

1.16: R/S Naming, Two or More Stereogenic Centers

Optical Activity

First, though, let's look at a property in which one enantiomer differs from another. Enantiomers are alike in all respects but one. They have the same melting point, the same boiling point and the same solubility in common solvents. The difference between the two enantiomers only shows up when we put them in a chiral environment. Our analogy with gloves can help here. In a pair of gloves, the left glove weighs the same as the right glove, it is the same size and typically the same color. It is made of the same material. The difference between them only shows up when we try one on. One fits the right hand better than the other. In this instance, the right hand is a chiral environment and the properties of the left and right gloves differ in that environment.

A specific "chiral environment" for molecules is provided by polarized light. The outcome of this is that if we pass a beam of polarized light through a solution of one enantiomer, the plane of that polarization will be rotated either to the left or the right. This phenomenon is called *optical activity*. If we do the same experiment, but use the other enantiomer (the mirror image of the first one) the plane of polarization will be rotated in the opposite direction. In either case, the amount of the rotation (the number of degrees in the angle between the plane of polarization before passage through the sample and the plane of polarization after passage through the sample) is the same but the directions are opposite.

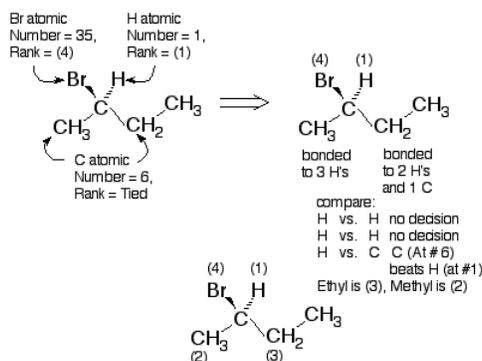
If the sample causes a rotation of the plane of polarization of the light in the clockwise direction (from the viewer's point of view) we say that the compound is dextrorotatory and we designate this by a plus sign in parentheses (+). Correspondingly, the terms for counter-clockwise rotation are levorotatory and (-).

R/S Naming

It has been possible to determine the *absolute configuration* of a chiral molecule since 1954. That is, we can know for a specific molecule which of the two mirror image structures is the one which represents the actual arrangement in three dimensions. We need a way to designate that information in the compound's name.

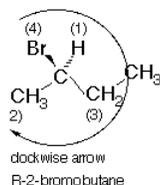
The system we use has two components. First we need to be able to list the four atoms or groups connected to the stereogenic carbon in a specific rank order. Then we need to have a way to distinguish the orientation of these groups or atoms in one enantiomer from the orientation in the other.

Ranking Groups or Atoms: We rank groups or atoms by the atomic number of the atom directly attached to the stereogenic carbon. The group or atom with the highest atomic number gets the highest rank number (4). In 2-bromobutane (below), this is bromine whose atomic number is 35. The lowest rank goes to hydrogen (atomic number one), so it gets rank number (1). That is fairly straightforward, but what do we do about the two carbons? They both have atomic numbers of six and are tied for ranking. The tie-breaker is to look next at the three atoms attached to each of these two carbons. We compare their atomic numbers until we find a difference. In 2-bromobutane one of these carbons is in a methyl group, so it is bonded to three hydrogens. The other "tied" carbon is carbon one of an ethyl group, so it is bonded to two hydrogens and a carbon. If we compare these two situations we find that there is no breaking the tie by comparing hydrogens, but the second carbon of the ethyl group has a higher atomic number than the hydrogen which is its competition on the methyl group. The tie is broken, the ethyl group has a higher (3) rank than the methyl group (2), so we have all of the atoms or groups attached to the stereogenic carbon ranked.



The "tie breaking" process can be extended to more complex situations. Study how it works for doubly bonded carbons in Section 4.3 (Rule 3) of Brown.

Orientation: Now that we have ranking for the four groups or atoms attached to the stereogenic carbon, we need to describe how they are oriented in space. We do this by turning our molecule so that the lowest (1) ranked atom or group is pointed behind the paper, away from us. Then we imagine a curved arrow which starts at the highest (4) ranked group, passes by the (3) group and ends at the (2) group. If this arrow points in a clockwise direction, we use the letter **R** (from Latin *rectus*) to describe the compound. If the arrow points counter-clockwise, we use the letter **L** (Latin *sinistrus*). These letters are prefixed to the IUPAC name of the compound, so our compound is *R*-2-bromobutane.



Practice this process using the problems in the text and bring up any questions in class. You can also practice with the on-line lab problems. Like other naming situations, it sometimes seems arbitrary and picky, but it isn't fundamentally hard. Practice is very necessary so that you can use the R/S system quickly and effectively.

One last point about the R/S system and optical activity: There is no direct relationship between a compound's absolute configuration (designated by R or S) and its optical activity. Some R compounds have clockwise (+) rotations, some have counter-clockwise (-) rotations, and the same is necessarily true of S compounds.

Diastereoisomerism

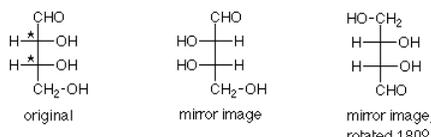
What happens if we have two (or more) stereogenic centers in the same compound?

Next time, we'll look at how these stereogenic atoms are included in naming, and then we'll go on to consider what complications arise if there are more than one stereogenic atom in a molecule. We'll use Fischer projections for this, since the next topic is sugars and Fischer projections are used routinely to describe sugar structures.

Let's take a compound with two stereogenic centers (designated with asterisks *):

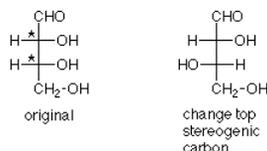


Does it have a mirror image? Yes. Is it superimposable on its mirror image? No. (Remember that we can rotate Fischer projections 180° in the plane of the paper.)

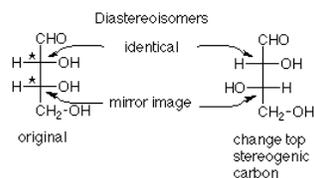


Notice that neither the mirror image nor the rotated mirror image is superimposable on the original structure. The original structure and its mirror image are enantiomers. Each will be optically active.

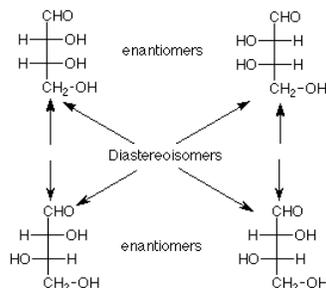
Now let's look at what the relationship would be if we did change the configuration at one of the stereogenic carbon atoms, but left the other one alone.



There isn't a mirror image relationship here, and the structures are not superimposable. Neither of the terms "enantiomer" or "identical" applies. The compounds are isomers though, and since they are connected identically, they are stereoisomers. The word we use for this relationship is *diastereoisomeric*. Diastereoisomers may be recognized because they are connected identically, they have two (or more) stereogenic atoms and comparison of those atoms reveals that the relationship at one (or more) atom is identical and the relationship at the other (or more) atom is mirror-image.



Since the diastereoisomer we made by changing the top stereogenic carbon of our original compound is not superimposable upon its mirror image, it too is optically active and has a mirror image enantiomer. Here is the complete set of enantiomeric and diastereoisomeric relationships for this case:

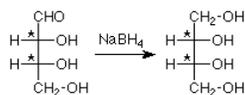


The horizontal relationships here are between enantiomers, compounds which are non-superimposable mirror images. The vertical and diagonal relationships are between diastereoisomers, stereoisomers which are neither identical nor mirror images.

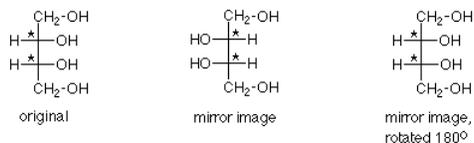
Diastereoisomers show differences in properties other than optical activity. They typically have different melting and boiling points and solubilities and they may show differences in how fast they react with other reagents. These differences are not usually as large as those shown by compounds which are not isomers. Here are some on-line problems on this topic

Meso Compounds

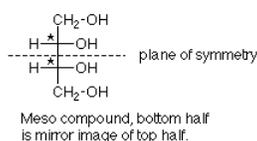
There is one more case to consider. What if the four atoms or groups bonded to one of the stereogenic atoms are the same as those bonded to the other. We can explore this in our example by considering what happens if we reduce the aldehyde (CHO) group with NaBH₄. The product is a primary alcohol (-CH₂OH) group, the same group as is at the bottom of this compound. The four atoms or groups attached to the top stereogenic carbon are the same as those attached to the bottom stereogenic carbon.



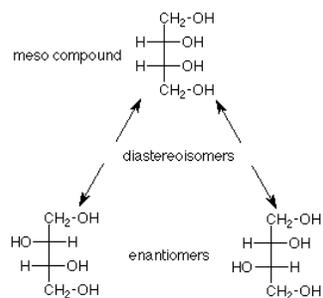
Now, let's test this molecule to see if it is superimposable upon its mirror image. As before, we make the mirror image and then we rotate it 180° in the plane of the paper. The original structure is identical to its mirror image, so we do not have enantiomers here. A compound like this is called a *meso* compound. Since it is superimposable upon its mirror image, it is not optically active, even though it has two (or more) stereogenic carbon atoms.



Another way to detect a meso compound is to look for a plane of symmetry within the molecule. This is particularly easy with Fischer projections, since what we have to do is to imagine a plane cutting the molecule precisely in two so that there is a bottom half and a top half. If the bottom half is the mirror image of the top half, we have a meso compound.



A meso compound will have diastereoisomers as well. We can generate these by changing one of the stereogenic carbons and then making its mirror image. The latter two compounds are enantiomers. Each is a diastereoisomer of the original meso compound.



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