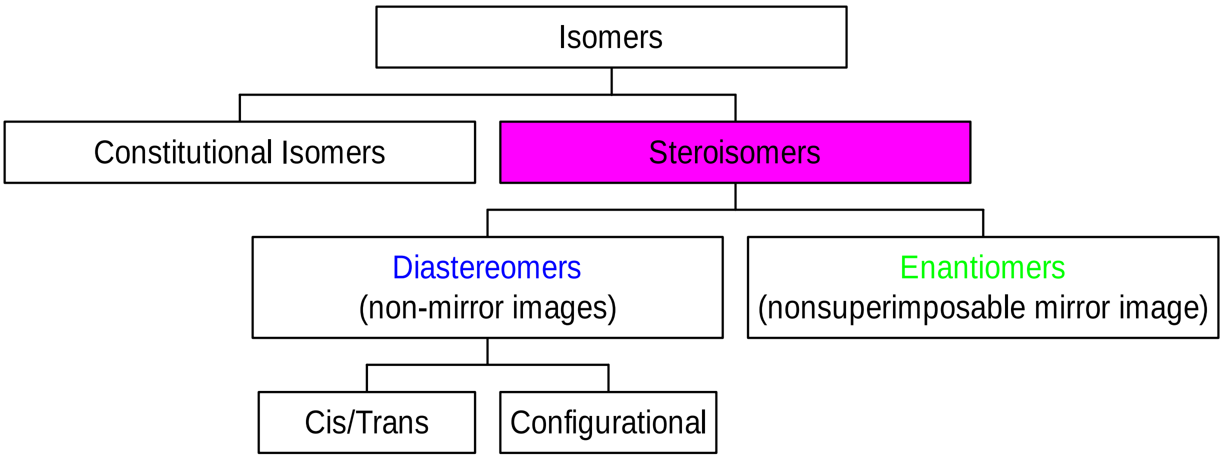
Stereochemistry

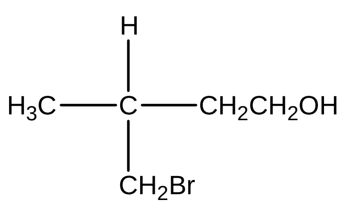


Stereoisomers—compounds in which atoms are connected in the same order but with different geometry.

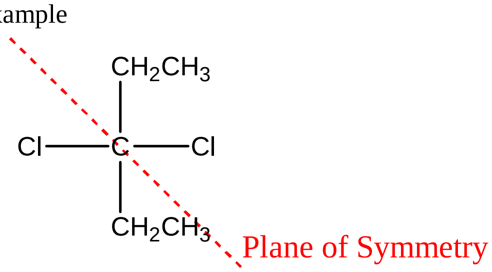
Chirality—molecules that are not superimposible with their mirror images are said to be chiral. Chiral molecules exist in two enantiomer forms, which can be thought of like left hand and a right hand.

A molecule is chiral if it does not contain a plane of symmetry.

Example



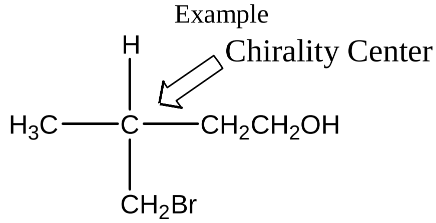
Chiral



Achiral

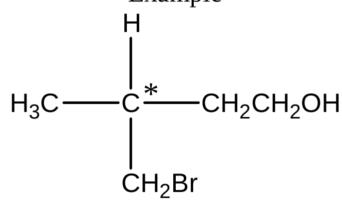
Carbons bonded to 4 different atoms or groups are known as chiral carbons/chirality centers. Chirality centers give rise to chirality. However, not all molecules with chirality centers are chiral.

Example



Chiral carbons are often indicated with an *.

Example



Optical Activity

Plane polarized light—light that is passed through a polarizer so that it only oscillates in a single plane.

When a beam of plane polarized light passes through a solution of certain organic molecules, the plane is rotated. Molecules that cause the plane to rotate are called Optically Active. Chiral molecules are optically active. The amount of rotation, written as α, can be calculated using a polarimeter and is given in degrees.

- Molecules that rotate the plane of polarized light to the left (counterclockwise) are levorotatory (-).
- Molecules that rotate the plane of polarized light to the right (clockwise) are dextrorotatory (+).

Specific Rotation $[\alpha]_D$—the observed rotation when the sample pathlength *l* is 1 dm, the sample concentration C is 1 g/mL, and the light's wavelength used is 589 nm.

$$[\alpha]_D = \frac{\text{Observerd Rotation (degrees)}}{\text{pathlength, } l \text{ (dm) x concentration, C (g/mL)}} = \frac{\alpha}{l \times C}$$

Practice Problem

1) Morphine has a specific rotation of –132. If a lab student uses a sample that has a concentration of .0128 g/mL and a path length of 1 dm, what would she expect the observed rotation to be?

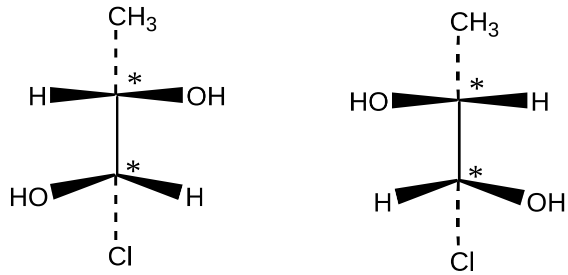
Answer

Enantiomers

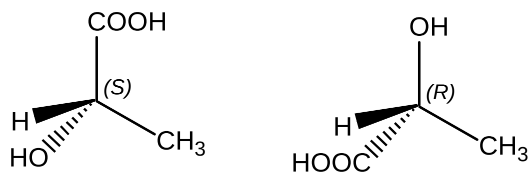
Enantiomers are superimposable mirror images

Examples

1)



2)



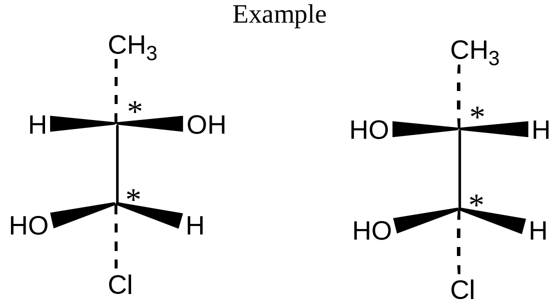
Enantiomers have the same physical properties and spectroscopic properties. They are identical in all respects except in how they affect plane polarized light.

Diastereomers

Molecules with more than one chiral carbon can exist not only as enantiomers, but also as diastereomers, another type of stereoisomer.

Diastereomers are non-superimposable non-mirror images

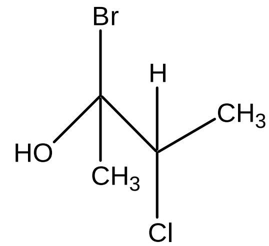
Example



The maximum number of stereoisomers a molecule can exist as is equal to 2^{n+m}, where n is the number of chiral carbons and m is the number of double bonds (primarily carbon-carbon double bonds).

Practice Problem

2) What is the maximum number of stereoisomers for:



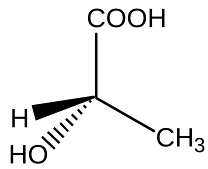
Answer

<u>R, S Configuration</u>

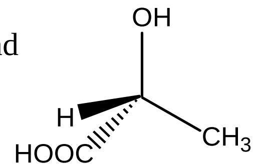
1) Assign priorities to each of the four atoms directly bonded to the chiral center with 1 being the highest and 4 the lowest. The atom with the highest atomic number is given first priority, as with E,Z designation.
2) If a decision about priority cannot be made by looking at the atoms bonded directly to the chiral carbon, consider the second atom in the substiuent, comparing each substituent atom by atom until a difference can be found.
3) Multiple-bonded atoms should be counted as having the same number of single-bonded atoms.
4) View the molecule so that the lowest priority atom is in the back.

- The chiral carbon is R if the first priority to third priority atoms are arranged in a clockwise direction.
- The chiral carbon is S if the first priority to third priority atoms are arranged in a counterclockwise direction.

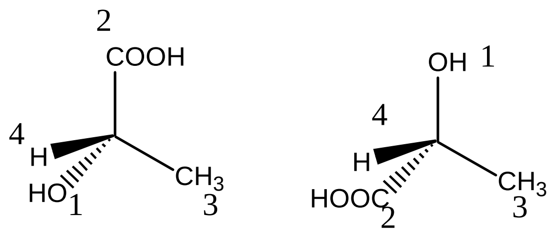
Example:



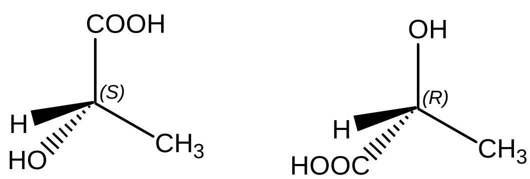
and



Assign Priorities



These enantiomers are drawn such that the lowest priority atom is in the front. It is coming towards you. In order to determine which is R or S you must either 1) imagine yourself to be standing behind the molecules looking out (so that the hydrogen is in the back), or 2) you can simply reverse whatever answer you would get from viewing the molecule as it is with the lowest priority atom in the front. For instance, the left molecule has the first to third priorities arranged clockwise, which would be an R if the hydrogen were in the back. However, since the lowest priority atom is in the front, reverse this answer to an S. By the same reasoning, the molecule on the right is an R.

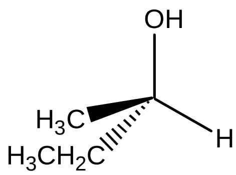


When dealing with molecules with more than one chiral carbon, assess each chiral carbon individually when determining whether it is R or S.

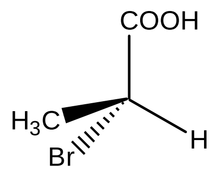
Practice Problems

3) Determine the R/S configuration for the following molecules:

a.



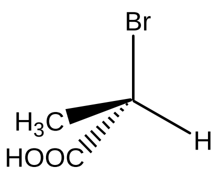
b.



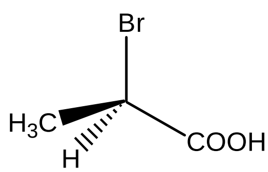
Answer

4) Which of the following are enantiomers?

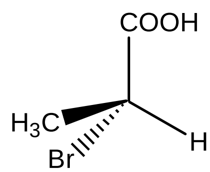
a.



b.

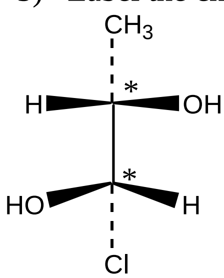


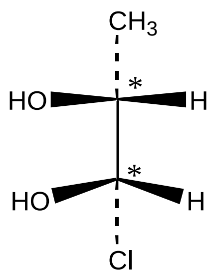
c.



Answer

5) Label the chiral carbons (indicated by an *) as R or S:



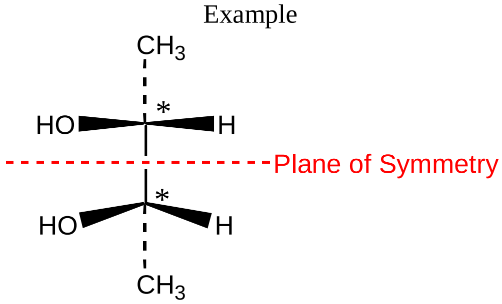


Answer

<u>Meso Compounds</u>

Meso Compounds are compounds that contain chirality centers but are achiral.

Example



Meso compounds are not optically active.

<u>Racemic Mixtures</u>

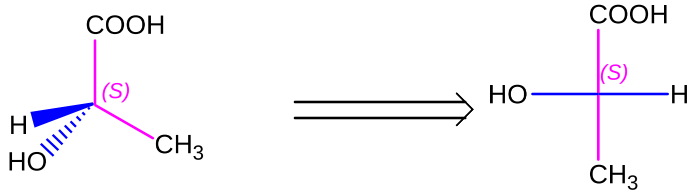
Racemic Mixtures—A 50:50 mixture of the two enantiomers.

Racemic Mixtures give a net rotation of plane polarized light equal to zero. The amount of each enantiomer is equal so that each cancels out the other's effects on plane polarized light.

<u>Fischer Projections</u>

Fischer Projections, like Newman Projections, are a way to represent the three dimensional arrangement of molecules. A Fischer Projection, representing a tetrahedral carbon consists of 2 crossed lines.

Example



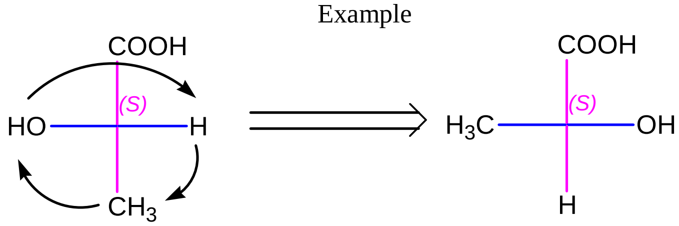
- Horizontal lines represent bonds coming out of the page.
- Vertical lines represent bonds going into the page.

To determine a molecules R or S configuration from a Fischer Projection, move the lowest priority atom to the top position, following the rules for movement listed below, before assessing whether the three highest priorities are in a clockwise (R) or counterclockwise (S) direction.

Allowable Moves:

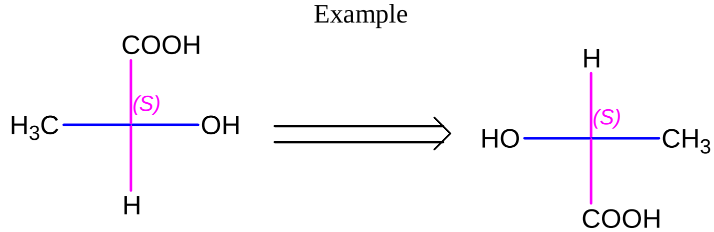
1) Hold one group fixed and rotate the other three in a clockwise or counterclockwise direction.

Example



2) Rotate the projection 180°

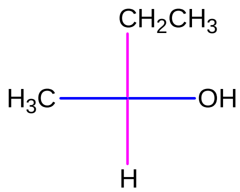
Example



Practice Problem

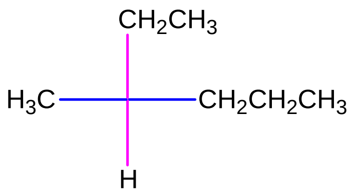
6) Assign R/S configurations to the following Fischer Projections:

a.



Answer

b.



Answer

Answer

1) Morphine has a specific rotation of –132. If a lab student uses a sample that has a concentration of .0128 g/mL and a path length of 1 dm, what would she expect the observed rotation to be?

$$C = .0128,\ l = 1,\ [\alpha]_D = -132$$

$$-132 = \frac{\alpha}{1 \times .0128}$$

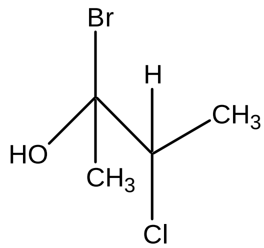
$$\alpha = -1.6896$$

approximately –1.69

Return to Problem

Answer

2) What is the maximum number of stereoisomers for:



2 chiral carbons. 0 double bonds.

n = 2, m = 0

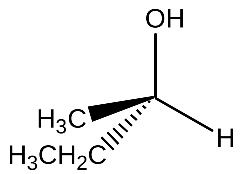
$2^{n+m} = 4$

Return to Problem

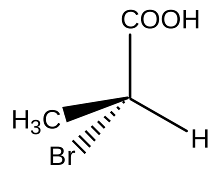
Answer

3) Label the following as R or S:

A



B.



A is S

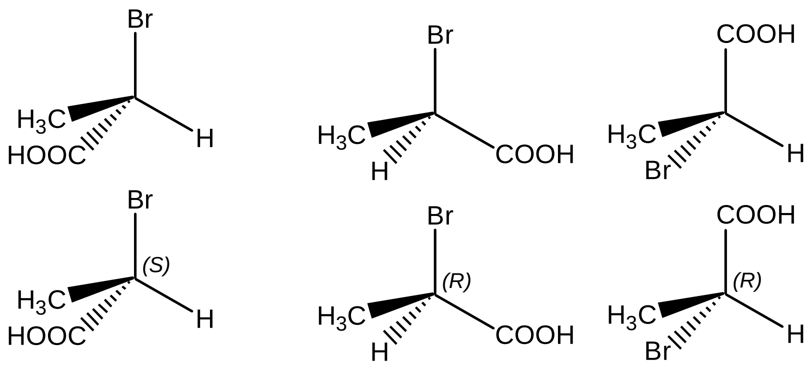
B is R

Return to Problem

Answer

4) Which of the following are enantiomers?

A B C

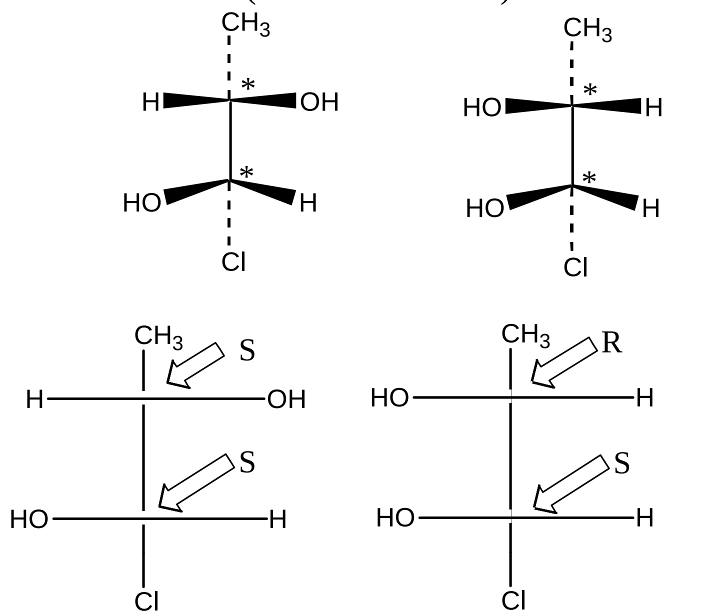


A and B are enantiomers. B and C are the same molecule. Therefore, A and C are also enantiomers.

Return to Problem

Answer

5) Label the chiral carbons (indicated with an *) as R or S:

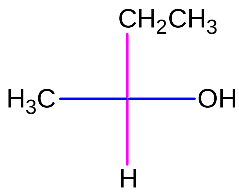


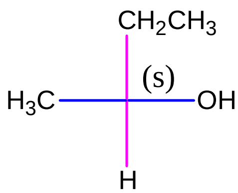
Return to Problem

Answer

6) Assign R/S configurations to the following Fischer Projections:

a.



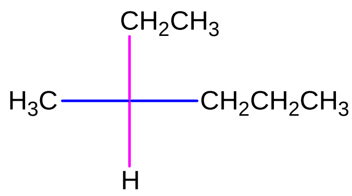


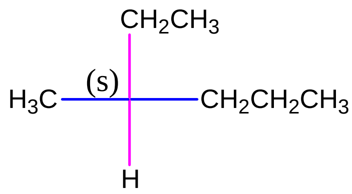
Return to Problem

Answer

6) Assign R/S configurations to the following Fischer Projections:

b.





Return to Problem