**Is R Right, or Is It Proper?**

Choice of the letter R presented a problem for Cahn, Ingold, and Prelog, the scientists who devised the R,S system. The letter S stands for *sinister*, one of the Latin words for left. However, the Latin word for right (in the directional sense) is *dexter*, and unfortunately the letter D was already being used in another system of configuration (the D,L system). It was difficulties with the D,L system that led to the need for a new system, and the last thing anyone needed was a system that confused the two! Fortunately, Latin provided another word for right: the participle *rectus*. But this “right” does not indicate direction: it means *proper*, or correct. (The English word *rectify* comes from the same root.) Although the Latin wasn’t quite proper, it solved the problem! In passing, it might be noted that R and S are the first initials of Robert S. Cahn, one of the inventors of the R,S system (Sec. 4.2B). A coincidence? Perhaps.

### PROBLEMS

**6.5** Draw perspective representations for each of the following chiral molecules. Use models if necessary. (D = deuterium = \( ^2\text{H} \), a heavy isotope of hydrogen.)

(a) \( (S)\text{-H}_3\text{C}—\text{CH}—\text{OH} \)  
(b) \( (\text{Z},4\text{R})\text{-4-methyl-2-hexene} \)

**6.6** Indicate whether the asymmetric atom in each of the following compounds has the R or S configuration.

- (a) \( \text{O}—\text{C}—\text{OH} \)
- (b) \( \text{O}—\text{C}—\text{OH} \)
- (c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+—\text{CH}—\text{OH} \)

**6.3 PHYSICAL PROPERTIES OF ENANTIOMERS: OPTICAL ACTIVITY**

Recall from Sec. 2.6 that organic compounds can be characterized by their physical properties. Two properties often used for this purpose are the melting point and the boiling point. *The melting points and boiling points of a pair of enantiomers are identical.* Thus, the boiling points of \((R)\)- and \((S)\)-2-butanol are both 99.5°C. Likewise, the melting points of \((R)\)- and \((S)\)-lactic acid are both 53°C.

\[
\text{H}_3\text{C}—\text{CH}—\text{C}—\text{OH}
\]

A pair of enantiomers also have identical densities, indices of refraction, heats of formation, standard free energies, and many other properties.
If enantiomers have so many identical properties, how can we tell one enantiomer from the other? A compound and its enantiomer can be distinguished by their effects on polarized light. Understanding these phenomena requires an introduction to the properties of polarized light.

A. Polarized Light

Light is a wave motion that consists of oscillating electric and magnetic fields. The electric field of ordinary light oscillates in all planes, but it is possible to obtain light with an electric field that oscillates in only one plane. This kind of light is called plane-polarized light, or simply, polarized light (Fig. 6.6).

Polarized light is obtained by passing ordinary light through a polarizer, such as a Nicol prism (a prism made of specially cut and joined calcite crystals). The orientation of the polarizer’s axis of polarization determines the plane of the resulting polarized light. Analysis of polarized light hinges on the fact that if plane-polarized light is subjected to a second polarizer whose axis of polarization is perpendicular to that of the first, no light passes through the second polarizer (Fig. 6.7a, p. 236). This same effect can be observed with two pairs of polarized sunglasses (Fig. 6.7b). When the lenses are oriented in the same direction, light will pass through. When the lenses are turned at right angles, their axes of polarization are crossed, no light is transmitted, and the lenses appear dark.

Photography enthusiasts may recognize the same phenomenon at work in a polarizing filter. A great deal of the glare in reflected skylight is polarized light. This can be filtered out by turning a polarizing filter so that the image has minimum intensity. The resulting photograph has much greater contrast than the same picture taken without the filter.

B. Optical Activity

If plane-polarized light is passed through one enantiomer of a chiral substance (either the pure enantiomer or a solution of it), the plane of polarization of the emergent light is rotated. A sub-
stance that rotates the plane of polarized light is said to be **optically active.** Individual enan-
tiomers of chiral substances are optically active.

Optical activity is measured in a device called a **polarimeter** (Fig. 6.8), which is basically
the system of two polarizers shown in Fig. 6.7. The sample to be studied is placed in the light
beam between the two polarizers. Because optical activity changes with the wavelength
(color) of the light, monochromatic light—light of a single color—is used to measure optical
activity. The yellow light from a sodium arc (the sodium D-line with a wavelength of
589.3 nm) is often used in this type of experiment. An optically inactive sample (such as air
or solvent) is placed in the light beam. Light polarized by the first polarizer passes through
the sample, and the analyzer is turned to establish a dark field. This setting of the analyzer defines
the zero of optical rotation. Next, the sample whose optical activity is to be measured is
placed in the light beam. The number of degrees $\alpha$ that the analyzer must be turned to reestab-
lish the dark field is the **optical rotation** of the sample. If the sample rotates the plane of po-
larized light in the clockwise direction, the optical rotation is given a plus sign. Such a sam-
ple is said to be **dextrorotatory** (Latin *dexter*, meaning “right”). If the sample rotates the
plane of polarized light in the counterclockwise direction, the optical rotation is given a minus sign, and the sample is said to be levorotatory (Latin laevus, meaning “left”).

The optical rotation of a sample is the quantitative measure of its optical activity. The observed optical rotation \( \alpha \) is proportional to the number of optically active molecules present in the path through which the light beam passes. Thus, \( \alpha \) is proportional to both the concentration \( c \) of the optically active compound in the sample as well as the length \( l \) of the sample container:

\[
\alpha = [\alpha]cl
\]  

The constant of proportionality, \( [\alpha] \), is called the specific rotation. By convention, the concentration of the sample is expressed in grams per milliliter (g mL\(^{-1}\)), and the path length is in decimeters (dm). (For a pure liquid, \( c \) is taken as the density.) Thus, the specific rotation is equal to the observed rotation at a concentration of 1 g mL\(^{-1}\) and a path length of 1 dm. Because the specific rotation \( [\alpha] \) is independent of \( c \) and \( l \), it is used as the standard measure of optical activity. The observed rotation is reported in degrees; hence, the dimensions of \( [\alpha] \) are degrees mL g\(^{-1}\) dm\(^{-1}\). (Often, specific rotations are reported simply in degrees, with the other

\[\text{Figure 6.8} \text{ Determination of optical rotation in a simple polarimeter. (a) First, the reference condition of zero rotation is established as a dark field. (b) Next, the polarized light is passed through an optically active sample with observed rotation } \alpha. \text{ The analyzer is rotated to establish the dark-field condition again. The optical rotation } \alpha \text{ can be read from the calibrated scale on the analyzer.}\]
units understood.) Because the specific rotation of any compound varies with wavelength and temperature, \([\alpha]\) is conventionally reported with a subscript that indicates the wavelength of light used and a superscript that indicates the temperature. Thus, a specific rotation reported as \([\alpha]^{20}_D\) has been determined at 20°C using the sodium D-line.

One decimeter = 10 centimeters. The reason for using the decimeter as a unit of length is that the length of a typical sample container used in polarimeters is 1 dm.

**Study Problem 6.3**

A sample of (S)-2-butanol has an observed rotation of +1.03°. The measurement was made with a 1.0 \(M\) solution of (S)-2-butanol in a sample container that is 10 cm long. What is the specific rotation \([\alpha]^{20}_D\) of (S)-2-butanol?

**Solution** To calculate the specific rotation, the sample concentration in g mL\(^{-1}\) must be determined. Because the molecular mass of 2-butanol is 74.12, the 1.0 \(M\) solution contains 74.1 g L\(^{-1}\) or 0.0741 g mL\(^{-1}\) of 2-butanol. This is the value of \(c\) used in Eq. 6.1. The value of \(l\) is 1 dm. Substituting in Eq. 6.1, \([\alpha]^{20}_D = (+1.03\text{ degrees})/(0.0741 \text{ g mL}^{-1})(1 \text{ dm}) = +13.9 \text{ degrees mL}^{-1} \text{ dm}^{-1}\).

### C. Optical Activities of Enantiomers

Enantiomers are distinguished by their optical activities because *enantiomers rotate the plane of polarized light by equal amounts in opposite directions*. Thus, if the specific rotation \([\alpha]^{20}_D\) of (S)-2-butanol is +13.9 degrees mL\(^{-1}\) dm\(^{-1}\) (Study Problem 6.3), then the specific rotation of (R)-2-butanol is −13.9 degrees mL\(^{-1}\) dm\(^{-1}\). Similarly, if a particular solution of (S)-2-butanol has an observed rotation of +3.5°, then a solution of (R)-2-butanol under the same conditions will have an observed rotation of −3.5°.

A sample of a pure chiral compound uncontaminated by its enantiomer is said to be enantiomerically pure. (The term optically pure is sometimes used to mean the same thing.) In a mixture of the two enantiomers, each contributes to the optical rotation in proportion to its concentration, as Eq. 6.1 shows. As a result, a sample containing equal amounts of two enantiomers has an observed optical rotation of zero.

Sometimes a plus or minus sign is used with the name of a chiral compound to indicate the sign of its optical rotation. Thus, (S)-2-butanol is sometimes called (S)-(+)2-butanol because it has a positive optical rotation, and (R)-2-butanol is sometimes called (R)-(−)-2-butanol.

*The sign of optical rotation is unrelated to the R or S configuration of the compound.* Thus, some compounds with the S configuration have positive rotations, and others have negative rotations. Although the S enantiomer of 2-butanol is dextrorotatory (\([\alpha]^{20}_D = +13.9 \text{ degrees mL}^{-1} \text{ dm}^{-1}\)), it is the R enantiomer of glyceraldehyde that is dextrorotatory.

\[
\begin{align*}
\text{(R)-(+)\text{-glyceraldehyde}} \\
[\alpha]^{20}_D & = +13.5 \text{ degrees mL}^{-1} \text{ dm}^{-1}
\end{align*}
\]

The development of methods to predict reliably the signs and magnitudes for the optical rotations of chiral compounds is a research problem of current interest.
A mixture containing equal amounts of two enantiomers is encountered so commonly that it is given a special name: a racemate or racemic mixture. (In older literature, the term racemic modification was used.) A racemate is referred to by name in two ways. The racemate of 2-butanol, for example, can be called either racemic 2-butanol or \((\pm)-2\)-butanol.

Racemates typically have physical properties that are different from those of the pure enantiomers. For example, the melting point of either enantiomer of lactic acid (p. 234) is 53 °C, but the melting point of racemic lactic acid is 18 °C. The reason for the different melting points is that the crystal structures differ. Recall from Sec. 2.6B that the melting point largely reflects interactions between molecules in the crystalline solid. (Imagine packing a dozen left shoes—a “pure enantiomer”—in a box, and then imagine packing six right shoes and six left shoes—a “racemate”—in the same box. The interactions among the shoes—the way they touch each other—are different in the two cases.) The optical rotations of enantiomers and racemates are another example of differing physical properties. The optical rotation of any racemate is zero, because a racemate contains equal amounts of two enantiomers whose optical rotations of equal magnitude and opposite sign exactly cancel each other.

The process of forming a racemate from a pure enantiomer is called racemization. The simplest method of racemization is to mix equal amounts of enantiomers. As you will learn, racemization can also occur as a result of chemical reactions.

Because a pair of enantiomers have the same boiling points, melting points, and solubilities—exactly the properties that are usually exploited in designing separations—the separation of enantiomers poses a special problem. The separation of a pair of enantiomers, called an enantiomeric resolution, requires special methods that are discussed in Sec. 6.8.