Molecular structure and your molecular model kit

Structure and Nomenclature

This manual is available at www.bluffton.edu/~bergerd/Models/. For a short tutorial on using online models, go to www.bluffton.edu/~bergerd/classes/jmol.html.

Thinking in three dimensions is one of the most important skills in organic chemistry. Most organic molecules (especially biological molecules) function through and because of their particular three-dimensional shapes. You must be able to translate flat pictures of molecules into three-dimensional models in your mind in order to do well in either organic or biochemistry. In order to develop this skill, you have been asked to purchase a molecular model kit. This series of exercises, aided by online models, will help you learn to use your model kit.

Using the *Molecular Visions* model kit

The Molecular Visions model kit was chosen for its combination of low price and ability to represent a great many molecules; many professional chemists prefer it as a research model kit. However, like the line-drawing method of representing molecular structures, it is highly stylized.

Three resources will help you learn to use your model kit: the kit manual, which has many color pictures; demonstration by the instructor; and online molecular models, which will allow you to compare the model you build to a more conventional representation. Demonstrations and online models will be provided throughout the course; reading the manual is, of course, up to you!

Some of the laboratory periods will be devoted to learning to use your model kit, and you may be required to identify molecular models during examinations.

Your kit contains several different types of pieces, but the ones that concern us at present are those which allow us to represent organic molecules.[1] These are the *tetrahedral* pieces, the gray *double-bond end-pieces* which go with the gray or red *double bond* pieces, and the *triple bonds.* There are also several *colored balls.*

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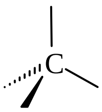
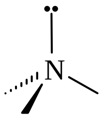
[1] The gray trigonal pieces will be used later, to represent certain reactive carbon species. Chemistry majors will find the gray trigonal and linear pieces, and the pink pieces, useful when they study *trigonal bipyramidal*, *square planar* and *octahedral* inorganic and organometallic molecules. The short pink pieces are "bond extenders" used for inorganic and organometallic compounds, which often have longer bonds.

Tetrahedral pieces should not be confused with the gray double-bond end-pieces! There are black, red and blue tetrahedral pieces, which are the standard (or CPK) colors for carbon, oxygen and nitrogen respectively. To assemble a *tetrahedral center*, take two tetrahedral pieces (usually of the same color) and snap them together. A tetrahedral center represents an atom with four *groups* attached. Remember from VSEPR[2] that a *group* can be either a bond or a lone pair of electrons.

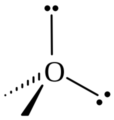
Assemble **tetrahedral centers** from tetrahedral pieces of each color. Notice that the four arms or "bonds" are arranged at angles of 109.5º. The black center represents a carbon atom, with four bonds. The blue center represents a nitrogen atom, with three bonds and a lone pair of electrons. The red center represents an oxygen atom, with two bonds and two lone pairs.



black



blue

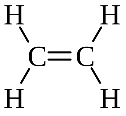


red

To represent methane (CH_4), you may use four white balls (representing hydrogen atoms) attached to the black tetrahedral center; ammonia (NH_3) and water (H_2O) can be represented by using three and two white balls, respectively. However, larger molecules will have too many hydrogens for this method to be practical, given your limited supply of white balls. One alternative is to represent a lone pair of electrons by a colored ball, and let blank ends represent hydrogen atoms! Also, divalent oxygen (as in water) can be represented by a *single* red tetrahedral piece.

> *Build models of methane, ammonia and water. Compare them to the online models (www.bluffton.edu/~bergerd/Models/vision2.html). Now build ethane* (CH_3CH_3)*, methanamine* (CH_3NH_2) *and methanol* (CH_3OH)*; again, compare your models to the online models (www.bluffton.edu/~bergerd/Models/vision3.html).*

Double-bond pieces include several types: *end-pieces,* which are gray; gray *double bonds*; and *half-bonds* which are either gray or red. The gray pieces are used to represent carbon atoms and carbon-carbon double bonds; in order to represent a carbon-carbon double bond, snap a gray end-piece into each end of one of the gray double bonds.

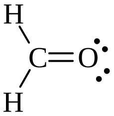


ethene

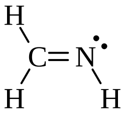
> *Build a model of ethene,[3] and compare it to the online model. The "bonds" are arranged at normal trigonal planar angles of 120º. Notice that the online model does not show the double bond! (www.bluffton.edu/~bergerd/Models/vision4.html) However, you can deduce the presence of a double bond from the trigonal planarity of its two carbon atoms.*

Carbon-oxygen double bonds - *carbonyl groups* - may be represented using the gray and red half-bonds. To represent a carbonyl group, first snap together one red and one gray half-bond; then snap a gray end-piece into the gray end of the double bond.

Carbon-nitrogen double bonds are rarer in organic chemistry, and the fact that the nitrogen's valence is not filled means that a group may be bonded to nitrogen. To represent a carbon-nitrogen double bond, take a gray double-



methanal



methanal imine

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[2] **V**alence **S**hell **E**lectron **P**air **R**epulsion, which says electron groupings (bonds or lone pairs) distribute themselves evenly around a central atom. See your textbook.

[3] Commonly known as *ethylene.*

bond piece. Snap a gray end-piece into one end to represent carbon, and a blue tetrahedral piece into the other end for nitrogen.

> *Build models of methanal[4] and methanal imine, and compare them to the online models (www.bluffton.edu/~bergerd/Models/vision4.html).*

Triple bonds are represented using the gray triple-bond pieces. **Each piece represents TWO carbon atoms with a triple bond between them and one *open valence* for each atom.** Notice that triple bonds have a normal bond angle of 180º. Carbon-nitrogen triple bonds are also possible (such bonds are referred to as *cyano* or *nitrile* groups), but there is no distinct way to represent them with this model kit.

$H-C\equiv C-H$

ethyne

> *Build a model of ethyne[5] and compare it to the online model (www.bluffton.edu/~bergerd/Models/vision4.html).*

Structure and nomenclature

> *Use your models in conjunction with the instructions and the online models. Build the models as you read each description so that you can **see** what is being discussed!*

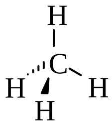
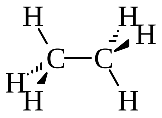
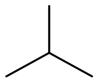
Alkanes can be represented entirely with the black tetrahedral pieces from your model kit, while alkenes and alkynes require double- and triple-bond pieces to be included. In this module, you will explore the relationship between all-atom representations, line drawings, and molecular models.

Alkanes, alkenes and alkynes

www.bluffton.edu/~bergerd/Models/structure.html

Review the sections in your texts concerning **alkane** nomenclature. Using your model kit, build **methane, ethane, propane** and **butane** and compare them to the online models. Rearrange the model of butane to its constitutional isomer, **2-methylpropane** (isobutane). This demonstrates that constitutional isomers use the same atoms, differently connected.

In the table below, line drawings have been used for butane and 2-methylpropane. Line drawings cannot be used for methane and are almost never used for ethane or propane. But line drawings make higher alkane structures much easier to read!

methane	**ethane**	**propane**	**butane**	**2-methylpropane**
		$H_3C-CH_2-CH_3$		

Alkenes (www.bluffton.edu/~bergerd/Models/struc2.html), of course, must have at least two carbon atoms since the central feature of an alkene is a carbon-carbon double bond. Build **ethene** (ethylene),

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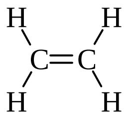
[4] Commonly known as *formaldehyde.*

[5] Commonly known as *acetylene.*

propene (propylene) and **1-butene** and compare them to the models online. Now reconnect your model of 1-butene to represent its *constitutional isomer*[6] **2-methylpropene** (isobutylene).

ethene

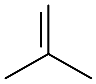


propene

$H_3C{-}CH{=}CH_2$

1-butene

2-methylpropene



Cycloalkanes (http://www.bluffton.edu/~bergerd/Models/struc3.html) are constitutional isomers of alkenes.[7] Since you need at least three vertices to form a closed figure in geometry, at least three carbon atoms are required for a cycloalkane.

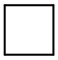
> *You should use the odd-colored flexible pieces in your model kit to form small (3- and 4-membered) rings, as* ***the strain is likely to break the normal, less flexible pieces****. See your kit manual for guidance.*

Build models of **cyclopropane** and **cyclobutane** using the flexible pieces to form the rings. Build **cyclopentane** and **cyclohexane** using the normal tetrahedral pieces.

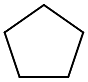
Notice, from the models you have built with your model kit, how the rings get "floppier" as they get larger. The molecules are shown below as line drawings, in which each vertex represents a carbon atom, and hydrogens are automatically assumed to exist at unfilled carbon valences. You will see that your *Molecular Visions* kit works very much like a line drawing.

cyclopropane

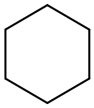
cyclobutane



cyclopentane



cyclohexane



Alkynes (www.bluffton.edu/~bergerd/Models/struc4.html) contain carbon-carbon triple bonds. An important feature of alkynes is their rigid linearity; four atoms are held firmly in a straight line. Build **ethyne** (acetylene), **propyne, 1-butyne** and **2-butyne.** Why is there no other triple-bonded isomer of butyne?

ethyne

$H{-}C{\equiv}C{-}H$

propyne

$H_3C{-}C{\equiv}C{-}H$

1-butyne

$H{-}C{\equiv}C{-}CH_2{-}CH_3$

2-butyne

$H_3C{-}C{\equiv}C{-}CH_3$

You probably noticed that, while we built 1-butene and 2-methylpropene, we left out one of the isomers of C_4H_8. **2-butene** can be represented in several ways:

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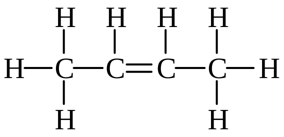
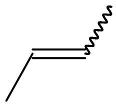
[6] Constitutional isomers have the same formula (for example, C_3H_7NO) but have different "skeletons" (arrangement of atoms along the "main chains").

[7] Both have the general formula C_nH_{2n}.



$H_3C-CH=CH-CH_3$



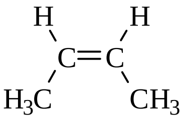
None of these indicates any particular geometry; the squiggly line in the third drawing makes that explicit. However, if you build a model of 2-butene you will quickly notice that there are two possible geometries.

Stereoisomers: Cis-trans diastereomers

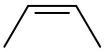
(www.bluffton.edu/~bergerd/Models/struc6.html)

The two possible isomers of 2-butene are *cis*-2-butene and *trans*-2-butene; *cis* indicates that substituents are arranged on the same side of the double bond, while *trans* indicates opposite sides. These are *stereoisomers;* the atoms are connected in the same way, but arranged differently in space.

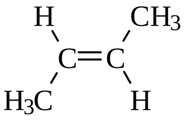
***cis*-2-butene**



or



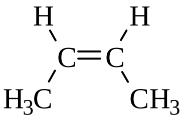
***trans*-2-butene**



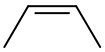
or

For alkenes, there is a more general way of indicating *cis*/*trans* orientation: E/Z nomenclature. *Z* stands for the German word *zusammen* (together) and corresponds to *cis*; *E* stands for *entgegen* (opposite) and corresponds to *trans*. The use of these designations is discussed in your text and will be covered in lecture; for our present purpose it is sufficient to point out that another way of naming the two *diastereomers*[8] of 2-butene is

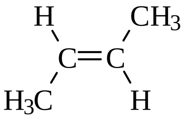
Z-2-butene



or



E-2-butene



or

In a similar fashion (www.bluffton.edu/~bergerd/Models/struc7.html), cycloalkanes which have two substituents on the ring can have them arranged on the *same* face of the ring *(cis)* or on *opposite* faces *(trans)*. Look at your model of any of the cycloalkanes discussed above, and notice that the hydrogen atoms project both above and below the "plane" of the ring. Now put two methyl groups on the ring at adjacent positions. Is what you have built *cis or trans*?[9]

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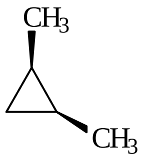
[8] Diastereomers are stereoisomers which are *not* mirror images of each other.

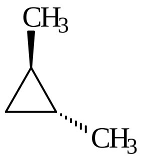
[9] *Z* and *E* are NEVER appropriate for cycloalkanes!!!

1,2-dimethylcyclopropane

cis

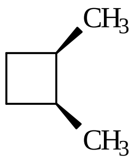


trans

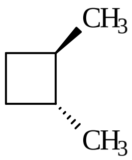


1,2-dimethylcyclobutane

cis

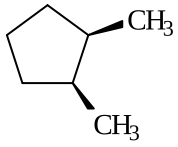


trans

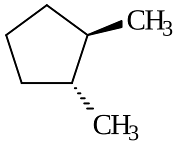


1,2-dimethylcyclopentane

cis

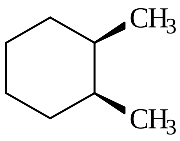


trans

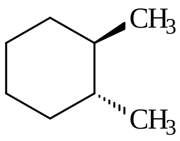


1,2-dimethylcyclohexane

cis



trans



Conformation and Newman projections

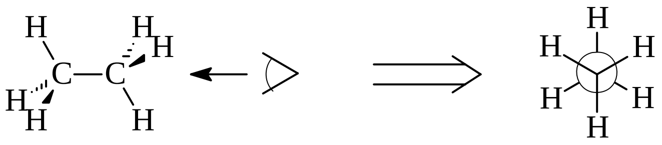
(www.bluffton.edu/~bergerd/Models/newman.html)

> *Use your models in conjunction with the instructions and the online models. Build the models as you read each description so that you can* ***SEE*** *what is being discussed!*

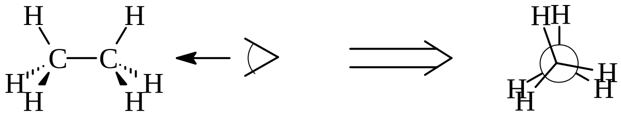
Look at your model of ethane. Notice that the central carbon-carbon bond rotates freely. This means that the hydrogens on the adjacent carbon atoms can be either alternating or all lined up; the appropriate terms are *staggered* and *eclipsed.* Since hydrogen atoms have size and thus can interfere with each other, the *staggered conformation* of ethane is lower in energy than the *eclipsed conformation.* The eclipsed conformation has what we call *torsional strain* because of the interactions of eclipsed hydrogen atoms.

The way we emphasize conformation about a particular bond is with a *Newman projection. To* understand a Newman projection, imagine that you are sighting down the carbon-carbon bond in ethane (take your model and do so now!) The carbon atom behind is represented by a large circle; the hydrogens attached to each carbon can be clearly seen in the projection.

staggered ethane

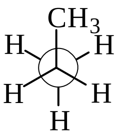


eclipsed ethane

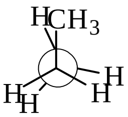


In the same way, propane can be staggered or eclipsed about either of the carbon-carbon bonds.

staggered propane

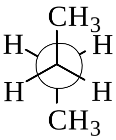


eclipsed propane

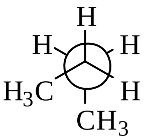


However, butane has another bit of conformational information: when you look down the central carbon-carbon bond, the staggered form can have the methyl groups either adjacent *(gauche)* or opposite *(anti)*. The *anti* conformation is lower in energy than the *gauche*. While this makes little difference in most of the chemistry of butane, conformational considerations become important when we consider cyclo-alkanes.

anti **butane**

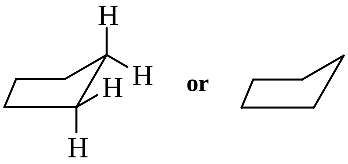


gauche **butane**



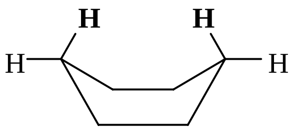
Unsubstituted cycloalkanes (www.bluffton.edu/~bergerd/Models/newman2.html), if planar, would not only have significant *angle strain* (caused by abnormal bond angles in the ring) but also considerable *torsional strain* (from eclipsing of adjacent hydrogens). Cyclopropane and cyclobutane cannot avoid having large amounts of strain in their structures, but cyclopentane and cyclohexane can easily adopt conformations in which not only the angles have normal values but eclipsing (and thus torsional strain) is minimized.

Planar *cyclopentane* has almost-normal bond angles of 108º. Nevertheless, to avoid torsional strain the molecule bends into the so-called *envelope* conformation, in which one of the carbon atoms is bent out-of plane. This staggers the hydrogens on that atom relative to those on adjacent carbon atoms.

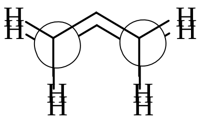


If *cyclohexane* (www.bluffton.edu/~bergerd/Models/newman3.html) were planar, there would be considerable angle strain as the angles in a planar hexagon are 120º (vs. 109.5º). However, when you use your model kit to build cyclohexane you will see that the ring is really rather "floppy." This floppiness allows both angle and torsional strain to be relieved, and cyclohexane has two main conformational types: *boat* (in which two opposite carbons are bend out-of-plane in the same direction) and *chair* (in which two opposite carbons are bent out-of-plane in opposite directions).

Boat cyclohexane has no angle strain, but there are several eclipsed interactions between neighboring hydrogens. The actual "boat" conformation is the so-called *twist boat*, in which the eclipsed interactions are alleviated by twisting around some of the carbon-carbon bonds. Nevertheless, the boat conformation is still relatively high in energy because of the unavoidable *flagpole* interactions between the hydrogens on the insides of the "prow" and "stern." The Newman projection below emphasizes the eclipsed interactions along the "gunwales" of the boat.



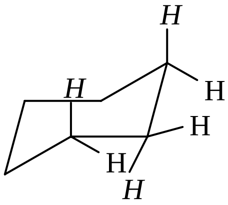
or

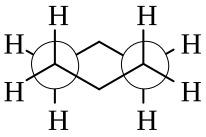


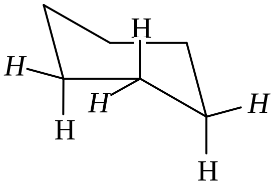
*The flagpole hydrogens are shown in **boldface**.*

> *The twist-boat conformation is very difficult to draw; however, it can be seen in the online models (www.bluffton.edu/~bergerd/Models/newman3.html) and you should be able to reproduce it using your model kit.*

Chair cyclohexane has neither angle strain nor eclipsed interactions! In fact, it has ***zero* strain *energy***. If you build a model of chair cyclohexane, you will notice that there are two types of hydrogens, depending on whether they point up or down with respect to the ring, or point along the ring "plane." These types are called, respectively, *axial* and *equatorial*, and are color-coded in the on-line version of this tutorial. The Newman projection emphasizes that all hydrogens are staggered; if you examine your model you will see that this is true all the way around the ring.

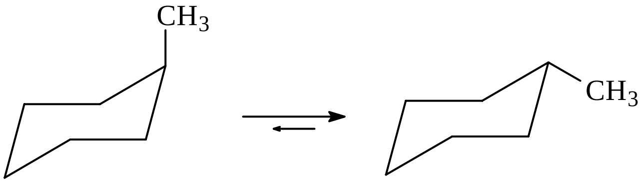






> *Mark one axial and one equatorial position on your model with colored balls. Now "ring-flip" to the other chair conformation. The colored balls have changed places: the one which was axial is now equatorial, and vice versa.*

For unsubstituted cyclohexane, the two chair conformations (or *conformers*) have the same energy. But when we begin to put substituents on the ring, this quickly comes to a halt: because of axial-axial *steric*[10] interactions, most substituents prefer to be in an equatorial position. Very large substituents, such as *t*-butyl groups, *lock* the ring into a particular conformation!



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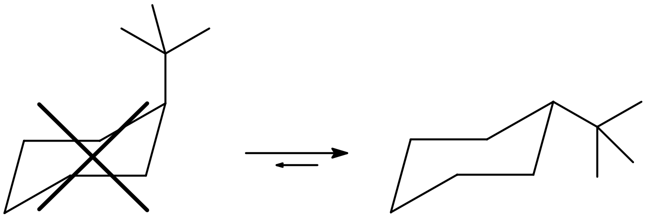
[10] Size-related.



Examine the online models of methylcyclohexane and t-butylcyclohexane in space-filling mode. (www.bluffton.edu/~bergerd/Models/newman4.html) Notice the steric interactions.

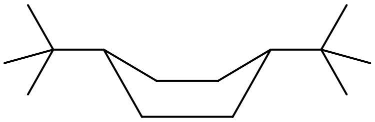
When more than one substituent is present, the ring will take on whichever conformation is lowest in energy; if possible, all substituents will be in equatorial positions. However, as you will see, this is not always possible in a chair conformation.

Build models of the following molecules, and report whether one chair conformation will be favored over the other (www.bluffton.edu/~bergerd/Models/newman5.html):

- Cis-*1,2-dimethylcyclohexane*
- Trans-*1,2-dimethylcyclohexane*
- Cis-*1,3-dimethylcyclohexane*
- Trans-*1,3-dimethylcyclohexane*
- Cis-*1,4-dimethylcyclohexane*
- Trans-*1,4-dimethylcyclohexane*

Now build cis-*1,4-di*-t-*butylcyclohexane. Do you expect it to be a low-energy molecule or a high-energy molecule from steric considerations?*

What is observed is that this molecule tends to exist in a **boat** *form because this is the only conformer which allows both* t-*butyl groups to be equatorial!*



Chirality

> *This manual is available at www.bluffton.edu/~bergerd/Models/chiral.html. Use your model kit in conjunction with the instructions and the online models. Build the models as you read each description so that you can* ***see*** *what is being discussed!*

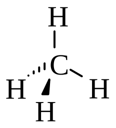
Chirality[11] is an attribute of objects that makes it impossible to superimpose them on their mirror images. Examples of chiral macroscopic objects include hands, feet, screws, automobiles and so on.

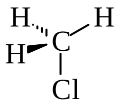
Molecules can also be chiral. Ways of measuring chirality are explained in your text and will be explored in the laboratory; the purpose of this module is to explore chirality using molecular models.

Chiral centers

For a single carbon atom to be chiral, there must be **four *different*** substituents attached. Such a carbon atom is called a *chiral center.*[12] Chirality may be illustrated by considering a series of substituted methanes.

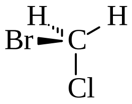
Methane itself (www.bluffton.edu/~bergerd/Models/chiral2.html) is obviously *achiral* (not chiral). It is easy to see that methane can be superimposed on its mirror image; nevertheless, you may want to test this. The same is true for chloromethane.

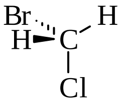




or CH_3Cl

Bromochloromethane, with *three* different substituents on carbon, may be more difficult to see; but if you build models of the two “different” molecules below you will find that they can be superimposed.





However, a methane with *four* different substituents, such as bromochlorofluoromethane, is chiral (www.bluffton.edu/~bergerd/Models/chiral3.html). Build models of the two different molecules below. You will see that they are mirror images and cannot be superimposed! Such molecules are *enantiomers*[13] of each other.

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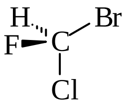
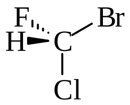
[11] “Handedness.”

[12] A chiral center need not be a carbon atom, as long as there are four different groups attached. For example, it is possible to have chiral ammonium ions or chiral silanes (compounds of silicon). In neutral nitrogen, a lone pair is formally able to serve as a fourth group but, because of the very low inversion barrier for amines, “chiral” neutral nitrogen compounds usually exist as racemic mixtures. Phosphines (phosphorus compounds analogous to amines) *can* be chiral because the inversion barrier at phosphorus is very high.

[13] Enantiomers are stereoisomers which *are* mirror images of each other.

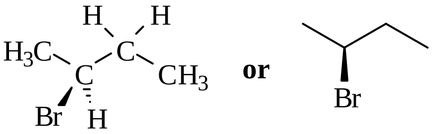


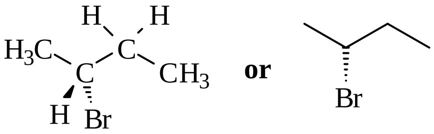


Use your models to explore the method explained in your text for determining whether configuration is R *or* S. *Which of the two molecules above is* R*? Which is* S*?*

Other molecules can be thought of as "substituted methanes." Those with four substituents – like 2-bromobutane and 2-butanol – are also chiral.

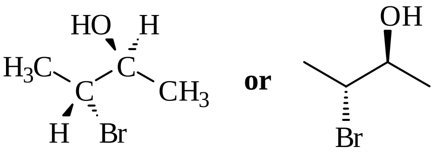
Build pairs of enantiomers for 2-butanol and 2-bromobutane. Draw the R *and* S *configurations of each. Of the two molecules shown below, which is* R *and which is* S*?*

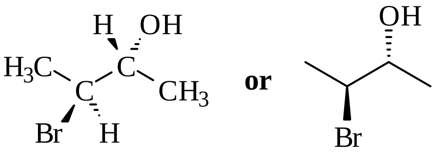


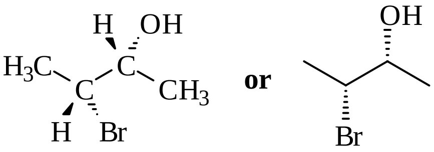


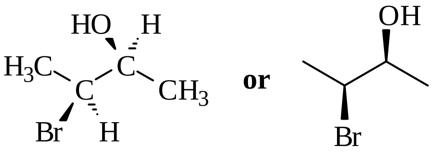
Molecules with more than one chiral center will obviously have more than two stereoisomers; in general, a molecule with *n* chiral centers will have 2^n stereoisomers. However, **this is a maximum** and is not always the case, as we will see.

For example, 3-bromo-2-butanol, with two chiral centers, will have $2^2 = 4$ stereoisomers. If each chiral center can be either *R* or *S*, obviously the stereoisomers will be *RR*, *SS*, *RS* and *SR*. These four are shown below; notice that each horizontal pair of isomers is a pair of enantiomers.







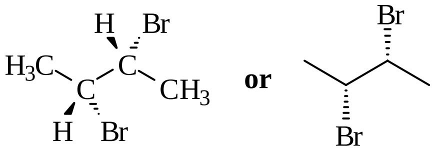


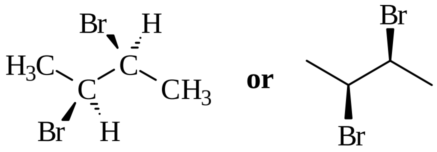
Assign the correct RS *designation to each of the chiral centers in the molecules above, and name the molecules correctly.*

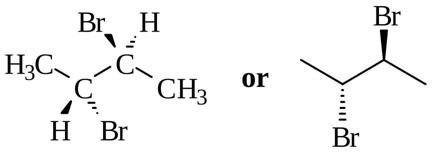
Remember that stereoisomers which are not mutual mirror images are called *diastereomers*. The top two molecules are diastereomers of the bottom ones.

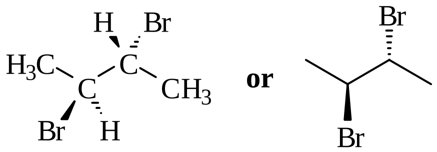
When both chiral centers in a molecule have the **same substituents**, the molecule as a whole may or may not be chiral. If one half of a molecule is the mirror image of the other half, the molecule contains a plane of symmetry and **cannot** be chiral *even though it may contain chiral centers*.

Consider 2,3-dibromobutane. Like 3-bromo-2-butanol it has two chiral centers and therefore four (2^2) possible configurations: *RR, SS, RS* and *SR*. However, if you examine models of the four molecules below you will see that the bottom pair are identical! Molecules which contain chiral centers but are not themselves chiral are called *meso,* and we refer to them as (for example) *meso*-2,3-dibromobutane.









Assign R *or* S *configuration to each of the chiral centers in the molecules shown above. Which molecules contain a plane of symmetry?*

Fischer projections

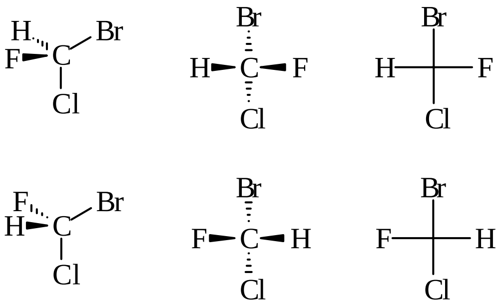
www.bluffton.edu/~bergerd/Models/chiral6.html

Around 1890-1900, organic chemists were getting used to the idea that organic molecules are three-dimensional things, and that different arrangements of substituents in space give different molecules. But they were not at all used to thinking in three dimensions (in fact, the wedge-dash system of "perspective" drawing did not come into general use for about another 50 years!)

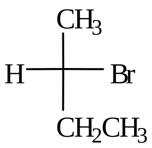
Emil Fischer devised the system of Fischer projections, which allows a 3-D molecule to be correctly represented by a plane figure. There are two conventions associated with Fischer projections, but only the first is essential:

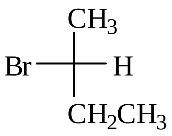
1. All vertical lines represent bonds going away from the viewer; all horizontal lines represent bonds coming toward the viewer.
2. The main chain of carbon atoms is laid out vertically by convention.

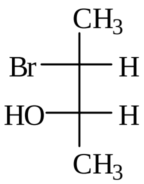
The two enantiomeric bromochlorofluoromethanes shown above can be represented thus:

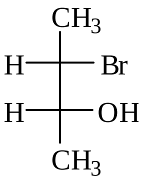


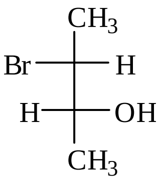
Satisfy yourself that the Fischer projections shown below correspond to the 2-bromobutanes, 3-bromo-2-butanols and 2,3-dibromobutanes shown in Section A.

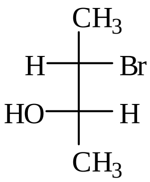


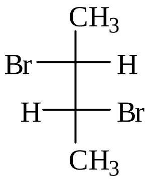




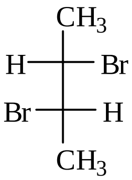




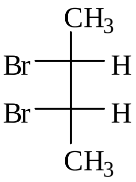




R,*R*-2,3-dibromobutane



S,*S*-2,3-dibromobutane



meso-2,3-dibromobutane

One advantage of a Fischer projection is that it becomes immediately obvious when a molecule is *meso*.

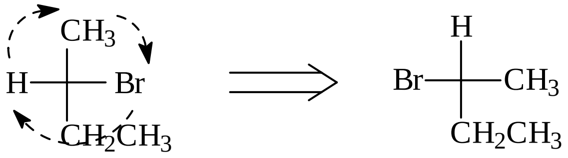
Rules for manipulating Fischer projections

www.bluffton.edu/~bergerd/Models/chiral7.html

The rules for manipulating Fischer projections as given in your text may be incomplete. The full rules are as follows.

1. Projections, as single units, may be rotated 180º only (**not** 90º), and *only in the plane of the paper*.

2. Any **three** groups may be rotated, with the fourth remaining fixed, and the result will be a molecule identical to the starting molecule.[14] If we take the Fischer projection of one of our 2-bromobutanes and perform such a rotation, we can easily see that it is S-2-bromobutane. (Remember that, in the projection on the right, the H atom is pointing away from us.)



Using your model kit or the online online models, you should satisfy yourself that the two Fischer projections above represent the **same molecule**.

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[14] This is equivalent to rotating around a single bond.