Stereoisomers Part II

As chemists studied organic compounds isolated from plants and animals, a new and subtle type of configurational stereoisomerism was discovered. For example, lactic acid (a $C_3H_6O_3$ carboxylic acid) was found in sour milk as well as in the blood and muscle fluids of animals. The physical properties of this simple



compound were identical, regardless of the source (m.p, 53 °C & pK_a 3.80), but there was evidence that the physiological behavior of the compound from the two sources was not the same. Another natural product, the fragrant C₁₀H₁₄O ketone carvone, was isolated from both spearmint and caraway. Again, all the physical properties of carvone from these two sources seemed to be identical (b.p. 230 °C), but the odors of the two carvones were different and reflected their source. Other examples of this kind were encountered, and suspicions of a subtle kind of stereoisomerism were confirmed by the different interaction these compounds displayed with plane polarized light. We now know that this configurational stereoisomerism is due to different right and left-handed forms that certain structures may adopt, in much the same way that a screw may have right or left-handed threads but the same overall size and shape. Isomeric pairs of this kind are termed **enantiomers** (from the Greek *enantion* meaning opposite).

Chirality and Symmetry

All objects may be classified with respect to a property we call **chirality** (from the Greek *cheir* meaning hand). A **chiral object** is not identical in all respects (i.e. superimposable) with its mirror image. An**achiral object** is identical with (superimposable on) its mirror image. Chiral objects have a "handedness", for example, golf clubs, scissors, shoes and a corkscrew. Thus, one can buy right or left-handed golf clubs and scissors. Likewise, gloves and shoes come in pairs, a right and a left. Achiral objects do not have a handedness, for example, a baseball bat (no writing or logos on it), a plain round ball, a pencil, a T-shirt and a nail. The chirality of an object is related to its symmetry, and to this end it is useful to recognize certain **symmetry elements** that may be associated with a

given object. A symmetry element is a plane, a line or a point in or through an object, about which a rotation or reflection leaves the object in an orientation indistinguishable from the original. Some examples of symmetry elements are shown below.



The face playing card provides an example of a center or point of symmetry. Starting from such a point, a line drawn in any direction encounters the same structural features as the opposite (180°) line. Four random lines of this kind are shown in green. An example of a molecular configuration having a point of symmetry is (E)-1,2-dichloroethene. Another way of describing a point of symmetry is to note that any point in the object is reproduced by reflection through the center onto the other side. In these two cases the point of symmetry is colored magenta.

The boat conformation of cyclohexane shows an axis of symmetry (labeled C_2 here) and two intersecting planes of symmetry (labeled σ). The notation for a symmetry axis is C_n , where n is an integer chosen so that rotation about the axis by 360/n^o returns the object to a position indistinguishable from where it started. In this case the rotation is by 180^o, so n=2. A plane of symmetry divides the object in such a way that the points on one side of the plane are equivalent to the points on the other side by reflection through the plane. In addition to the point of symmetry noted earlier, (E)-1,2-dichloroethene also has a plane of symmetry (the plane defined by the six atoms), and a C_2 axis, passing through the center perpendicular to the plane. The existence of a reflective symmetry element (a point or plane of symmetry) is sufficient to assure that the object having that element is **achiral**. Chiral objects, therefore, do not have any reflective symmetry elements, but may have rotational symmetry axes, since these elements do not require reflection to operate. In addition to the chiral vs achiral distinction, there are two other terms often used to refer to the symmetry of an object. These are:

(i) Dissymmetry: The absence of reflective symmetry elements. All dissymmetric objects are chiral.
 (ii) Asymmetry: The absence of all symmetry elements. All asymmetric objects are chiral.

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