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Ajit J Thakkar

Chapter 1

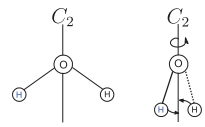
Molecular symmetry

1.1 Symmetry operations and elements

Symmetry is all around us. Most people find symmetry aesthetically pleasing. Molecular symmetry imposes constraints on molecular properties[1]. A *symmetry operation* is an action that leaves an object looking the same after it has been carried out. A *symmetry element* is a point, straight line, or plane (flat surface) with respect to which a symmetry operation is carried out. The center of mass must remain unmoved by any symmetry operation and therefore lies on all symmetry elements. When discussing molecular symmetry, we normally use a Cartesian coordinate system with the origin at the center of mass. There are five types of symmetry operation. The identity operation E does nothing and is included only to make a connection between symmetry operations and *group theory*. The other four symmetry operations—rotations C_n, reflections σ, inversion i, and improper rotations S_n—are described next.

1.1.1 Rotations around axes

A symmetry axis C_n, of order n, is a straight line about which $(1/n)$th of a full 'turn' (a rotation by an angle of $360°/n$) brings a molecule into a configuration indistinguishable from the original one. A C_n axis must pass through the center of mass.



[1] As Eugene Wigner said, symmetry provides 'a structure and coherence to the laws of nature just as the laws of nature provide a structure and coherence to a set of events'.

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A C_1 axis corresponds to a 360° rotation and so it is the same as the identity operation: $C_1 = E$. A C_2 axis has a 360°/2 = 180° rotation associated with it. In H_2O, the line bisecting the HOH angle is a C_2 axis; rotation about this axis by 180° just interchanges the two hydrogen nuclei. If the z axis is a C_2 axis, then its action on a nucleus is to move it from its original position (x, y, z) to $(-x, -y, z)$. Thus

$$C_2(z)\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}. \tag{1.1}$$

A C_2 axis generates only one unique symmetry operation because two 180° rotations bring an object back to its original configuration; that is, $C_2C_2 = C_2^2 = E$. Each of the objects A, B and C in figure 1.1 has exactly one C_2 axis. The C_2 axis is along the x axis in object A, along the y axis in object B, and along the z axis in object C. The more symmetrical object D in figure 1.1 has three C_2 axes, one along each of the x, y and z axes.

A square has a C_4 axis of symmetry as illustrated in figure 1.2. Performing two successive C_4 or 360°/4 = 90° rotations has the same effect as a single C_2 or 180° rotation; in symbols, $C_4^2 = C_2$. Hence for every C_4 axis there is always a collinear C_2 axis. Moreover, $C_4^4 = C_2^2 = E$ and so a C_4 axis generates only two unique symmetry operations, C_4 and C_4^3. A clockwise C_4^3 rotation is the same as a counter clockwise C_4 rotation. We adopt the convention that all rotations are clockwise. A C_4 axis can be found, for example, along each S–F bond in the octahedral molecule SF_6, and along the axial I–F bond in the square pyramidal IF_5 molecule. (Tip: nuclei not on C_n occur in sets of n equivalent ones.)

In NH_3, the line passing through the nitrogen nucleus and the center of the triangle formed by the hydrogen nuclei is a C_3 axis; rotation by 360°/3 = 120° permutes the H nuclei ($a \to b$, $b \to c$, $c \to a$). Methane has a C_3 axis along each C–H bond.

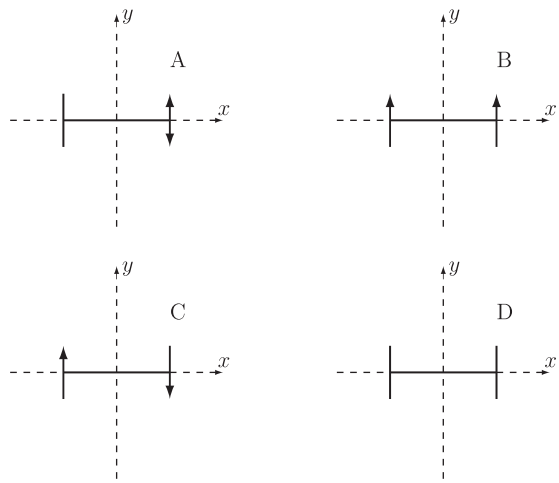


Figure 1.1. Can you see the C_2 axes in objects A, B, C, and D?

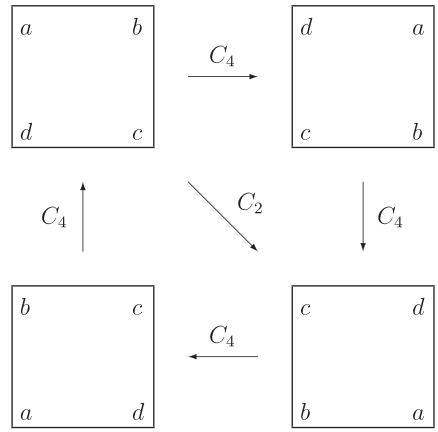
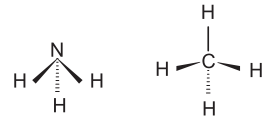
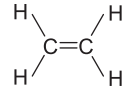


Figure 1.2. C_4 symmetry in a square.



A C_3 axis generates two unique symmetry operations, C_3 and C_3^2. Benzene has a C_6 axis perpendicular to the ring and passing through its center. A C_6 axis generates only two unique symmetry operations, C_6 and C_6^5, because a C_3 and a C_2 axis are always coincident with it, and $C_6^2 = C_3$, $C_6^3 = C_2$, $C_6^4 = C_3^2$, and $C_6^6 = E$. In O=C=O, the molecular axis is a C_∞ axis because rotation by any angle, however small, about this axis leaves the nuclei unmoved.

The z axis is taken along the *principal symmetry axis* which is defined as the C_n axis with the highest order n. For example, the C_6 axis is the principal axis in benzene. If there are several C_n axes of the highest n, then the principal axis is the one passing through the most nuclei. For example, ethene (C_2H_4) has three C_2 axes and the principal axis is the one passing through both carbons. A planar molecule that has its principal axis in the molecular plane, like ethene but unlike benzene, is placed in the yz plane.



1.1.2 Reflections through symmetry planes

A plane is a symmetry plane σ if reflection of all nuclei through this plane sends the molecule into an indistinguishable configuration. A symmetry plane contains the center of mass and bisects a molecule. If the symmetry plane is the xy plane, then its action on a nucleus is to move it from its original position (x, y, z) to $(x, y, -z)$. Thus,

$$\sigma_{xy}\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}. \tag{1.2}$$

A symmetry plane generates only one unique symmetry operation because reflecting through it twice brings a molecule back to its original configuration. Hence $\sigma^2 = E$. A symmetry plane is also called a mirror plane.

The xy plane is a symmetry plane for each of the planar objects A, B, C and D in figure 1.1. Objects A and D also have the xz plane as a plane of symmetry. Objects B and D have a yz symmetry plane. Object C has no other planes of symmetry. Thus object D has three planes of symmetry, objects A and B each have two but object C has only one plane of symmetry. Any planar molecule, such as benzene, has its molecular plane as a plane of symmetry because reflection across the molecular plane leaves all nuclei unmoved.

NH_3 has three planes of symmetry each of which contains an N–H bond and is perpendicular to the plane containing the three hydrogen atoms. (Tip: nuclei not on σ occur in equivalent pairs.) The three symmetry planes are geometrically equivalent, and the corresponding reflections are said to form a *class*. Operations in the same class can be converted into one another by application of some symmetry operation of the group or equivalently by a suitable rotation of the coordinate system. The identity operation always forms a class of its own.

A symmetry plane perpendicular to the principal symmetry axis is called a *horizontal* symmetry plane σ_h. Symmetry planes that contain the principal symmetry axis are called *vertical* symmetry planes σ_v. A vertical symmetry plane that bisects the angle between two C_2 axes is called a *dihedral* plane σ_d. The distinction between σ_v and σ_d planes is unimportant, at least in this book. For example, H_2O has two vertical symmetry planes: the molecular plane and one perpendicular to it. The intersection of the two planes coincides with the C_2 axis. The molecular plane of a planar molecule can be either horizontal as in C_6H_6 or vertical as in H_2O. Benzene also has six symmetry planes perpendicular to the ring and containing the C_6 axis. These six planes separate into two classes: three containing CH bonds and three containing no nuclei. One class of planes is called vertical and the other dihedral; in this example, either class could be called vertical. Linear molecules like HCl and HCN have an infinite number of vertical symmetry planes. Some of them, such as N_2 and CO_2, have a horizontal symmetry plane as well. Reflection in σ_h is always in a class by itself.

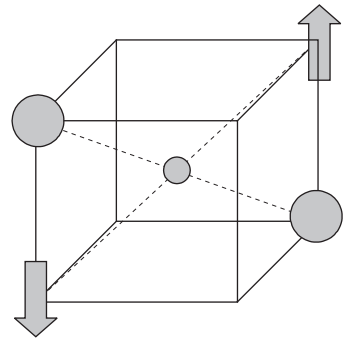


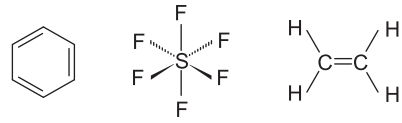
Figure 1.3. This object has a center of symmetry. There would be no center of symmetry if the arrows pointed in the same direction.

1.1.3 Inversion through a center of symmetry

If an equivalent nucleus is reached whenever a straight line from *any* nucleus to the center of mass is continued an equal distance in the opposite direction, then the center of mass is also a center of symmetry. Since the center of mass is at the coordinate origin (0, 0, 0), the inversion operation i moves an object from its original position (x, y, z) to $(-x, -y, -z)$. Thus

$$i\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}. \tag{1.3}$$

Objects C and D in figure 1.1 have a center of symmetry but objects A and B do not. C_6H_6, SF_6, C_2H_4 and the object in figure 1.3 have a center of symmetry but CH_4 does not. (Tip: nuclei not on i occur in equivalent pairs.) Inversion generates only one unique symmetry operation because $i^2 = E$. Inversion forms a class by itself.



1.1.4 Improper rotations around improper axes

An improper rotation S_n is a rotation by $360°/n$ about an axis followed by a reflection in a plane perpendicular to the axis. Thus $S_n = \sigma C_n$. No unique symmetry operations are generated by an S_1 or S_2. Note that $S_1 = \sigma C_1 = \sigma$ because $C_1 = E$, and that $S_2 = \sigma C_2 = i$ as can be seen by combining equations (1.1)–(1.3). Hence only S_n with $n \geqslant 3$ are normally called S_n. Molecules which have both a C_n and a σ_h must have an S_n. For example, benzene has an S_6 axis coincident with its C_6 axis because it has a σ_h.

However, an object or molecule need not have a σ or a C_n to have an S_n. Non-trivial S_4 axes are illustrated in figure 1.4 for a crossed stack of erasers and for

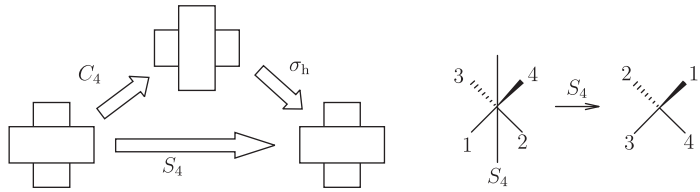


Figure 1.4. A non-trivial S_4 axis with no coincident C_4 axis is shown for stacked erasers on the left and for methane on the right.

methane. Figure 1.4 shows that methane has three S_4 axes, each of which bisects two HCH angles, even though it has neither a C_4 axis nor any symmetry planes perpendicular to an S_4 axis. An S_4 axis generates only two unique symmetry operations, S_4 and S_4^3, because $S_4^2 = \sigma C_4 \sigma C_4 = \sigma^2 C_4^2 = EC_2 = C_2$ and $S_4^4 = S_4^2 S_4^2 = C_2^2 = E$.

1.2 Classification of molecular symmetry

Objects cannot have an arbitrary collection of symmetry elements. For example, it is impossible to have a molecule in which there is a C_3 axis and only one σ_v. A rotation by 120° about the C_3 axis carries the σ_v into a different plane, say P. Since C_3 is a symmetry axis, this new configuration of the molecule must be indistinguishable from the original one. However, for this to be so, the plane P must be a σ_v plane as well. Clearly, a C_3 axis and one σ_v plane imply the existence of two more σ_v planes.

Mathematicians have worked out all possible groups of symmetry operations. Their results can be used to classify molecules by symmetry. Since all the symmetry elements of a molecule must intersect in at least one point, the symmetry groups are called *point groups*. Each group is designated by a symbol called the *Schoenflies symbol*.

An atom has spherical symmetry and belongs to the K point group. To assign a molecule to a point group, use the flow chart given in figure 1.5. The first step is to decide whether the molecule is linear (all atoms on a straight line). If it is linear, then it has $C_{\infty v}$ or $D_{\infty h}$ symmetry depending on whether or not it has an inversion center. For example, carbon dioxide (O=C=O) has $D_{\infty h}$ symmetry but HCN has $C_{\infty v}$ symmetry.

If the molecule is not linear, then search for non-trivial axes of rotation C_n with $n > 1$. It helps to know that if there is a C_n axis, then all the off-axis nuclei can be separated into sets of n equivalent nuclei. If there are multiple C_n with $n > 2$, then the molecule belongs to a high-symmetry 'Platonic' group. Six C_5 axes indicate I_h, the point group of a perfect icosahedron or pentagonal dodecahedron, or the rare I, which has only the pure rotations of an icosahedron. Buckminsterfullerene C_{60} has I_h symmetry. Three C_4 axes indicate O_h, the point group of a cube or a perfect octahedron like SF_6, or the rare O which has only the pure rotations of an octahedron. Four C_3 axes and no C_4 axes indicate T_d, the group of a perfect tetrahedron like methane, or the rare T which has only the rotations of T_d, or T_h obtained by combining an inversion center with the rotations of T. The I, O, T_h, and T point groups are chemically rare.

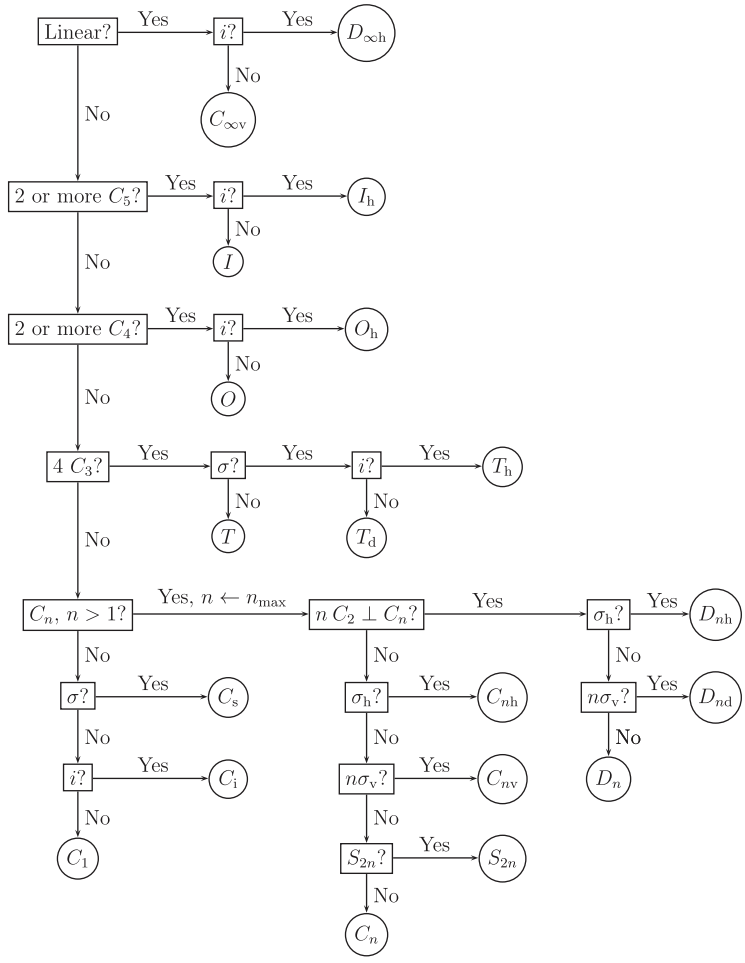


Figure 1.5. Flow chart for determining point group symmetry.

If there are no C_n axes at all with $n > 1$, the molecule is of low symmetry and belongs to (a) C_s if there is a symmetry plane, (b) C_i if there is a center of inversion, and (c) C_1 otherwise. If there are some C_n with $n > 1$, choose a principal axis with the maximum n. From this point on, n is the fixed number that you determined in this step. Check for nC_2 axes perpendicular to the principal axis of symmetry. Next, search for a horizontal plane of symmetry, σ_h. Don't assume that the molecular plane in a planar molecule is a σ_h. For example, the molecular plane in benzene is a σ_h but the molecular plane in H_2O is a σ_v. On those rare occasions when you have to look for an S_{2n} axis, bear in mind that $2n$ is always even and that $2n \geqslant 4$ because $n > 1$. Molecules with D_n or S_{2n} symmetry are uncommon. For example, $C(C_6H_5)_4$ has S_4 symmetry, and ethane in a conformation that is neither staggered nor eclipsed has D_3 symmetry. Use table 1.1 to check for all the symmetry elements characteristic of the point group.

Table 1.1. Characteristic symmetry elements of point groups. $n \geqslant 2$.

Simple		Single-axis groups		Dihedral groups	
C_1	E	C_n	C_n	D_n	C_n, nC_2 ($\perp C_n$)
C_s	σ	C_{nv}	C_n, $n\sigma_v$	D_{nd}	C_n, nC_2 ($\perp C_n$), $n\sigma_d$, S_{2n}
C_i	i	C_{nh}	C_n, σ_h	D_{nh}	C_n, nC_2 ($\perp C_n$), $n\sigma_v$, σ_h
		Infinite groups		Platonic groups	
		$C_{\infty v}$	C_∞, $\infty\sigma_v$	T_d	$4C_3$, $3C_2$, $6\sigma_d$, $3S_4$
		$D_{\infty h}$	C_∞, $\infty\sigma_v$, i, σ_h	O_h	$3C_4$, $4C_3$, i, $6\sigma_d$, $3\sigma_h$
		K	∞ C_∞	I_h	$6C_5$, $10C_3$, i, 15σ

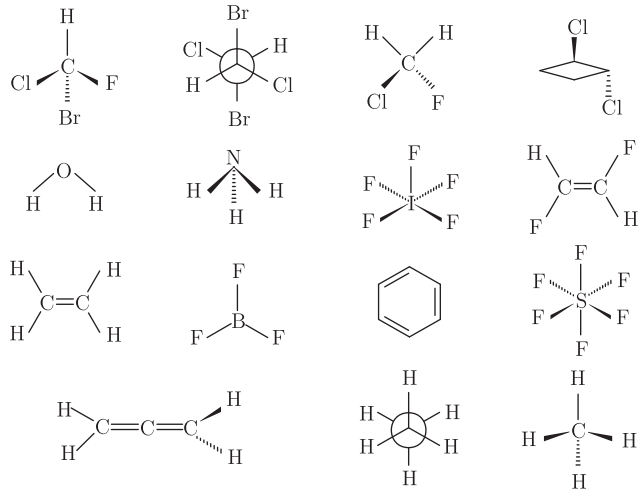


Figure 1.6. Molecules with various symmetries.

Practice finding the point groups[2] for the molecules in figure 1.6. Visualization software that allows rotation of a molecule's ball-and-stick image in three dimensions is helpful. Newman projections, as taught in organic chemistry, help you see D_n, D_{nd}, and D_{nh} symmetry.

1.3 Implications of symmetry

The dipole moment of a molecule should not be changed either in direction or in magnitude by a symmetry operation. This invariance to symmetry operations can be realized only if the dipole moment vector is contained in each of the symmetry elements. For example, an inversion center, more than one C_n axis, and a horizontal symmetry plane all eliminate the possibility of a dipole moment. Therefore, a

[2] From left to right, first row: C_1, C_i, C_s, C_2; second row: C_{2v}, C_{3v}, C_{4v}, C_{2h}; third row: D_{2h}, D_{3h}, D_{6h}, O_h; fourth row: D_{2d}, D_{3d}, T_d.

molecule can have a non-zero dipole moment only if it belongs to one of the point groups C_1, C_s, C_n or C_{nv}. Thus H_2O with C_{2v} symmetry can and does have a non-zero dipole moment, but CO_2 with $D_{\infty h}$ symmetry cannot and does not have a non-zero dipole moment.

A *chiral* molecule is one that cannot be superimposed on its mirror image. Thus, a molecule can be chiral only if it does not have a symmetry element that converts a right-handed object to a left-handed one. In other words, a molecule can be chiral only if it does not have a plane of symmetry or an inversion center or an improper axis of symmetry S_n. Since $S_1 = \sigma$ and $S_2 = i$, we can simply say that the presence of an improper axis of symmetry rules out chirality. A molecule can be chiral only if it belongs to a C_n or D_n point group.

In discussions of rotational spectroscopy, it is usual to classify molecules into four kinds of *rotors* or *tops*. The correspondence between that classification and point groups is simple. *Linear rotors* are $C_{\infty v}$ or $D_{\infty h}$ molecules. *Spherical tops* contain more than one C_n axis with $n \geqslant 3$ as in T_d, O_h or I_h molecules. *Symmetric tops* are molecules that contain one and only one C_n axis with $n \geqslant 3$ or an S_4 axis, and thus belong to C_n, C_{nv}, C_{nh}, D_n, D_{nh} or D_{nd} with $n \geqslant 3$ or D_{2d} or S_n ($n = 4, 6, 8, \ldots$). *Asymmetric tops* are molecules that do not contain any C_n axis with $n \geqslant 3$ or S_4 axis, and thus belong to C_1, C_i, C_s, C_2, C_{2v}, C_{2h}, D_2 or D_{2h}.

Two symmetry operations, $\mathcal{O}_1$ and $\mathcal{O}_2$, are said to commute if the result of carrying out one after the other does not depend upon the order in which they are carried out. That is $\mathcal{O}_1$ and $\mathcal{O}_2$ commute if $\mathcal{O}_1\mathcal{O}_2 = \mathcal{O}_2\mathcal{O}_1$ where $\mathcal{O}_1\mathcal{O}_2$ means first do $\mathcal{O}_2$ and then do $\mathcal{O}_1$. Symmetry operations do not always commute. For example, figure 1.7 shows that, in an equilateral triangle, reflections in the σ_v do not commute with one another; in symbols, we write $\sigma_v'\sigma_v \neq \sigma_v\sigma_v'$. Figure 1.7 also shows that $\sigma_v'\sigma_v = C_3$ and $\sigma_v\sigma_v' = C_3^2$.

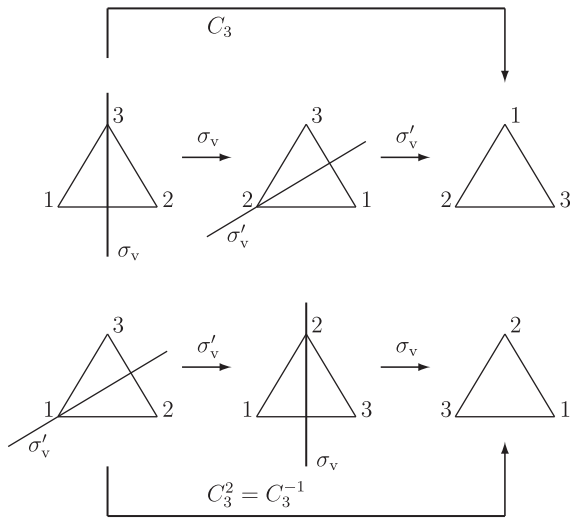


Figure 1.7. Non-commutativity of reflections in an equilateral triangle.

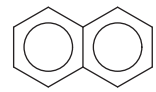
Groups in which each symmetry operation commutes with every other symmetry operation are called *Abelian*. Every element of an Abelian group forms a class by itself. Note that the symmetry group of an asymmetric top molecule is always an Abelian point group. The energy levels of molecules with Abelian symmetry have a special simplicity as we shall see in section 4.2.

Problems (see appendix B for hints and solutions)

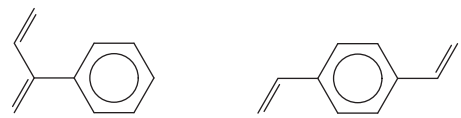
1.1 Which of the molecules in figure 1.6 has a center of inversion?

1.2 Suppose the z axis is a C_4 axis of symmetry. What will be the coordinates of a nucleus after a clockwise C_4 rotation if its coordinates were (x, y, z) before the rotation?

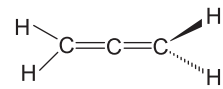
1.3 Use sketches to show all the symmetry elements in naphthalene.



1.4 Use sketches to show all the symmetry elements in the following molecules:

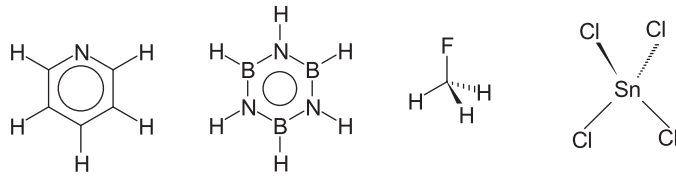


1.5 Find two planes of symmetry and three C_2 axes in allene (C_3H_4).

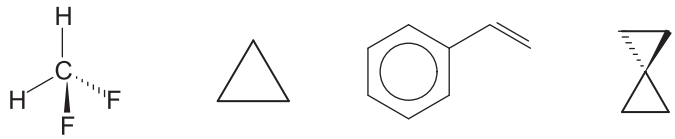


Use sketches to show the symmetry elements. Drawing Newman diagrams (projections) in the manner of organic chemistry books is helpful.

1.6 Find the symmetry point group for each of the following molecules. Which molecules are polar and which are chiral?



1.7 Find the symmetry point group for each of the following molecules. Which molecules are polar and which are chiral?



1.8 A molecule has three C_2 axes that are perpendicular to each other, and no other non-trivial symmetry elements. Can such a molecule have a non-zero dipole moment? Can it be chiral? Explain without reference to the point group of the molecule.