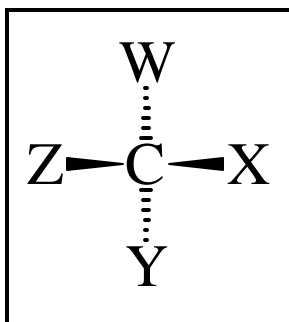


STEREOGENIC CENTER (Chiral Center, Asymmetric Center)

Atom (usually carbon) to which 4 different groups are attached:



Many, *but not all*, molecules which contain a stereogenic center are chiral. (A molecule which contains just one stereogenic center will be chiral.)

Many, *but not all*, chiral molecules contain a stereogenic center.

The *configuration* of the atoms at a stereogenic center refers to their orientation in space. (Do not confuse with *conformation*; bonds must be broken to change configuration, conformations are changed by rotation around single bonds.)

Specification of Configuration at a Stereogenic center:
R,S

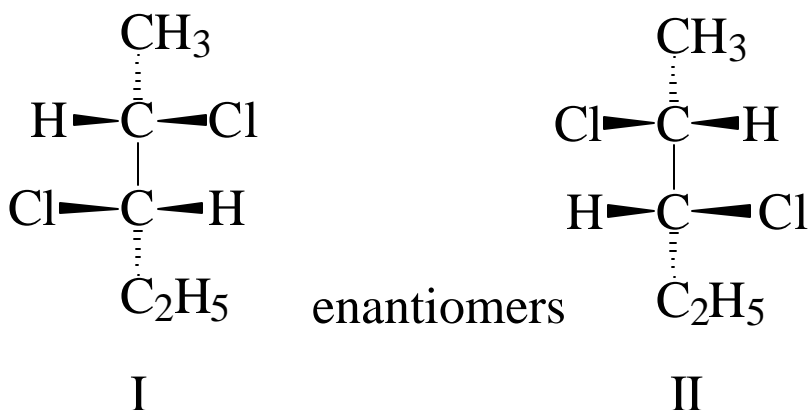
1. Establish priorities for the four groups attached to the stereogenic center in question (1 [highest], 2, 3, 4 [lowest]) in the same way as is done for E, Z.
2. Orient the molecule so that the group of lowest priority is BEHIND the stereogenic center from your viewpoint.
3. If, in moving from group 1 to 2 to 3, the motion is clockwise, the stereogenic center is R; if the motion is counterclockwise, the stereogenic center is S.

The arrangement of atoms in space that characterizes a particular stereoisomer is called its configuration (eg R or S for a compound with one stereogenic center). The configuration of a chiral substance is not related in any simple way to its sign of optical rotation.

Diastereomers —

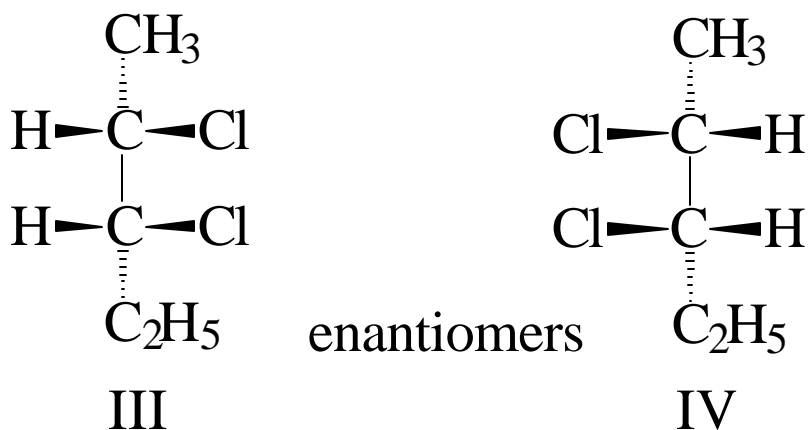
[Enantiomers: Mirror-image stereoisomers.

Diastereomers: Stereoisomers which are not enantiomers.]



(2S, 3S)-2,3-dichloropentane

(2R, 3R)-2,3-dichloropentane



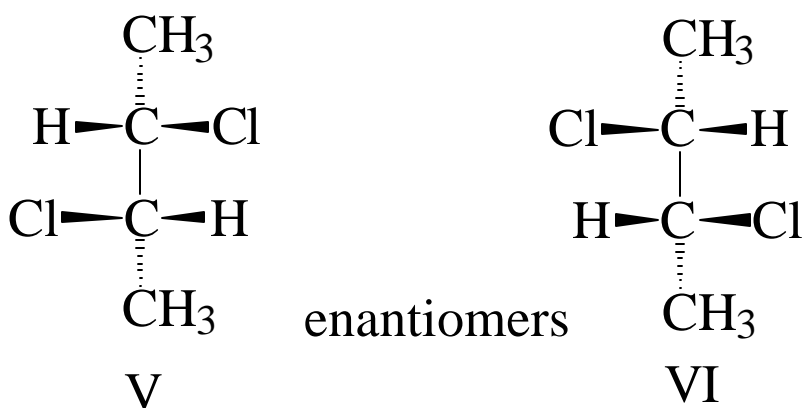
(2S, 3R)-2,3-dichloropentane

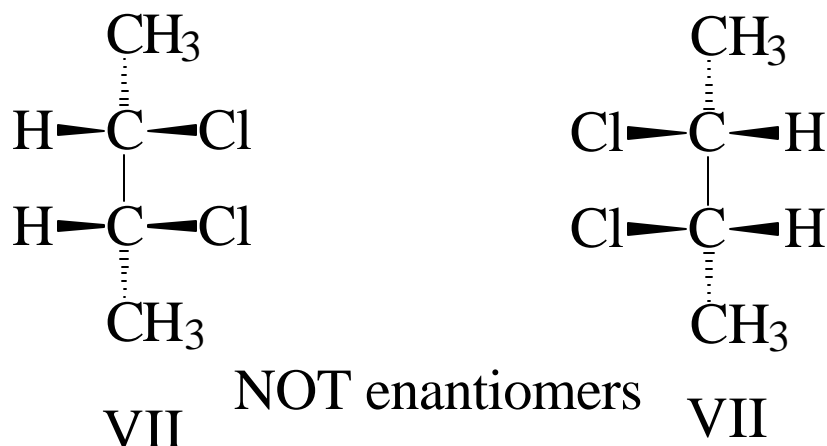
(2R, 3S)-2,3-dichloropentane

I is a stereoisomer of III & IV.
 II is a stereoisomer of III & IV.
 I is not a mirror image of III or IV.
 II is not a mirror image of III or IV.
 Therefore,
 I is a diastereomer of III & IV.
 II is a diastereomer of III & IV.

Diastereomers often have similar, but not identical, chemical properties. They have different physical properties, and can be separated from one another by ordinary physical means.

Meso Structures —





superimposable (same compound):
a *meso* structure

Meso compounds are superimposable on their mirror images even though they contain stereogenic centers. They are not chiral and cannot be optically active. They have a plane or center of symmetry.

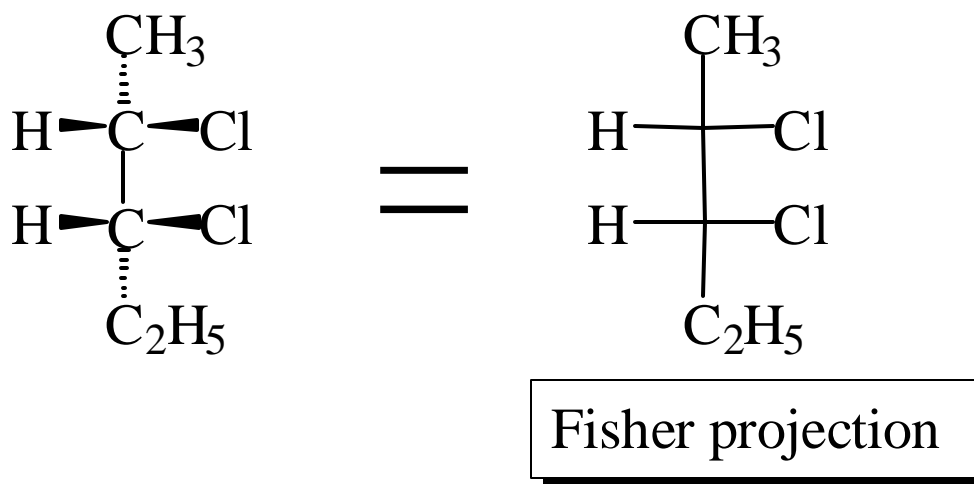
Fisher Projections —

☞ A method of representing stereogenic centers without using wedged or dashed bonds.

Horizontal bonds come from the stereogenic center toward you.

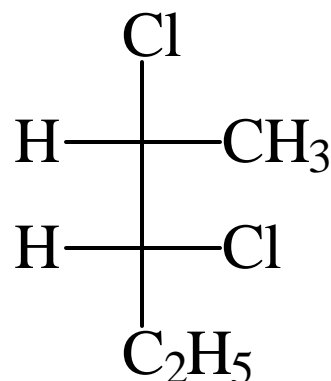
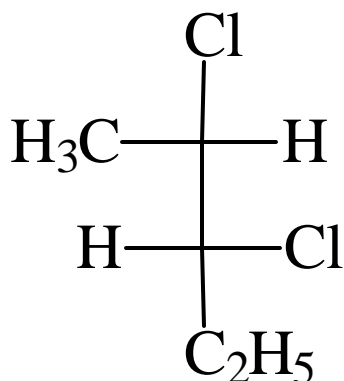
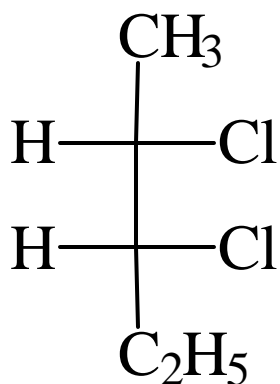
Vertical bonds go from the stereogenic center away from you.

eg



To determine if the configuration around an atom is the same or opposite in two Fisher projections you can

- ☞ determine the R,S configuration of each.
- ☞ interchange pairs of groups around the stereogenic center of one until both projections are identical. Since each exchange inverts the configuration an odd number of exchanges means the configurations were opposite; an even number means they are the same.



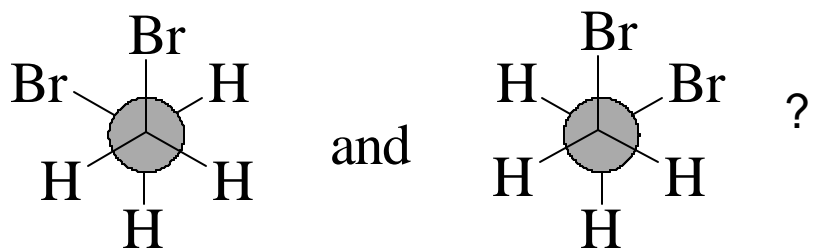
Reactions/Stereogenic centers/Chiral Molecules

- 1) If no bond to a stereogenic center is broken configuration is retained in going from reactant to product since the four groups have the same spatial orientation (but R may become S & *vice versa* owing to group priority changes.)
- 2) If a bond to a stereogenic center is broken the outcome will depend on the mechanism of the reaction.
- 3) If achiral reagents react to form chiral molecules racemic mixtures will result.

Optically inactive reactants \longrightarrow
optically inactive products,



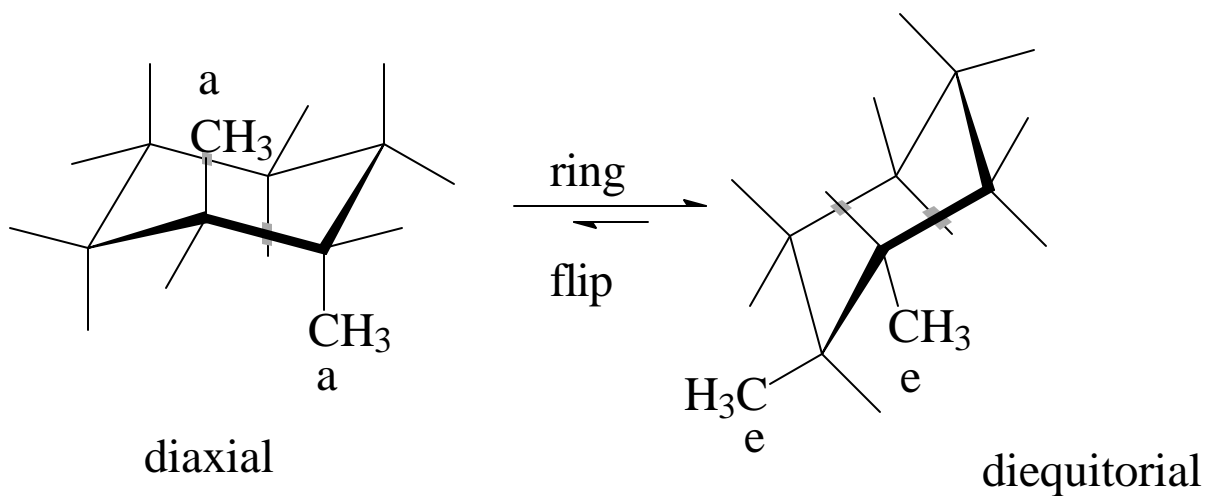
What is the relationship between



They are conformational enantiomers.

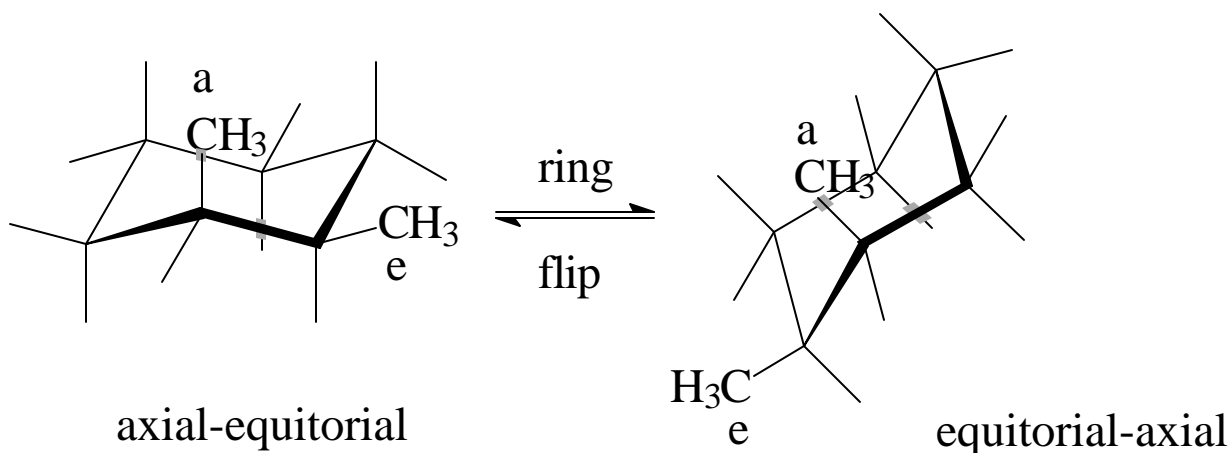
Disubstituted cyclohexanes —

Trans-1,2-dimethylcyclohexane can exist as two possible chair conformers:



[diequatorial] > [diaxial] because of 1,3-diaxial interactions

This is a pair of *conformational diastereomers*.
Cis-1,2-dimethylcyclohexane can exist as two possible chair conformers:



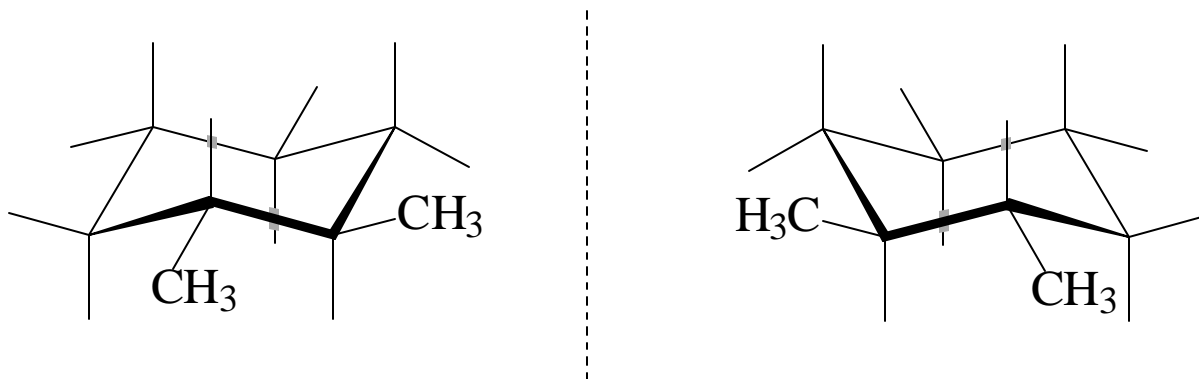
These conformations are of equal energy and therefore present in equal amount.

This is a pair of *conformational enantiomers*. These cannot be resolved because of rapid interconversion. *Cis*-1,2-dimethylcyclohexane is an achiral molecule.

Note that either of the *cis*-1,2-dimethylcyclohexane conformers is a **configurational diastereomer** (geometric isomer) of either of the *trans*-1,2-dimethylcyclohexane conformers.

Of the four isomers shown, the diequatorial *trans*-1,2-dimethylcyclohexane is most stable.

Trans-1,2-dimethylcyclohexane is a chiral molecule: it is not superimposable on its mirror image.



These structures are not interconvertible *via* rotation around single bonds (ring flip): they are configurational enantiomers (and resolvable).