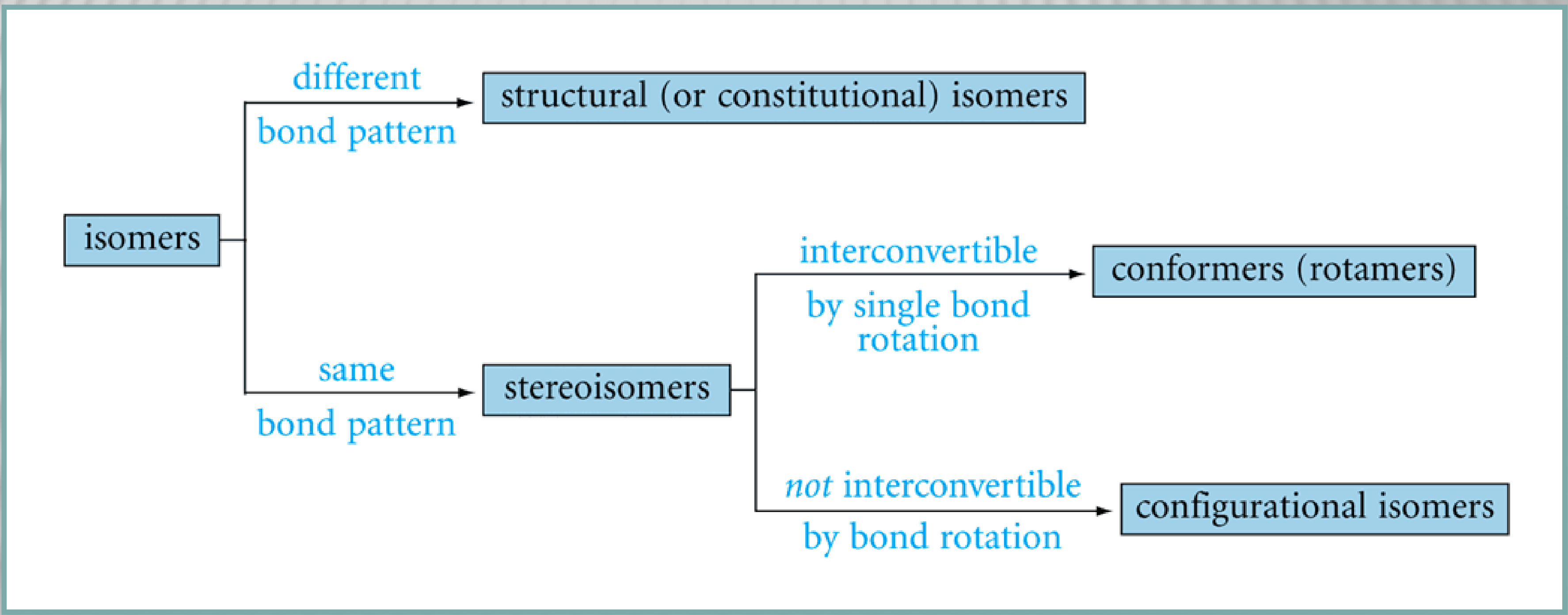

The odors of caraway seeds (left) and mint leaves (right) arise from the enantiomers of carvone, which differ in arrangement of the atoms attached to the indicated (*) carbon.
5
Stereoisomerism
O
*
Carvone

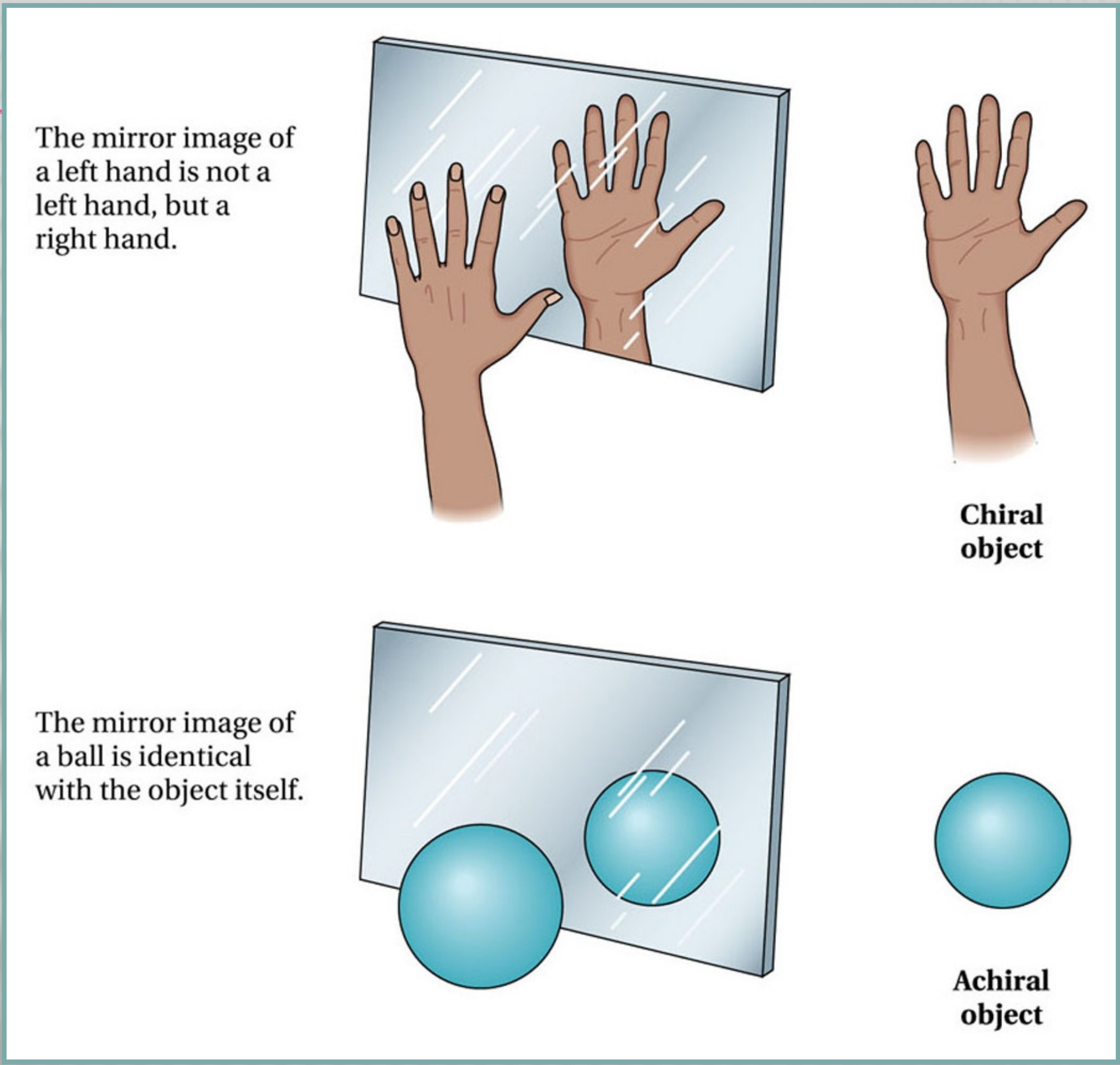
Isomerism: Constitutional Isomers and Stereoisomers

- Stereoisomers are isomers with the same molecular formula and same connectivity of atoms but different arrangement of atoms in space

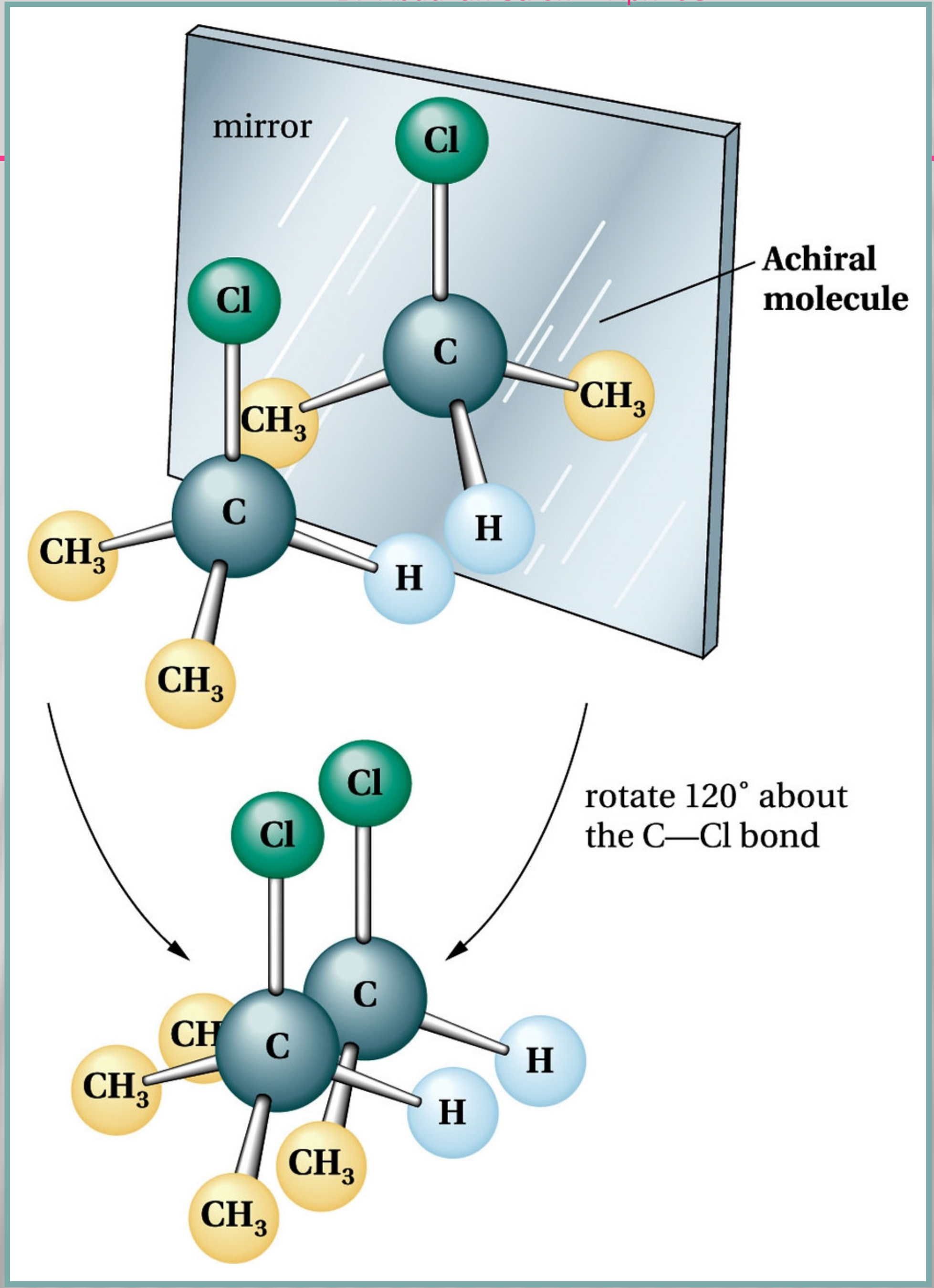


5.1 CHIRALITY AND ENANTIOMERS

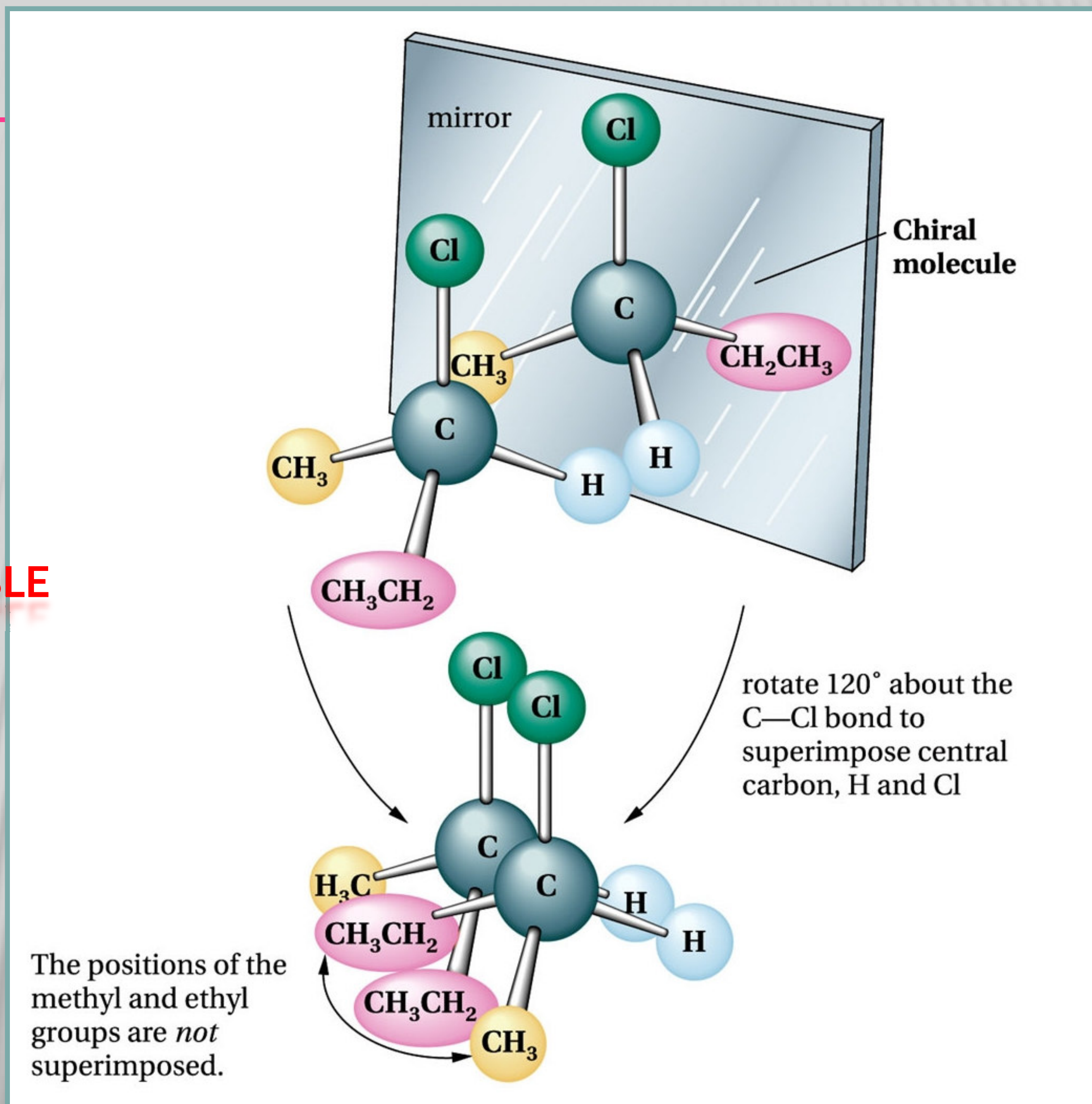
- A molecule (or an object) is either chiral or achiral.
- A chiral molecule (or object) is one that exhibits the *property of handedness*. An achiral molecule does not have this property.
- To tell whether a molecule (or object) is chiral or achiral, examine the molecule (or object) and its mirror image:
  - The mirror image of a chiral molecule cannot be superimposed on the molecule itself.
  - The mirror image of an achiral molecule, however, is identical with or superimposable on the molecule itself.


The mirror image of a left hand is not a left hand, but a right hand.
Chiral object
The mirror image of a ball is identical with the object itself.
Achiral object

MODEL OF 2-CHLOROPROPANE AND ITS MIRROR IMAGE — *SUPERIMPOSABLE*

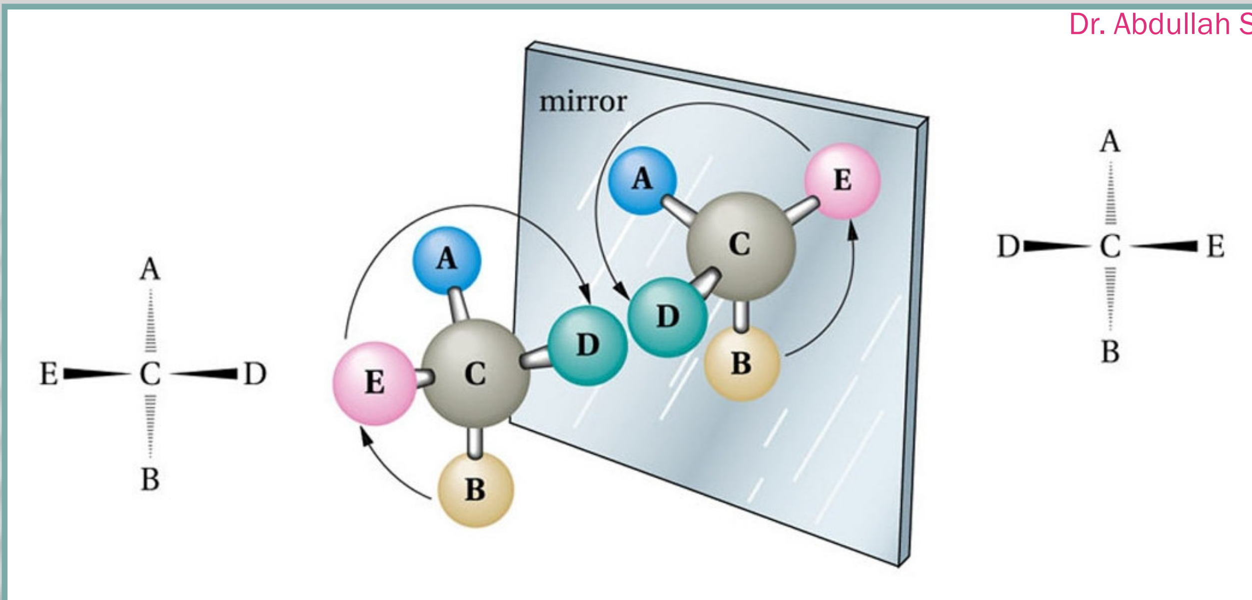


MODEL OF 2-CHLOROBUTANE AND ITS MIRROR IMAGE — NONSUPERIMPOSABLE

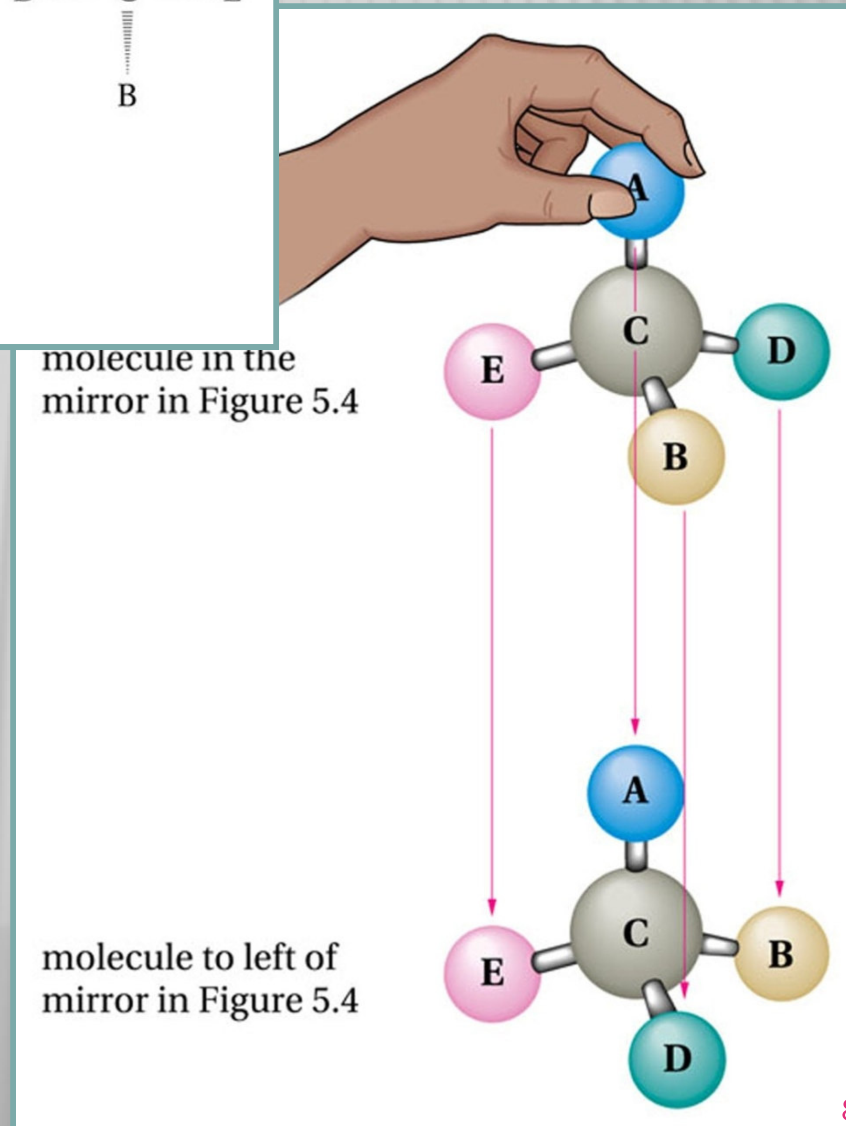


5.2 STEREOGENIC CENTERS, THE STEREOGENIC CARBON ATOM

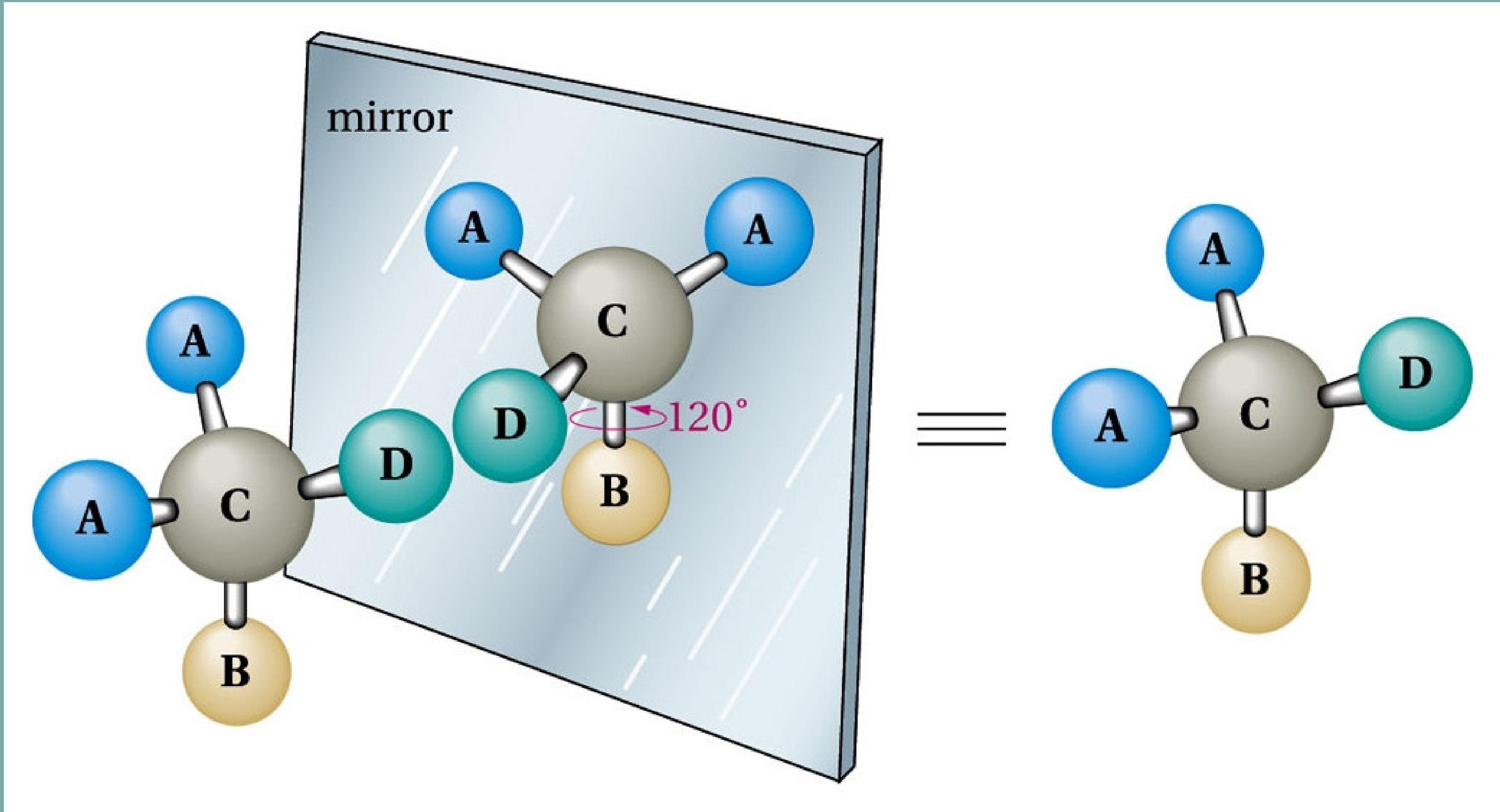
- *Enantiomers* are a pair of molecules related as nonsuperimposable mirror images.
- A carbon atom with four different groups attached is called a *stereogenic center because it gives rise to stereoisomers*.
- Any molecule with a *plane of symmetry* is achiral. Chiral molecules do not have a plane of symmetry.
- *Configuration* refers to the arrangement of groups attached to a stereogenic center.



THE CHIRALITY OF ENANTIOMERS

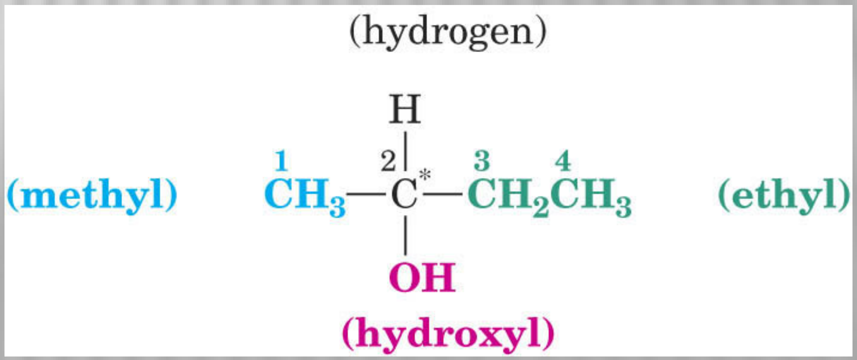


PLANE OF SYMMETRY



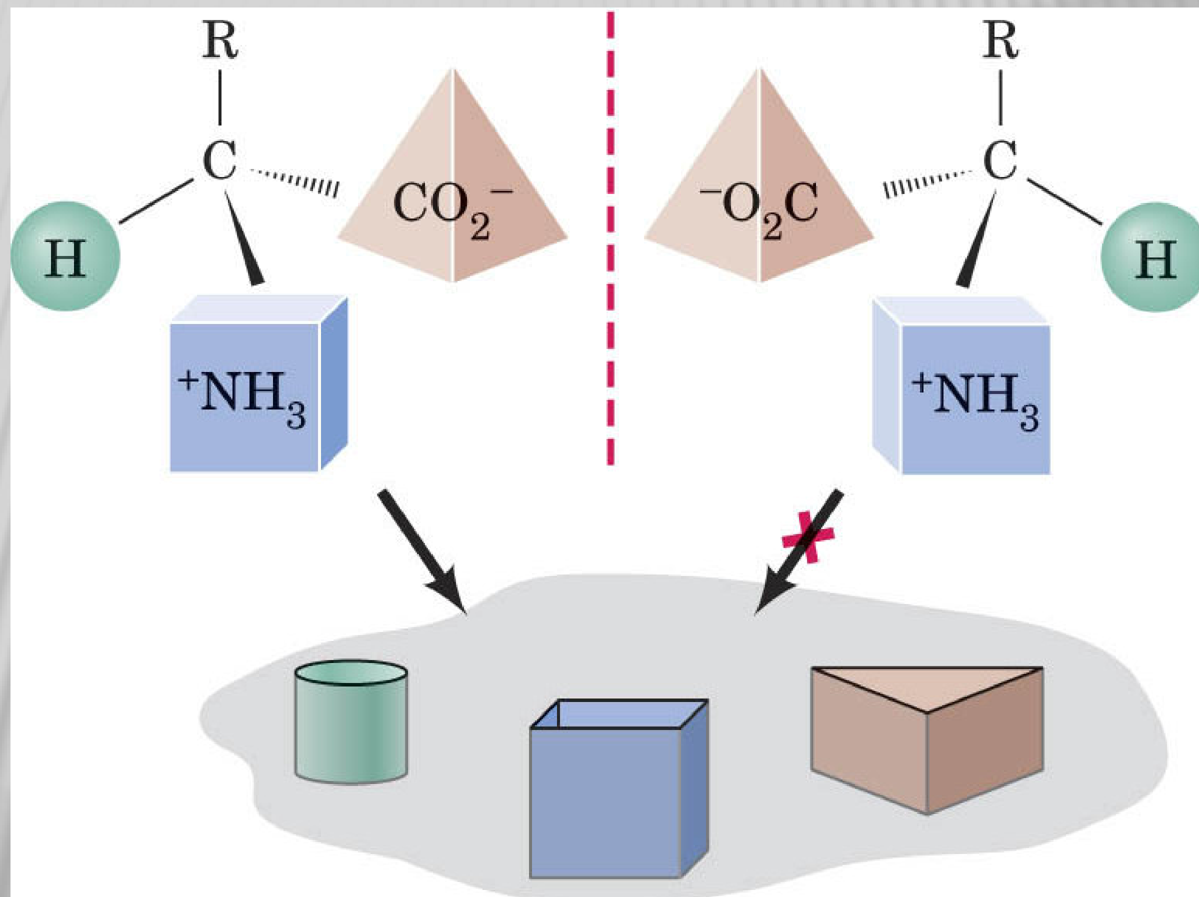
Plane of symmetry: a plane that passes through a molecule (or object) in such a way that what is on one side of the plane is the exact reflection of what is on the other side.

- Chiral molecule
  - A molecule with a single tetrahedral carbon bonded to four different groups will always be chiral
  - A molecule with more than one tetrahedral carbon bonded to four different groups is not always chiral
  - Switching two groups at the tetrahedral center leads to the enantiomeric molecule in a molecule with one tetrahedral carbon
- Stereogenic center
  - An atom bearing groups of such nature that an interchange of any two groups will produce a stereoisomer
  - Carbons at a tetrahedral stereogenic center are designated with an asterisk (*)
- Example: 2-butanol



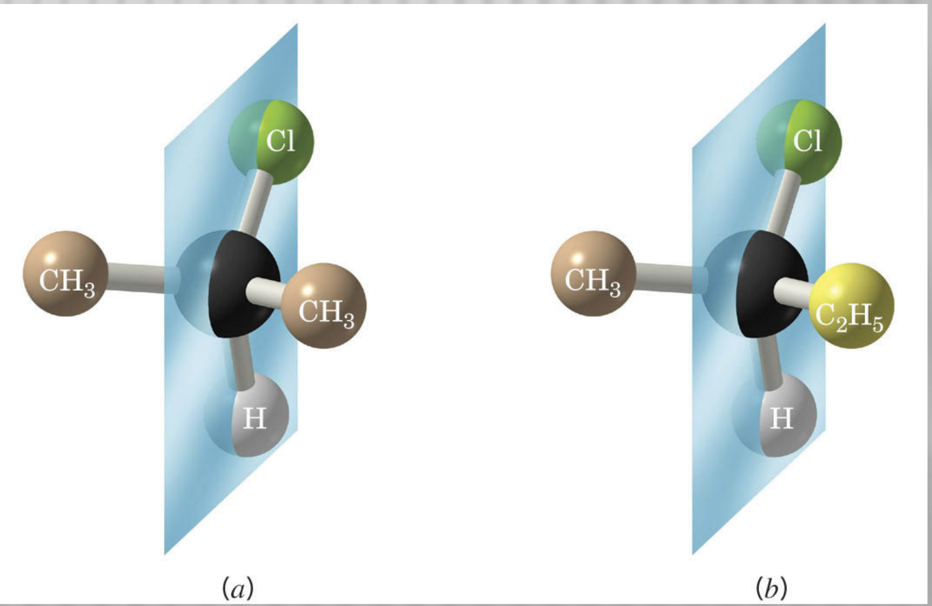
The Biological Importance of Chirality

- The binding specificity of a chiral receptor site for a chiral molecule is usually only favorable in one way



Tests for Chirality: Planes of Symmetry

- Plane of symmetry
  - An imaginary plane that bisects a molecule in such a way that the two halves of the molecule are mirror images of each other
  - A molecule with a plane of symmetry cannot be chiral
- Example
  - 2-Chloropropane (a) has a plane of symmetry but 2-chlorobutane (b) does not



EXAMPLE 5.1

Locate the stereogenic center in 3-methylhexane.

SOLUTION Draw the structure, and look for a carbon atom with four different groups attached.

$$\begin{array}{l} 1\quad\;\; 2\quad\;\; 3\;\;\; 4\quad\;\; 5\quad\;\; 6 \\ CH_3CH_2\underset{\displaystyle \begin{array}{c}|\\ CH_3\end{array}}{C}HCH_2CH_2CH_3 \end{array}$$

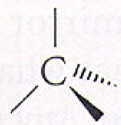
All of the carbons except carbon-3 have at least two hydrogens (two identical groups) and therefore cannot be stereogenic centers. But carbon-3 has four different groups attached (H, CH_3—, CH_3CH_2—, and $CH_3CH_2CH_2$—) and is therefore a stereogenic center. By convention, we sometimes mark such centers with an asterisk.

$$CH_3CH_2\underset{\displaystyle \begin{array}{c}|\\ CH_3\end{array}}{\overset{*}{C}}HCH_2CH_2CH_3$$

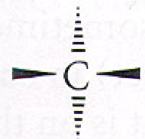
EXAMPLE 5.2

Draw the two enantiomers of 3-methylhexane.

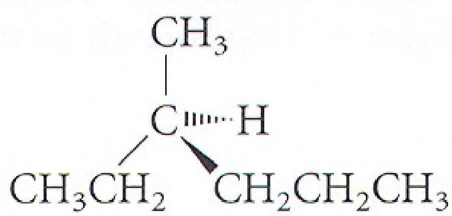
SOLUTION There are many ways to do this. Here are two of them. First draw carbon-3 with four tetrahedral bonds.



or



Then attach the four different groups, in any order.



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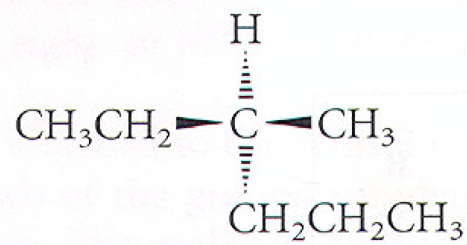
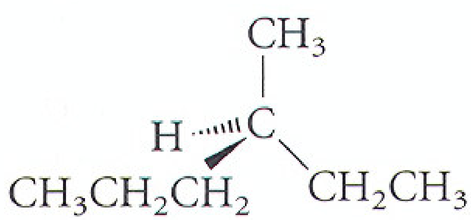


Now draw the mirror image, or interchange the positions of any two groups.



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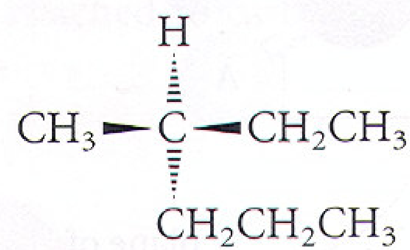
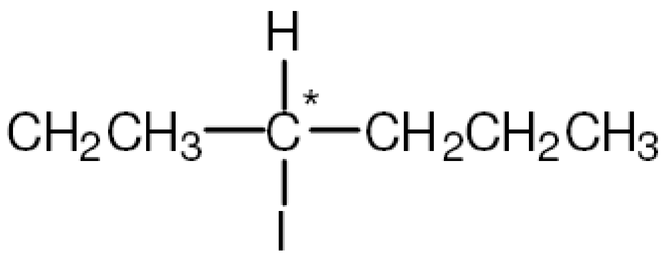


PROBLEM 5.2 Find the stereogenic centers in

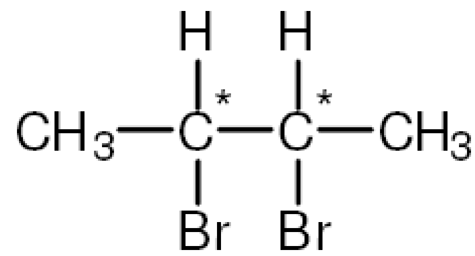
a. $CH_3CH_2CHICH_2CH_2CH_3$ b. $BrFCHCH_3$
c. 3-methylcyclohexene d. 2,3-dibromobutane

5.2 The stereogenic centers are marked with an asterisk. Note that each stereogenic center has four different groups attached.

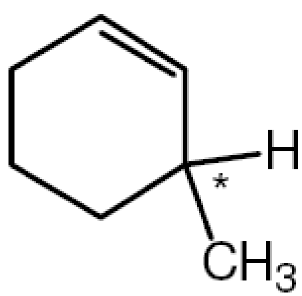
a.



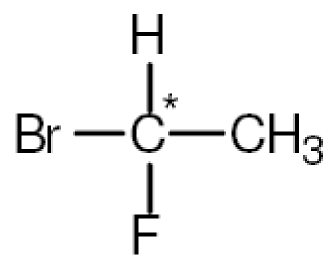
d



c.



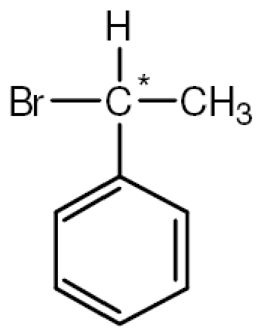
b



PROBLEM 5.3 Which of the following compounds is chiral?

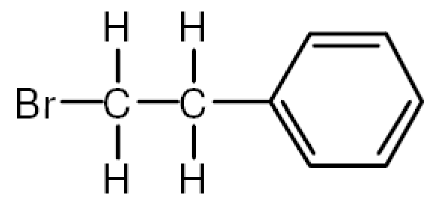
a. 1-bromo-1-phenylethane b. 1-bromo-2-phenylethane

5.3 a.



chiral

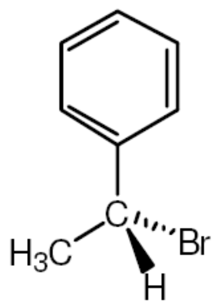
b.

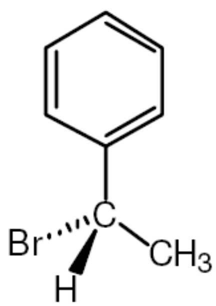


no stereogenic centers; achiral

PROBLEM 5.4 Draw three-dimensional structures for the two enantiomers of the chiral compound in Problem 5.3.

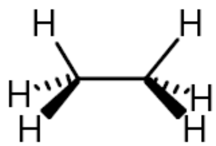
5.4 Note that if the right structure is rotated 180° about the carbon-phenyl bond, the methyl and phenyl groups can be superimposed on those of the left structure, but the positions of the hydrogen and bromine will be interchanged.





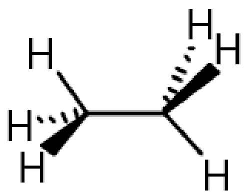
PROBLEM 5.5 Locate the planes of symmetry in the eclipsed conformation of ethane. In this conformation, is ethane chiral or achiral?

5.5 The planes of symmetry are (a) the three planes that pass through any pair of eclipsed hydrogens and (b) the perpendicular bisector of the C–C bond. Ethane in this conformation is achiral.



PROBLEM 5.6 Does the staggered conformation of ethane have planes of symmetry? In this conformation, is ethane chiral or achiral? *(Careful!)*

5.6 There are three planes of symmetry that pass through any pair of anti-hydrogens. Ethane in this conformation is achiral.



PROBLEM 5.7 Locate the planes of symmetry in *cis*- and *trans*-1,2-dichloroethene. Are these molecules chiral or achiral? *(Careful!)*

5.7 *cis*-1,2-Dichloroethene has a plane of symmetry that bisects the double bond. The molecular plane is also a symmetry plane. *trans*-1,2-Dichloroethene is planar. That plane is a symmetry plane. Both *cis*- and *trans*-1,2-dichloroethane are achiral.