Appendix VII: Determination of the Molecular Symmetry Group

A systematic approach to the determination of the point group that describes the symmetry of a molecular is suggested by the flow diagram of Fig. 1. If any difficulty is encountered in finding the symmetry group of a given structure, it is recommended that a molecular model be constructed – the familiar "sticks and stones" version that is employed in elementary courses in organic chemistry. It is then sufficient to follow the diagram and respond to the questions, as indicated. In general the answer is yes (**Y**) or no (**N**).

Play the symmetry game! Follow the flow diagram (Fig. 1). When you arrive at a point where there is a number in parenthesis, refer to the following comments:

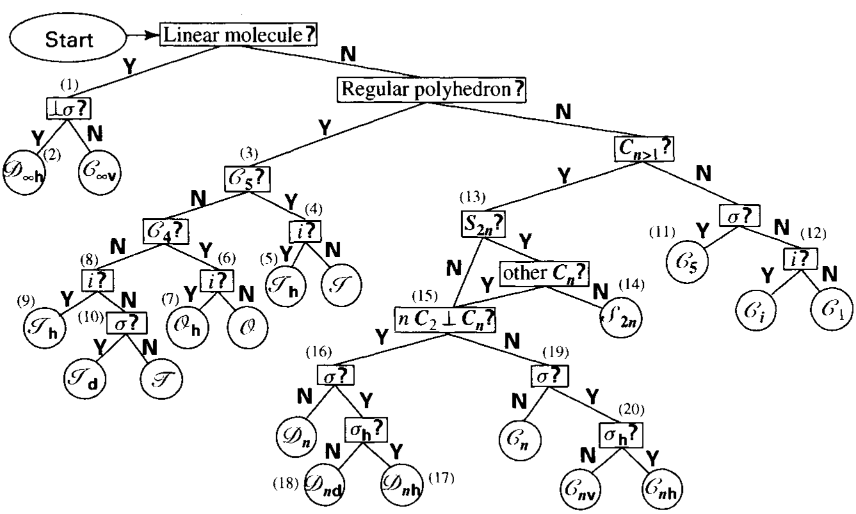

Fig. 1 Flow diagram for the determination of the symmetry group of a molecule.

(1) If the equilibrium structure of your molecule is linear, verify that it has a proper rotation axis of infinite order and an infinite number of planes of symmetry.

(2) If your molecule belongs to the group $\mathcal{D}_{\infty\mathbf{h}}$, it also has an infinite number of binary axes of rotation and a center of inversion. Please check.

(3) You say that your nonlinear molecule has the high symmetry of a regular polyhedron, such as a tetrahedron, cube, octahedron, dodecahedron, icosahedron, ... sphere. If it is a sphere, it is monatomic. On the other hand, if it is not monatomic, it has the symmetry of one of the Platonic solids (see the introduction to Chapter 8).

(4) You have replied that your molecule has a 5-fold axis of rotation. Verify that it also has 15 binary axes and ten ternary axes. Note that it belongs to one of the icosahedral groups. If you play soccer, consider the ball. Before you kick it, look at it. What is its symmetry?

(5) If your molecule has a center of inversion, as you have now indicated, it also must have 15 planes of symmetry. Can you find them?

(6) OK, your molecule does not have a C_5 axis. However, if it has a C_4 axis, it also has three binary rotation axes collinear with the C_4 and six other binary axes. Look carefully to be sure that your molecule indeed belongs to one of the octahedral groups.

(7) If your octahedral molecule has a center of symmetry, it also has nine planes of symmetry (three "horizontal" and six "diagonal"), as well as a number of improper rotation axes or orders four and six. Can you find all of them? If so, you can conclude that your molecule is of symmetry $\mathcal{O}_{\mathbf{h}}$.

(8) If there is neither a C_5 axis nor a C_4 axis, the symmetry of your molecule is that of one of the tetrahedral groups. Check that it also has four 3-fold and three binary rotation axes.

(9) If your molecule has a center of symmetry, it is of point group $\mathcal{T}_{\mathbf{h}}$.

(10) If, as in comment (8), your molecule has any planes of symmetry, it has six of them, as well as three improper axes of order four. If you find them, you can conclude that your molecule is of symmetry $\mathcal{T}_{\mathbf{d}}$. If not, it is of symmetry $\mathcal{T}$.

(11) You have replied that your molecule, that is not a regular polyhedron, does not have a proper rotation axis of order greater than one. If its only symmetry element is a plane, it belongs to the group $\mathcal{C}_{1\mathbf{h}} \equiv \mathcal{C}_{\mathbf{s}}$.

(12) However, if it has center of inversion, it belongs to the group $\mathcal{C}_{\mathrm{i}} \equiv \mathcal{S}_2$. It is then a very rare specimen. It is suggested that you repeat the analysis of its symmetry. On the other hand if your molecule does not have a center of inversion, its symmetry (or lack thereof) is described

by the group $\mathcal{C}_1$ and group theory cannot help you! Unfortunately, many molecules are in this category.

(13) You have specified the order of the proper rotation axis C_n is $n \geq 2$. Is there, then, an improper axis S_{2n}? (Note that if $n > 2$, the n-fold rotation axis C_n is by convention taken to be the vertical (z) axis).

(14) You have replied that there is indeed an axis S_{2n}. However, are there other binary axes C_2 perpendicular to the S_{2n}? If not, the symmetry of your molecule is described by one of the groups $\mathcal{S}_{2n}$ (Note that if n is odd, there is a center of inversion). However, this result is subject to doubt, as there are very few molecules of symmetry $\mathcal{S}_{2n}$.

(15) If you have arrived at this point, you have found no improper axis S_{2n}, but more than one proper axis of order n Or, you have identified at least one other axis of order n in addition to that collinear with S_{2n}. Now, look for n binary axes perpendicular to C_n. If you do not find any, the point group is one of the $\mathcal{C}$-type. Otherwise, there are n binary axes and the group is one of type $\mathcal{D}$.

(16) If there is no plane of symmetry, your molecule belongs to one of the $\mathcal{D}_\mathbf{n}$ groups.

(17) If there is a plane of symmetry perpendicular to the C_n axis, it is denoted by σ_h. Then, if your molecule is of symmetry $\mathcal{D}_\mathbf{nh}$, it also has n planes of symmetry in addition to the horizontal one. Furthermore, it must have an n-fold improper rotation axis (note that $i \equiv S_2$). In general if n is even, there is also a center of symmetry.

(18) If you have arrived at point group $\mathcal{D}_\mathbf{nd}$, your molecule must have n (diagonal) planes of symmetry in addition to the horizontal one. If n is odd, there is also a center of symmetry. The simplest case is that with $n = 2$. Look at the seams on a baseball or a tennis ball and verify that its symmetry is that of $\mathcal{D}_\mathbf{2d}$.

(19) The absence of n binary axes will lead you to one of the three $\mathcal{C}$-type point groups shown. Your molecule has the symmetry of one of the $\mathcal{C}_\mathbf{n}$ groups if it has no planes of symmetry.

(20) The presence or absence of a horizontal plane of symmetry will characterize the groups $\mathcal{C}_\mathbf{nh}$ or $\mathcal{C}_\mathbf{nv}$, respectively. To verify these possible results note that the former groups must have an improper rotation axis of order n ($\mathcal{C}_\mathbf{1h} \equiv \mathcal{C}_\mathbf{s}$). However, for the latter (groups $\mathcal{C}_\mathbf{nv}$), you will hopefully find n vertical planes, but no center of symmetry.