Homework problems – Chapter 4


See your solutions manual for answers to these problems.

2. Draw out the structures and indicate with an asterisk the stereogenic carbons in each of the following molecules.
   (a) (E)-4-methyl-2-hexene
   (b) 4-methyl-1-pentene
   (c) 3-methylcyclohexene
   (d) (Z)-4-methyl-2-pentene

   ![Structures](image)

3. How many stereocenters are there in 3,4,5,6-tetramethyl-4-octene? Show all of the carbon stereocenters in the structure of this compound

   ![Structures](image)

There are two stereocenters in 3,4,5,6-tetramethyl-4-octene (the two possible isomers are shown).
4. Identify all of the stereocenters in each of the following structures

a. 

b. 

c. none present

d. 

e. 

5. Give the configuration of each stereocenter in the following compounds

a. 

b. 

c. meso-3,4-dimethylhexane
A number in parenthesis indicates group priority. Remember that when lowest priority group is directed you, the actual configuration is opposite to what it appears to be.
6. Indicate whether each of the following is true (T) or false (F). If false, explain why.

(a) In some cases constitutional isomers are chiral (T)

(b) In every case, a pair of enantiomers have a mirror image relationship (T)

(c) Mirror-image molecules are in all cases enantiomers. (F). Because some mirror image molecules are superimposable.

(d) If a compound has an enantiomer it must be chiral (T)

(e) Every chiral compound has a diastereomer. (F) A compound with only one stereocenter is chiral and only has an enantiomer but no diastereomers. Remember: A compound with n stereogenic centers has exactly $2^n$ configurational stereoisomers, unless some of its diastereomers are meso compounds; then it has fewer than $2^n$ configurational stereoisomers.

(f) If a compound has a diasteromer it must be chiral. (F). Remember that meso compounds are achiral but have diastereomers

(g) Any molecule containing a stereocenter must be chiral (F). Again meso-compounds contain stereocenters but are not chiral

(h) Some chiral molecules are optically inactive. (F). Chiral molecules have a handedness and hence are always optically active.

(i) Some diastereomers have a mirror-image relationship (F). Mirror images have the same atom to atom connectivities and internal dimensions, diastereomers do not have the same internal dimensions

(j) If a structure has no plane of symmetry it is chiral. (F). A structure may have no plane of symmetry but possess a point of symmetry and hence be achiral. See
for example, staggered conformation of meso-3,4-dimethylhexane in problem 5 (above).

(k) All chiral molecules have no plane of symmetry (T)

7. Explain why compound A can be resolved into enantiomers but compound B cannot.

\[ \begin{align*}
\text{A} & \quad \text{Me} \quad \text{N}^+ \quad \text{C} \quad \text{H}_2 \quad \text{Et} \quad \text{C} \quad \text{H} \quad \text{CH}_2 \quad \text{Cl}^- \\
\text{B} & \quad \text{Me} \quad \text{N} \quad \text{C} \quad \text{H}_2 \quad \text{Et} \quad \text{C} \quad \text{H} \quad \text{CH}_2
\end{align*} \]

\( \text{A} \) contains a stereogenic nitrogen atom due to the substitution of four non-identical groups. Thus, it can be resolved into enantiomers. In contrast, compound \( \text{B} \) possesses a lone pair and undergoes rapid lone pair inversion to interconvert the enantiomers. Thus, it can't be resolved into enantiomers.

8. The specific rotation of the R enantiomer of the following alkene is \( \left[ \alpha \right]_D^{25} = +76^\circ \), its molecular mass is 146.2.

\[ \begin{align*}
\text{H}_3\text{C} & \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{CH}_2
\end{align*} \]

(a) What is the observed rotation of a 0.75 M solution of the S enantiomer of this compound in a 1-dm sample path?

The specific rotation of the S enantiomer of the alkene is \( \left[ \alpha \right]_D^{25} = -76 \) (since it will rotate plane-polarized light the opposite direction)
\[ [\alpha]_\lambda^T = \alpha / l \cdot c \]

where \( \alpha \) is the measured rotation, \( T \) is the temperature (in °C), \( \lambda \) is the wavelength (in nm), \( l \) is the path length (in dm), and \( c \) is the concentration of the chiral compound in solution (in g/mL). **Note:** the units of the specific rotation is actually degrees • mL • g\(^{-1}\) • dm\(^{-1}\) but specific rotations are generally cited in degrees (°) and the remaining units are omitted for convenience.

First, the sample concentration in g/mL must be determined

\[
c \text{ in g/mL} = \frac{0.75 \text{ mol}}{\text{L mol}} \times \frac{146.2 \text{ g}}{\text{mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.11 \text{ g/mL}
\]

Thus,

\[\alpha = \frac{-76 \degree}{1 \text{ dm} \times 0.11 \text{ g/mL}} = -76 \degree \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1} \times 0.11 \text{ (dm \cdot g \cdot mL}^{-1}) = -8.36 \degree \]

(b) What is the observed rotation of a 0.5 M solution of this compound in a 5-cm sample path?

\[
c \text{ in g/mL} = \frac{0.5 \text{ mol}}{\text{L mol}} \times \frac{146.2 \text{ g}}{\text{mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.073 \text{ g/mL}
\]

\[\alpha = \frac{-76 \degree}{0.5 \text{ dm} \times 0.073 \text{ g/mL}} = -76 \degree \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1} \times 0.036 \text{ (dm \cdot g \cdot mL}^{-1}) = -2.78 \degree \]
9. Identify the stereocenters in each of the following structures and tell whether each structure is chiral.

Structures a–c are chiral because they contain stereocenters and no plane- or center of symmetry. Structure d contains two stereocenters but has a plane of symmetry that contains the C=C bond and bisects the cyclopropyl ring. Hence it is a meso compound.