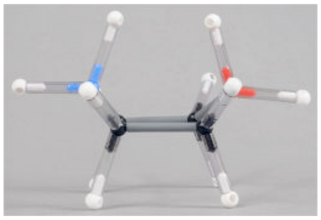
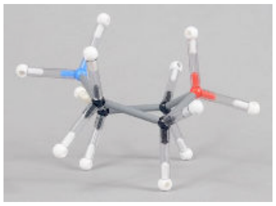
Super Models





Organic Stereochemistry Model Kit

Ryler Enterprises, Inc.

Recommended for ages 10 - adult.

⚠**Caution:** Atom centers and vinyl tubing are a choking hazard. Do not eat or chew model parts.

Kit Contents:

15 black 4-peg carbon atom centers
10 black 3-peg carbon atom centers
8 red 4-peg oxygen atom centers
3 blue 4-peg nitrogen atom centers
3 red 1-peg oxygen atom centers
12 green 1-peg chlorine atom centers
2 dark green 1-peg iodine atom centers
2 blue-green 1-peg bromine atom centers
3 blue 1-peg nitrogen atom centers
36 white 1-peg hydrogen atom centers
3 silver 6-peg metal atom centers
3 purple 5-peg phosphorus atom centers
50 clear, 1.25″ tubes (single bonds)
8 clear, 4 cm tubes (double/triple bonds)
2 clear, .875″ tubes (sigma bonds)
4 white, 2″ tubes (pi bonds)
10 grey, rigid bonds (for easily rotated bonds)

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Organic Stereochemistry

INTRODUCTION TO ORGANIC STEREOCHEMISTRY.

This model kit provides you with an inexpensive expedient for visualizing molecular architecture in three dimensions, as well as giving you the tactile sensations that enhance your ability to learn and to recall important information about the stereochemistry of carbon compounds.

Isomers are compounds that share the same formula but have different arrangements of their atoms. There are two main categories of isomers: constitutional (structural) and stereoisomers. See Fig. 1.

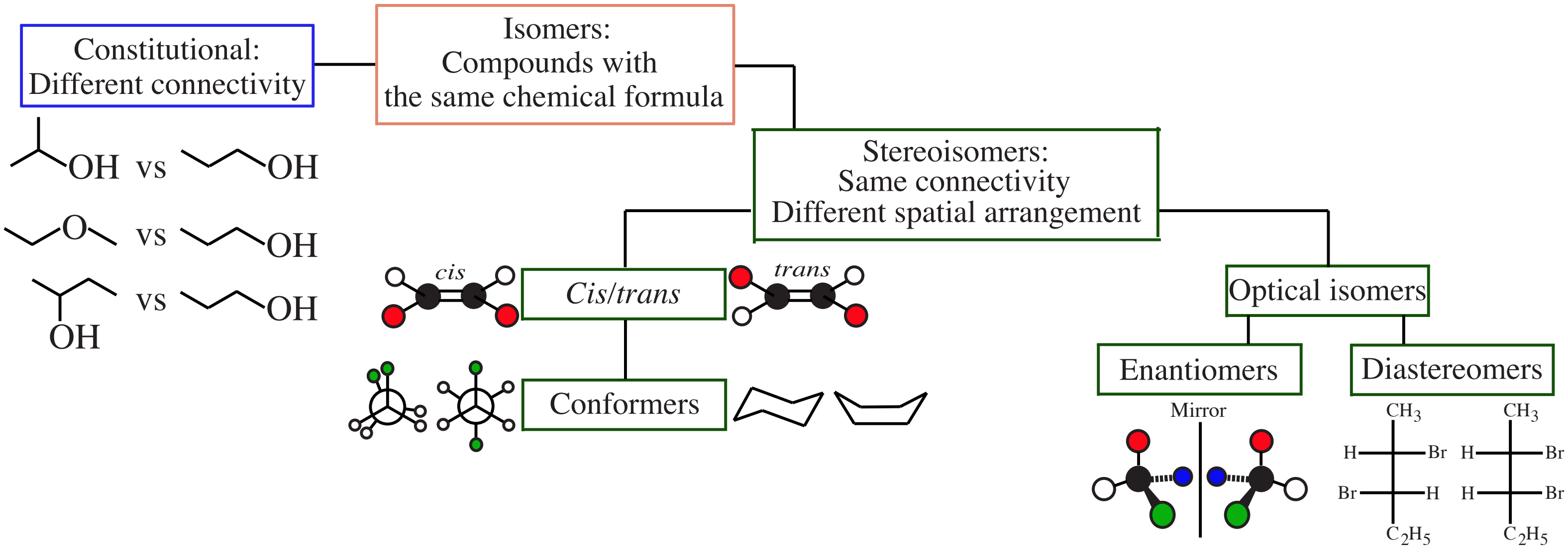


Fig. 1 Classification scheme for isomers.

Constitutional isomers are different compounds with the same chemical formula. Isomers in this category differ in that at least one atom in molecule A is bonded to a different atom in molecule B. In other words, atoms have different connectivity.

Fig. 2 shows two constitutional isomers of C_3H_8O. (a) is 1-propanol, and (b) is ethyl methyl ether.

(a) (b)

Fig. 2 Two constitutional isomers of C_3H_8O.

In these instructions, we will focus on stereoisomers. Stereoisomers share the same chemical formulas and bonding, atom to atom, i.e. they share the same connectivity. However, they differ in the positions of their atoms in three dimensional space.

The grey bonds will slip more readily and they are meant to be used when you must rotate atoms to show particular molecular geometries (e.g. boat and chair, or 1,3-diaxial interactions). Use the clear bonds for more permanent connections that do not have to rotate.

EXERCISE I: ECLIPSED AND STAGGERED CONFORMATIONS OF ETHANE: NEWMAN PROJECTIONS.

A. Construct a model of ethane using a grey bond between two black, tetrahedral carbon atoms. Using the 1.25´´ clear bonds, attach two white and one green, one peg atoms to each carbon atom. Observe the eclipsed and staggered conformers by looking at one carbon atom which covers the second carbon atom, as illustrated in Fig. 3.

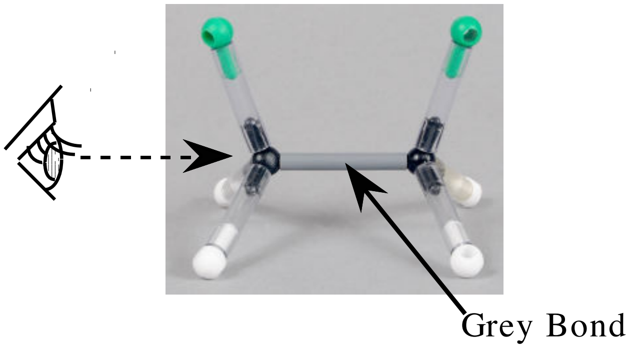
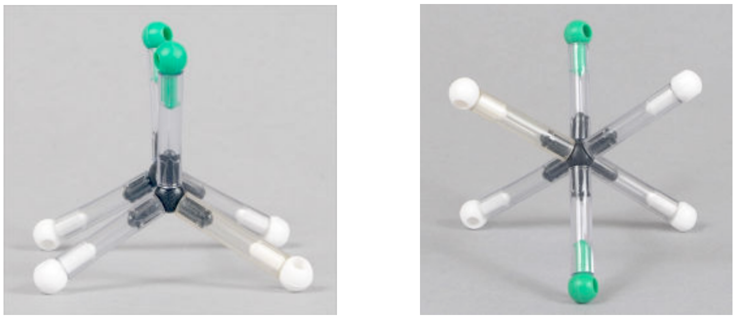


Fig. 3. Observing an eclipsed ethane conformer.

B. Align the single peg atoms to form an eclipsed structure, and then rotate the single bond to make the staggered form. See Fig. 4.



eclipsed staggered

Fig. 4 Eclipsed and staggered models.

C. Now we will convert the above photos into Newman projections. 1) Draw a circle to represent the carbon in the back, and add three short lines 120° apart to represent the three bonds to the carbon. If you are making an eclipsed conformer, tilt the lines slightly counterclockwise. 2) Draw in the front carbon, as a dot, in the middle of the circle, and add three long lines at 120° from each other. 3) Add colored circles to represent substituents, or write chemical symbols. See Fig. 5.

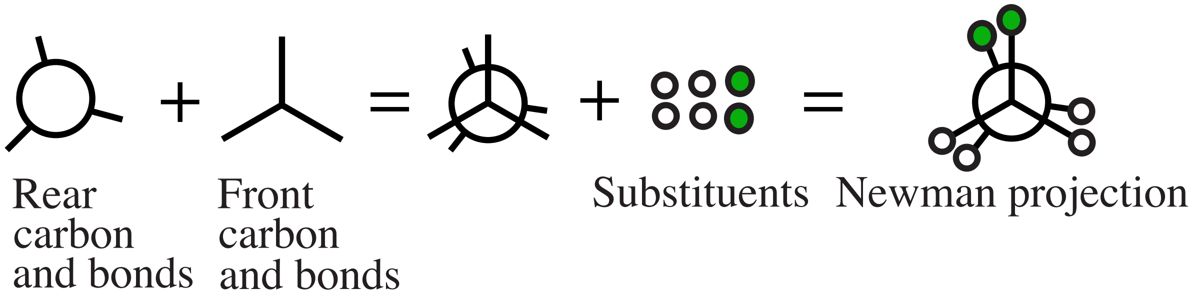


Fig. 5 Constructing a Newman projection of an eclipsed ethane molecule.

D. Draw the Newman projection for a staggered ethane molecule.

E. Keep in mind that the infinite number of angles between the substituents on the carbon atoms is due to the free rotation of the sigma bond between the two carbon atoms.

EXERCISE II: OBSERVING CONFORMERS OF BUTANE.

A. Make a model of butane using the clear bonds, but use one grey bond between the second, C2, and third, C3, carbons. Align the second and third carbons with your eye so that the second covers the third carbon. See Fig 6.

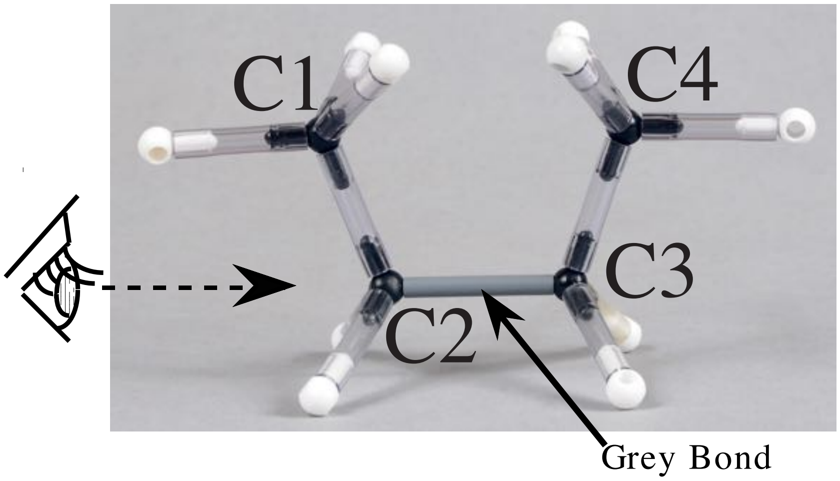


Fig. 6 Observing butane conformers

B. Turn the fourth carbon (C4) 180° so that it points down. This is the anti or staggered conformer pictured in Fig. 7. It is also called anti-periplanar, a term you will encounter later in your study of organic chemistry.

You will now make a series of 60° clockwise turns as you continue looking at C2.

C. Turn the third carbon 60° clockwise and observe the eclipsed conformation. See Fig. 8.

D. Another 60° clockwise turn of the third carbon produces the gauche conformer. See figure 9.

E. One more 60° twist to the right aligns the two methyl groups in the eclipsed methyl conformation. It is also known by the term syn-planar. See figure 10.

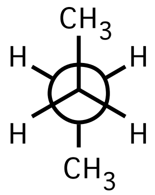


Fig. 7 anti

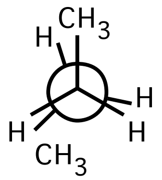


Fig. 8 Eclipsed

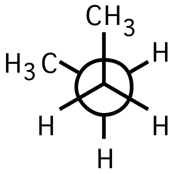


Fig. 9 gauche

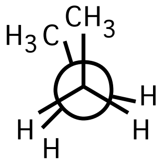


Fig. 10 fully eclipsed methyls

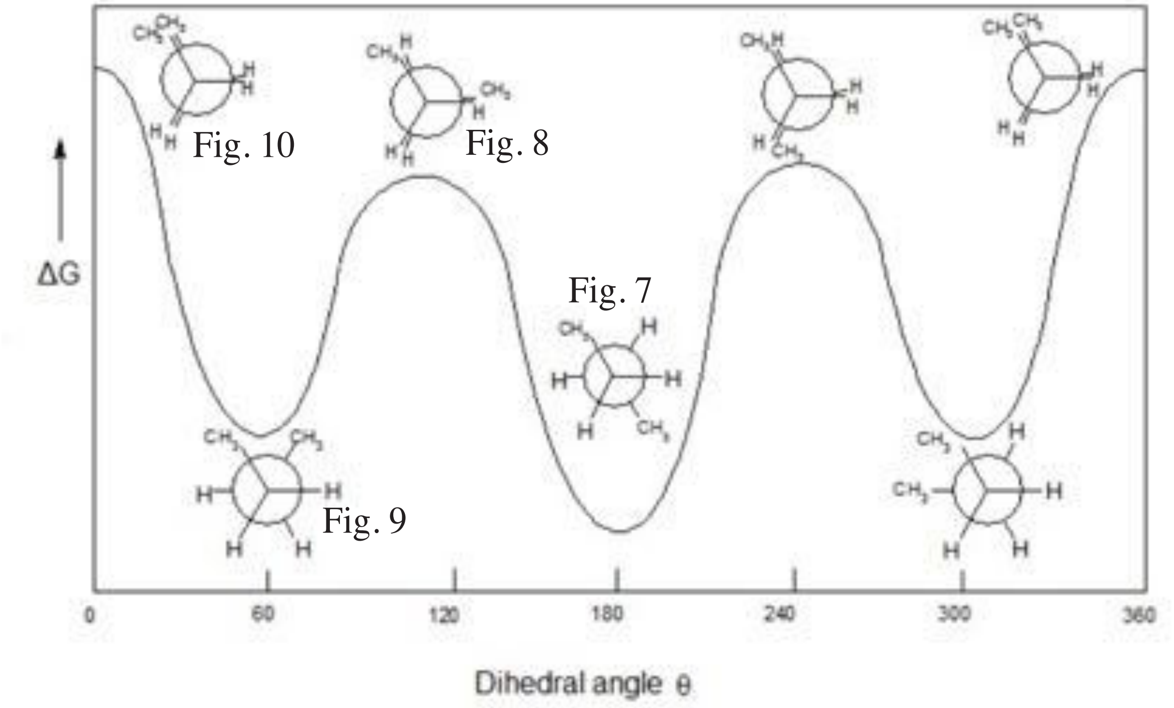
F. Work the following problems.

1. How many discrete positions of C4 are possible making only 60° turns? How many are staggered, and how many are eclipsed?

2. Rank the four above conformations of butane on the basis of their energy levels, from lowest to highest.

Answers:

1. 360°/60° = 6. Three are staggered, and three are eclipsed.
2. Use the following graph to help answer the question.



EXERCISE III: TORSIONAL, STERIC, AND ANGLE STRAIN.

A. The term strain refers to an increase in energy in a molecule due to unstable structures.

B. Torsional strain is due to the repulsions among the electrons in bonds that are separated by two atoms as indicated in Fig. 11.

Torsional strain
due to these electrons
interacting

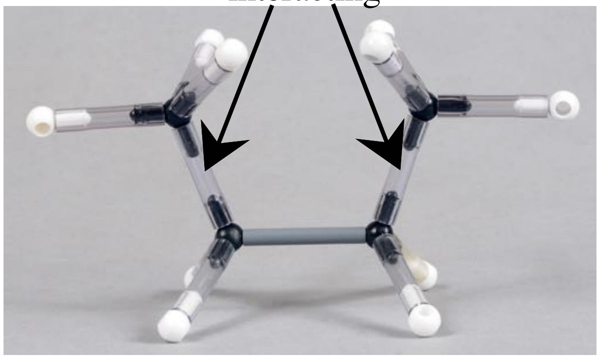


Fig. 11 Illustrating the cause of torsional strain.

C. Steric strain occurs when two or more atoms get close to and repel each other. See Fig. 12.

Steric strain
due to these atoms
interacting

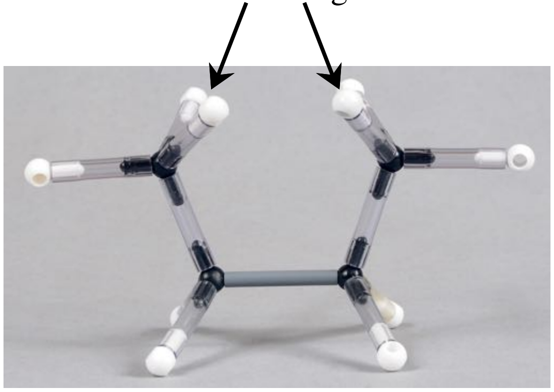
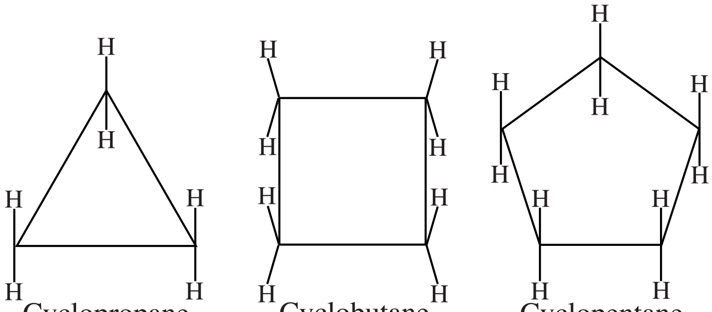


Fig. 12 The cause of steric strain.

D. To observe angle strain, you can build a series of three cyclic models. Using the clear bonds, construct a molecule of cyclopropane. Observe the strain put on the C-C bonds which make them bend. Now make a model of cyclobutane, and notice that there is much less strain on the C-C bonds. Finally, make a model of cyclopentane, and make note of the reduced bond strain in the ring of this molecule.
In these examples, strain forces can be called, ring strain. See Fig. 13.



Cyclopropane Cyclobutane Cyclopentane

Fig. 13 Three cyclic compounds used to study angle strain.

E. These rings will naturally attempt to relieve their strain by “puckering,” i.e. They twist pushing some atoms up and others down. Try it with your models, and observe the reduction of strain.

EXERCISE IV: PLANAR AND CHAIR CONFORMERS OF CYCLOHEXANE.

A. Using grey bonds within the ring, four black atoms, one blue atom (at C1), and one red atom (at C4), construct a model of cyclohexane. Use clear bonds to join two white hydrogen atoms to each atom of the ring. Arrange the all of atoms so that the grey bonds are all in the same plane (i.e. in the planar form). Notice that every hydrogen atom is eclipsed (Fig. 14) and that the grey bonds are slightly bent, indicating strain. These conditions raise the energy level of the molecule.

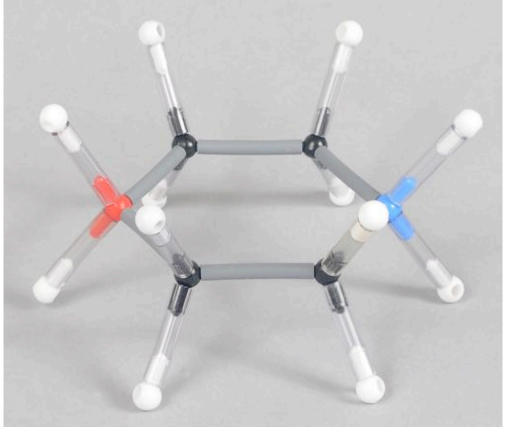


Fig. 14 Planar cyclohexane.

B. Rotate the blue atom up and the red atom down to produce the chair conformation as in Fig. 15. Your model will now reveal fewer eclipsed hydrogens and reduced bond strain within the ring. Both of these factors reduce the energy of the molecule. Notice that there are six hydrogens that are axial (three straight up, and three straight down). There are also six hydrogens that point away from the plane, or axis of the model. These are called equatorial hydrogens.

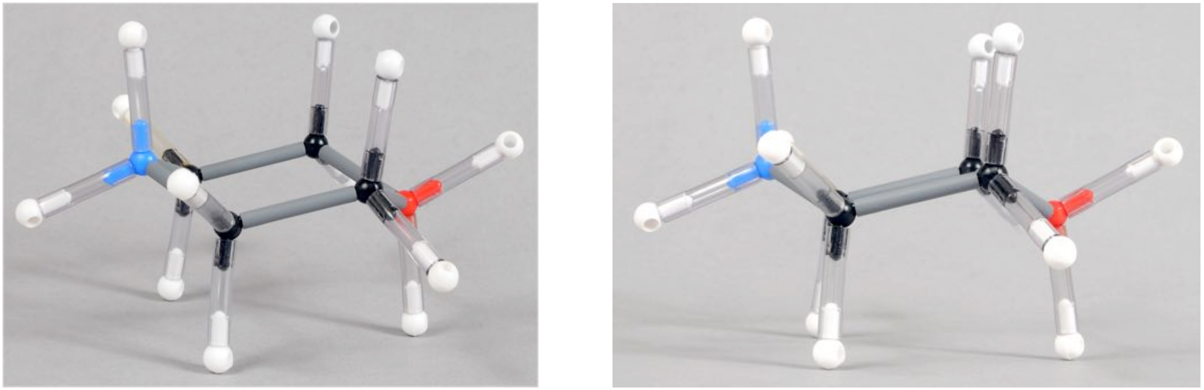


Fig. 15 Two views of the chair conformer of cyclohexane.

EXERCISE V: THREE ADDITIONAL CONFORMATIONS OF CYCLOHEXANE.

A. Return the cyclohexane to the planar form (Fig. 14). Rotate the blue carbon (C1) up to form a half-chair (Fig. 16) and observe the strain in four of the six bonds within the ring, and the eclipsed hydrogens.

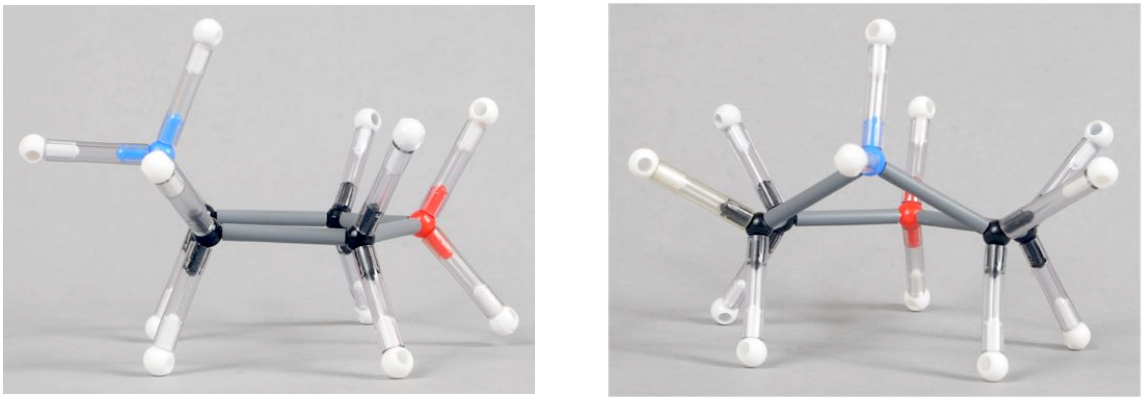


Fig. 16 Two views of the half-chair conformer of cyclohexane.

B. To produce the twist-boat conformation (Fig. 17), hold the blue carbon in the up position, grasp the red carbon (C4) in your other hand, and as you flip the red carbon up, twist it away from yourself.

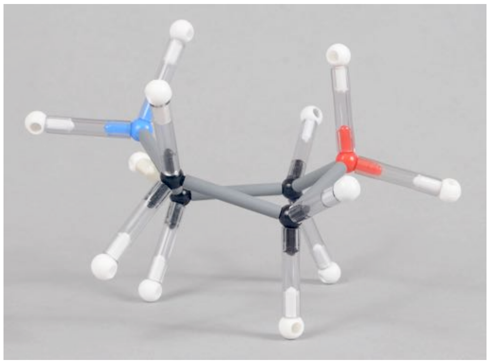


Fig. 17 Twist-boat

Check to see whether your model has the correct shape by placing it on a table. The red and blue atoms should be above the plane of the black atoms and the entire model should rock when you gently press down alternately on the red and blue carbons.

C. You will see eclipsing of the hydrogens when you change your model to the boat conformer. To make a boat (Fig. 18) from the twist-boat, simply twist the red carbon to a vertical position immediately opposite the blue carbon. When placed on a flat surface, the model cannot be rocked as it could be in the twist-boat form.

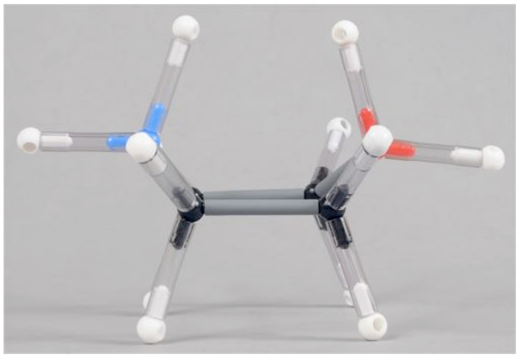


Fig. 18 Cyclohexane in a boat conformation.

D. See whether you can rank the energy levels of the chair, the half-chair, the twist-boat, the planar, and the boat conformers based on your observations of bond deformation and hydrogen eclipsing. Check your determinations against the graph in Fig. 19.

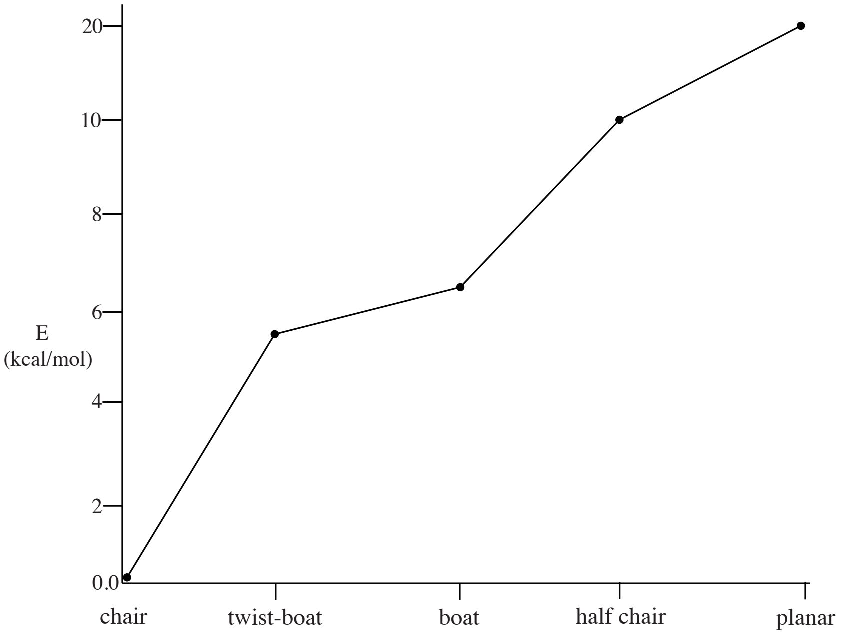


Fig. 19 Energy increase associated with conformers of cyclohexane.

EXERCISE VI: EQUATORIAL AND AXIAL POSITIONS IN CYCLOHEXANE.

A. Make the chair conformation with your cyclohexane model, with the blue atom "up", and the red atom "down." Place the model on a table. Replace the three hydrogens touching the table and the three hydrogens pointing straight up with green, single peg atoms. All six of the green atoms are in the axial position. The remaining six hydrogen atoms are called equatorial. In Fig. 20, the equatorial positions are indicated with white atoms, and the axial with green atoms.

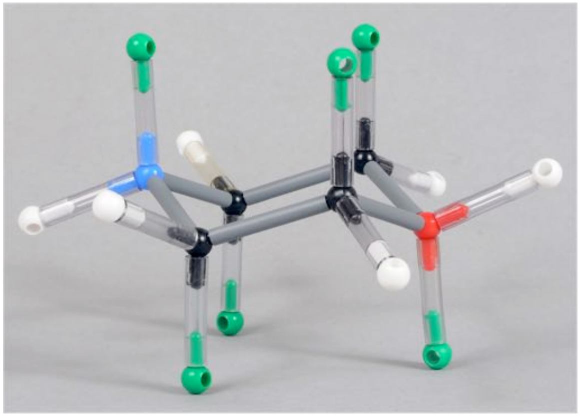


Fig. 20. Axial and equatorial positions of substituents on cyclohexane.

B. Now rotate the red carbon up, and rotate the blue carbon down. Observe that each green atom has become equatorial and vice versa. See Fig. 21.

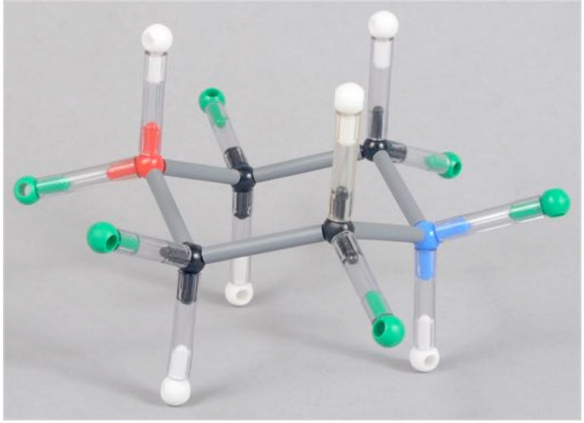


Fig. 21 Rotation of the ring atoms changes axial and equatorial orientation.

EXERCISE VII: 1,3-DIAXIAL INTERACTION.

A. Make a methyl group using three clear bonds, three white hydrogen atoms, a black-tetrahedral carbon atom, and a grey tube. Rotate the cyclohexane so that the blue atom is "up" again. Remove the green axial hydrogen and its clear bond from the blue carbon in the cyclohexane ring. Replace the hydrogen with the methyl group using the grey, rigid bond to attach it to the blue carbon. See Fig. 22.

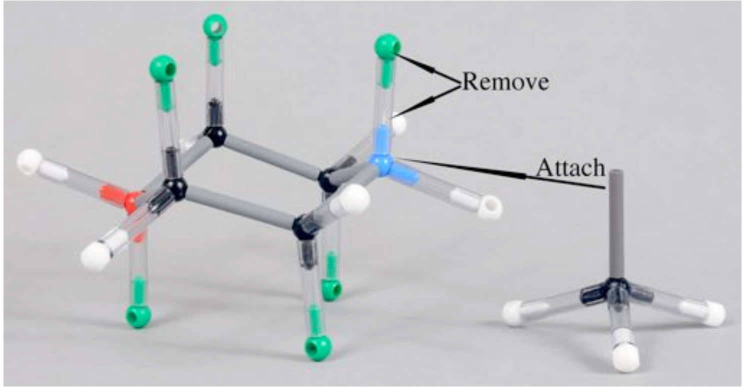


Fig. 22 Substituting a methyl group for a hydrogen on cyclohexane.

The substituting of the methyl for a hydrogen forms methylcyclohexane as you can see in Fig. 23.

Fig. 23 Methylcyclohexane.

B. Spin the methyl around on the rigid bond, and notice how close the methyl's hydrogens come to the hydrogens on the third and fifth carbons, creating 1,3-diaxial repulsions. See Fig. 24.

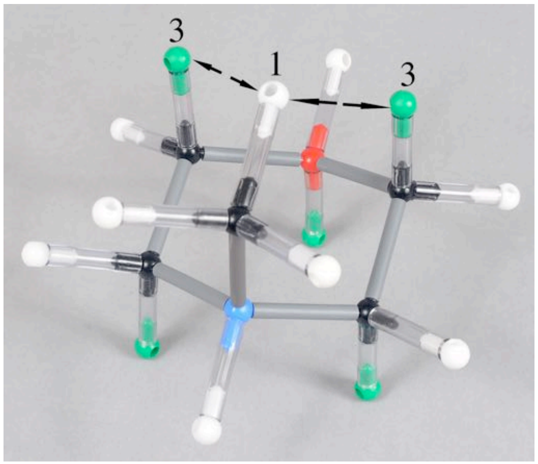


Fig. 24 1,3 Diaxial repulsions in a molecule of methylcyclohexane.

C. Now rotate the blue carbon down and the red carbon up. You will see the methyl group in the equatorial position and the elimination of the 1,3-diaxial hydrogen repulsions. See Fig. 25.

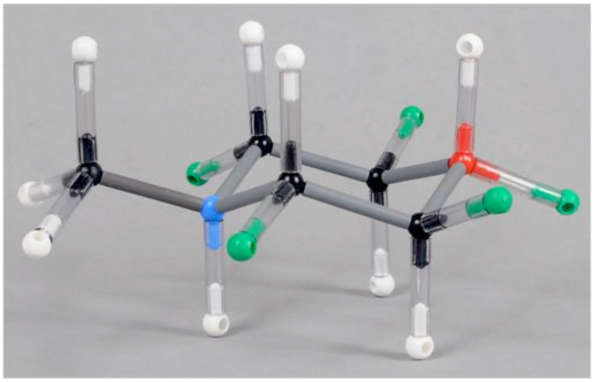


Fig. 25 Equatorial methylcyclohexane.

EXERCISE VIII: COMPARISON OF METHYLCYCLOHEXANE AND BUTANE.

Now hold the model of methylcyclohexane (in the chair conformation with the methyl in the axial position on the “up” blue carbon) so that the second carbon (black) obscures the first carbon (blue) as in the Newman projection in Fig. 26, and compare it to the Newman projection of butane in the gauche configuration.

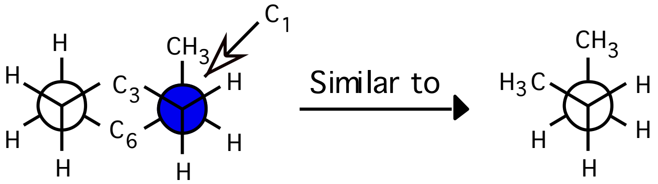


Fig. 26 Newman projections of methylcyclohexane and gauche butane.

If you remove the methyl and hydrogen from the blue carbon and switch their positions, you will see that the methyl (which is now equatorial), the blue carbon, and carbons 2 and 3 approximate anti butane. See Fig. 27.

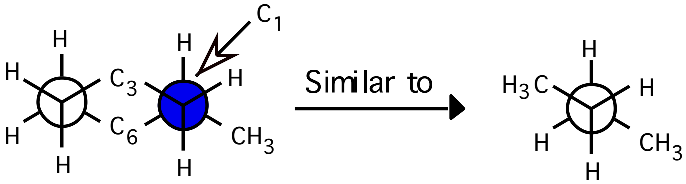


Fig. 27 Newman projections of methylcyclohexane and anti butane

Based on what you know of the energies of gauche and anti butane, which form of methylcyclohexane would have the lower energy level?

EXERCISE IX: DISUBSTITUTED CYCLOHEXANE.

A. Make three *cis*-dimethylcyclohexanes using a second methyl group each with three clear bonds, three white hydrogen atoms, a red-tetrahedral carbon atom, and a grey tube. Leave the methyl group with the black carbon on the blue atom (in the down position) on the ring.

Place the red methyl group in a *cis*-1,2-(Fig. 28) position in one model, a *cis*-1,3-(Fig. 29) position in a second model, and a *cis*-1,4-(Fig. 30) position in a third model.

When you are finished building the models, complete the table in Fig. 31. Write in the axial (a) or equatorial (e) position of each methyl group, first with the BLUE atom in the ring down, and then, after flipping the ring (BLUE UP; RED DOWN), determine the equatorial and axial positions again. The first blank has been filed in for you with e/a, meaning C1 is equatorial, and C2 is axial.

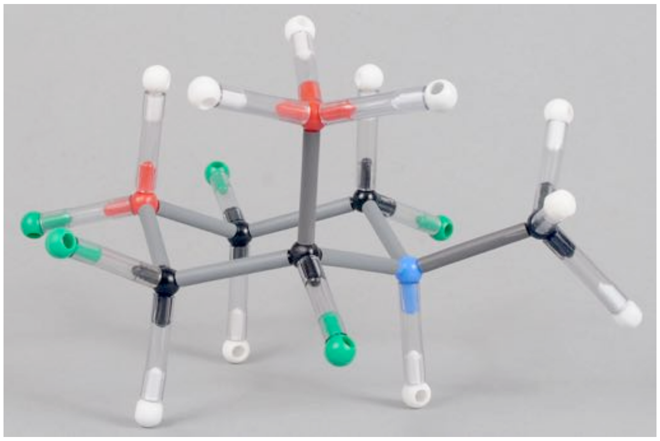


Fig. 28 *cis*-1,2-dimethylcyclohexane.

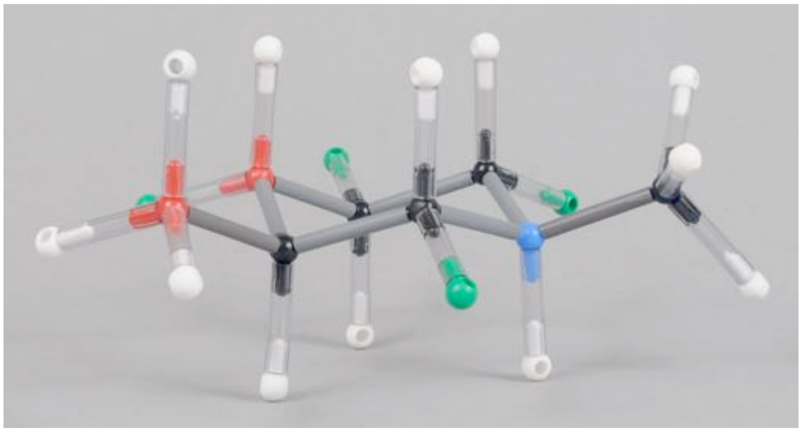


Fig. 29 *cis*-1,3-dimethylcyclohexane.

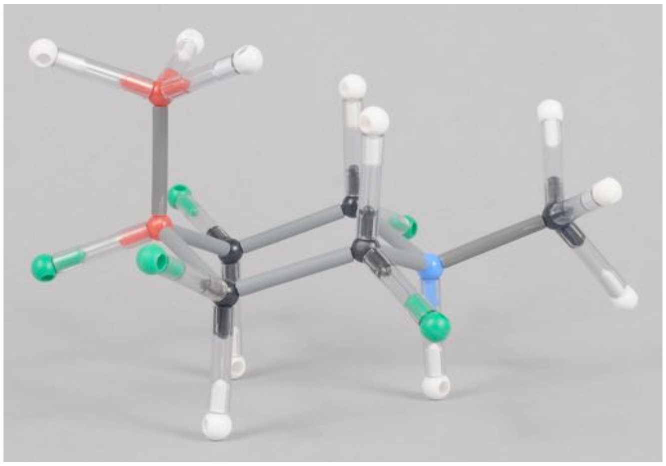


Fig. 30 *cis-1*,4-dimethylcyclohexane.

Cis-dimethylcyclohexane Chair Conformations

METHYLS ON CARBONS	*CIS*-DIMETHYLS	
	BLUE DOWN	BLUE UP
1,2	e/a	________
1,3	________	________
1,4	________	________

Fig. 31 A table used to describe the equatorial or axial position of a methyl group.

B. Make three *trans*-dimethylcyclohexanes using a second methyl group each with three clear bonds, three white hydrogen atoms, a red-tetrahedral carbon atom, and a grey tube. Leave the methyl group with the black carbon on the blue atom (in the down position) on the ring.

Place the red methyl group in a *trans*-1,2-(Fig. 32) position in one model, a *trans*-1,3- (Fig. 33) position in a second model, and a *trans* -1,4-(Fig. 34) position in a third model.

When you are finished building the models, complete the table in Fig. 35. Write in the axial (a) or equatorial (e) position of each methyl group, first with the BLUE atom in the ring down, and then, after flipping the ring (BLUE UP; RED DOWN), determine the equatorial and axial positions again. The first blank has been filed in for you with e/a, meaning C1 is equatorial, and C2 is axial.

Which of the above axial-equatorial combinations has the lowest energy?

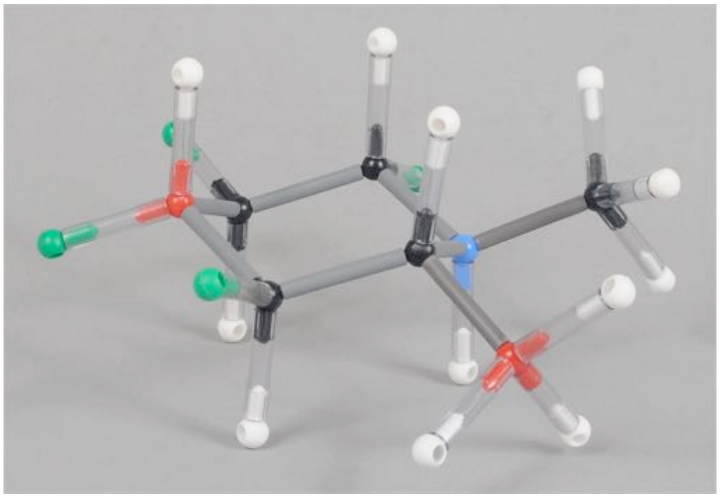


Fig. 32 *trans*-1,2-dimethylcyclohexane

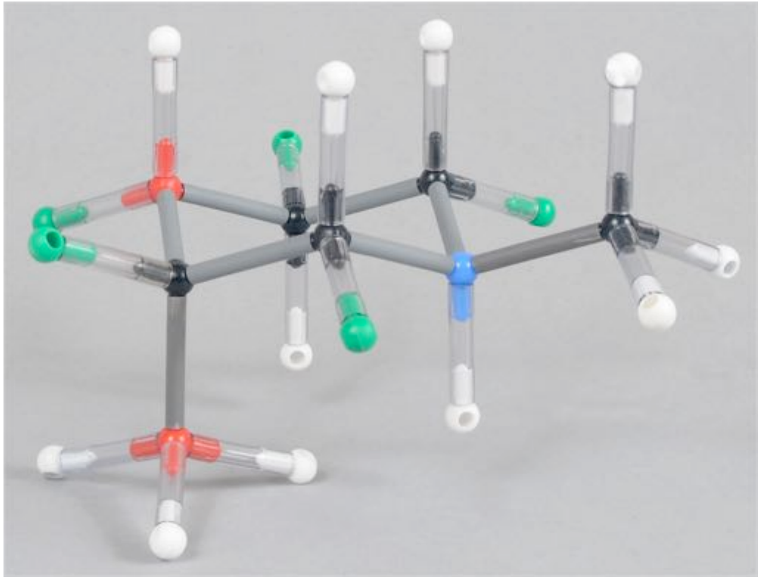


Fig. 33 *trans*-1,3-dimethylcyclohexane

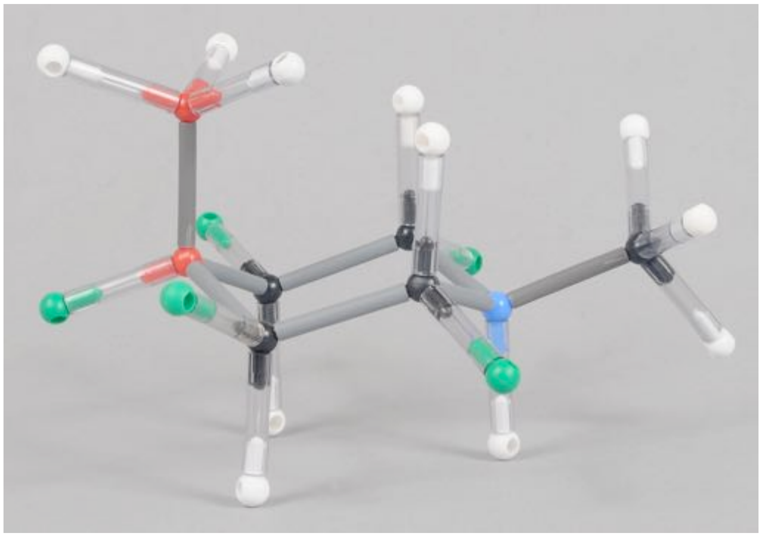


Fig. 34 *trans*-1,4-dimethylcyclohexane

Trans-dimethylcyclohexane Chair Conformations

METHYLS ON CARBONS	*TRANS*-DIMETHYLS	
	BLUE DOWN	BLUE UP
1,2	e/e	________
1,3	________	________
1,4	________	________

Fig. 31 A table used to describe the equatorial or axial position of a methyl group.

Which of the above axial-equatorial combinations has the lowest energy?

EXERCISE X: CHEMICAL SYMBOLISM.

A. It is expedient sometimes to show a complex biochemical structure in an abbreviated form. For example, cyclohexane (C_6H_{12}) can be drawn as a simple hexagon. A carbon atom is understood to be located where two lines intersect. We also assume two hydrogen atoms are bonded to each carbon, since carbon atoms always make four bonds. On the left in Fig. 35, all of the bonds and atoms are drawn in. On the right, the skeletal structure only shows bonds.

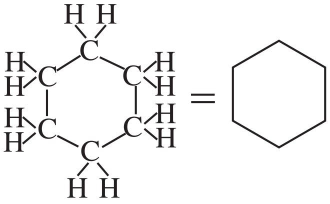


Fig. 35 A shorthand method of drawing a molecule of cyclohexane.

There are four methods of making a molecular diagram of a benzene ring. This also applies to a phenyl group which is benzene minus one hydrogen atom. This structure should be assembled by using six of the black, three-peg carbon atoms. See Fig. 36.

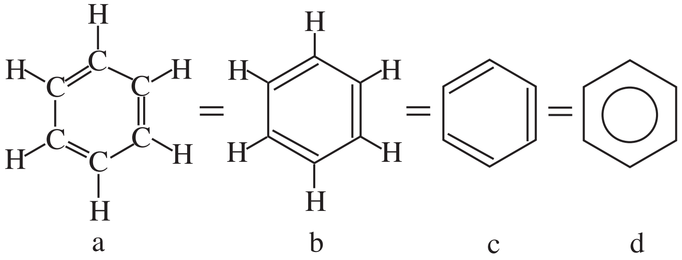


Fig. 36 Four ways to draw a benzene ring or a phenyl group.

The display of bonds and H atoms is also avoided in other structures as illustrated below. See Figs. 37, 38, 39, and 40.

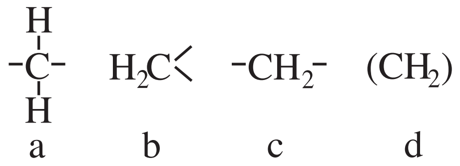


Fig. 37 Four examples of a methylene group.

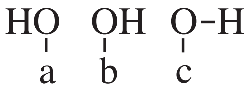


Fig. 38 Three examples of an hydroxyl, or hydroxy group.

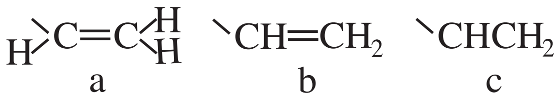


Fig. 39 Three examples of an alkene (double bonded carbons) group.

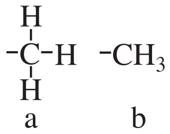


Fig. 40 Two examples of a methyl group.

Greater simplification is possible when we leave out carbon and hydrogen atoms as you can see in Fig. 41.

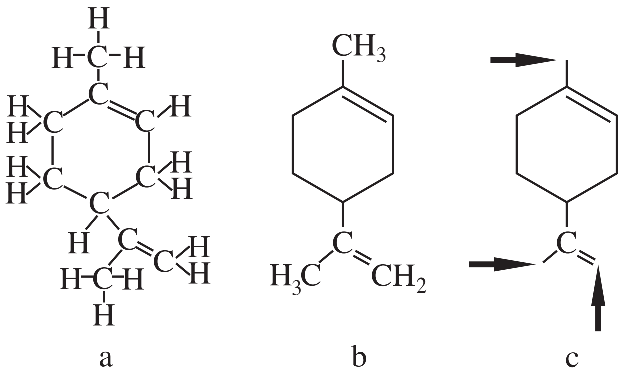


Fig. 41 From complex to simpler diagrams as we move from letter a to letter c.

Notice that at the “open” end of a bond, indicated by the arrows in “c,” above, you will find a carbon atom. Count the bonds shown attached to a carbon atom, then subtract this number from four. The result is the number of hydrogen atoms you should consider attached to the carbon atom.

Count the numbers of carbons, hydrogens, oxygens, single bonds, double bonds, and the total number of bonds in the structural formula of elemicin below in Fig. 42.

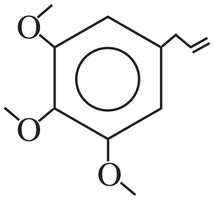


Fig. 42 Elemicin

Answers: carbons—12; hydrogens—16; oxygens—3; single bonds—31; double bonds—4; total number of bonds—35.

Next consider the method for simplifying the formulas of organic acids and aldehydes which are both composed of atoms of carbon, hydrogen and oxygen as you see below in expanded (a) and condensed (b) forms. See Fig. 43.

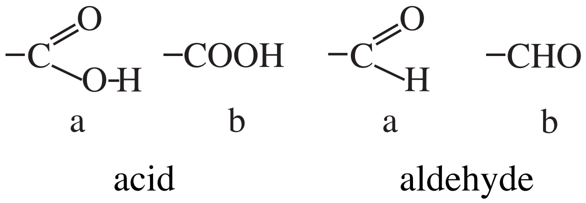


Fig. 43 Expanded and condensed forms of organic acids and aldehydes.

EXERCISE XI: CHIRALITY.

As you study this section, make models to aid in your visualizing the concepts.

A. We will start with enantiomers which are chiral molecules that have at least one chiral carbon. Chiral carbon atoms have four different atoms or groups of atoms bonded to them. In some instances, it is possible to have two different arrangements of the same four bonded groups on a carbon atom. A carbon atom of this description is known by several names such as stereogenic center, stereocenter, chirality center, asymmetric carbon, chiral carbon, or chiral center. We will call it a chiral carbon, and start our discussion of optical isomers with some simple compounds. Fig. 44 has a list of symbols that will be helpful in visualizing molecular structures.

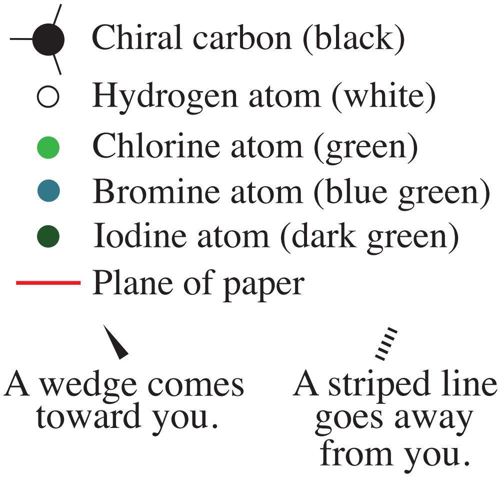


Fig. 44 Symbols for understanding chirality.

A molecule with two or more groups of the same type will not be chiral due to the presence of an internal plane of symmetry. The molecule will be in perfect alignment with its mirror image. The drawing at the top of Fig. 45 is a view of the molecule looking down on the chlorine atom..

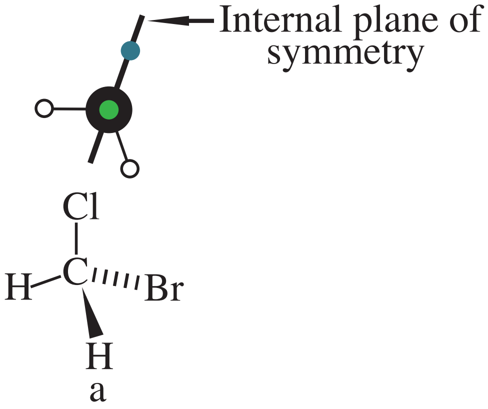


Fig. 45 A molecule with no chiral carbon and is not chiral.

A molecule with only one chiral carbon will not be in perfect alignment (be superimposable) on its mirror image. The molecule itself is called chiral. Chiral comes from the Greek word for hand, so chiral molecules have “handedness,” (i.e. a left and a right handed form). Chiral molecules are called enantiomers.

In structural diagrams, solid lines are bonds that link atoms which lie in the plane of the paper; those that are in front of the plane are connected by solid wedges; those that go behind the plane are bonded by a series of stripes. An asterisk (*) identifies a chiral carbon.

Use the key presented in Fig. 44 to make a model of bromochloroiodomethane. Also make its enantiomer. See Fig. 46.

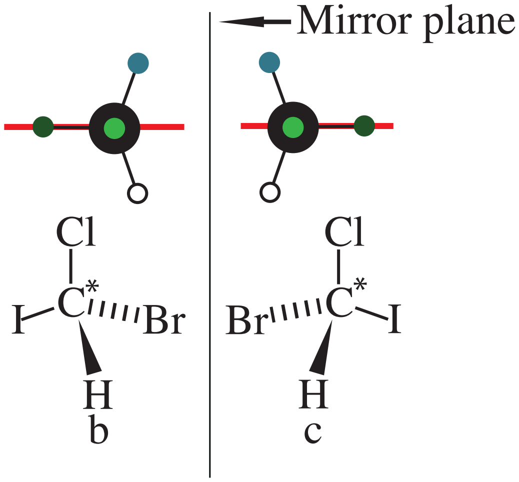


Fig. 46 Enantiomers of CHBrClI (bromochloroiodomethane).

At the top of Fig. 46, you see the view of the two molecules looking down on the chlorine atoms. Notice that “b” and “c” are mirror images of one another. The two different forms of CHBrClI share the same sets of chemical and physical properties with only a few exceptions which depend on chirality.

B. Now we would like to know which one is left hand and which one is right handed. In this section we will learn the procedure for determining the “handedness,” that is, the absolute configuration of “b” and “c.”

Step 1. Make sure that the atom with the lowest atomic weight on the chiral carbon is pointing away from you. In most, but not all, of the molecules you will encounter, it will be a hydrogen atom (at. wt. 1). In order to get “b” into the correct position, grab the chlorine of “b” and turn it clockwise 180° so that it looks like “e.” See Fig. 47.

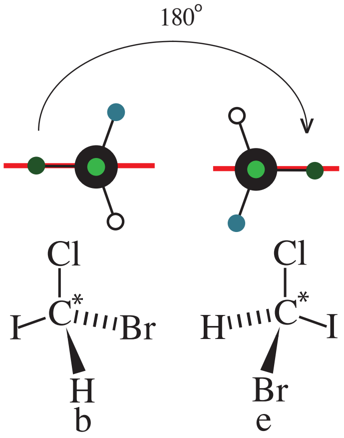


Fig. 47 Positioning –H behind the plane of the paper.

Step 2. Find the atomic weight of each other atom immediately bonded to the chiral carbon.

Step 3. Assign values from 1 to 4 to the atoms based on their atomic weights. The lower the weight, the lower the priority. Here, H = 4 (lowest priority). The other atomic weights are Cl = 35, Br = 80, I = 127. Therefore, Cl gets a 3, Br gets 2, and I has priority 1.

Step 4. We already placed H = 4 in back, so now we trace a path from 1 to 2 to 3. The path travels clockwise, so we have discovered that “b” is right handed. See Fig. 48.

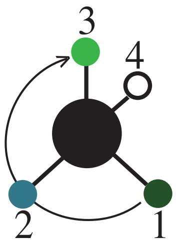


Fig. 48 Right handed CHBrClI.

Step 5. The way we indicate handedness is by using the Cahn-Ingold-Prelog (CIP) system naming a right handed molecule with the prefix (*R*)-, and a left handed molecule with the prefix (*S*)-. The CHBrClI "b" which we used to learn the procedure would then, be called (*R*)-bromochloroiodomethane. Its "c" enantiomer in Fig. 46 is called (*S*)-bromochloroiodomethane.

The same parts are present, just the way they are arranged in space is different.

In Fig. 49, there is a photograph of the isomers of bromochloroiodomethane. Which one is (*R*), and which one is (*S*)?

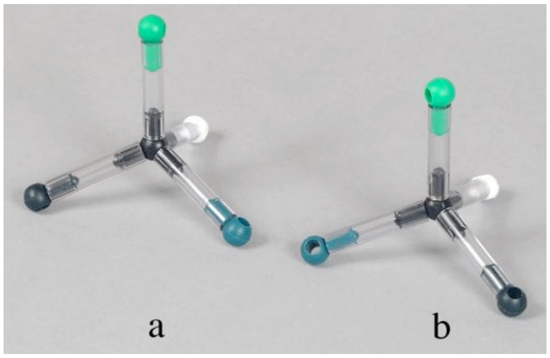


Fig. 49 Identify the chirality of "a" and "b."

Answers: "a" is the (*S*) isomer. "b" is the (*R*) isomer.

B. The following photograph in Fig. 50 presents a problem which is a little more challenging. Which one is (*R*), and which one is (*S*)?

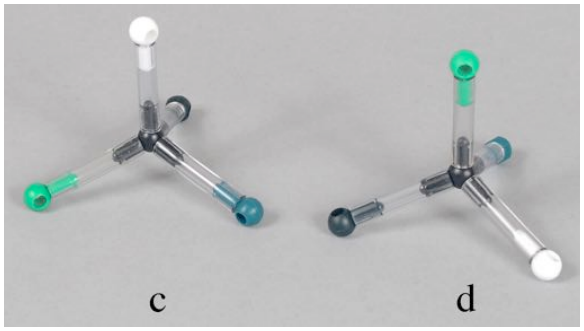


Fig. 50 Identify the chirality of "c" and "d."

There are three approaches you can try here. 1) Make models, and turn them to see the H in the back. 2) In your mind, flip the pictures around so that the H is in the back, and then make your determination. 3) Again using your imagination, switch the H and any other atom so that the H is in the back. Determine the clockwise or counterclockwise path from 1 to 3. You will find an (*R*) or (*S*) answer, but since you made the allowable switch of atoms, you must switch your answer to the opposite chirality.

Answers: "c" is (*S*), and "d" is (*R*).

C. The molecules you just looked at were quite simple, but most of the chemicals you will encounter have many more atoms. Therefore, we should learn about the chirality of molecules with greater complexity. Are there any chiral carbons in Fig. 51?

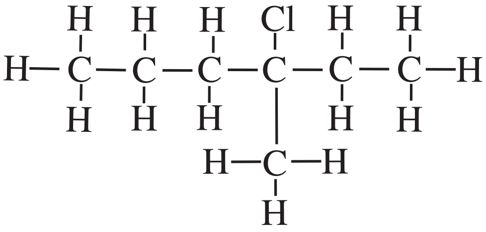


Fig. 51 Do you see any chiral carbons here?

Answer: Fig. 51 has only one chiral carbon which is marked with an asterisk (*).

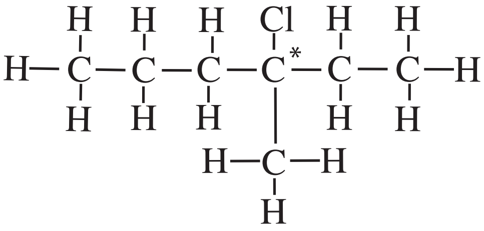
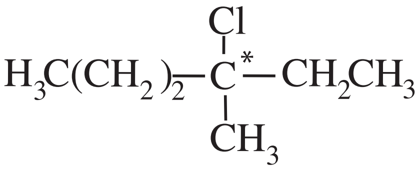


Fig. 52 3-chloro-3-methylhexane with one chiral carbon.

Converting the molecule in Fig. 52 to a condensed formula, we will see Fig. 53.



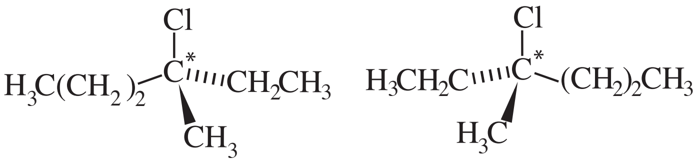
$$H_3C(CH_2)_2-\overset{Cl}{\underset{CH_3}{C^*}}-CH_2CH_3$$

Fig. 53 Condensed form of 3-chloro-3-methylhexane.

Using straight lines in the plane of the paper, a dashed line, and a wedge, draw one of the isomers of 3-chloro-3-methylhexane. There are only two isomers of the compound, so you can not make a mistake.

A valuable fact you might want to know is that there are a maximum of 2^n isomers for a compound with n chiral carbons. However, some of the isomers may not exist. So, with one chiral carbon, a compound might have two isomers. With two chiral carbons, four isomers are possible, and so on.

Your structural formulas should look like the two enantiomers in Fig. 54.



a

b

Fig. 54 The two enantiomers of 3-chloro-3-methylhexane.

Is "a" (*R*), or (*S*)?

Answer: "a" is (*S*), so then "b" is (*R*).

Here is how we determined the answers. Inspection of the atoms immediately bonded to C* shows that the chlorine atom (Cl) has the highest atomic weight (35), so Cl has highest priority value of 1. The other three atoms are tied at atomic weight 12 each. See Fig. 55.

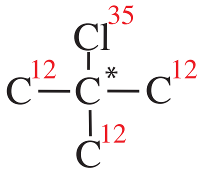


Fig. 55 The first step in finding chirality.

In order to break the tie among the three carbon atoms, we set up the following diagrams in Fig. 56.

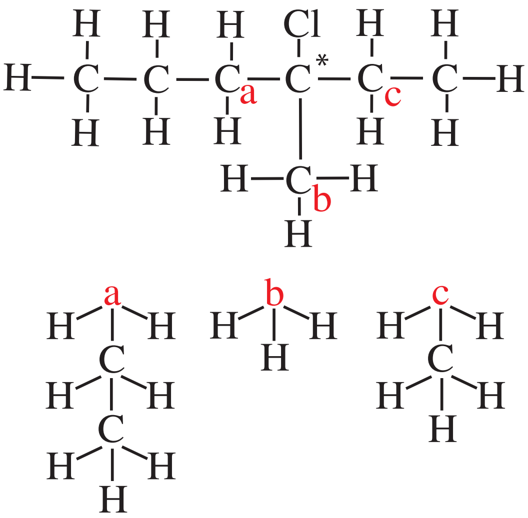


Fig. 56 Finding the distribution of mass.

"a" has the second most mass, so its priority is 2; "c" is next, and "b" has the lowest priority. $-CH_3$ should be placed in back of the plane of the paper in order to determine (*R*), and (*S*) enantiomers.

D. Now we will demonstrate the concept with an even more complex molecule; carvone. See Fig. 57.

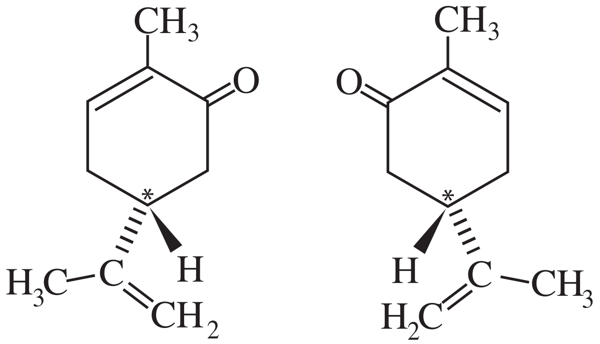


Fig. 57 Carvone.

Make models of the two structures. Can one be superimposed on the other by flipping the carvone that is on the right side of Fig. 57 so that it looks like Fig. 58? Are they enantiomers? If they are enantiomers which one is (*R*), and which one is (*S*)? Observe the labeling of the carbons in Fig. 58.

The chiral carbon is marked with an *, and the H atom can immediately be assigned the lowest priority (4).

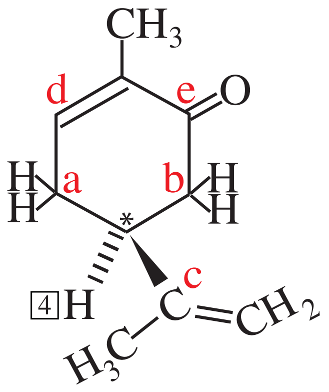


Fig. 58 Carvone set up for (*R*), (*S*) determination.

Fig. 59 shows what is found following the bonds from "a" and from "b."

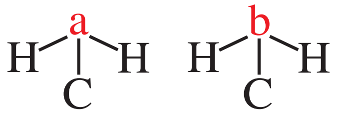
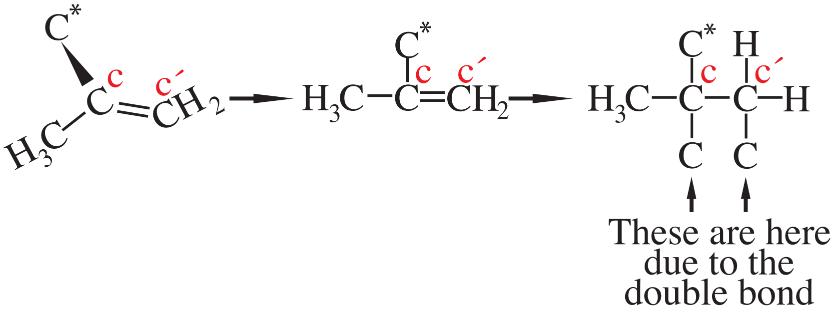


Fig. 59 The same results at "a" and "b."

The atoms at "c" make up a group called methylethenyl. Because the group has a double bond, we must make some changes in its structure before we can determine its weight value.

The "c" carbon is joined with another carbon, c-prime (c´), through a double bond. Each carbon is treated as though it were bonded with **two** other carbon atoms, not one. On the right side of Fig. 60, the two additional carbon atoms are shown.



These are here due to the double bond

Fig. 60 Expanding methylethenyl to include extra carbon atoms.

Now we can better compare “a,” “b,” and “c.” “c” clearly has the highest priority of the three. Its priority is a 3. See Fig. 61.

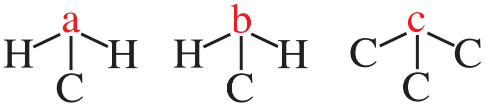


Fig. 61 With three carbons joined to it, “c” has the highest priority.

We still have a tie between “a” and “b” to break, so we use the same analytical technique on them as we used on “c.” See Figs. 62 and 63.

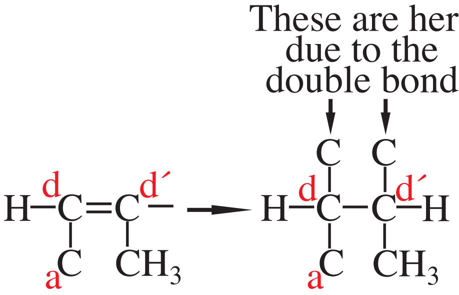

These are here due to the double bond

Fig. 62 Expanding groups around “d” to include extra carbon atoms.

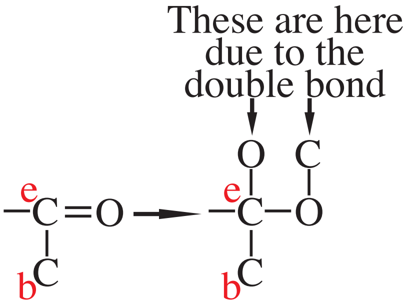

These are here due to the double bond

Fig. 63 Expanding groups around “e” to include an extra carbon and oxygen atom.

Fig. 64 is a summary of what we found in making Figs. 62 and 63.

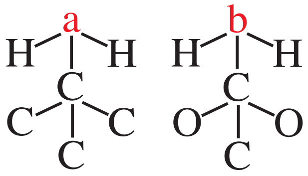


Fig. 64 Showing the preference of “b” as priority 2 and “a” as priority 3.

So, the structure we worked so hard on is the(*S*) enantiomer, the one that tastes like caraway seeds. The (*R*) enantiomer has the taste of spearmint. This is just one example of how important chirality is in biological molecules. See Fig. 65.

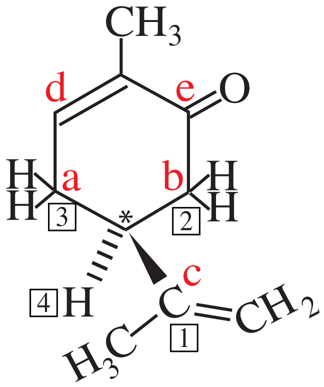
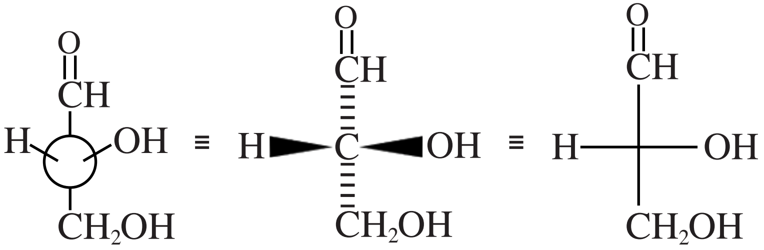


Fig. 65 (*S*)-carvone.

E. Glyceraldehyde, a chiral molecule, can be represented by a ball and stick formula (Fig. 66a), a dimensional formula (Fig. 66b), and a Fischer projection (Fig. 66c). The three illustrations are equivalent, i.e., they show the same groups arranged in the same way.



a. Ball and stick formula

b. Dimensional formula

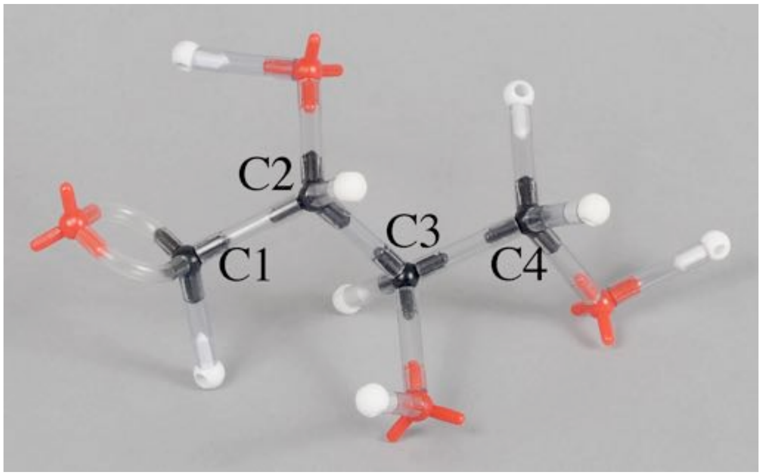
c. Fischer projection

Fig. 66 Equivalent representations of glyceraldehyde.

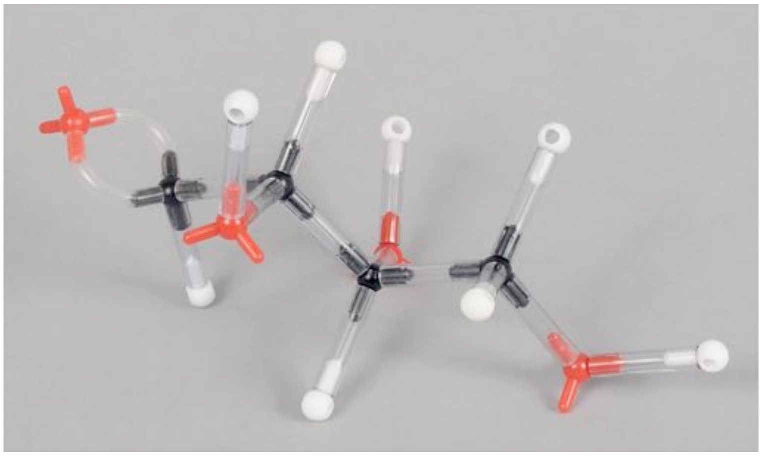
Make a determination of the absolute configuration glyceraldehyde you see in Fig. 66, and then Make a model of it in order to prove your evaluation. Is it (*R*) or (*S*)?

EXERCISE XII: TWO CHIRAL ATOMS IN ONE MOLECULE.

A. Construct a molecule of erythrose (2,3,4-trihydroxybutanal) and its enantiomer (Fig. 67).



a

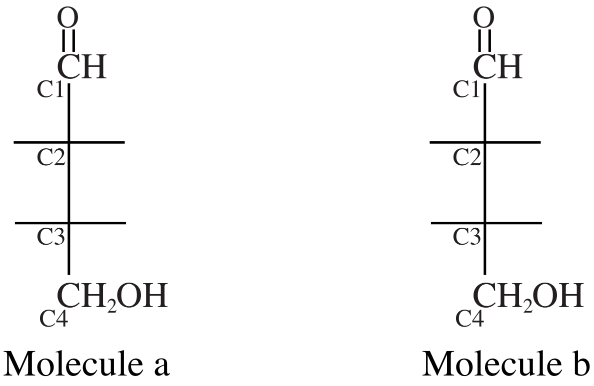


b

Fig. 67 Two enantiomers of erythrose, each with two chiral carbons.

B. By placing one isomer model on the other, you can confirm that they are enantiomers because they are mirror images, and one cannot be superimposed on the other. Now determine the absolute configuration of the isomers shown in Fig. 67. You should have found that “a” is (2*R*,3*R*). Molecule “b” has the configuration (2*S*,3*S*). Note that enantiomers will always have the opposite absolute *R* and *S* chiral carbons.

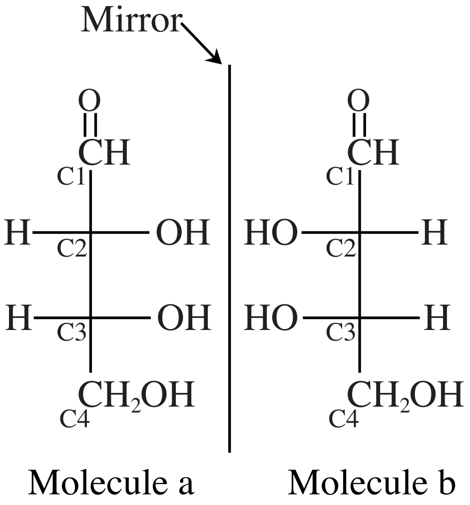
C. If you had difficulty in determining the *R* and *S* configurations, convert the above photos into Fisher projections first. C1 and C4 will be pointing away from you, so just put them at the ends of the vertical line. Fill in the “a” and “b” diagrams in Fig. 68. To make a determination of where to place the hydroxy groups (—OH), just look at the carbon it is bonded to in an “up” position. C2 is already up, and the —OH is on the right, so put it on the right in the diagram for “a” in Fig. 68. To find the placement of —OH on C3 in “a,” turn the molecule over so that C3 is “up.” The C3 —OH is on the right, so put it in the proper place in Fig. 68, “a.” With some practice, you will be able to “flip” a molecule in your mind.



Molecule a Molecule b

Fig. 68 Complete the Fisher projections above.

This what you projections should look like, side by side. Note that they are mirror images (enantiomers). See Fig. 69.

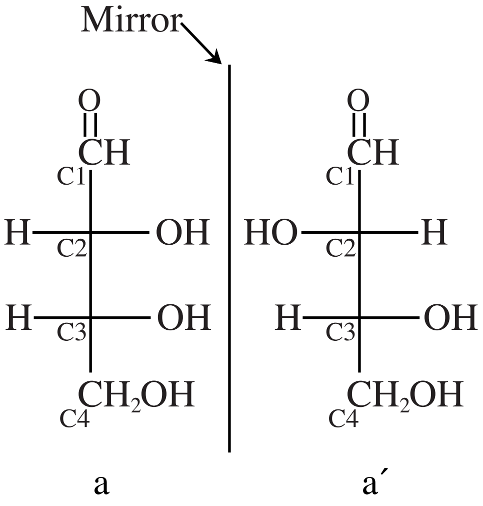


Molecule a Molecule b

Fig. 69 D-erythrose on the left, and L- erythrose on the right.

EXERCISE XIII: DIASTEREOMERS.

Switch the —OH and —H groups bonded to C3 of Molecule b shown in Fig. 69b. Is this new model, Molecule “a′” a mirror image of “a”? Is “a′” an enantiomer of “a”?



a a′

Fig. 70 D-erythrose (a) and a stereoisomer, D-threose (a′).

D-erythrose (a) and a **stereoisomer** D-threose (a′) are stereoisomers that are **not** enantiomers; they are **not** mirror images of one another. They are **diastereomers**.

EXERCISE XIV: *MESO* COMPOUNDS.

Build a model of tartaric acid, its mirror image, and its diastereomer (Fig. 71).

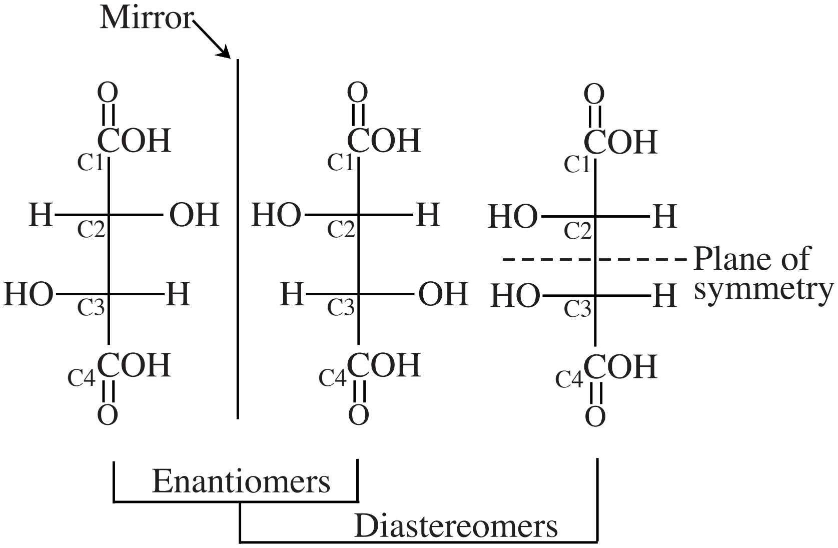


Fig. 71 Tartaric acid, its mirror image, and the diastereomer of both.

Since an internal plane of symmetry can be drawn through the diastereomer, it is not a chiral molecule. The upper half is the mirror image of the lower half, and each half will cancel the chirality of its internal mirror image. Molecules with this property are called *Meso* compounds. This is an example of an achiral with more than one chiral carbon.

EXERCISE XV: CYCLIC ALKANES WITH CHIRAL CARBONS.

A. Now we turn our attention to models of *cis*- and *trans*-1,2-dimethyl-cyclopropane. Make the *cis*- form first, then construct its mirror image, try to superimpose the models (Fig. 72). Are you able to superimpose them?

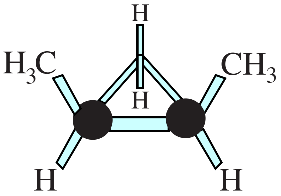


Fig. 72 *cis*-1,2-dimethylcyclopropane.

Can you see a plane of symmetry in the molecule? Look at Fig. 73.

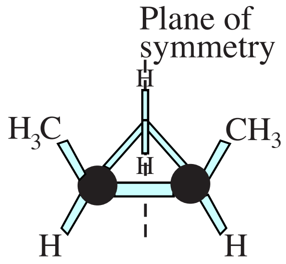
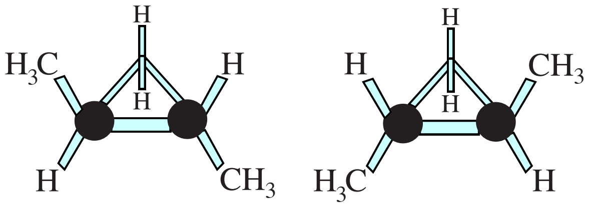


Fig. 73 *cis*-1,2-dimethylcyclopropane with an internal plane of symmetry.

B. Rearrange one methyl group in both models so that you have the *trans* isomer and its mirror image (Fig. 74). Do the molecules have an internal plane of symmetry? Do you now have a pair of enantiomers? Are there chiral carbons in the models? Do they have different properties?



a b

Fig. 74 *trans*-1,2-dimethylcyclopropane enantiomers.

There is no plane of symmetry in either molecule. “a” and “b” are enantiomers. There are two chiral carbons in each molecule. Except for rotating polarized light in opposite directions and reacting with other chiral molecules differently, they have the same chemical and physical properties.

<u>EXERCISE XVI: GEOMETRIC (*CIS/TRANS*) ISOMERISM.</u>

A. The presence of one or more double bonds in an organic compound could, if the right conditions obtain, result in another type of stereoismerism. If there is asymmetry on both carbons of a double bond, diastereomers will exist. That is if “a” and “a´” are different, **and** if “b” and “b´” are different, then *cis*- or *trans*-diastereomers will exist. See Fig. 75.

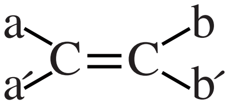
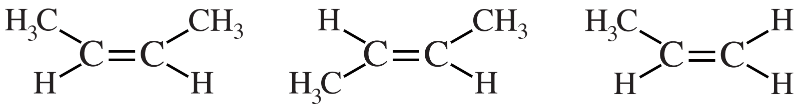
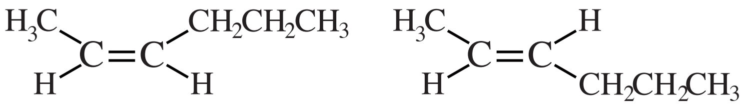


Fig. 75 The conditions that must be met for *cis/trans* isomerism to exist.

B. When the groups bonded to the carbons of the double bond are not too complex naming geometric isomers using *cis/trans* terms is not difficult. *cis* means “on the same” side, and *trans* means “on the opposite” side. Examine these molecules in Fig. 76 on the next page for examples.



cis-2-butene *trans*-2-butene Neither *cis* nor *trans*
This is propene



cis-1-hexene *trans*-1-hexene

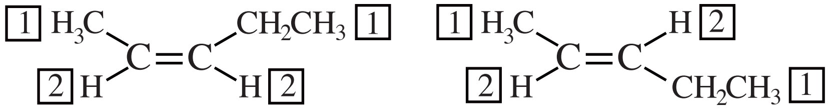
Fig. 76 Some examples of using *cis/trans* naming protocol.

C. Naming geometric isomers when confusion might result using *cis/trans* terms is facilitated by the use of the *E/Z* system instead. What prefix can we use for the 3-methyl-2-pentene molecules in Fig. 77?

a b

Fig. 77 Is “a” *cis* or *trans*? Is “b” *cis* or *trans*?

The solution to the naming problems is to use the CIP priority system we used to name *R/S* structures. Find the heaviest group on each carbon, and give it priority 1. The other group on the same carbon gets a 2. If the 1’s are on the same side, across the double bond, the molecule gets the prefix *Z* (for the German word zusammen, meaning together). If the 1’s not on the same side across the double bond, use the prefix *E* (for the German word entgegen, meaning opposite). How, then, would you name “a” and “b” in Fig. 77. Fig. 78 gives the solution.



a b

Fig. 78 “a” is (2*Z*)-3-methyl-2-pentene. “b” is (2*E*)-3-methyl-2-pentene.