove are different, so also optical isomers are mirror images of each other and cannot be superimposed identically upon each other.

### A BROAD CLASSIFICATION OF ISOMERS

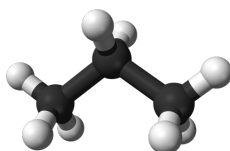


Source: Wikipedia

- Different people name the classification of isomers in different ways. The above is a good starting point.
- Please note that no matter how you may write a formula, all that is achieved by using a formula is to write on a piece of paper a very poor representation of how a molecule is actually put together in reality **in 3 dimensions!**
- For example the molecular formula  $C_3H_8$  is but a poor representation of

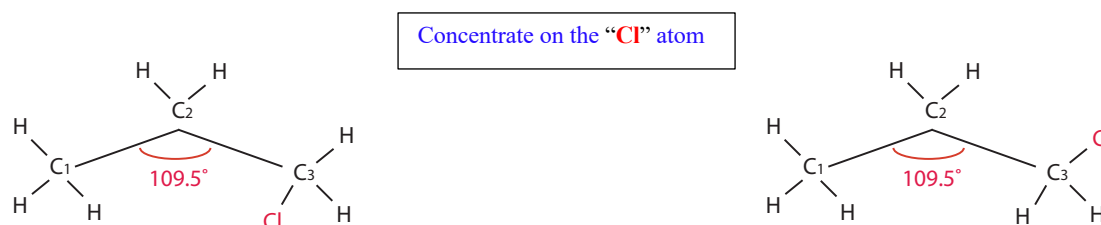


and even these two representations are themselves but a poor representation of the fact that ALL the bond angles in each of the separate Carbon configurations in  $C_3H_8$  are approximately  $109.5^\circ$  and occupy 3-dimensional space, and the molecule could therefore be drawn as follows.



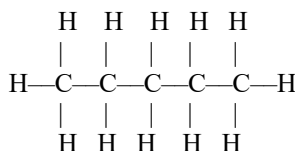
Source: venngage

- EVERY SINGLE BOND ANGLE here is approximately  $109.5^\circ$ . Please remember that this diagram depicts the molecule on TWO dimensional paper – but in reality the molecule exists in THREE DIMENSIONS!
- Moreover, in alkane molecules it is as though there is a universal joint linking each of the adjoining C atoms – and this allows them to rotate in relation to each other so long as the  $109.5^\circ$  bond angle is maintained. The diagram below attempts to show the effect of rotating the Carbon atom marked C3 *around the single bond which joins it to the C2 atom*. After C3 is rotated around its bond with C2, the Cl atom is now located in a different place in space *but the substance has not changed chemically!* In other words, **the two molecules below are not isomers**, and instead **they are exactly the same molecule**. Rotation around a single bond does NOT alter the substance in any way. However, when we come to examine the 3-dimensional structure of double bonds we will see that **rotation around a double bond DESTROYS the substance**.



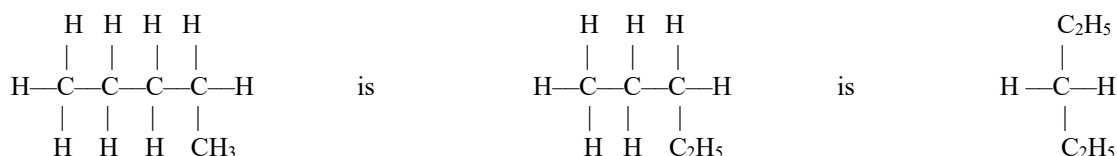
### Structural Isomers

- Structural isomers *have the same molecular formula but have different structural formulae*.<sup>6</sup>
- However, if we consider the entities that possess the Molecular Formula  $C_5H_{12}$ , we can see that although all the structures (on the next page) *appear to be different from each other*, nevertheless **they are NOT different**. The rule is that if you imagine all the C atoms positioned on one long piece of wire (as in the first diagram below), and **if you can bend the wire into the required shape without cutting the wire and soldering the cut piece back on, then the resultant molecule is not an isomer. It is the SAME molecule**. If you have to cut and solder the wire back on, **then it is an isomer**.

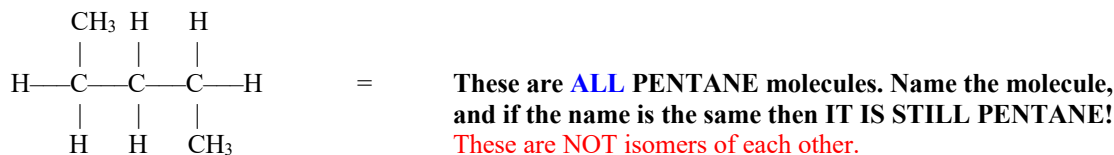


- **The molecules below are NOT isomers of  $C_5H_{12}$** . They ARE all Pentane molecules – and they look different merely because the C atoms have been rotated around single bonds. **(Please name the molecule, and if the name is the same then it is not a different molecule.)**

<sup>6</sup> It is possible to call all the isomers of pentane “chain isomers”, indicating that the differences occur merely in the structure of the chain.



In order to name a molecule, remember to first look for the longest C chain that you can find.

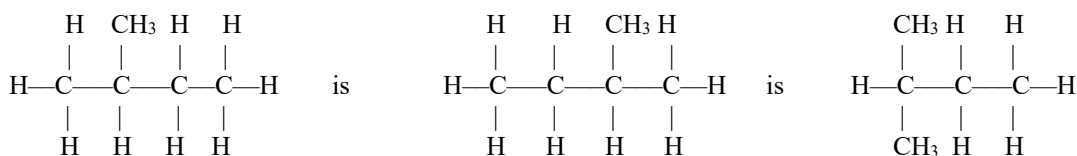


And now for the true isomers of Pentane (a) 2-methyl butane, and (b) 2,2-dimethyl propane.

a) **2-methyl BUTANE** (these next three diagrams all represent EXACTLY the SAME molecule)

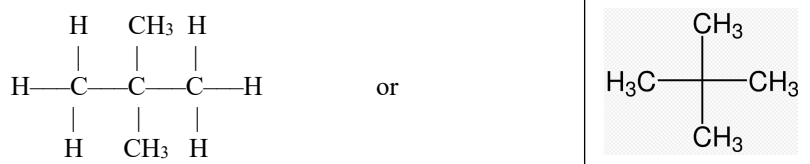
For the molecule in the middle, I have just gone round the back of the first molecule and I am now looking at it from the back of it.

This one is NOT a propane!  
It is still a butane.



- You might at first sight think that the molecule on the right is different from the one in the middle and the one on the left – **but it is NOT different**. It is exactly the same molecule. Name it and you will see this. The molecule below IS different, but the ones above are all **2-methyl butane**.

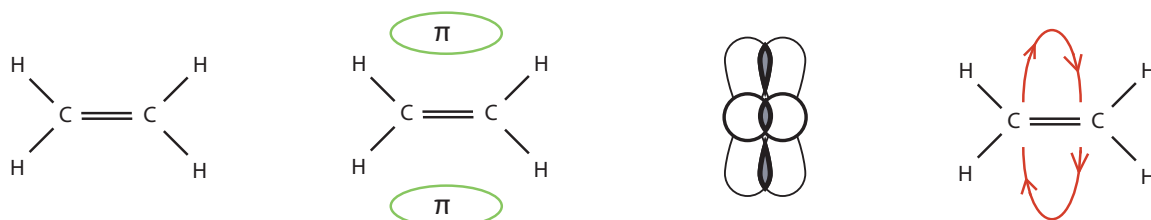
b) **2,2-dimethyl PROPANE**



- That's it. There are three isomers with the molecular formula  $\text{C}_5\text{H}_{12}$ . They are pentane, 2-methyl butane, and 2,2-dimethyl propane. There are NO OTHER ISOMERS OF  $\text{C}_5\text{H}_{12}$  ! Try drawing it for yourself and you will see that this is so! **Name the molecule that you draw, and if it has the same name as one of the three above, then IT WILL BE EXACTLY THE SAME MOLECULE.**
- Now let us look at "Cis-trans isomerism". In Latin "cis" means "on the same side" and "trans" means "across" or "on the other side". You DO need to remember which word means which – and you can do so by remembering that if you "transport" someone across a river, then you are taking that person to *the other side*. (Similarly, 'trans-atlantic' means on the other side of the Atlantic.)

## Cis-trans isomerism

- If you were to go back to Chapter 1 you would see that in Organic Chemistry, a double bond is created by the overlap of two unhybridised 'p' orbitals (one from each of two bonded Carbon atoms), and consequently if you were to rotate the two Carbon atoms in relation to each other, then the overlap between the two 'p' orbitals would be broken and there would no longer be a double bond where one existed previously – and, if the molecule no longer has a double bond, *then at that point it is no longer the molecule that it formerly was*. You would probably agree that if your head were removed from your body, then you would cease to be who you currently are – and so also, **breaking a double bond inside a molecule stops the molecule from being the substance that it formerly was!** Moreover, *if your head were turned back to front (as in cis/trans isomerism), then you would no longer be you*.
- Inside a molecule that has a double bond (e.g.  $C_2H_4$  or  $H_2C=CH_2$ ), the double bond consists of a  $\sigma$  bond and a  $\pi$  bond, and if one C atom were rotated against the other one, then the overlap of the 'p' orbitals would be broken and thus the double bond would be broken **and the molecule would no longer be the molecule that it was**. However, the four H atoms in the molecule below are the same species (they are all H atoms) therefore cis/trans isomerism is not possible in Ethene ( $C_2H_4$  or  $H_2C=CH_2$ ).



- However, if we substituted two Chlorine (Cl) atoms for two of the H atoms, then we could certainly create cis/trans isomers as below. Each of these two molecules is 1,2-dichloroethene, but they are two different isomers of 1,2-dichloroethene and they will therefore have different boiling and melting points/etc.



- OK, let us now try to define cis/trans-isomerism.
- Cis/trans isomerism** arises from the fact that when two Carbon atoms are double bonded, they cannot rotate in relation to each other without breaking the  $\pi$  and (thus) the double bond, and thus changing the nature of the substance under consideration; therefore, atoms or groups of atoms that are attached to each one of the two C atoms on the SAME (**cis**) side of the double bond may form a different configuration from the same attachments when they are placed on OPPOSITE (**trans**) sides of the double bond – **and a different configuration would then form a different substance from the original one**.
- When two C atoms are double bonded to each other, it is not possible to rotate one C atom around the double bond without breaking the  $\pi$  overlap and thus destroying the substance – and this lies at the heart of the explanation of cis-trans isomerism!**
- These days in 'A' Level exams in England they do not ask for definitions, but for a different exam you might want to memorise the following wording:

“Cis-trans isomerism results from the fact that a  $\pi$  bond is formed by the overlap of two unhybridised ‘p’ orbitals, and if the overlap of these orbitals is broken then the molecule and thus the substance will be destroyed. **The rotation of one C atom around the other C atom in a double bond breaks the  $\pi$  bond and thus destroys the substance. Rotation through  $180^\circ$  will re-establish another  $\pi$  bond but it might also create a different substance.**”

- Now let us look at some examples of cis-trans isomers, but before we do so let us remind ourselves of what is and what is NOT an isomer of a substance that has a double bond. **The two molecules in (A) are NOT isomers – they are the SAME molecule looked at from differing viewpoints (i.e. from the back and from the front), and the same is true for the molecules in (B).**

**These are not isomers. They are the same molecule.**

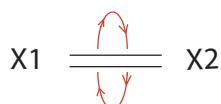
**A)**



**B)**



- The two molecules in (A) and in (B) are NOT isomers. In each instance they are EXACTLY the same molecule looked at from the FRONT and from the BACK of the molecule.*
- In what follows,



constitutes an instruction to rotate  $X_1$  against  $X_2$  through  $180^\circ$  around the double bond that links the two atoms.

- The following molecules ARE cis/trans isomers!*

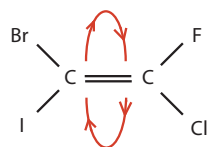
**C)**



and

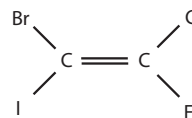


**D) CIS (with regard to Br and F)**



*“Z” isomer (with regard to I and Cl)*

**TRANS (with regard to Br and F) <sup>7</sup>**



*“E” isomer with regard to I and Cl<sup>8</sup>*

- “Z” for “zusammen” is Chemistry German for being on the same side, and “E” for “entgegen” is Chemistry German for being on opposite sides. (*Poor Goethe must be looking down and crying his eyes out!*) I will talk about the E/Z Cahn-Ingold-Prelog (CIP) rules next year, but Jim Clark has an excellent explanation of the rules on <https://www.chemguide.co.uk/basicorg/isomerism/ez.html> . The Chemistry Department at UCL used to housed in the Sir Christopher Ingold Building (and may still be so.)

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<sup>7</sup> In a situation such as the one above, some chemists use the E/Z classification where if the two species with the highest “CIP” priorities regarding Atomic Number are on the same side of the axis of rotation then the isomer is termed a “Z” isomer, and if they are on opposite sides then it becomes an “E” isomer.

<sup>8</sup> I has a higher Atomic Number than Br, and Cl than F. (Atomic Number = the number of protons in the nucleus.)

- OK, the examiners sometimes throw in a question about Yield and also about Atom Economy (or Atom Efficiency) so now let us look at that topic.

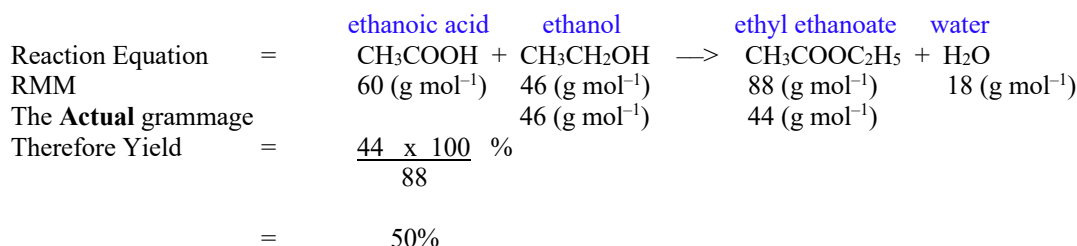
### YIELD

- Students are required to know how to calculate the **yield** of reactions, and there are many different reasons why the **Actual** output of a particular reaction may not be the same as its **Theoretical** output.
- Yield is a measure of how **successful** a process may be.

$$\text{Yield} = \frac{\text{Actual Output}}{\text{Theoretical Output}} \times 100 \%$$

If we obtain  $44 \text{ g mol}^{-1}$  out of a theoretical output of  $88 \text{ g mol}^{-1}$ , then the yield would be 50%.

- Calculating the “Yield” of a particular experiment is very easy and it is best shown by doing the calculation involved. Let us look at a sample question viz. “Only 44g of Ethyl Ethanoate were obtained by reacting 1 mole of  $\text{CH}_3\text{COOH}$  (ethanoic acid) with 1 mole of  $\text{CH}_3\text{CH}_2\text{OH}$  (ethanol) in the presence of conc. Sulphuric Acid. What was the Yield?” (The reaction below takes place in the presence of concentrated Sulphuric Acid.)



### ATOM ECONOMY/EFFICIENCY

- AE is a measure of how **wasteful or how fruitful** a process may be. Here we have used  $106 \text{ g mol}^{-1}$  to obtain  $44 \text{ g mol}^{-1}$ . The AE is 41.5%, viz. we used 58.5% of the materials without obtaining anything that we desired.

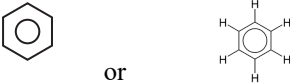
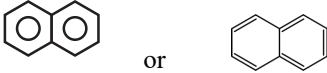
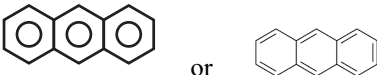
$$\text{Atom Economy} = \frac{\text{Actual Output}}{\text{Total Mass of the Reactants}} \times 100 \%$$

$$= \left( \frac{44}{106} \times 100 \right) \% = 41.5 \%$$

NB The Conservation of Mass Law requires that the total mass of the reactants = the total mass of the products.

## Postscript

- You may occasionally see the words “Aliphatic/Alicyclic/and Aromatic”, and the difference between these groups of compounds is very simple

Aliphatic compounds	Alicyclic compounds	Aromatic compounds/Arenes <sup>9</sup>
	Cyclical organic substances with <b>no</b> delocalised $\pi$ ring	(these do have delocalised $\pi$ rings)
e.g.		
Alkanes	• Cyclical Alkanes	• Benzene (C <sub>6</sub> H <sub>6</sub> )
• Alkenes	• Cyclical Alkenes	(and Benzene compounds)
• Alkynes		
		• Naphthalene (C <sub>10</sub> H <sub>8</sub> ) <sup>10</sup>
		(and Naphthalene compounds)
		
		• Anthracene (C <sub>14</sub> H <sub>10</sub> )
		(and Anthracene compounds)
		

*The diagrams on the right of this column are from Wikipedia*

<sup>9</sup> An “arene” is an aromatic hydrocarbon.

<sup>10</sup> There is far too much detail for you in it, but would you like to try clicking on to <http://en.wikipedia.org/wiki/Naphthalene>

It is good practice for you to see how other people describe/view things. Be flexible in your thought processes and always try to develop an “open” mind. The reason that human beings spend so much time killing each other is because they have closed minds – and always think that they are in the right, even when they may possibly be in the wrong!