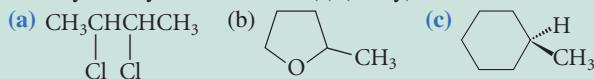


Figure 6.4 Center of symmetry. (a) If a molecule has a center of symmetry, forming the mirror image (1, *top arrow*) and then rotating the entire molecule 180° about an axis perpendicular to the mirror (2, *bottom arrow*) reproduces the molecule. (b) Any line through the center of symmetry (*black dot*) contacts equivalent points on the molecule at equal distances from the center.

6.3 Show the planes and centers of symmetry (if any) in each of the following achiral objects.

- (a) the methane molecule (b) a cone
 (c) the ethylene molecule (d) the *trans*-2-butene molecule
 (e) the *cis*-2-butene molecule (f) the staggered conformation of ethane
 (g) the anti conformation of butane

6.4 Identify the asymmetric carbon(s) (if any) in each of the following molecules.



6.2

NOMENCLATURE OF ENANTIOMERS: THE R,S SYSTEM

The existence of enantiomers poses a special problem in nomenclature. How do we indicate in the name of 2-butanol, for example, which enantiomer we have? It turns out that the same Cahn–Ingold–Prelog priority rules used to assign *E* and *Z* configurations to alkene stereoisomers (Sec. 4.2B) can be applied to enantiomers. (The Cahn–Ingold–Prelog rules were, in fact,

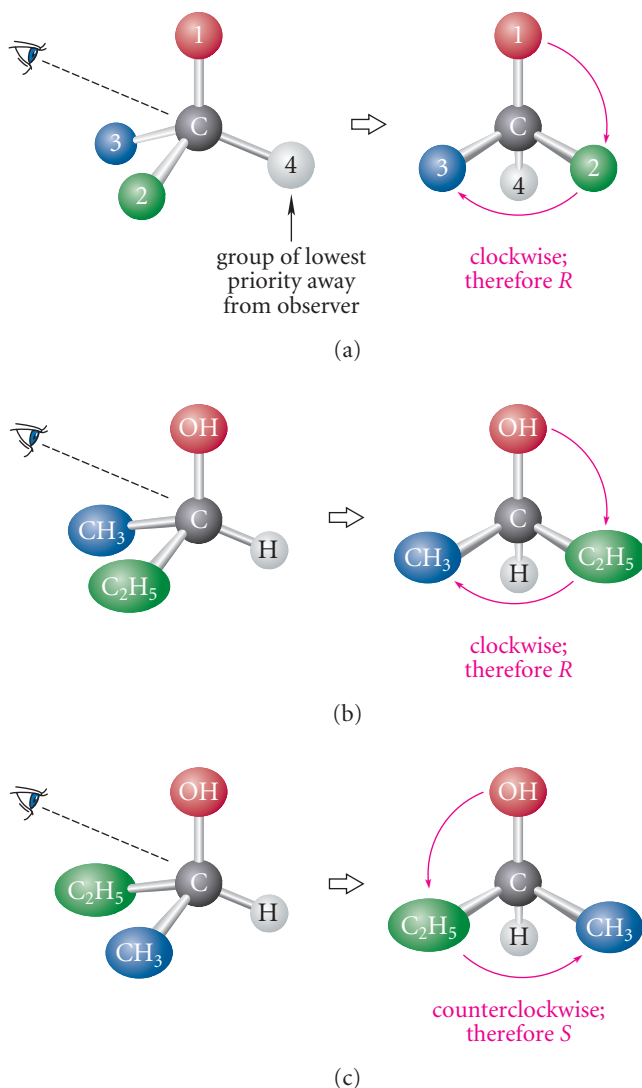


Figure 6.5 Use of the Cahn–Ingold–Prelog system to designate the stereochemistry of (a) a general asymmetric carbon atom, (b) (*R*)-2-butanol, (c) (*S*)-2-butanol. The direction of observation in each part is shown by the eye, and what the observer sees is shown on the right. Priority 1 is highest and priority 4 is lowest.

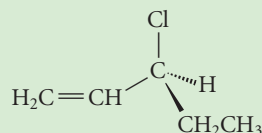
first developed for asymmetric carbons and then later applied to double-bond stereoisomerism.) A *stereochemical configuration*, or arrangement of atoms, at each asymmetric carbon in a molecule can be assigned using the following steps, which are illustrated in Fig. 6.5.

1. Identify an asymmetric carbon and the four different groups bound to it.
2. Assign priorities to the four different groups according to the rules given in Sec. 4.2B. The convention used in this text is that the highest priority = 1 and the lowest priority = 4.
3. View the molecule along the bond *from the asymmetric carbon to the group of lowest priority*—that is, with the asymmetric carbon nearer and the lowest-priority group farther away.

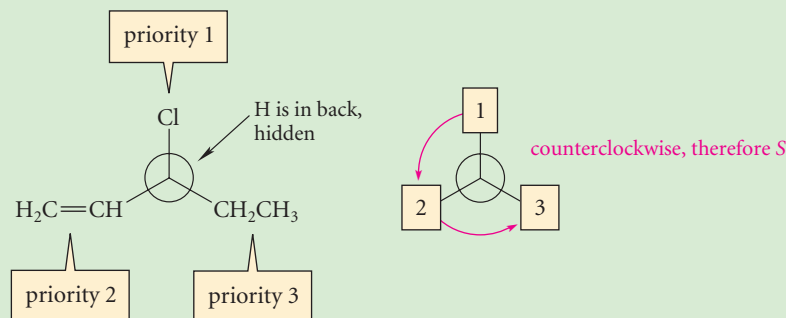
4. Consider the clockwise or counterclockwise order of the remaining group priorities. If the priorities of these groups decrease in the *clockwise* direction, the asymmetric carbon is said to have the *R* configuration (*R* = Latin *rectus*, for “correct,” “proper”). If the priorities of these groups decrease in the *counterclockwise* direction, the asymmetric carbon is said to have the *S* configuration (*S* = Latin *sinister*, for “left”).

Study Problem 6.2

Determine the stereochemical configuration of the following enantiomer of 3-chloro-1-pentene:

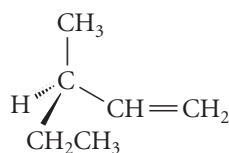


Solution First assign relative priorities to the four groups attached to the asymmetric carbon. These are (1) —Cl, (2) H₂C=CH—, (3) —CH₂CH₃, and (4) —H. Then, *using a model if necessary*, sight along the bond from the asymmetric carbon to the lowest-priority group (in this case, the H). The resulting view is essentially a Newman projection along the C—H bond:

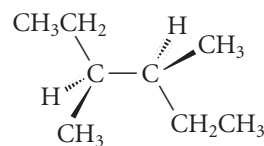


Because the priorities of the first three groups decrease in a counterclockwise direction, this is the *S* enantiomer of 3-chloro-1-pentene.

A stereoisomer is named by indicating the configuration of each asymmetric carbon before the systematic name of the compound, as in the following examples:



(R)-3-methyl-1-pentene

(3*S*,4*S*)-3,4-dimethylhexane

(Be sure to verify these and other *R,S* assignments you find in this chapter.) As illustrated by the second example, numbers are used with the *R,S* designations when a molecule contains more than one asymmetric carbon.

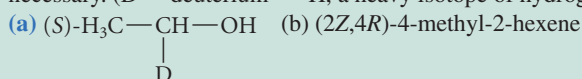
The *R,S* system is not the only system used for describing stereochemical configuration. The *D,L* system, which predates the *R,S* system, is still used in amino acid and carbohydrate chemistry (Chapters 24 and 26). With this exception, the *R,S* system has gained virtually complete acceptance.

Is *R* Right, or Is It Proper?

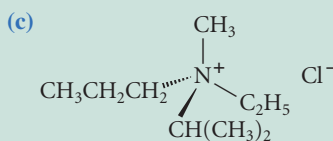
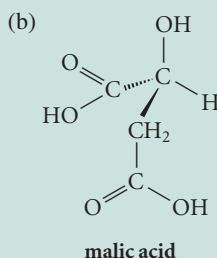
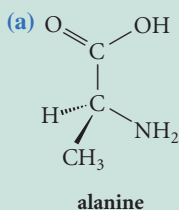
Choice of the letter *R* presented a problem for Cahn, Ingold, and Prelog, the scientists who devised the *R,S* system. The letter *S* stands for *sinister*, one of the Latin words for *left*. However, the Latin word for *right* (in the directional sense) is *dexter*, and unfortunately the letter *D* 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

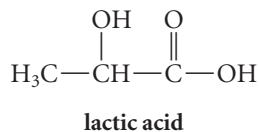
6.5 Draw perspective representations for each of the following chiral molecules. Use models if necessary. (D = deuterium = ^2H , a heavy isotope of hydrogen.)



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

**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.



A pair of enantiomers also have identical densities, indices of refraction, heats of formation, standard free energies, and many other properties.