

Chapter 7 – Stereochemistry (more about stereoisomerism)

Introduction

This chapter deals further with molecules as three-dimensional objects. The type of three-dimensionality involved also applies to objects from your daily life, so we will start with what is familiar.

An exaggerated assertion: *All objects in the universe can be regarded as one of two kinds, based on their idealized, external shapes.* Examples are given below.

This Kind



ping-pong ball



plain water glass



new piece of chalk



CO₂ molecule



baseball bat



fish

That Kind



shoe (or foot)



glove (or hand)



screw or spring (helix)



ear



golf club



a pebble

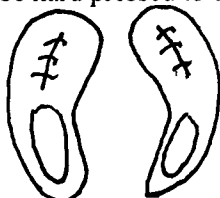
Note that the objects of That Kind include some that you recognize as "handed". There is a left variety and a right variety. It isn't obvious, but a pebble as well as any other irregular object is also handed in a similar way, as can be shown. In this case, a left and right pair doesn't exist in the real world.

All of the objects included in the This Kind list are "not handed". A left and right variety can't exist. A baseball bat or a ping-pong ball would serve left- or right-handed players equally well.

Objects that are handed are referred to as *chiral*. Objects that are not handed are *achiral*.

How do the two objects in a handed pair differ?

We know from experience that there is something different about a left shoe and a right shoe, for example. But we might be hard pressed to define exactly how they differ. Consider the two shoes in a pair (idealized).



1. They have the same mass.
2. They have the same dimensions (length, width, etc.).
3. They have the same volume.
4. They have the same component parts.

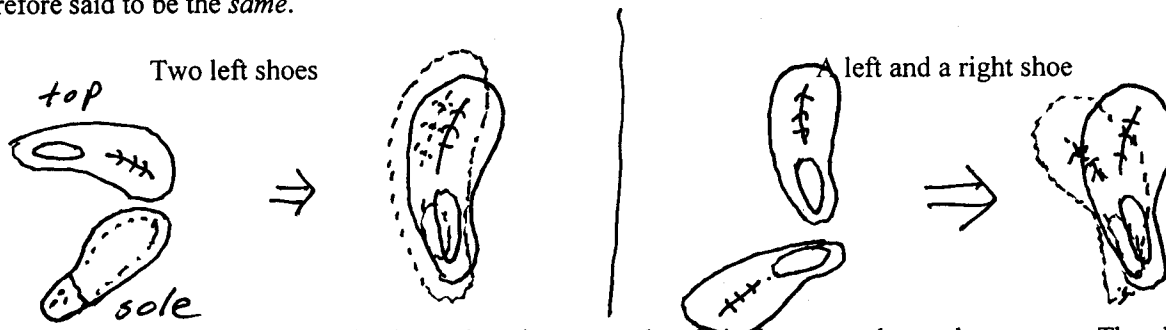
How is it that they differ? *They differ in the spatial arrangement of their component parts.* They differ in their *topography*. They are topographically *not the same*. We also say that they differ in their *configurations*. When we refer below to the sameness of two objects, it is topographical (configurational) sameness that is meant.

How to test for the topographical (configurational) sameness of two objects?

We will have occasion to decide whether or not two objects or shapes are the same. The general rule is as follows:

1. If two objects have shapes that are *superimposable*, they are the same (topographically).
2. If two objects have shapes that are *non-superimposable*, they are not the same (topographically).

Consider two left shoes (same size and style). We can pick them up and move them around in such a way that their shapes could be merged (a mental process, not permitted in reality). They have superimposable shapes and are therefore said to be the *same*.



Now consider a left shoe and a right shoe. There is no way that their shapes can be made to merge. They have non-superimposable shapes and are therefore *not the same*.

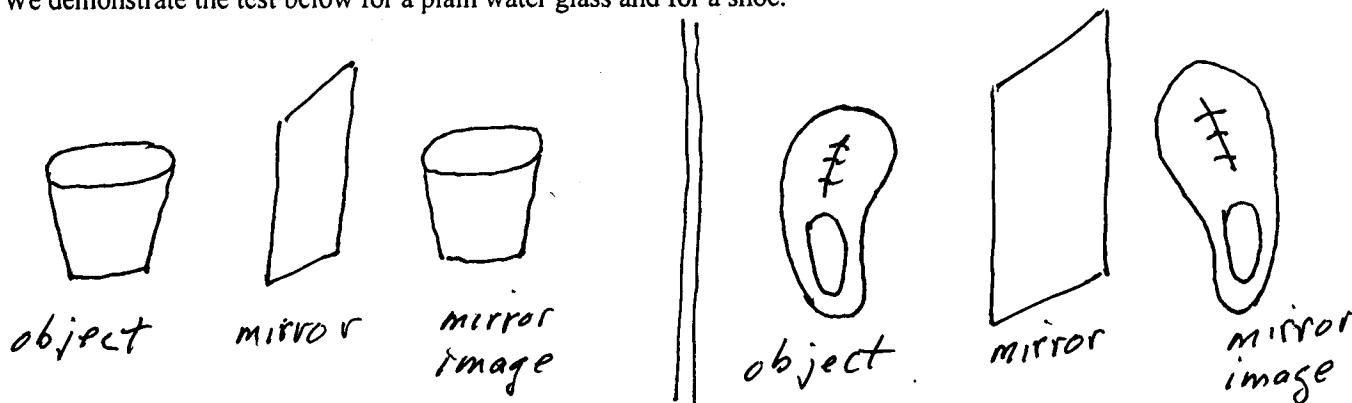
How to test whether or not an object is chiral (handed)?

Now that we have a test for the sameness of two objects, we are prepared to test for the chirality of any object. Is it chiral or isn't it?

The general procedure is to imagine or construct the mirror image of the object. Then:

1. If an object and its mirror image have *superimposable* shapes, the object is *achiral*.
2. If an object and its mirror image have *non-superimposable* shapes, the object is *chiral*. There will be a "left" and "right" variety of the object. If the original object is of the left variety, the shape of the mirror image represents the right variety.

We demonstrate the test below for a plain water glass and for a shoe.

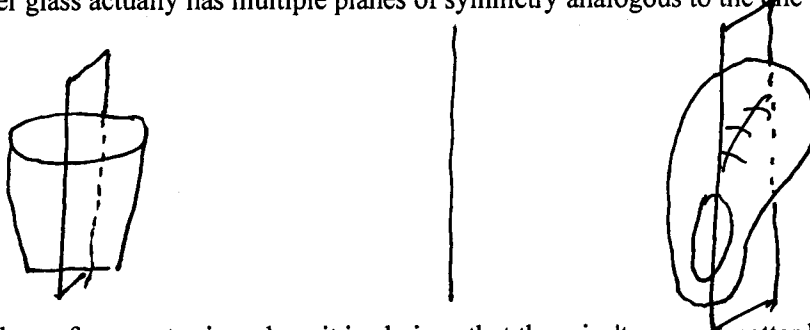


It's not hard to see that the water glass and its mirror image have superimposable shapes. Therefore, the water glass is achiral. The mirror image of the original shoe, which happens to be a left shoe, has the shape of a right shoe. We have already shown above that these shapes are non-superimposable. Therefore, the original shoe is a chiral object.

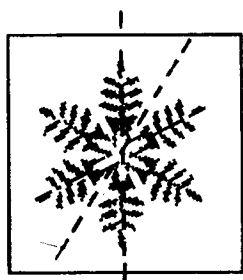
Another test for chirality.

The test described above works every time, but it is sometimes hard to tell whether or not the object and its mirror image are superimposable. A different test, which is usually easier to perform, involves looking for what is called a *plane of symmetry* or a *center of symmetry*. We will start with a plane of symmetry.

A plane of symmetry is an imaginary plane ("slicer") that can slice anywhere through an object in such a way that the two halves of the object are mirror images of each other. (It is sometimes called a *mirror plane*.) The diagram below shows that the water glass does have a plane of symmetry. Each half is a mirror reflection of the other. The presence of a plane of symmetry means that the object is achiral. Sometimes there is more than one plane of symmetry in an object. The water glass actually has multiple planes of symmetry analogous to the one shown.



Looking for a plane of symmetry in a shoe, it is obvious that there isn't one, no matter how you slice. Therefore, the shoe is a chiral object.



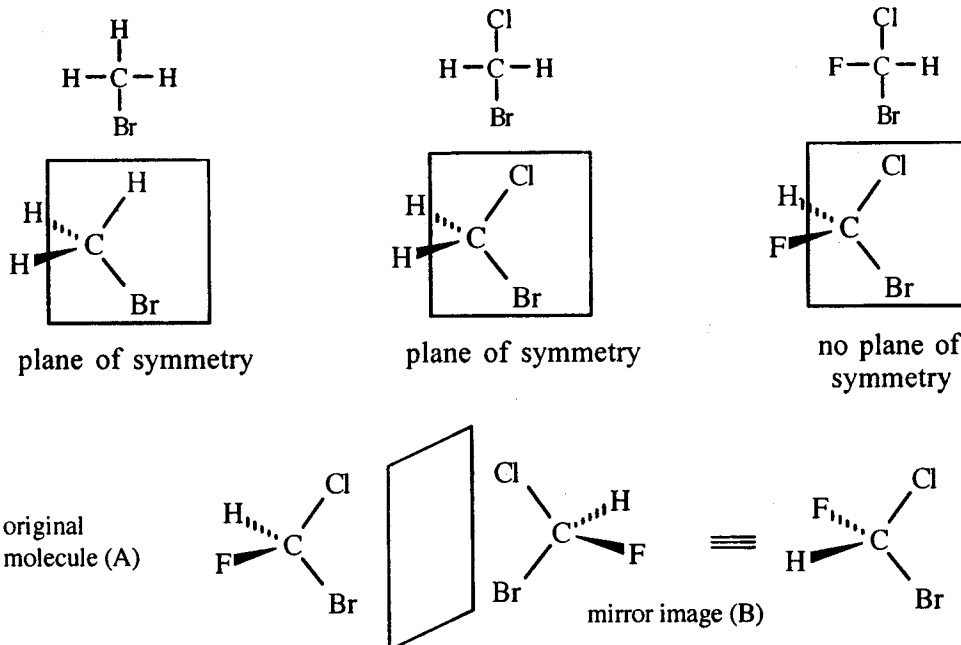
Some objects have one or more planes of symmetry as well as a *center of symmetry*. ~~A~~ The snowflake (idealized) has six planes of symmetry that can slice it as shown. There is another plane of symmetry, not shown, that slices through the edge of the snowflake from one side to the other (analogous to a bagel slicer). The center of symmetry in the snowflake is a point right in the middle. If a straight line is drawn from the center of symmetry to any other place on the snowflake, then extended in the opposite direction, the extended line will encounter an exactly equivalent place in the snowflake.

There are some objects that have no plane of symmetry, but do have a center of symmetry. Such an object is achiral. The plane of symmetry test by itself would give a false result. Examples will be given later, using molecules.

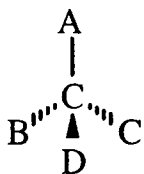
Chiral and achiral molecules.

A molecule is an object like any other object; some are chiral, some are achiral. We will focus on organic molecules, but the concept applies to inorganic molecules as well.

Consider the three halogenated methanes shown below. The first two can be seen to have a plane of symmetry, but the third doesn't. Also, if the mirror image of this molecule is constructed, the molecule and its mirror image are not superimposable.



The original molecule (A) and its mirror image (B) are not superimposable. Therefore, the molecule is chiral, and the mirror image represents the "other" form. A and B are stereoisomers of CHFCIBr. They are called *enantiomers* of CHFCIBr (enanti- = opposite). They are also sometimes called *mirror image isomers* or *optical isomers* of CHFCIBr.

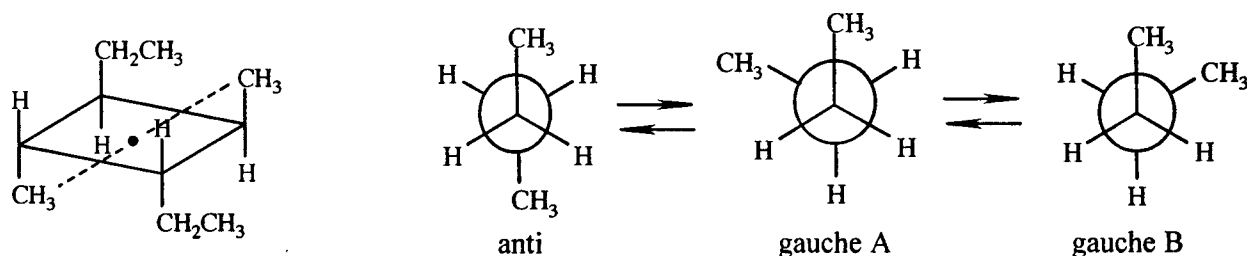


In CHFCIBr, the carbon has four different things attached to it. A molecule that possesses such a carbon atom (generalized on the left) will typically be chiral and can exist in two enantiomeric forms (but not always, as we shall see). A carbon atom of this kind is called by several names, as follows:

1. a chiral carbon
2. a chiral center
3. a stereogenic center (preferred)
4. a stereogenic carbon
5. a stereocenter
6. an asymmetric carbon atom (discouraged)

Overview

1. Many organic molecules have one or more chiral carbon atoms.
2. Some organic molecules have no chiral carbons, but *are* chiral because of their overall shape; for example, built like a spiral staircase.
3. a) A molecule is chiral if it *is not* superimposable on its mirror image. b) A molecule is achiral if it *is* superimposable on its mirror image.
4. A molecule is achiral if it has a) a plane of symmetry or b) a center of symmetry. The molecule illustrated at the left below has no plane of symmetry, but it does have a center of symmetry, which is a spot exactly in the middle of the ring.



5. A nominally achiral molecule can have chiral conformations. For example, butane, above, is regarded as achiral, but there are two chiral, enantiomeric conformations of gauche butane. They interconvert rapidly and cannot be isolated. A large molecule may have hundreds of irregular conformations, each of which is chiral.
6. A mixture of equal amounts of both enantiomers of a molecule is called a *racemic mixture* or *racemate*. Most typical reactions in organic laboratories involve racemic mixtures, because there is usually no reason to use a pure enantiomer. Methods are available for separating a racemic mixture into the pure enantiomers.
7. The majority of chiral molecules found in nature exist as one enantiomer only.
8. Enantiomers have identical physical properties, (mp, bp, density, solubility, etc.) except for *optical activity* as measured in a *polarimeter*.