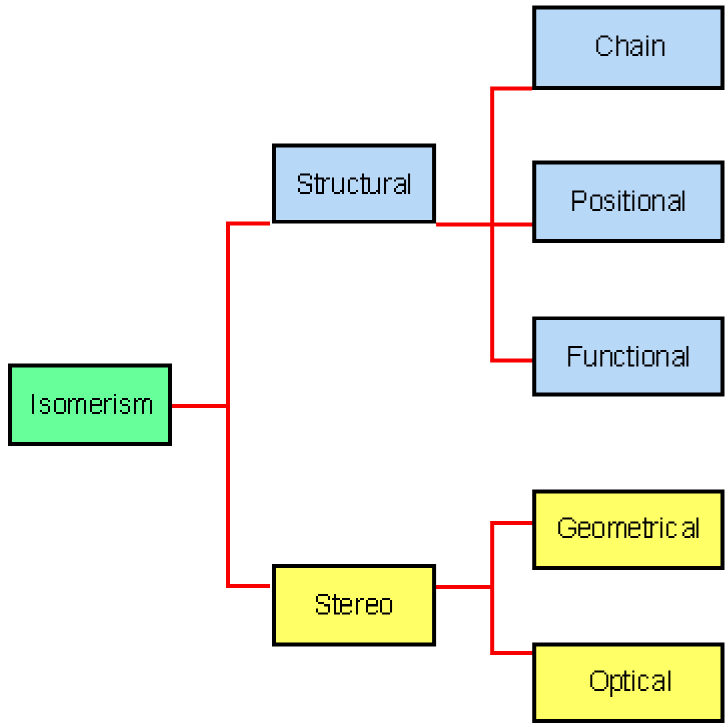
Chemistry 102

Organic Chemistry: Introduction to Isomers Workshop

What are isomers?

Isomers are molecules with the same molecular formula, but different arrangements of atoms. There are different types of isomers, shown by the diagram on the right.

“Structural” isomers are widely called “conformational” isomers. The latter term is preferred in the IUPAC system of nomenclature.



Structural Isomerism

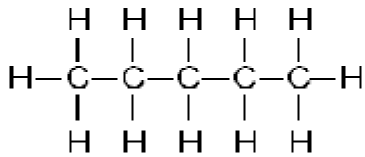
Structural isomerism occurs when two or more organic compounds have the same molecular formulae, but different structures. These differences tend to give the molecules different chemical and physical properties. There are three types of structural isomerism that you need to be aware of: chain isomerism, positional isomerism and functional isomerism. There is a fourth type, known as **tautomerism** (where there are two isomers are known as the **keto** and **enol** isomers) that will not be introduced here.

Chain Isomerism

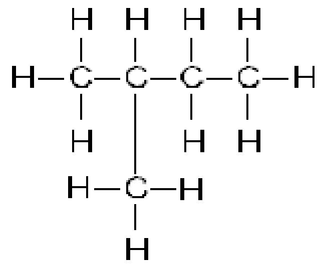
Chain isomerism occurs when the way carbon atoms are linked together is different from compound to compound. It is also called nuclear isomerism.

There are three chain isomers of C_5H_{12} shown below. Note that these isomers have the same empirical formula as pentane, but different conformations.

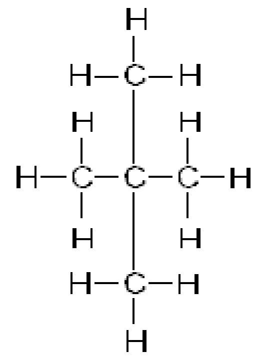
pentane



2-methylbutane



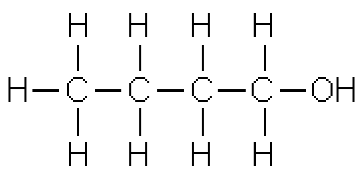
2,2-dimethylpropane



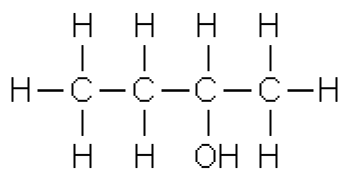
Positional Isomerism

Positional isomerism, another type of structural isomerism, occurs when functional groups are in different positions on the same carbon chain. Positional isomers of alcohols, alkenes, and aromatics are common. Below are models of the positional isomers of butanol, butene and methylphenol:

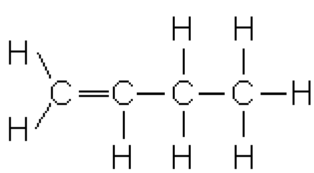
1-butanol



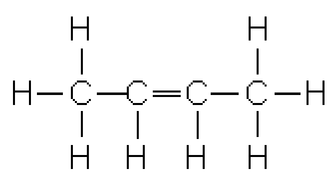
2-butanol



1-butene

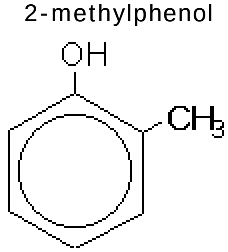


2-butene

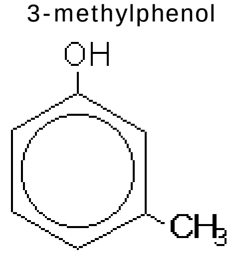


Note: this is *cis*-2-butene, which has a geometric isomer called *trans*-2-butene

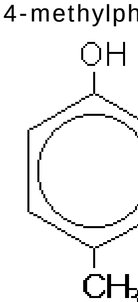
2-methylphenol



3-methylphenol



4-methylphenol



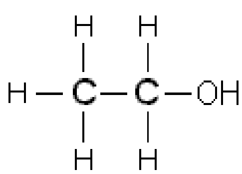
Functional Isomerism

Functional isomerism, another kind of structural isomerism, occurs when substances have the same molecular formula but different functional groups. This means that functional isomers belong to different homologous series. There are two functional group isomers of which you need to be aware:

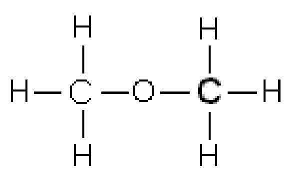
- alcohols and ethers
- aldehydes and ketones

Below are models of the functional isomers ethanol and methoxymethane, and propanal and propanone.

ethanol



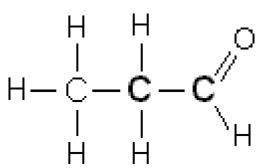
methoxymethane



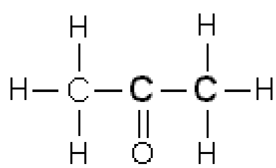
C_2H_6O

Alcohols have the **hydroxyl** group, **–OH**. Ethers have the functional group **R–O–R'**.

propanal



propanone (acetone)



C_3H_6O

Aldehydes and ketones both have the **carbonyl** group **C=O**. In ketones this is attached to two carbon atoms; in aldehydes it is attached to 1 or 2 hydrogen atoms.

Stereo-isomerism

Stereo-isomerism occurs when the atoms in a molecule can have different arrangements in space. There are two types of stereo-isomerism: geometrical isomerism and optical isomerism. Geometrical isomers can have very different physical properties, such as different melting points, but they tend to have the same chemical properties. Optical isomers have the same chemical and physical properties, except that one structure rotates the plane of polarized light to the right and the other rotates it to the left.

Geometric Isomerism

Geometric isomerism occurs when substances have the same molecular formula, but a different arrangement of their atoms in space. There are three ways that this can happen:

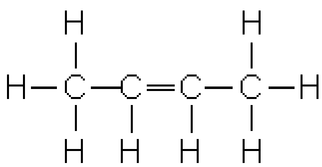
- where there is a C=C bond in the molecule;
- where a molecule has rings; or

- where there is a >C=N bond.

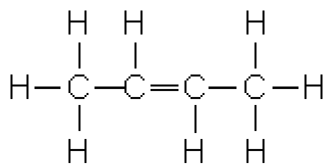
An interesting example of geometric isomerism caused by rings is found in sugars such as glucose, fructose, mannose and galactose.

Below are models of the geometric isomers of 1- butene and 2-butene. 1-Butene does not form geometric isomers, even though it has a C=C bond, because one of the double-bonded carbon atoms has two identical groups on it (hydrogen atoms in this case). 2-Butene does form geometric isomers because each double-bonded carbon atom has two different groups on it. The cis- and trans- prefixes are used to differentiate the positions of the functional groups.

cis-1-butene

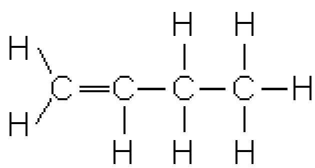


trans-2-butene



Where like groups are on the same side of the double bond, we call it a *cis* isomer; where they are on opposite sides we call it a *trans* isomer.

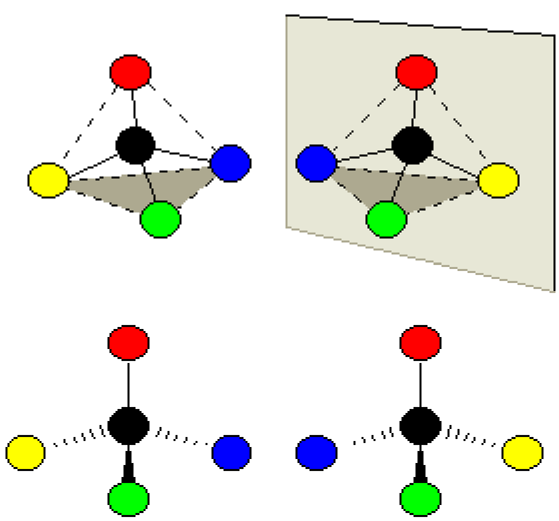
1-butene



Although 1-butene contains a C=C bond, it does not form geometrical isomers.

Take care - look for **different** groups on the double-bonded carbon atoms!

Optical Isomerism



Optical isomerism occurs when substances have the same molecular and structural formulae, but one cannot be superimposed on the other. Put simply, they are mirror images of each other (see the diagram on the right). No matter how hard you try, the molecule on the left will not turn into the molecule on the right – unless you break and make some bonds! Molecules like this are said to be chiral (pronounced ky-ral), and the different forms are called **enantiomers.**

Optical isomers can occur when there is an **asymmetric** carbon atom. An asymmetric carbon atom is one which is bonded to four different groups. The groups can be something hideously complex, or something comfortably simple like a hydrogen or chlorine atom. Remember:

- there must be **four groups**, and
- they must be **different**.

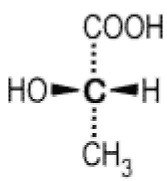
Optical isomers can rotate the plane of polarization of plane-polarized light:

- one enantiomer rotates the polarized light clockwise (to the right) and is the (+) enantiomer;
- the other rotates the polarized light anticlockwise (to the left) and is called the (–) enantiomer.

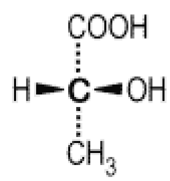
A mixture containing equal concentrations of the (+) and (–) enantiomers is not optically active (it will not rotate the plane of polarization). It is called a **racemic mixture** or **racemate**.

Below are models of the optical isomers of 2-hydroxypropanoic acid (lactic acid). Lactic acid is a fairly common and simple example of optical isomerism. The (+) enantiomer of lactic acid is found in muscle. Sour milk contains a racemic mixture of the two enantiomers.

(+)-lactic acid



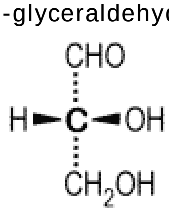
(–)-lactic acid



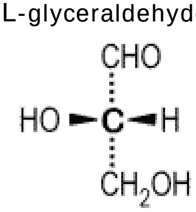
The dashed lines show bonds going into the screen; the wedges show bonds coming out of the screen.

Below is 2,3-dihydroxypropanal (glyceraldehyde). Glyceraldehyde is used as a standard by which other chiral molecules are compared. There are two enantiomers of glyceraldehyde, depending on the position of the –OH (hydroxyl) group on the molecule. These are known as D-glyceraldehyde and L-glyceraldehyde. The little capital letters D and L are deliberate. The positions of the hydroxyl groups on other chiral molecules can be compared with glyceraldehyde to see if they are the D-enantiomer or the L-enantiomer. This is very common in biochemistry. For example, natural sugars are D-enantiomers and amino acids are L-enantiomers. However, knowing whether a molecule is the D or L-enantiomer does **not** tell us whether it is the (+) or (–) enantiomer – so be careful!

D-glyceraldehyde



L-glyceraldehyde



Remember – these are reference molecules; the D and L signs do not tell you if the enantiomer is (+) or (–).

Exercises:

1. Draw 2-methylpentane. Make a molecular model of 2-methylpentane and convince yourself that 4-methylpentane is the same molecule.

2. Draw all the structural (chain) isomers of C_6H_{14}. How many are there? Verify that they are all different using molecular models. Name the isomers.

3. Draw and name all the positional isomers of propanol. The symmetrical isomer is commonly called isopropanol or rubbing alcohol.

4. Draw the functional isomers of C_3H_8O and C_4H_8O. Verify that they are all different using molecular models. Name the isomers.

5. Draw and name the cis- and trans- isomers of a) dibromoethene and b) 1-chloro-1-propene. Compare molecular models of each pair of isomers.

6. Compare pairs of molecular models of the + and – forms of lactic acid. Convince yourself that these molecules cannot be superimposed: that they are mirror images of each other. Do the same for the D- and L- forms of galactose. Draw 2-chloro-3-methylbutane and 2-chloro-2-methylbutane. Which of these molecules has an optical isomer? Draw it.