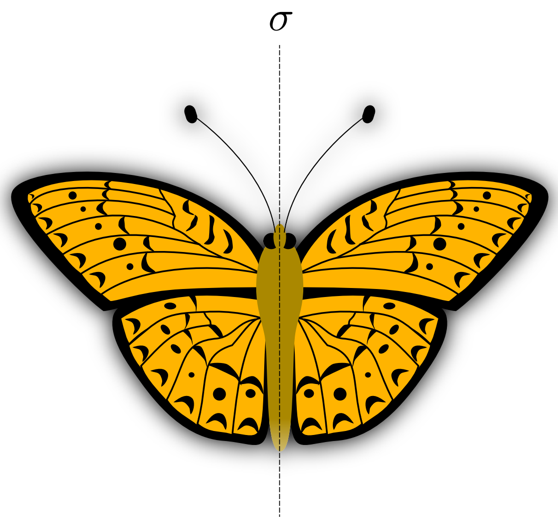
Introduction

Chemists have a nice, compact language for discussing the shapes of finite three-dimensional objects. The shapes of things can be referenced conveniently in terms of what we call symmetry "elements", some of which will already be familiar to you, and "operations". It will become clear that symmetry operations are carried out with respect to the symmetry elements that happen to be present. A symmetry element is present if, upon carring out a corresponding operation, the 3D finite object appears not to have moved or changed in any way.

Mirror Planes and Reflection

The operation of reflection is carried out with respect to a symmetry element known as a mirror plane, to which we give the symbol σ.

A simple example of a 3D finite object having mirror symmetry is a butterfly. This type of symmetry is also called "bilateral". The left half of the butterfly is equivalent to the right half. The mirror plane, σ, is perpendicular to the page, and bisects the butterfly as indicated by the dotted line.

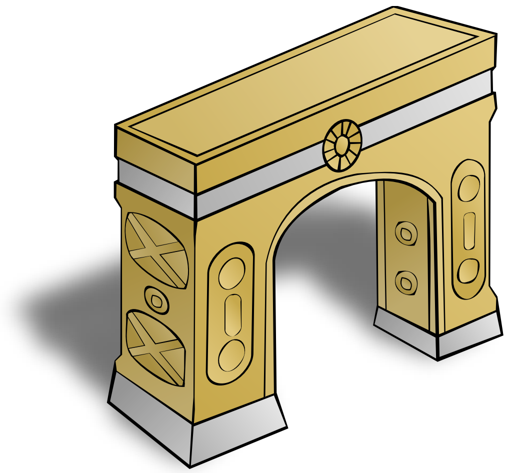


If we carry out the operation of reflection on the butterfly, then the left half exchanges places with the right half. Pick any dot on the butterfly's top left wing, and imagine it exchanging places with the corresponding dot on the butterfly's top right wing. This is the operation of reflection, since nothing appears to have changed or moved after the operation was carried out. Only dots that were equivalent exchanged their places.

If the butterfly's mirror plane indicated by the dotted line is taken to be the Cartesian yz plane, for example, then the operation of reflection amounts to inverting the value of the z coordinate for every point on the surface and the interior of the 3D butterfly solid object. Reflection then exchanges every butterfly point in space on the left side, or $-z$, with every butterfly point in space on the right side, $+z$.

Studying the shape of the butterfly, or indeed any finite 3D object having only bilateral symmetry, we can conclude that there is only present a single mirror plane. Another object with bilateral symmetry is a boomerang. Since a boomerang is shaped like a wing, the top is not shaped like the bottom, but the left is shaped and patterned like the right.

If a 3D finite object has top-bottom symmetry in addition to left-right symmetry, then most likely two mirror planes are present. An example of such an object is an arch. Another example of such an object is the water molecule in its equilibrium geometry. When we talk about the symmetry properties of molecules, we will normally be referring to the equilibrium geometry, even though it is the case that the structures get distorted during processes such as molecular vibrations or chemical reactions. Draw a ball-and-stick diagram of the water molecule, and see if you can convince yourself that it has two mirror planes, same as an arch.



Consider carrying out reflection operations on the water molecule that you drew. Reflection through one of the mirror planes exchanges the left hydrogen with the right hydrogen. The two H nuclei swap their positions, while the O nucleus stays in place. The O nucleus resides on the line of intersection of the two mirror planes, and these are mutually perpendicular.

Proper Axes and Rotation

If a 3D finite object can be rotated by $2\pi/n$ and not appear to have moved or changed in any way, then that object is said to possess an n-fold proper axis of rotation.

As an example, consider a steering wheel with three spokes. This wheel can be rotated by $2\pi/3$ or 120° whereupon it arrives at a configuration indistinguishable from the starting one. Therefore, this particular wheel has a type of principal rotation axis given C_3 as a label. In general, the labeling scheme for n-fold proper axes of rotation is C_n.

Now, unlike the case with a σ plane, notice that the C_3 proper axis of rotation generates more than just one corresponding operation. We can rotate that wheel by 120° (the C_3 operation), but we can also rotate it by 240° about the same axis to achieve yet another configuration equivalent to the original one. This second operation generated by the C_3 axis we call the ${C_3}^2$ operation.

What if the wheel is rotated by 360°? Well, this returns not just a configuration equivalent to the starting one, it returns the *identical* configuration that we started with. This operation, ${C_3}^3$, is not classified as a rotation, but rather it is labeled as the "identity" operation, E. In the case of a mirror plane, we could achieve the same effect as provided by the identity operation upon two sequential reflections through the same mirror plane:

$$E = {C_3}^3 = \sigma^2$$

Going back to the water molecule or the arch, is there present a proper rotation axis? What is its label, and how many operations (not including the identity) does it generate?

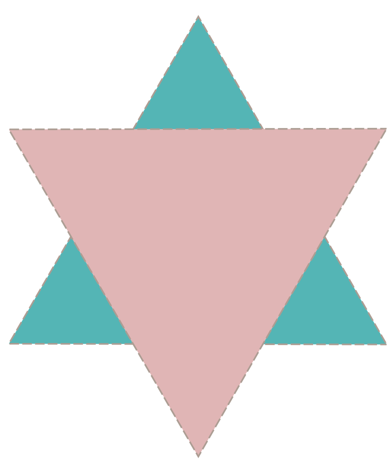
Improper Axes and Improper Rotations

The symmetry operation referred to as improper rotation can be thought of as going "up-down up-down as you go around". Another way to define improper rotation is as a rotation-reflection sequence. For example, a C_2 rotation followed by a reflection through a plane perpendicular to the C_2 axis is referred to as an S_2 operation. Mathematically, the particular case of the S_2 operation has the effect of inverting all the Cartesian coordinates of the points on the surface and inside the body of the object undergoing this operation, so that the special label i is used in this case, and a "center of inversion" is the symmetry element that is said to be present:

$$C_2 \text{ then } \sigma_\perp = S_2 = i$$

A molecule that has an inversion center is octahedral SF_6. The inversion operation applied to SF_6 exchanges pairs of identical *trans*-disposed fluorine atoms.

What would be the effect of carrying out an S_1 operation? This would be a 360° rotation (identity, nothing happened) followed by a reflection. So, an S_1 operation would be just a reflection, σ.



The graphic here represents the top and bottom faces of a trigonal antiprism. In the case of this solid shape, there is a proper three-fold axis of rotation (a C_3 axis) perpendicular to the page. Coincident with this C_3 axis there is an improper axis of rotation, S_6, the corresponding operation for which is rotation by $2\pi/6$ followed by reflection through a plane parallel to the page. What is the effect of carrying out two S_6 operations sequentially? That is the same as carrying out a single C_3 operation:

$$S_6{}^2 = C_3$$

For this trigonal antiprism there is an operation we would be tempted to refer to as $S_6{}^3$, but since this is actually the same as an inversion, we will call it i:

$$S_6{}^3 = i$$

So, the S_6 symmetry element generates only two new operations beyond E (the identity) and i (the inversion), these being S_6 and $S_6{}^5$. Some books call these $S_6{}^+$ and $S_6{}^-$ to indicate opposite directions of rotation.

Summary

Now we have introduced all the different kinds of symmetry elements (and corresponding operations) needed to describe the shapes of solid 3D finite bodies. Every object has the identity, E, and some also have one or more mirror planes, σ. Proper axes of rotation, C_n, can generate more than one new symmetry operation, while an inversion center (i) is a special case of an improper axis of rotation. In general, S_n operations (up-down, up-down as you go around) consist of a rotation-reflection sequence.