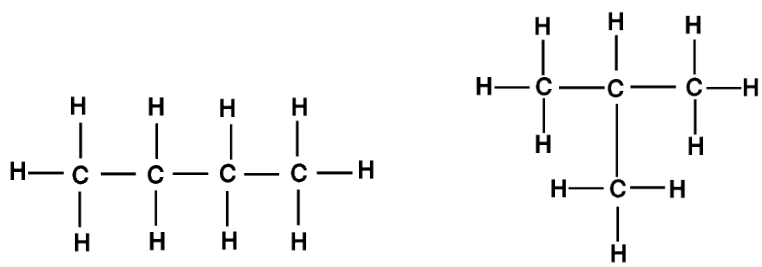
Chapter 16

WHY ARE THERE SO MANY CARBON COMPOUNDS II?

In Chapter 15, it was shown how there is an enormous number of hydrocarbons as a result of the ability of carbon compounds to catenate. These compounds can have structures which are straight chains, branched chains, or rings. The number of possibilities is increased many times by the existence of isomers, such as cis- trans- isomers. In this Chapter, it will be shown that organic compounds also containing oxygen atoms, nitrogen atoms, or halogen atoms result in an even larger range of possibilities.

16.1 Background

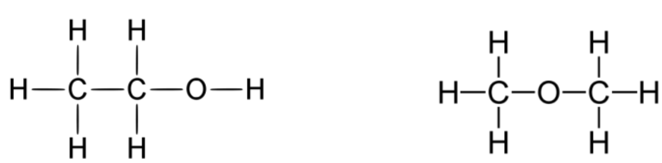
In Chapter 15, it was shown how two hydrocarbons could have the same molecular formula but differ in the bond organization to give different isomers. An example is the alkane, C_4H_{10}, which has two isomers, butane, and 2-methylpropane (Figure 16.1). These isomers differ slightly in melting points and boiling points, but have few other differences. They both burn in air, and are immiscible with water.



(a) (b)

Figure 16.1 The condensed formula for the two structural isomers of C_4H_{10} (a) butane, and (b) 2-methylpropane

By contrast, organic compounds containing elements other than carbon and hydrogen can have structural isomers with very different properties. For example, the molecular formula, C_2H_6O, represents two structural isomers shown in Figure 16.2. The first, commonly called ethyl alcohol, is a liquid at room temperature which is ingested by many as a socially-acceptable intoxicant. The second, commonly called dimethyl ether, is a gas at room temperature which has anesthetic properties when inhaled.



(a) (b)

Figure 16.2 The condensed formula for the two structural isomers of C_2H_6O

There is a second way in which organic compounds containing other elements differ from hydrocarbons. Adding an additional substituent, such as a methyl group, to a hydrocarbon slightly alters the melting and boiling point of the compound. For molecules also containing other elements, very small changes in structure can produce major changes in the properties. An interesting pair of examples is that of caffeine and theobromine (confusingly, the latter does not contain the element bromine). Caffeine is the stimulant in the coffee bean, tea leaves, and other sources while theobromine is the active ingredient in chocolate derived from the cacao bean. The corresponding ball-and-stick models are shown below in Figure 16.3. The only difference between them is that the caffeine molecule has a methyl, CH_3-, group to the lower right while the theobromine molecule has a hydrogen atom.

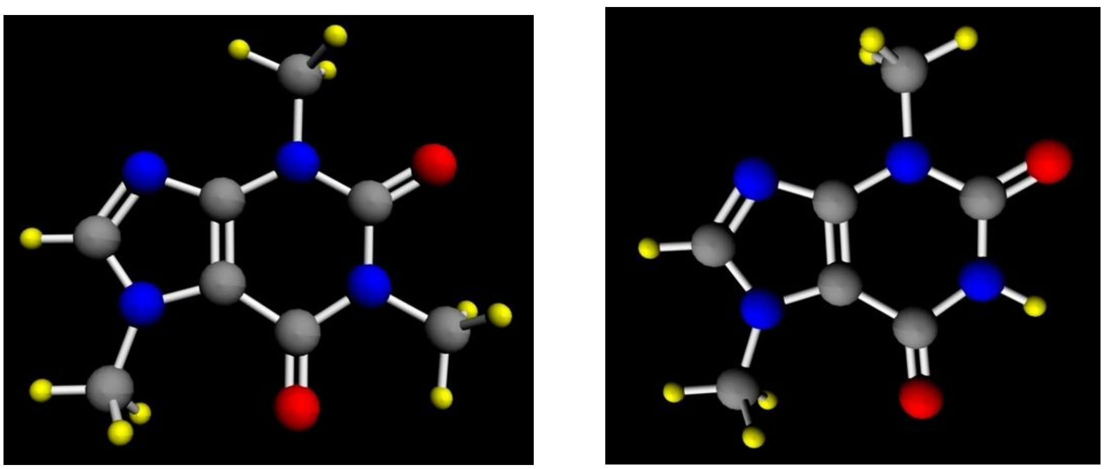


Figure 16.3 The ball-and-stick models of (a) caffeine and (b) theobromine. The atom colours are: carbon – grey; nitrogen – blue; oxygen – red; and hydrogen – yellow.

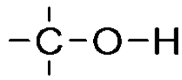
This difference has a major effect on the comparative properties of the compounds as can be seen in Table 16.1.

Table 16.1 A comparison of the properties of caffeine and theobromine

Caffeine	**Theobromine**
Strong effect on central nervous system	Mild effect on central nervous system
Fast acting	Slow onset
Rapid dissipation	Long lasting
Increases alertness	Increases feeling of well-being
Stimulates respiratory system	Stimulates muscular system
Addictive with documented withdrawal symptoms	Not addictive (though some may disagree!)

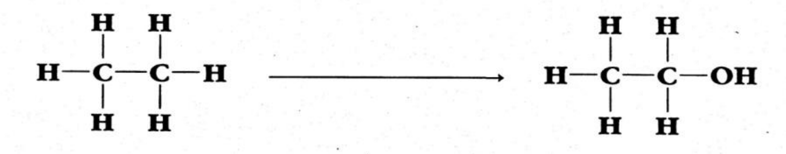
16.2 Alcohols

The substituents on the carbon chain are called ***functional groups***. The first group to be discussed is that of ***alcohols***. The characteristic functional group of an alcohol is:



NAMING ALCOHOLS

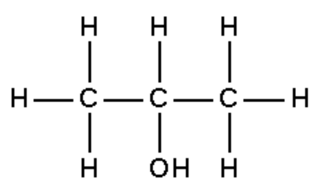
As with hydrocarbons, the first part of the name denotes the length of the carbon chain, preceded by the number and the type of any hydrocarbon substituents. The functional group is identified by the suffix, *–ol*, as can be seen below:



ethane ethanOL

EXAMPLE 16.1

Provide the name of the following alcohol shown as a structural formula:



Answer

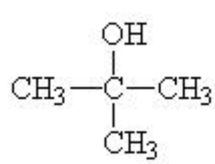
The chain has a length of three carbon atoms, thus the first part of the name will be: *propan-*.

The functional group is an alcohol, thus the suffix will be: *-ol*.

The alcohol group is on the second carbon atom in the chain, thus the complete name will be: *2-propanol*.

EXAMPLE 16.2

Provide the name for the following alcohol, shown as a condensed formula:



Answer
The chain has a length of three carbon atoms, thus the first part of the name will be: *propan-*.
The functional group is an alcohol, thus the suffix will be: *-ol*.
The alcohol group is on the second carbon atom in the chain, thus adding to the name as: *2-propanol*.
There is a methyl substituent, also on the second carbon of the chain. Thus the final name will be: *2-methyl-2-propanol*.

METHANOL

Methanol is the alcohol with the shortest carbon chain length. Commonly called methyl alcohol, this alcohol is highly poisonous by ingestion and also by skin absorption. This second point is particularly important as methanol is a major component of most windshield-washer anti-freeze solutions and it is easy to accidentally spill some on one's skin when filling a vehicle's reservoir. Methanol is also used as gas-line anti-freeze. The molecule is displayed below as space-filling model, ball-and-stick model, and as a structural formula (Figure 16.4).

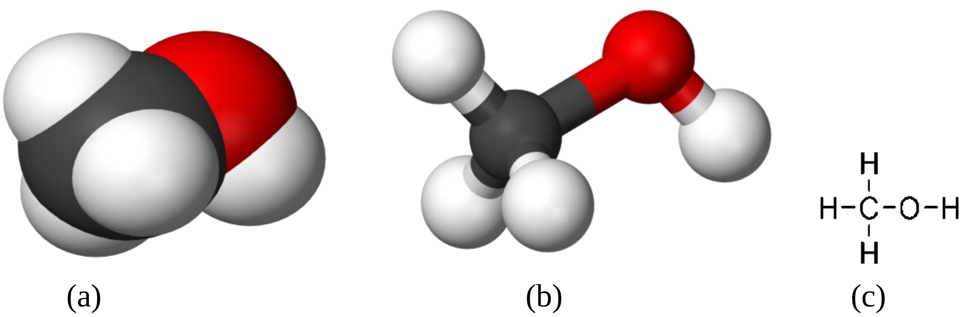
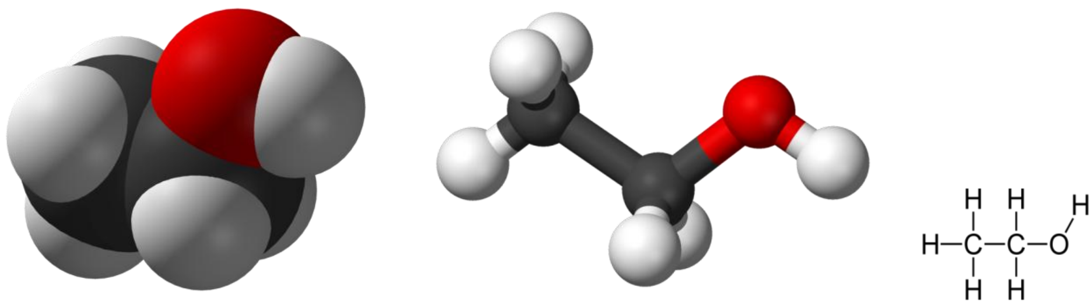


Figure 16.4 The CH_3OH, methanol, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

ETHANOL

Addition of a methyl group results in a change of properties from a highly toxic compound to one that is toxic only in large quantities. Commonly called ethyl alcohol, in addition to human consumption, ethanol is also used as a vehicle fuel. A vehicle labelled "E85" indicates that it can utilize a gasoline-ethanol mixture containing up to 85% ethanol. The molecule is displayed below as space-filling model, ball-and-stick model, and as a structural formula (Figure 16.5).

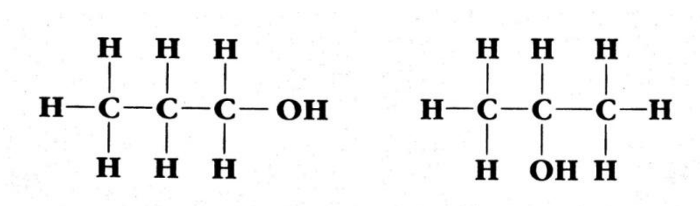


(a) (b) (c)

Figure 16.5 The CH_3CH_2OH, ethanol, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

STRUCTURAL ISOMERS

In Chapter 15, Section 15.5 Alkanes, the topic of structural isomers was introduced. In the context of hydrocarbons, the carbon atoms can be arranged in different ways, with a straight-chain, or as several or many branched-chain possibilities. As functional groups can be placed in different locations, there is additional ways of constructing structural isomers. For example, in Figure 16.6, both alcohols have the propane structure. However, the structural formula displayed in Figure 16.6a has the alcohol functional group on the first carbon atom in the chain, while the structural formula displayed in Figure 16.6b has the functional group on the second carbon atom in the chain. These molecules, 1-propanol and 2-propanol, respectively are structural isomers.

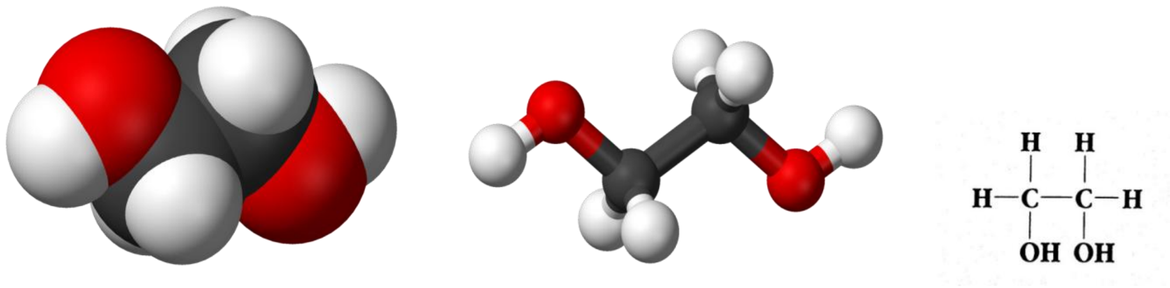


(a) (b)

Figure 16.6 Two structural isomers of the alcohol C_3H_8OH

1,2-ETHANEDIOL

It is possible to have more than one alcohol functional group in a molecule. 1,2-ethanediol, commonly called ethylene glycol, is an example of a molecule containing two alcohol groups. This highly-toxic compound is used in the coolant radiators of internal combustion engines as an antifreeze. The molecule is displayed below as space-filling model, ball-and-stick model, and as a structural formula (Figure 16.7).

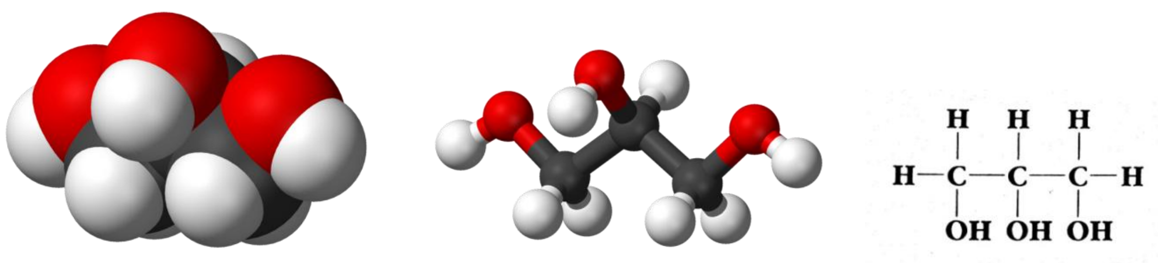


(a) (b) (c)

Figure 16.7 The CH_2OHCH_2OH, 1,2-ethanediol, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

1,2,3-PROPANETRIOL

Whereas 1,2-ethanediol is toxic, the simplest three-alcohol molecule is non-toxic. In fact, 1,2,3-propanetriol, commonly called glycerol or propylene glycol, is used in cosmetics and as a sweetener in the food industry. The molecule is displayed below as space-filling model, ball-and-stick model, and as a structural formula (Figure 16.8).

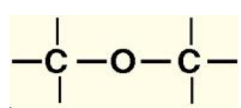


(a) (b) (c)

Figure 16.8 The $CH_2OHCHOHCH_2OH$, 1,2,3-propanetriol, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

16.3 Ethers

The second functional group to be studied is that of ***ethers***. An ether has an oxygen atom covalently-bonded on each side to a hydrocarbon chain:



NAMING ETHERS

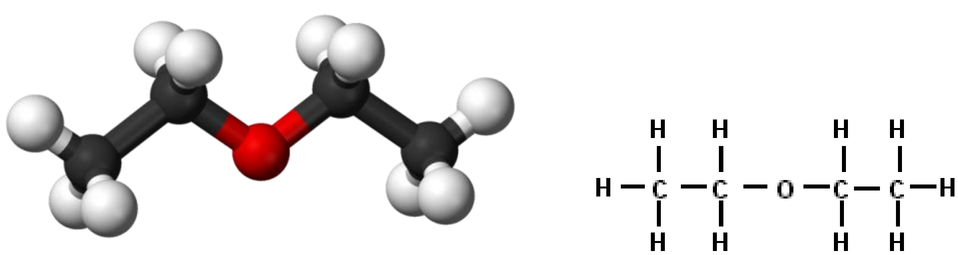
Unfortunately, there are two systems for naming ethers, and both are still widely used. In the IUPAC system, the longer chain is the stem name, the shorter chain is treated as a substituent with *–oxy–*bridging the two parts. In the Traditional system, the two carbon chains are named as substituents followed by the word *ether*. Table 16.2 shows a comparison of the names for two ethers.

Table 16.2 A comparison of the names of two ethers in the IUPAC and traditional naming systems

Condensed formula	$CH_3{-}O{-}CH_3$	$CH_3{-}O{-}CH_2CH_3$
IUPAC name	methoxymethane	methoxyethane
Traditional name	dimethyl ether	ethylmethyl ether

ETHOXYETHANE

The only widely-encountered ether is ethoxyethane, commonly called diethyl ether. Ethoxyethane was traditionally used as an early anæsthetic as it has a very high vapour pressure at room temperature. Inhaling the vapour leads to a rapid loss of consciousness. The molecule is shown in Figure 16.9 as a ball-and-stick model and as a structural formula.



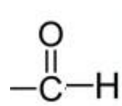
(a) (b)

Figure 16.9 The $CH_3CH_2OCH_2CH_3$, ethoxyethane, molecule represented as (a) a ball-and-stick model, and (b) a structural formula.

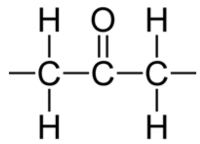
16.4 Aldehydes and Ketones

For both alcohols and ethers, the oxygen atom is singly-bonded: in alcohols, to one carbon atom and one hydrogen atom; and in ethers, to two carbon atoms. It is also possible for the oxygen atom to be doubly-bonded to a carbon atom. The C=O fragment is called a ***carbonyl*** unit. An added complication is that the property of the resulting molecule depends upon whether that carbon atom is bonded to two carbon atoms, or to one carbon atom and one hydrogen atom.

If the carbonyl fragment is bonded to a hydrogen atom, the functional group is called an ***aldehyde***:



If the carbonyl fragment is bonded to two carbon atoms, the functional group is called a ***ketone***:

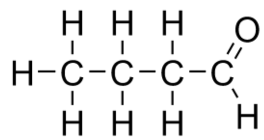


NAMING ALDEHYDES AND KETONES

Aldehydes and ketones have different suffixes. The aldehyde functional group is indicated by the suffix −*al*. As the carbon atom already has three covalent bonds utilized (one to the hydrogen atom and two to the oxygen atom), then the aldehyde function always has to be on the end of the carbon chain of a molecule.

EXAMPLE 16.3

Provide the name corresponding to the structural formula shown below:



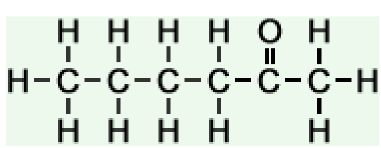
Answer

There is a four carbon chain with all single bonds, hence the first part of the name is *butan–*
The functional group is that of an aldehyde, hence the suffix is *–al*.
The complete name is *butanal*.

The ketone functional group is indicated by the suffix *–one* (pronounced as "own"). As a ketone has to have a carbon atom on each side of the carbonyl fragment, the simplest ketone has to have a three-carbon chain.

EXAMPLE 16.4

Provide the name corresponding to the structural formula shown below:



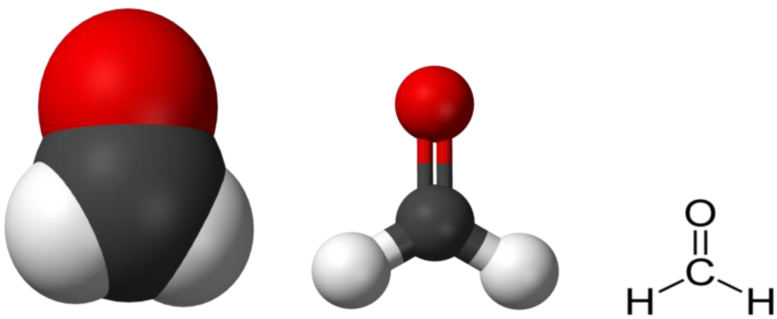
Answer

There is a six carbon chain with all single bonds, hence the first part of the name is *hexan–*.
The functional group is that of a ketone, hence the suffix is *–one*.

Counting from the lowest (left) end, the name must be preceded by the carbonyl location, namely "2."
The complete name is <u>*2-hexanone*</u>.

METHANAL

The simplest aldehyde is methanal, commonly called formaldehyde. Methanal was formerly used as a preservative of biological specimens, but with concerns about the toxicity of methanal, safer compounds are now used. The molecule is displayed below as space-filling model, ball-and-stick model, and as a structural formula (Figure 16.10).

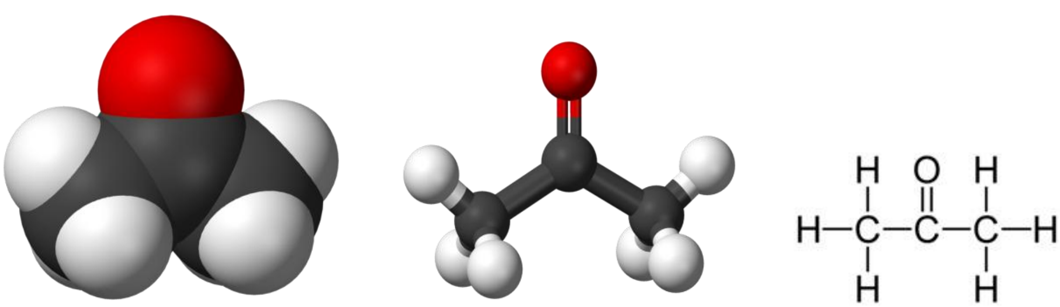


(a) (b) (c)

Figure 16.10 The CH_2O, methanal, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

PROPANONE

Usually given its common name of acetone, propanone is the simplest ketone. The compound is sometimes used as a solvent, such as a nail polish remover. The molecule is displayed below as space-filling model, ball-and-stick model, and as a structural formula (Figure 16.11).

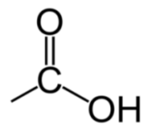


(a) (b) (c)

Figure 16.12 The CH_3COCH_3, propanone, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

16.5 Carboxylic Acids

The ***carboxylic acid*** functional group combines an alcohol fragment with a carbonyl fragment.



Yet the resulting functional group does not have a mixture of properties of these two groups. Instead, the combination has very different physical and chemical properties, those of an acid. This organic acid is different to the inorganic acids, such as hydrochloric acid, discussed in previous chapters.

When hydrogen chloride dissolves in water, essentially all of the molecules break apart to give hydrogen ions and chloride ions. It is the hydrogen ions which make the solution acidic. As essentially all the hydrogen is present as the hydrogen ions, hydrochloric acid is called a ***strong acid***.

$$HCl(g) \xrightarrow{\text{dissolve in water}} HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$$

However, when organic acids are dissolved in water, most of the molecules stay intact and only a small proportion break down into ions. This is an equilibrium, as was mentioned in Chapter 9, Section 9.3 Writing a Chemical Equation. As only a small portion of the hydrogen is present as the hydrogen ions, such acids are called a ***weak acid***. For example, CH_3COOH, commonly called acetic acid, dissolves in water as follows:

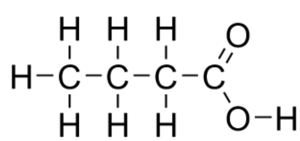
$$CH_3COOH(l) \xrightarrow{\text{dissolve in water}} CH_3COOH(aq) \rightleftharpoons H^{+}(aq) + CH_3COO^{-}(aq)$$

NAMING CARBOXYLIC ACIDS

The carboxylic acid functional group is indicated by the suffix ***−oic acid***. In working out the name, the carbon atom of the carboxylic acid is included in the chain name.

EXAMPLE 16.5

Provide the name corresponding to the structural formula shown below:



Answer

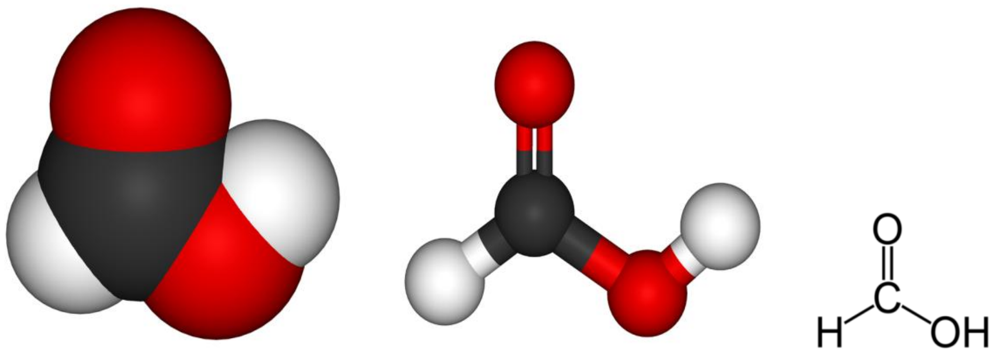
There is a four carbon chain with all single bonds, hence the first part of the name is *butan–*

The functional group is that of a carboxylic acid, hence the suffix is *–oic acid*.

The complete name is *butanoic acid*.

METHANOIC ACID

Commonly called formic acid, methanoic acid is the simplest carboxylic acid. It is methanoic acid that ants inject when they sting a prey. The molecule is displayed below as space-filling model, ball-and-stick model, and as a structural formula (Figure 16.13).

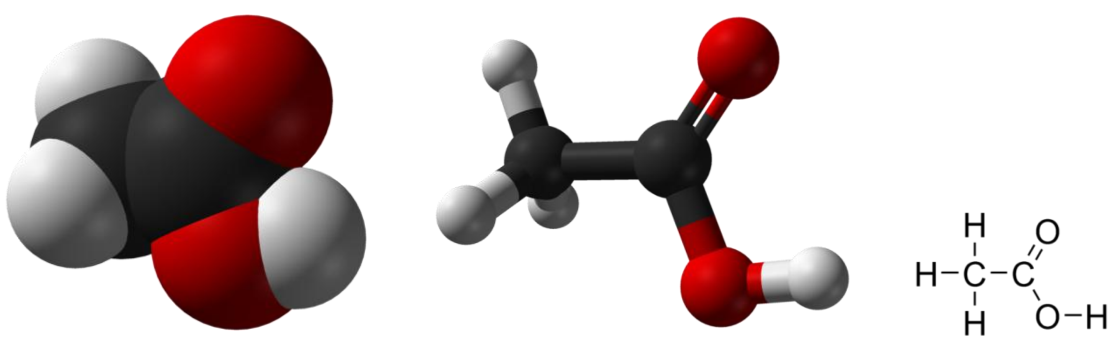


(a) (b) (c)

Figure 16.13 The HCOOH, methanoic acid, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

ETHANOIC ACID

Commonly called acetic acid, a dilute solution of ethanoic acid is known as vinegar. It is because ethanoic acid is a weak acid that it can be placed on foods to acidify them. That is, the number of hydrogen ions is far lower than would be the case with the same concentration of, for example, hydrochloric acid. The molecule is displayed below as a space-filling model, ball-and-stick model, and as a structural formula (Figure 16.14).

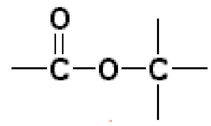


(a) (b) (c)

Figure 16.14 The CH_3COOH, ethanoic acid, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

16.6 Esters

The ***ester*** functional group combines a carbonyl fragment with an ether linkage.



NAMING ESTERS

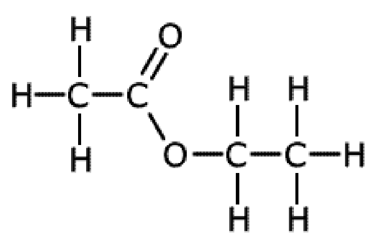
Esters are named in two parts. The carbon chain containing the carbonyl group is named as if it were derived from the related carboxylic acid, but with the suffix being *–oate*. The hydrocarbon chain bonded to the ether-like oxygen atom is treated as a substituent. Below are the structural formulas of two esters which are structural isomers (Figure 16.15). The two names are given for comparison.

(a) (b)

Figure 16.15 The name of each of these structural isomers is (a) ethyl methanoate and (b) methyl ethanoate.

EXAMPLE 16.6

Provide the name corresponding to the structural formula shown below:



Answer

The functional group is that of an ester.

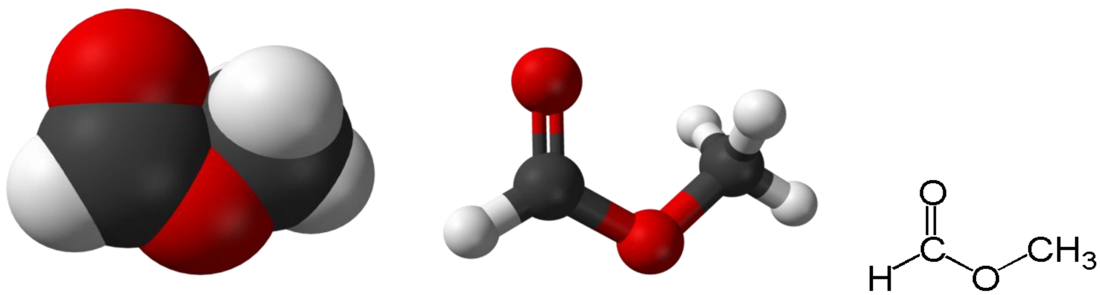
There is a two-carbon chain containing the carbonyl fragment. This second half of the name will be *ethanoate*.

It is a two-carbon chain attached to the ether linkage, hence the first half of the name is *ethyl*.

The complete name is <u>*ethyl ethanoate*</u>.

METHYL METHANOATE

The simplest ester is methyl methanoate, traditionally known as methyl formate. The molecule is displayed below as a space-filling model, ball-and-stick model, and as a structural formula (Figure 16.16).



(a) (b) (c)

Figure 16.16 The $HCOOCH_3$, methyl methanoate, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

ESTERS IN NATURAL PRODUCTS

The odours and flavours which we associate with fruit are nearly all mixtures of esters. The following table lists a few of the simple esters and the fruit to which they contribute odours and flavours.

Table 16.3 Some of the esters which contribute to the odours and flavours of fruit

Ester	**Fruit**
Butyl butanoate	pineapple
Ethyl nonanoate	grape
Ethyl pentanoate	apple
Pentyl pentanoate	apple
Propyl pentanoate	pear

16.7 Amines

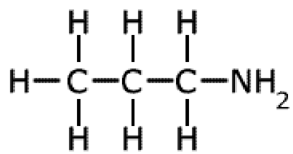
Up to this point, organic compounds containing oxygen have been covered. Other chemical elements are also involved in organic chemistry, the second most common being nitrogen. The nitrogen atom can bond to one, two, and even three hydrocarbon groups. These compounds NH_2 are called ***amines***. Amines have pungent and obnoxious odours. The smell of rotting fish is largely a result of amines produced during the bacterial decomposition.

NAMING AMINES

Unfortunately, there are several different ways of naming amines. This diversity is, in part because the nitrogen atom can bond to more than one hydrocarbon group. However, in this course, it will be more useful to focus on nitrogen atoms which are bonded to two hydrogen atoms and a single hydrocarbon chain. For these molecules, the prefix ***amino−*** is used to indicate the presence of an NH_2− group.

EXAMPLE 16.7

Provide the name corresponding to the structural formula shown below:



Answer

The functional group is that of an amine.

There is a three carbon chain (with all single carbon-carbon bonds) giving the second part of the name as *propane*.

There is an amine functional group giving the first part of the name as *amino-*.

The amino group is on the first carbon atom from the right in the chain.

Thus the complete name is *1-aminopropane*.

AMINOMETHANE

Also called methyalamine, aminomethane is the simplest of the amines. The molecule is displayed below as a space-filling model, ball-and-stick model, and as a structural formula (Figure 16.17).

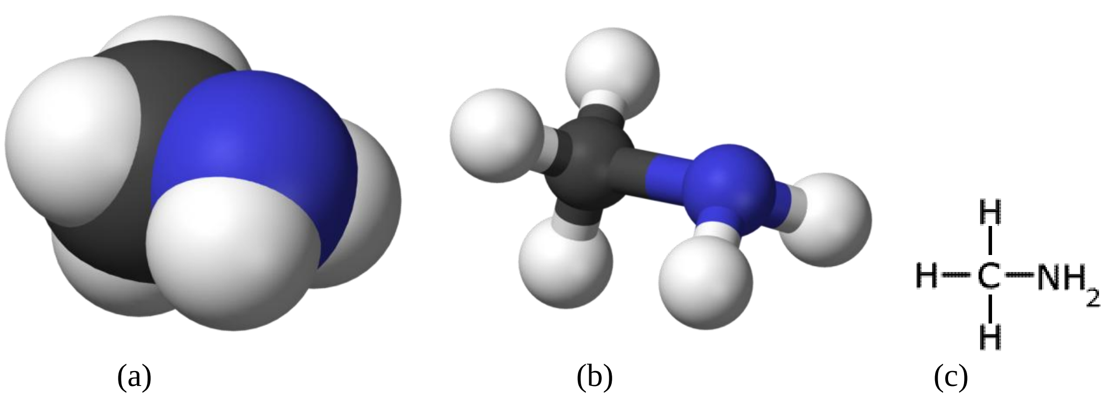
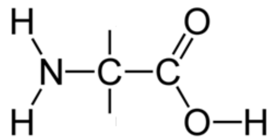


Figure 16.17 The CH_3NH_2, aminomethane, molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

16.8 Amino acids

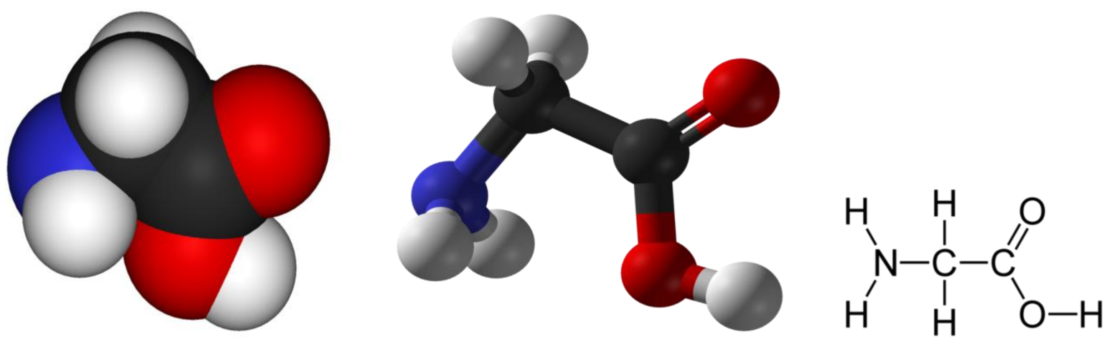
In Section 16.5, carboxylic acids were discussed and in Section 16.7, amines. Among the most important molecules in living organisms are ***amino acids***. Amino acids contain both carboxylic acid and amine functional groups.



The identity of the amino acid depends upon the groups attached to the carbon atom between the two functional groups. Each of the amino acids is known by its common name, thus the remainder of this Section will introduce a few of the simpler amino acids.

GLYCINE

The simplest amino acid is glycine. This has two hydrogen atoms attached to the central carbon atom. The molecule is displayed below as a space-filling model, ball-and-stick model, and as a structural formula (Figure 16.18).

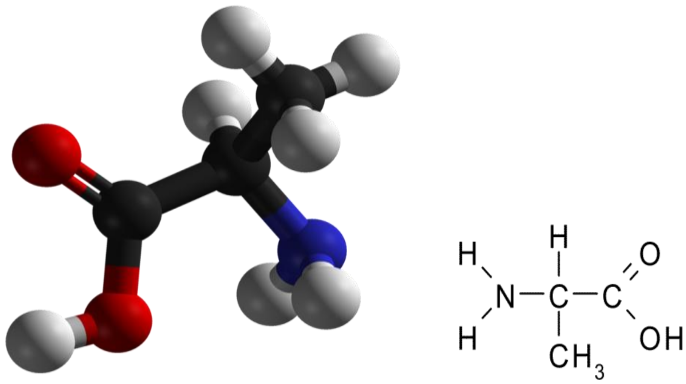


(a) (b) (c)

Figure 16.18 The glycine molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

ALANINE

The next simplest amino acid is alanine, in which a methyl group is attached to the central carbon atom. The molecule is displayed below as a ball-and-stick model and as a structural formula (Figure 16.19).

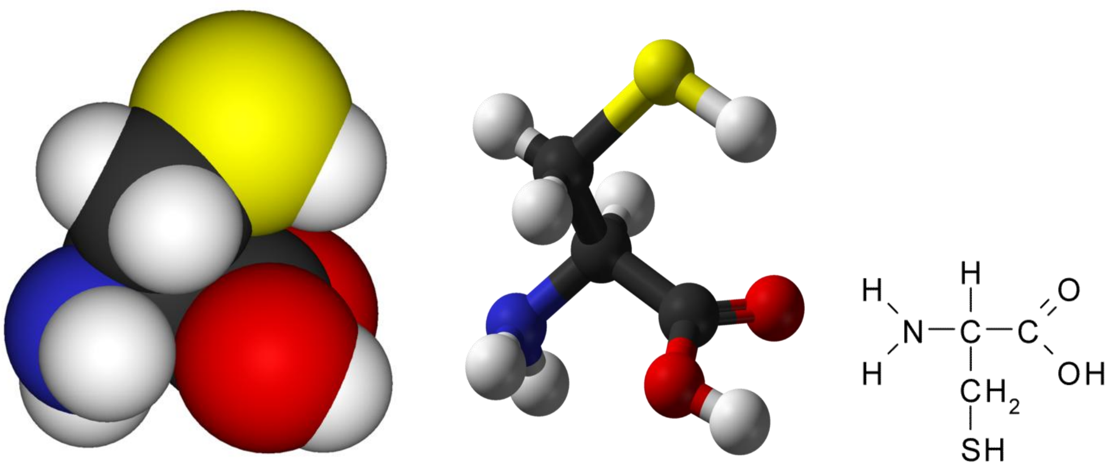


(a) (b)

Figure 16.19 The alanine molecule represented as (a) a ball-and-stick model, and (b) a structural formula.

Cysteine

Amino acids can contain other elements. A sulfur-containing amino acid of particular importance is cysteine. The molecule is displayed below as a space-filling model, ball-and-stick model, and as a structural formula (Figure 16.20).



(a) (b) (c)

Figure 16.20 The cysteine molecule represented as (a) a space-filling model, (b) a ball-and-stick model, and (c) a structural formula.

Optical (Chiral) Isomers

In Chapter 15, Section 15.5 Alkanes, the concept of structural isomers was introduced. Then in Chapter 15, Section 15.6 Alkenes, geometric (cis-trans) isomers were discussed. Here, a third type of isomerism, ***optical, or chiral, isomerism***. The topic is introduced in this section as amino acids are the most important molecules to exhibit this type of isomerism.

If four different groups are attached to a central carbon atom, then there are two different ways in which these substituents can be arranged. These two different arrangements are shown in Figure 16.21 where each coloured sphere represents a different attached group. The molecule on the left, when reflected in a mirror, becomes the mirror image, which cannot be superimposed over the real molecule.

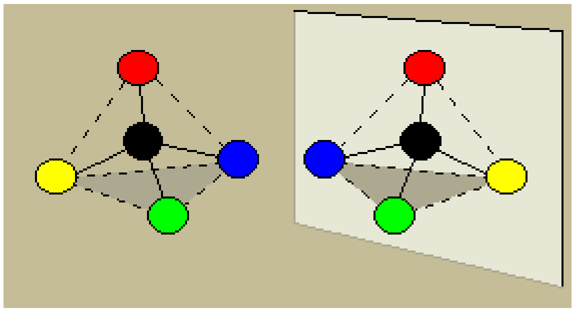


Figure 16.21 A molecule having four different groups (indicated as different coloured spheres) attached to a central carbon atom and its non-superimposable mirror image.

As mentioned above, amino acids are chiral compounds (see Figure 16.22). When an amino acid is synthesized in a chemical laboratory, an equal proportion of the two forms is obtained. However, amino acids synthesized by living organisms are always of one specific chiral form.

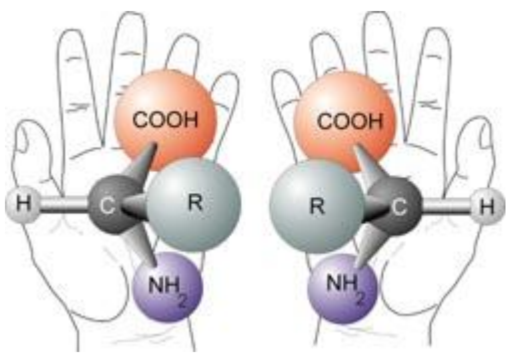


Figure 16.22 The two chiral forms of an amino acid

16.9 Halogen-containing organic compounds

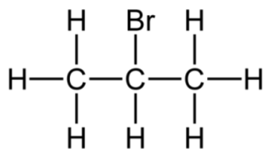
It is possible for any hydrogen atom in an organic compound to be replaced by a halogen atom – fluorine, chlorine, bromine, or iodine. Compounds can contain several of one halogen atom, or a mixture of halogen atoms.

NAMING HALOGEN-CONTAINING COMPOUNDS

The carbon chain of the compound is named as usual. The halogen functional group is indicated by the prefix of the halogen: *fluoro−*, *chloro−*, *bromo−*, or *iodo−*.

EXAMPLE 16.8

Provide the name corresponding to the structural formula shown below:



Answer

There is a three carbon chain (with all single carbon-carbon bonds) giving the second part of the name as *propane*.

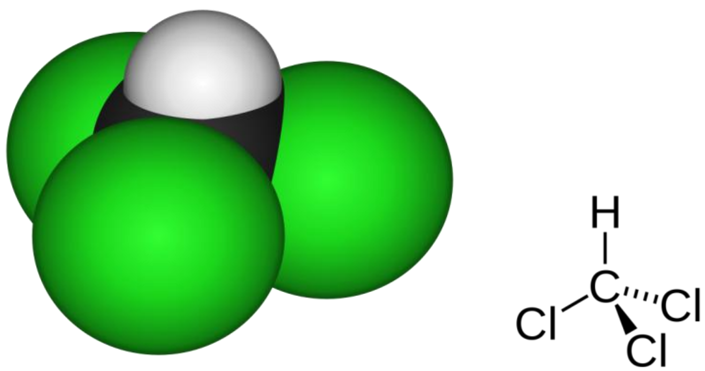
There is a bromine functional group, giving the first part of the name as *bromo*-.

The bromine atom is on the second carbon atom in the chain.

Thus the complete name is *2-bromopropane*.

TRICHLOROMETHANE

Commonly known as chloroform, trichloromethane vapour was formerly used as an anæsthetic during medical operations. The molecule is displayed below as a space-filling model and as a structural formula (Figure 16.23).

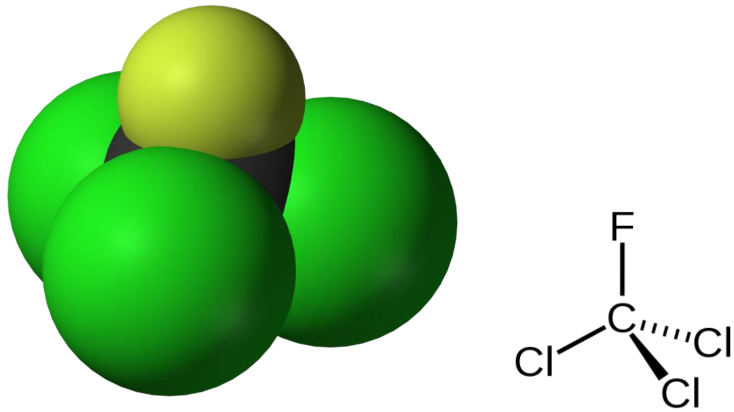


(a) (b)

Figure 16.23 The trichloromethane, $CHCl_3$, molecule represented as (a) a space-filling model, (b) a structural formula.

TRICHLOROFLUOROMETHANE

Trichlorofluoromethane is one of the chlorofluorocarbons (CFCs) which was used in air conditioning systems. Unfortunately, it is also a potent ‘greenhouse gas.’ The molecule is displayed below as a space-filling model and as a structural formula (Figure 16.24).

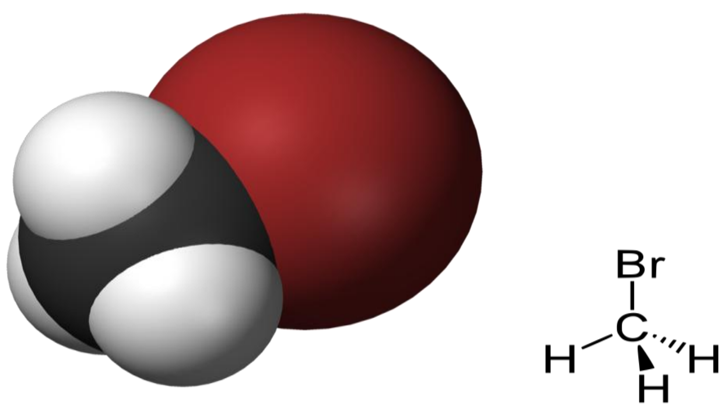


(a) (b)

Figure 16.24 The trichlorofluoromethane, $CFCl_3$, molecule represented as (a) a space-filling model, (b) a structural formula.

BROMOMETHANE

Bromomethane is produced by marine organisms and it is also synthesized and used as a pesticide in agriculture. Unfortunately, this compound is not only toxic in high concentrations, but it, too, is a greenhouse gas. The molecule is displayed below as a space-filling model and as a structural formula (Figure 16.25).



(a) (b)

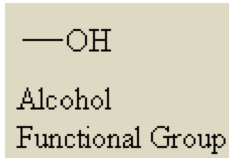
Figure 16.25 The bromomethane, CH_3Br, molecule represented as (a) a space-filling model, (b) a structural formula.

16.10 An Organic Review

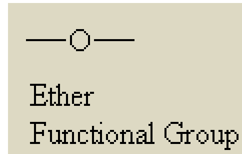
The diversity of organic chemistry is a result of two factors: the variety of functional groups and the types of isomerism. This section will be a review of these two factors.

OXYGEN-CONTAINING FUNCTIONAL GROUPS

In addition to the ability to form carbon-carbon double and triple bonds, the incorporation of oxygen atoms in organic molecules results in six different possible functional groups. Two of the functional groups contain singly-bonded oxygen atoms:

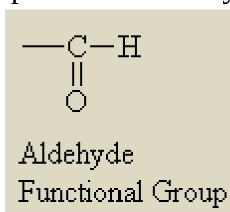


Alcohol Functional Group

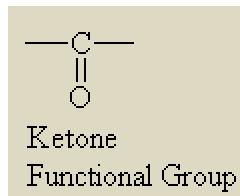


Ether Functional Group

Two of the functional groups contain doubly-bonded oxygen atoms:

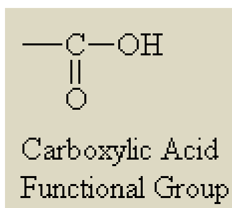


Aldehyde Functional Group

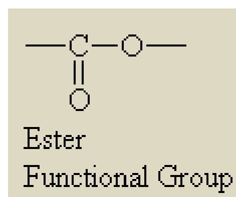


Ketone Functional Group

And the final two function groups contain one doubly-bonded oxygen atom and one singly-bonded oxygen atom:



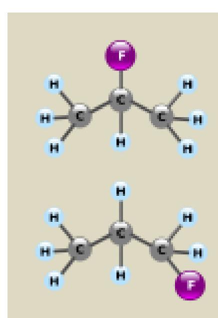
Carboxylic Acid Functional Group



Ester Functional Group

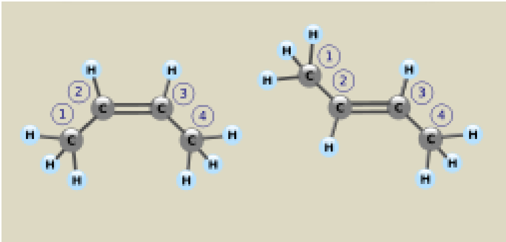
TYPES OF ISOMERISM

The most all-encompassing type of isomerism is structural isomerism. For any given molecular formula, there are often several or many ways to arrange the carbon chain and substituent side chains together with different possible locations for any functional groups.



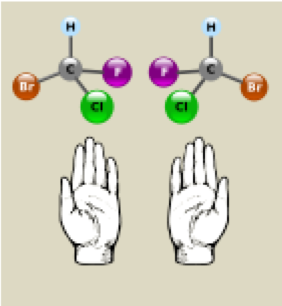
Structural isomers

For molecules which contain a carbon-carbon double bond, the rigidity of the bond results in the possibility of cis-trans (geometric) isomers.



cis-trans (geometric) isomers

If a carbon atom in a molecule has four different groups attached to that carbon atom, then there will be a pair of mirror-image molecules possible. Such compounds are said to be chiral compounds.



Optical (chiral) isomers

16.11 The End

In this on-line book, each of the fundamental concepts in chemistry has been covered. By mastering this material, you should now feel confident to proceed on with your studies, wherever they might take you.