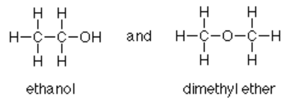
1.15: Chirality, Three Dimensional Structure

Isomerism

Let's begin by reminding ourselves of some of the ideas involved in the topic of isomerism. Structural understanding of organic chemistry begins with the statements that carbon makes four bonds and each carbon can bond to another carbon (the Kekule-Couper-Butlerov theory of organic structure). In even very small molecules (try C_2H_6O) this means that there is more than one way to connect the atoms. Each of these connection patterns represents a different compound. Here are two for C_2H_6O:



There are two things to notice about this. First, the structural difference between the two molecules can be described in terms of "what's connected to what." For example, the oxygen in ethanol is connected to a CH_3CH_2 group and to a hydrogen while the oxygen in dimethyl ether is connected to two methyl groups. Connectivity is the key difference here. Second, and this is new, we can describe this connectivity quite nicely using just the usual two dimensions we can conveniently represent on paper, a chalkboard, or a computer monitor.

There are many types of organic compounds for which this description is inadequate. This is particularly true for compounds involved in biological processes such as sugars and amino acids (carbohydrates and proteins). For these compounds and many others we will need to use three dimensions in order to have an adequate description of the structure.

Chiral Objects

Let's look at some familiar objects so as to get a sense of when we will need to think about three dimensions. Consider the way in which a sock differs from a glove. It doesn't matter which foot you put a sock on, it will fit just as well. That certainly can't be said about a glove. A glove fits one hand much better than the other.

One quick way to differentiate between sock-like objects and glove-like objects is to ask whether an object is identical with its mirror image or not. Consider a pair of socks. One of the socks is a mirror image of the other (Think of holding one sock up to a mirror. What you see is identical to the other sock, and to the original sock.) Now consider a pair of gloves. The right glove is the mirror image of the left glove, but they are not identical. They can't be superimposed -- merged so they completely match. Objects like gloves which cannot be superimposed upon their mirror images are called *chiral*, from the Greek word for hand. Objects like socks which can be superimposed upon their mirror images are called *achiral*.

Now notice that we need three dimensions to describe the difference between a left glove and a right glove. If you hold up two gloves so that you are looking at the edge nearest the thumb, you notice that the difference lies in which way the thumb points. The rest of the glove can be pretty well described by a plane (two dimensions), just as a sock can be described by a plane, but the describing which way the thumb points requires a third dimension, out of the plane. Make up a list of your own of familiar objects and decide whether they are *chiral* or *achiral* by testing each for superimposability on its mirror image.

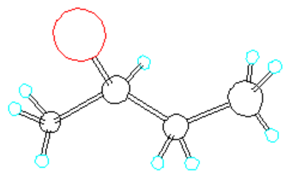
Stereogenic Centers

Now, how does this apply to molecules? You can satisfy yourself by playing with models that the following statement is true: **A molecule which contains one carbon which is directly bonded to four different groups or atoms is not superimposable on its mirror image.** Such a molecule is *chiral* just the same way that a glove is *chiral*and a carbon which is bonded to four different groups is called a *stereogenic center*. The lab for next week has a good example of a carbon bonded to four different atoms. You can move one of the two molecules to verify the mirror image relationship and you can check for superimposability.

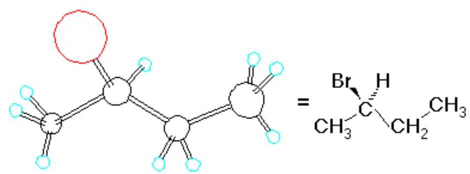
So, if we wish to find out whether a candidate molecule is chiral or achiral, we check for stereogenic centers -- carbons which are bonded to four different groups or atoms. One question which always comes up at this point is "How different do the groups or atoms have to be?" If the groups have the same composition they are different if they are isomeric -- if they are connected differently. For example, propyl and iso-propyl are different.

Structural Representations

Once we've convinced ourselves that a stereogenic carbon atom makes a compound chiral, we need to think about how we will represent the three dimensional structures of these compounds when we are restricted to two dimensions. For example, the following sketch represents a 2-bromobutane. It is not superimposable upon its mirror image (see the three dimensional representations earlier).

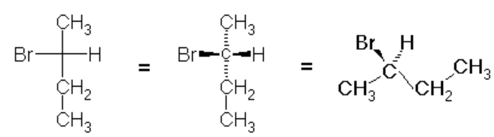


How do we represent this structure? There are two conventional representations. The first is called a "perspective view." In this view, bonds represented by solid wedges are taken to point toward the viewer (in front of the plane of the paper), bonds represented by dashed line wedges are taken to point away from the viewer (behind the plane of the paper, and bonds represented by ordinary straight lines are taken to lie in the plane of the paper. In a perspective view the 2-bromobutane above would be represented as:



The Br is in front of the plane, the H is behind it, and the methyl (to the left) and ethyl (to the right) groups are taken as being in the plane (at least the carbons of those groups).

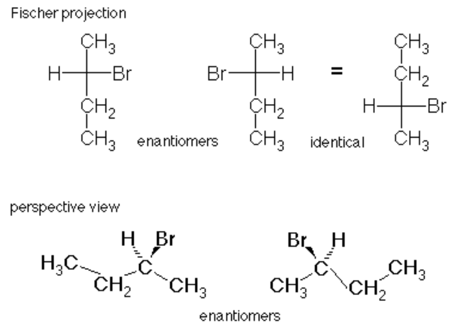
The other representation is known as the Fischer projection. This is a convention in which the stereogenic carbon atom is represented by the junction of two crossed lines. The horizontal line is taken to represent bonds which come from the carbon to an atom toward the viewer (in front of the plane) and the vertical lines are taken to represent a bond which goes from the carbon to an atom away from the viewer (behind the plane). This can be converted to a perspective view by drawing in the appropriate solid and dashed wedges:



The last "equals" sign says that the Fischer projection and the perspective view are representations of the same molecule. You may wish to verify this by imagining yourself as looking down from above the perspective view with the methyl group toward the top of your head. Can you see the wedge interpretation of the Fischer projection?

Because of the special meaning of horizontal and vertical lines in the Fischer projection, they can only maintain their meaning if we restrict manipulations to 180º rotations in the plane of the paper. You can demonstrate this for yourself by converting a Fischer projection to a perspective view, then rotating the Fischer projection by 90º and converting the new Fischer projection to another perspective view. The two perspective views are mirror images.

The term which describes the relationship between an object (molecule) and its non-superimposable mirror image is *enantiomeric*. An object and its non-superimposable mirror image are *entantiomers* of each other. If the object is superimposable on its mirror image, then there is really only one object and the term used is *identical*. These relationships are illustrated below:


Fischer projection
CH3
H
Br
CH2
CH3
enantiomers
CH3
Br
H
CH2
CH3
=
identical
CH3
CH2
H
Br
CH3
perspective view
H
Br
H3C
C
CH2
CH3
Br
H
C
CH3
CH2
CH3
enantiomers