

# Molecular Symmetry

DAVID J. WILLOCK

*Cardiff University*

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*Cardiff University*



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# Preface

Symmetry is central to spectroscopy, chemical bonding theory and many other aspects of the molecular sciences. The idea of this book is to introduce the topic in a graduated way, from molecular structure, through point groups, leading into the powerful tools that group theory provides. Example models and applications are used at all stages to show how the sometimes abstract ideas are relevant to practical problems. It is designed to be a useful companion at all levels of undergraduate study and beyond.

Chapters 1 and 2 introduce the ideas of symmetry elements and operations for the description of molecular geometry; this sets up the required symbols through examples of particular molecules. Chapter 3 looks from a slightly different perspective, laying out all the sets of operations that are contained in the common point groups and discussing why only certain sets are possible. For all three chapters Appendices 1, 2 and 4 give some paper models that can be used for visualization of the shapes that are not easily built using a molecular modeling kit. These paper models will also be available from the website. The reader interested in the applications of symmetry, without too much detail of the background, may wish to skip over Chapter 3 on the first reading.

Chapters 4 and 5 introduce the concepts of group theory, which makes symmetry indispensable for understanding many areas of chemistry. This book concentrates on applications in vibrational spectroscopy and molecular orbital theory and so illustrative examples are drawn from these areas.

Chapter 6 covers applications in vibrational spectroscopy, specifically dealing with infra-red and Raman. The chapter explains how symmetry is used to rationalise experimental data to help determine the shape and structure of molecules. To do this some background on the physical origin of spectral bands and the role of symmetry in determining selection rules is given.

Finally, Chapter 7 deals with molecular orbital theory. Molecular orbital pictures are quite straightforward to produce with modern software and the results of such calculations are used as illustrations throughout. The aim of this chapter is to demystify how molecular orbitals are obtained from sets of atomic orbitals. Some fundamental concepts, such as the idea of electronegativity and the factors that influence the strength of bonding are reviewed.

Further appendices are linked to each chapter to provide a more detailed coverage of material such as spectroscopic selection rules, the mathematics of matrices and background quantum mechanics. The flow of the text will work without these, but curiosity should hopefully draw the reader to them.

Many people have helped me in the production of this book, most notably those that have reviewed various parts of the manuscript; Mike Hewlins, Peter Knowles, Massimo Mella, Jamie Platts and Edward Jeffery. They have been thorough in their reading of the

text and frank in their comments on it, for which I am very grateful. Dai Hibbs, Bernard Richardson and Mike Coogan also provided some images from their own research, which has notably enlivened the presentation of the practical implications of symmetry. I have also taught the topic for a number of years with Simon Aldridge and Chris Morley, and have benefited greatly from their ideas.

David J. Willock  
Cardiff, November 2008.

Powerpoint slides of all figures from this book, along with other supplementary material can be found on this book's webpage at [www.wileyeurope.com/college/willock](http://www.wileyeurope.com/college/willock)

# 1

## Symmetry Elements and Operations

### 1.1 Introduction

Symmetry and group theory provide us with a formal method for the description of the geometry of objects by describing the patterns in their structure. In chemistry, it is a powerful method that underlies many apparently disparate phenomena. Symmetry allows us to describe accurately the types of bonding that can occur between atoms or groups of atoms in molecules. It also governs the transitions that may occur between energy levels in molecular systems, which in turn allows us to predict the absorption properties of molecules and, hence, their spectra.

This book will lay out the formal language used in the area, using illustrative examples of particular molecules throughout. We will then apply the ideas of symmetry to describe molecular structure and bonding in molecules and to consider the implications in spectroscopy.

Even in our surroundings we often look for symmetry, Figure 1.1 shows a picture of a wood engraving entitled *Fish, Vignette* made in 1955 by the artist M.C. Escher. In this work, the intertwined fish are shown set inside a hexagonal border. All of the fish illustrated have the same shape and they are designed to fit together perfectly. Six of the fish touch fins in the centre of the image and each of these has a partner with a fin on a corner of the hexagon. If we imagine rotating the picture by  $60^\circ$  about the central point, each fish would move to a new position and exactly replace a fish of opposite colour. This property gives the picture an attractive quality, but it also tells us that we could reconstruct the whole image by knowing the shape of the fish and the initial position of any pair, simply using six equivalent sections placed according to the rotation. At each step all we need do is remember to change the colours of the fish. The image is said to have rotational symmetry, and the techniques of this book provide a concise method of stating the rules for the construction of the picture.



**Figure 1.1** M.C. Escher's 'Fish, Vignette' Copyright 2008 The M.C. Escher Company-Holland. All rights reserved. [www.mcescher.com](http://www.mcescher.com).

Figure 1.2 shows the ceiling of the Arab Room of Cardiff Castle. It is clear that the decorators have gone to a lot of trouble to use symmetry. In this case, a rotation of the image through  $90^\circ$  would interchange the positions of the windows; but, since they are identical, the pattern would appear unchanged. Four such rotations are possible, with the last returning each part of the ceiling to exactly its initial location. This image also has additional symmetry properties not possessed by Escher's fish. Imagine a line drawn horizontally across the image so that it passes through the centre of the left- and right-hand windows. The two sections of the image are now reflections of each other, with each feature in the upper part of the picture repeated in the lower half, as if reflected in a mirror standing





**Figure 1.2** Arab Room ceiling, Cardiff Castle. Copyright: Cardiff Council.

perpendicular to the line. The mirror can be thought of as a plane of symmetry, and this image contains four such planes.

We can also look for planes of symmetry in nature. The fern frond shown in Figure 1.3 looks perfectly normal at first glance. However, on close inspection it can be seen that the left side of the leaf is just a reflection of the right-hand side on the surface of a pond. The picture is shown with the water surface vertical, which enhances the illusion. From half the leaf and its reflected image we can easily imagine the complete structure.

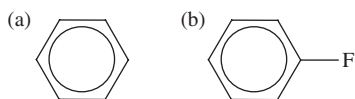
In chemistry, symmetry is not simply to do with beauty. It affects the properties of molecules and, in particular, influences the spectra we observe. For instance, most people would say that benzene is a ‘more’ symmetric molecule than fluorobenzene (Figure 1.4), since the fluorinated carbon should be different to the other carbon atoms. Figure 1.5 shows that this simple substitution has a profound affect on the infrared (IR) spectra of the two molecules.

The IR spectrum of benzene is very simple, showing only four main bands. On substitution with a single fluorine atom to give fluorobenzene, the spectrum becomes much more complex, with many more bands appearing between  $400$  and  $1600\text{ cm}^{-1}$ .

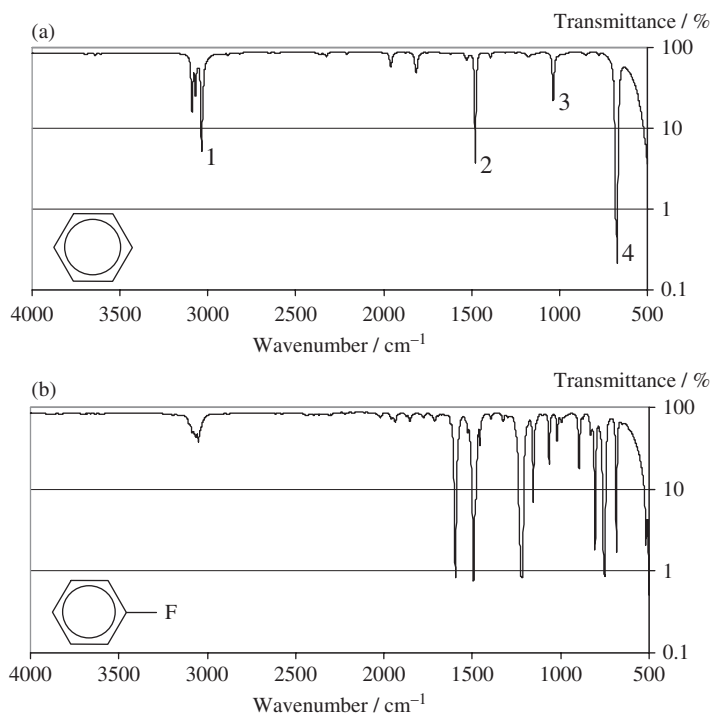
We know that IR spectra are the result of radiation exciting vibrational modes in a molecule. The number of possible lines is related to the number of vibrational modes for the molecule in question. Since each atom in a molecule can move in three dimensions ( $X, Y, Z$ ), both benzene and fluorobenzene will have a total of 36 degrees of freedom. For



**Figure 1.3** The frond of a fern imaged at the surface of a pond. Although we see a complete leaf, the left-hand side is actually a reflection. In fact, the segments (or pinna) on opposite sides of a frond are usually not quite mirror images of one another, as the points at which the pinna attach to the stem are staggered.



**Figure 1.4** The structures of (a) benzene and (b) fluorobenzene.



**Figure 1.5** The infra-red spectra of (a) benzene and (b) fluorobenzene. Note that the transmittance scale is logarithmic and the drop in the base line between around 700 and 500  $\text{cm}^{-1}$  is a feature of the instrument. Data kindly provided by Dr Mike Coogan, School of Chemistry, Cardiff University.

a nonlinear molecule there are six degrees of freedom associated with the motion of the molecule as a whole (three translations and three rotations), and these are not vibrations. So, we expect the number of vibrational modes for a molecule containing  $N$  atoms to be  $3N - 6$ . Both benzene and fluorobenzene have 12 atoms, and so have 30 vibrational modes. The fact that this does not result in 30 IR absorptions is a result of the symmetry of the molecules; and because benzene is ‘more’ symmetric than fluorobenzene, fewer modes of vibration are detected in the spectrum of benzene than in that of fluorobenzene.

To understand and quantify these differences in spectra we need more rigorous definitions of symmetry than simply saying benzene is ‘more’ symmetric than fluorobenzene. The geometric constructs of molecular symmetry help us to define a molecule’s symmetry and the use of group theory allows us to predict the number of absorption lines that will be observed.

To achieve this we look for features in the geometry of a molecule that give rise to its symmetry. The most easily recognized of these features, or *symmetry elements*, are rotational axes (lines of symmetry) and mirror planes (planes of symmetry). These will be discussed in the remaining sections of this chapter, along with the inversion centre, which is a point of symmetry. There are other symmetry elements and operations that are possible, and we will meet these in Chapter 2. The symmetry elements imply that

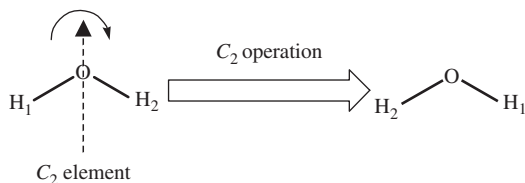
there are symmetry operations: actions that can be carried out which appear to leave the molecule unchanged. If a molecule has multiple symmetry elements then there will be at least one point in space which lies within them all. For example, Figure 1.8 shows that all the rotation axes of ferrocene meet at the central point where the Fe atom is located. For this reason, the symmetry of molecules is often referred to as *point group symmetry*. The idea of this book is to introduce the ideas of point group symmetry and its application in vibrational spectroscopy and the molecular orbital (MO) description of chemical bonding.

In periodic systems (such as crystal structures), other symmetries exist to do with translation between equivalent molecules. See the Further Reading section at the end of this chapter for a book on this topic.

## 1.2 Symmetry Elements and Operations

### 1.2.1 Proper Rotations: $C_n$

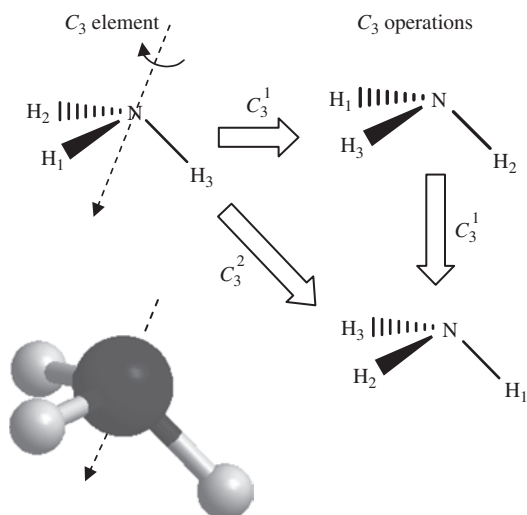
The geometric properties of shapes that make them symmetric can be classified by their symmetry elements. The validity of a symmetry element can be checked by carrying out the corresponding operation and then comparing the object with the starting point. For example, imagine constructing an axis for a water molecule which runs through the oxygen atom, bisecting the H—O—H angle, with the axis in the plane of the molecule. This construction is shown in Figure 1.6, which also illustrates the result of rotating the molecule by  $180^\circ$  around the axis. After the rotation, we end up with a view of the water molecule identical to the starting point, so much so that if we had not labelled the hydrogen atoms it would be indistinguishable from the original. This result shows that the axis we have drawn is a symmetry element of the molecule and the act of rotating the molecule is the corresponding symmetry operation. The rotation operation also shows that the two hydrogen atoms in the water molecule are equivalent; if a symmetry operation can interchange two atoms, then the atoms must occupy identical chemical environments.



**Figure 1.6** The  $C_2$  symmetry element of water and the result of the  $C_2$  operation.

Rotational elements and operations are labelled using a capital  $C$ . For rotations by  $180^\circ$  there are two positions of the molecule which appear identical, the starting point and the molecule after the rotation, so a subscript 2 is added to the label:  $C_2$ . This subscript is known as the *order* of the rotation axis.

To emphasize the difference between elements and operations further, consider the structure of ammonia shown in Figure 1.7. A  $C_3$  axis is present: the symmetry element is a line running through the nitrogen atom and the centre of the triangle formed by the three hydrogen atoms.

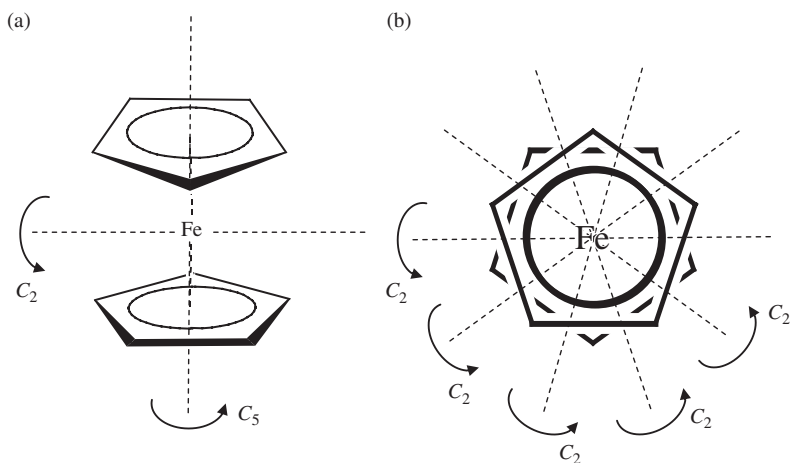


**Figure 1.7** The  $C_3$  axis of ammonia and the corresponding operations. The lower image shows a ball-and-stick model of ammonia in roughly the same orientation as the chemical drawing pictures above. The superscript on the operations gives the number of rotations starting from the initial configuration.

The  $C_3$  axis actually has two symmetry operations associated with it, as can be seen in Figure 1.7: a rotation by  $120^\circ$  and a rotation by  $240^\circ$ . By convention, a rotation operation moves the atoms clockwise when looking down the axis direction. In the first step of the operation sequence shown in Figure 1.7, a clockwise rotation by  $120^\circ$  takes each hydrogen atom to the position of one of its neighbours. A second application of the operation takes each hydrogen atom to the original position of its other neighbour. To distinguish the two operations we add a superscript to indicate how many times the operation has been applied. So  $C_3^2$  means that, starting from the original configuration, two successive rotations of  $120^\circ$  are applied, i.e. a total of  $240^\circ$ .

Molecules may contain more than one rotation axis, and those axes may have different orders. In this situation, the highest order axis is termed the *principal axis*. As an example, Figure 1.8 shows the structure of ferrocene (di-cyclopentadienyl iron(II)). This complex has a  $C_5$  axis, which is the line joining the centres of the cyclopentadiene rings through the Fe centre (Figure 1.8a). In addition, there are five  $C_2$  axes that run through the Fe atom parallel to the ring systems and perpendicular to the principal axis. These are best seen looking down the principal axis direction, as shown in Figure 1.8b. The  $C_2$  rotation operations cause the exchange of the cyclopentadiene rings, whereas the  $C_5$  operation simply rotates each cyclopentadiene ring around its centre. There is a convention that molecules are orientated so that the principal axis defines the vertical direction and that this is also aligned with the Cartesian Z-axis. This means that the vertical direction in Figure 1.8a runs up the page, whereas ‘vertical’ in Figure 1.8b is into the page.

The symmetry elements for a molecule are fixed in space: as we move the atoms under a given operation the symmetry elements are not shifted. For ferrocene, the atoms of the complex can be moved between any of five arrangements using the principal axis. In any



**Figure 1.8** The structure of ferrocene, illustrating (a) the  $C_5$  axis and an example  $C_2$  axis; (b) a plan view of the molecule showing all five  $C_2$  axes.

of these, each of the  $C_2$  axes remains a symmetry element. The five  $C_2$  axes meet at a point on the principal axis and they have an angular spacing of  $72^\circ$ , i.e. the angle of rotation for the  $C_5^1$  operation. So, after a  $C_5^1$  operation, the arrangement of the atoms around any of the  $C_2$  axes is shifted to one of its neighbours; this implies that all the  $C_2$  axes have an equivalent environment of atoms, and so they are treated as equivalent axes.

It is also possible for a molecule to contain axes of the same order that are not equivalent to one another. Figure 1.9 shows the structure of benzene, a molecule which has a  $C_6$  principal axis perpendicular to the molecular plane. Each of the carbon atoms in benzene can be placed at any of the six positions by successive applications of the  $C_6$  rotation and so all of the carbon atoms are in identical environments. Each  $C_6$  operation rotates the molecule about its centre by  $60^\circ$ . Two  $C_6$  operations,  $C_6^2$ , will give a rotation of  $120^\circ$ , which we have already seen corresponds to a  $C_3^1$  rotation. We will usually use the lowest order alternative when listing symmetry operations, so that the  $C_6$  axis has associated with it:

$C_6^1$ , which is unique

$C_6^2 = C_3^1$

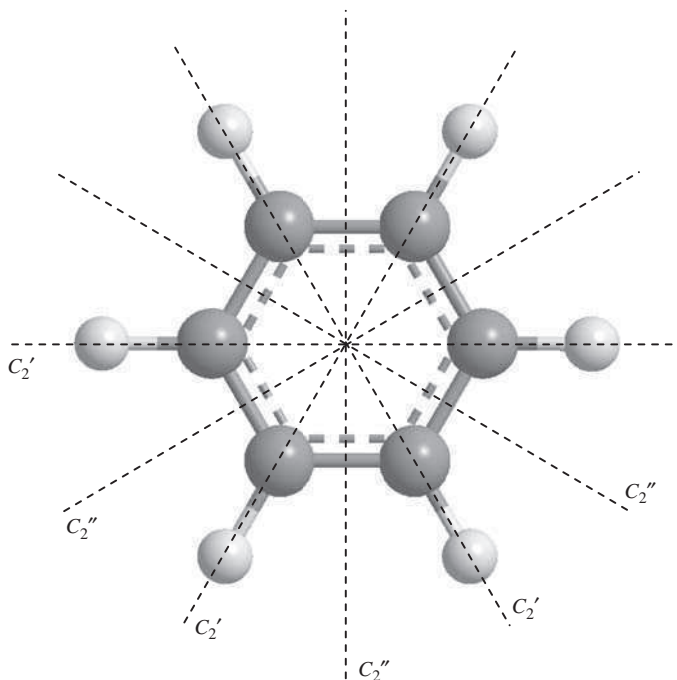
$C_6^3 = C_2$

$C_6^4 = C_3^2$

$C_6^5$ , which is unique.

This means that the  $C_6$  axis gives rise to two  $C_6$  operations, two  $C_3$  operations and a  $C_2$  operation, and so there must always be  $C_3$  and  $C_2$  axes collinear with a  $C_6$ .

In the plane of the benzene molecule there are also  $C_2$  axes that pass through opposite carbon atoms. The rotations about these axes must not be confused with the  $C_2$  operation from the principal axis, and so the axes are labelled  $C_2'$ , as shown in Figure 1.9. The  $C_2'$



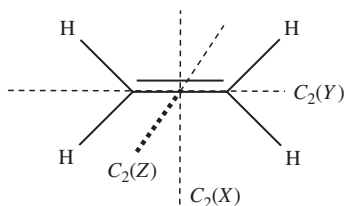
**Figure 1.9** The structure of benzene showing the two sets of three  $C_2$  axes in the molecular plane; the principal  $C_6$  axis is perpendicular to the plane and passes through the centre of the molecule at the crossing point of the  $C_2'$  and  $C_2''$  axes.

axes are  $60^\circ$  apart, and so successive  $C_6$  operations will alter which particular atoms are on which  $C_2'$  axes. However, each  $C_2'$  axis always contains two C and two H atoms, and so the three axes are equivalent. There is a second set of axes which join opposite bond centres, and these are labelled  $C_2''$  to distinguish them from the  $C_2'$  axes. We can tell that the  $C_2''$  and  $C_2'$  axes form distinct sets both from their chemical environments (one set join bond centres and one set join atoms) and from the fact that the  $C_6$  operations never interchange a bond centre and an atom position. We have made the choice that the axes joining opposite atoms should be labelled  $C_2'$  and that those between the bond centres that do not contain any atoms in the symmetry element are labelled  $C_2''$ .

A further possibility for multiple rotation axes is to have more than one candidate for the principal axis. For example, the highest order axis for ethene is a twofold axis, but there are three nonequivalent  $C_2$  axes, as shown in Figure 1.10. The choice of principal axis is now arbitrary, and it is usual to assign each axis a Cartesian label ( $X, Y$  or  $Z$ ) so that they can be referred to explicitly.

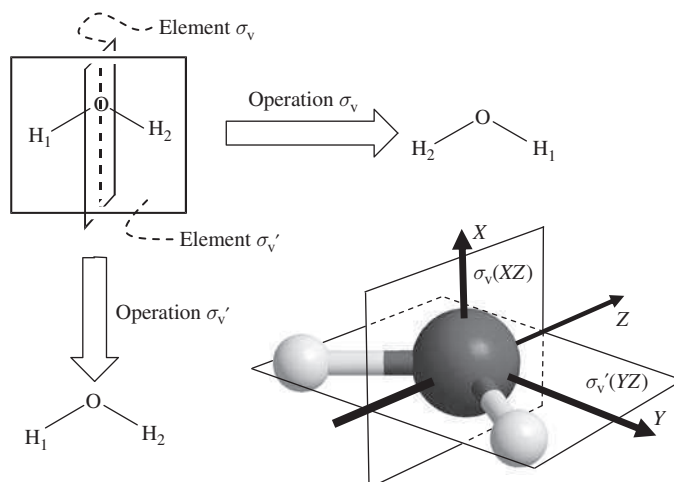
### 1.2.2 The Plane of Symmetry: $\sigma$

If a plane exists for which reflection of each atom in a molecule gives an indistinguishable configuration, the molecule is said to have a plane of symmetry, which is given the label  $\sigma$ .



**Figure 1.10** The structure of ethene showing three distinct  $C_2$  axes.

The symmetry element is the plane itself, since all points in the plane remain unchanged by the operation of reflection. For the water molecule there are two planes of symmetry, as shown in Figure 1.11. These are distinguished by labelling the plane perpendicular to the molecule  $\sigma$  and the plane of the molecule itself  $\sigma'$ . The  $C_2$  axis of water is the only axis, and so it is also the principal axis defining the vertical direction. This means that the mirror planes are standing vertically, and so a subscript is added to remind us of this, giving  $\sigma_v$  and  $\sigma_v'$ .



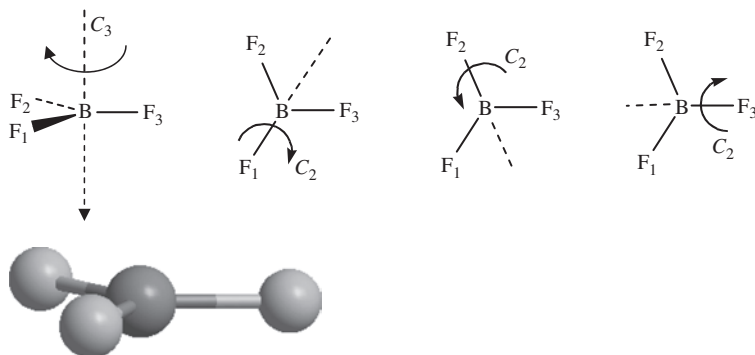
**Figure 1.11** The two mirror planes for the  $H_2O$  molecule showing the difference between  $\sigma_v$  and  $\sigma_v'$  operations. The inset shows the relationship between the mirror planes and a reference axis system.

Which plane is which is a somewhat arbitrary choice; however, the designation described here is quite widely used and is based on the alignment of the symmetry planes with the Cartesian axis system. Figure 1.11 shows that the two planes intersect in the line of the  $C_2$  axis we identified earlier; the planes of symmetry are said to *contain* the rotational axis. The principal axis gives us the Cartesian  $Z$ -direction, which, in this case, is in



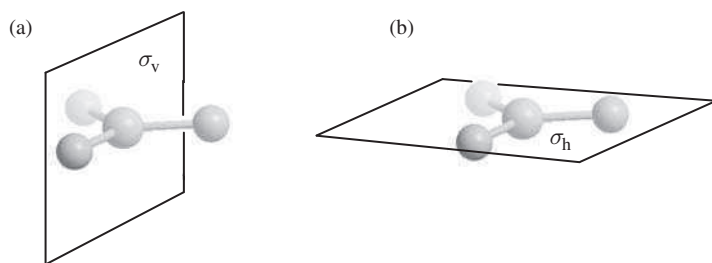
the molecular plane. We also take  $Y$  to be in the molecular plane, and so  $X$  must be perpendicular to it. The full labels for the mirror planes of water become  $\sigma_v(XZ)$  and  $\sigma_v'(YZ)$ , but it is common to omit the Cartesian parts of these labels.

Some molecules have multiple axes and mirror planes. For example, boron trifluoride ( $\text{BF}_3$ ) is a planar molecule with a  $C_3$  axis perpendicular to the plane and passing through the boron atom, as shown in Figure 1.12. However, there are also  $C_2$  axes in the plane of the molecule which run along each of the B—F bonds.



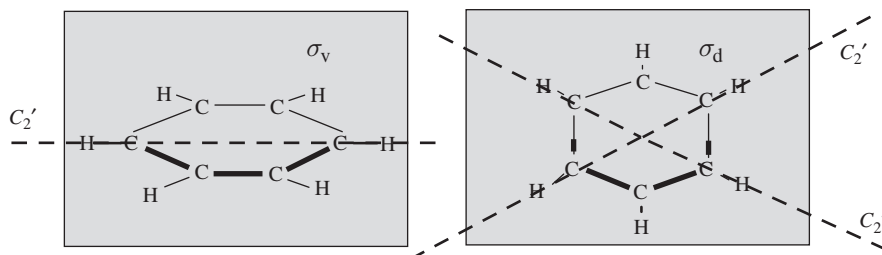
**Figure 1.12** The rotational symmetry elements of  $\text{BF}_3$ . To the left is a flying wedge drawing looking from the side of the molecule in the same orientation as the perspective ball-and-stick model below it. The  $C_2$  axes are shown with the molecule viewed looking down on the molecular plane.

The highest order axis present is taken to be the principal axis and gives us the ‘vertical’ direction. So,  $\text{BF}_3$  has three vertical mirror planes, each of which contains a B—F bond; an example of a vertical mirror plane in  $\text{BF}_3$  is shown in Figure 1.13a. The  $C_3$  operations will move the fluorine atoms between these planes, but each will always contain one fluorine atom and reflect the other two into one another. So, although there are three vertical planes, they are identical, requiring only the single label  $\sigma_v$ , and there are three  $\sigma_v$  operations. The plane of the molecule for  $\text{BF}_3$  is also a plane of symmetry, as illustrated in Figure 1.13b. This contains all three of the B—F bonds, but not the principal axis. In fact, the plane is perpendicular to the  $C_3$  axis, i.e. the plane is horizontal and so is labelled  $\sigma_h$ .



**Figure 1.13** The two types of symmetry plane for  $\text{BF}_3$ : (a) an example of a vertical plane; (b) the horizontal plane  $\sigma_h$ .

More complex collections of rotation axes and planes require the definition of an additional type of mirror plane. To illustrate this we can return to the case of benzene. In Figure 1.9 we showed that there are two sets of rotation axes in the molecular plane of benzene and labelled these  $C_2'$ , for the axes passing through opposite atoms, and  $C_2''$ , for the axes passing through opposite bonds. There are also two sets of three mirror planes which each contain the principal axis and either a  $C_2'$  or  $C_2''$  axis. Both types of mirror plane are vertical, but we need to distinguish them from one another. Each of the first set contain a  $C_2'$  axis and these are labelled  $\sigma_v$ . Planes in the second set are vertical, but are also in between the  $C_2'$  axes; this sort of vertical plane is called a dihedral plane and is given the symbol  $\sigma_d$ . The relationship of the  $\sigma_v$  and  $\sigma_d$  planes to the  $C_2'$  axes in benzene is shown in Figure 1.14.

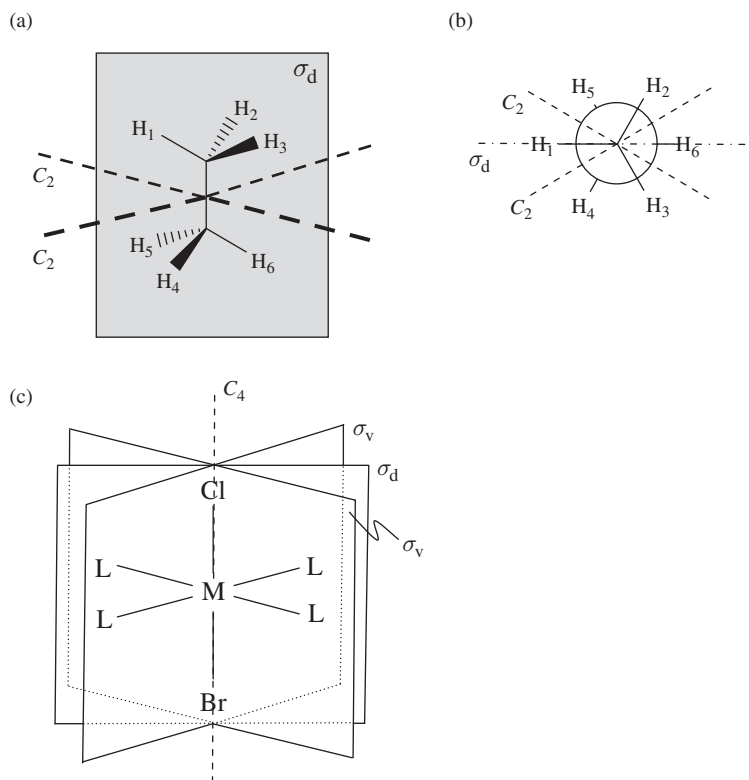


**Figure 1.14** The vertical ( $\sigma_v$ ) and dihedral ( $\sigma_d$ ) planes of benzene and their relation to the  $C_2'$  axes. The bonds in front of the planes have been thickened.

The dihedral plane has been introduced using an example where there is more than one type of vertical plane. However,  $\sigma_d$  planes are defined by their relationship to the horizontal  $C_2'$  axes; this means that molecules do exist in which  $\sigma_d$  is the only type of vertical plane.

An example of a molecule with  $\sigma_d$  but no  $\sigma_v$  planes is ethane in its staggered conformation. The principal axis in this case is a  $C_3$  axis running along the C—C bond, and the molecule is shown orientated vertically in Figure 1.15a. The illustrated dihedral plane of symmetry contains the two carbon atoms,  $H_1$  and  $H_6$ . There are horizontal  $C_2$  axes passing through the C—C bond centre, but they are not in the mirror planes, as can be seen from a Newman projection along the principal axis in Figure 1.15b. Figure 1.15a and b shows two of the three  $C_2$  axes: one rotates the molecule so that  $H_1$  and  $H_4$  interchange, while with the other  $H_1$  and  $H_5$  are swapped. The mirror plane in the diagram bisects the angle between these two axes and so is labelled  $\sigma_d$ . The  $\sigma_d$  operation would swap  $H_5$  with  $H_4$  and  $H_2$  with  $H_3$ . There are three  $C_2$  axes for ethane and, correspondingly, there are three  $\sigma_d$  planes.

The dihedral plane also occurs when there is more than one type of vertical mirror plane even if there are no horizontal  $C_2$  axes. Figure 1.15c shows a metal complex with four equivalent equatorial ligands. The internal structure of these ligands L will be assumed not to affect the symmetry properties of the complex. The complex has a principal axis of order 4, so there is a vertical  $C_2$  axis ( $C_4^2 = C_2$ ). However, the two axial halogen atoms are different (Cl and Br) and so there are no horizontal  $C_2$  axes. There are two mirror planes that each contain two *trans*-L ligands; these are labelled  $\sigma_v$ . The figure also shows one



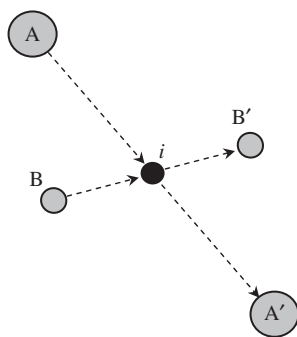
**Figure 1.15** (a) An example dihedral plane  $\sigma_d$  for ethane in the staggered conformation and the two  $C_2$  axes it lies between. (b) A Newman projection view showing the  $\sigma_d$  plane bisects the angle between the  $C_2$  axes. (c) An example metal complex with no horizontal  $C_2$  axes.

example of another pair of planes that only contain  $M$  and the halogen atoms, and reflect *cis*- $L$  ligands into one another. This plane bisects the angle between the two  $\sigma_v$  planes and so is labelled  $\sigma_d$ . The other  $\sigma_d$  plane would be perpendicular to the page.

**Problem 1.1:** In Section 1.2.3, Figure 1.19 shows the structure of the square planar complex  $[PtCl_4]^{2-}$ , find and label all the proper rotation axes and planes of symmetry for this structure. Remember to consider the full set of operations for high-order axes.

### 1.2.3 The Inversion Centre: $i$

So far, we have looked at symmetry operations for which the corresponding elements are the plane (a reflection operation) and a line (the rotation operation). The next symmetry element is the *inversion centre*, labelled  $i$ . The operation of inversion leaves only a single point unchanged, and so it is often referred to as a centre, or point, of symmetry. The inversion operation is illustrated in Figure 1.16 with two pairs of points,  $A, A'$  and  $B, B'$ , which represent atoms in a hypothetical molecule. For each pair, the points are equidistant

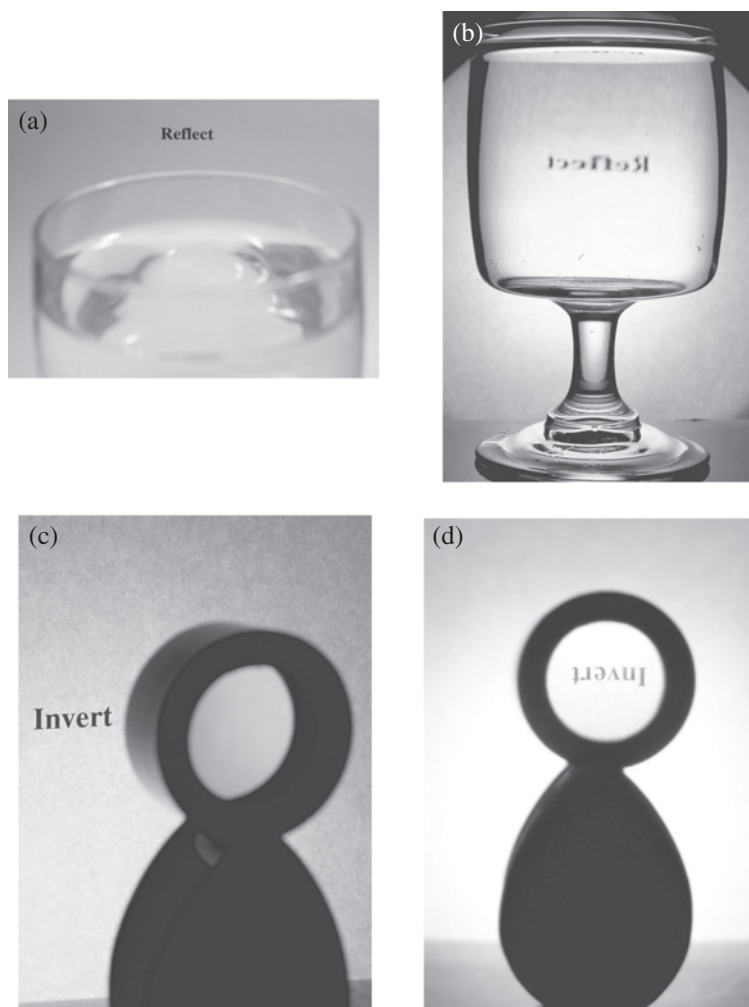


**Figure 1.16** An illustration of the inversion centre operation. Under inversion, each point in a molecule is moved through the inversion centre to a position on the opposite side of the centre and at the same distance from the centre as the original point. In this case, atom pairs  $A-A'$  and  $B-B'$  are linked by the inversion centre  $i$ .

from the inversion centre, and the lines between  $A$  and  $A'$  and between  $B$  and  $B'$  include  $i$ . To perform the inversion operation we imagine moving each atom in the molecule along a straight line to the inversion centre and then moving them along the same line beyond the centre to a distance equivalent to their starting point. For the hypothetical example,  $A$  and  $A'$  would be interchanged, as would  $B$  and  $B'$ . If the inversion operation result is indistinguishable from the initial geometry, then the molecule has an inversion centre. The inversion operation can be thought of as similar to the reflection operation, but referred to a point rather than a plane.

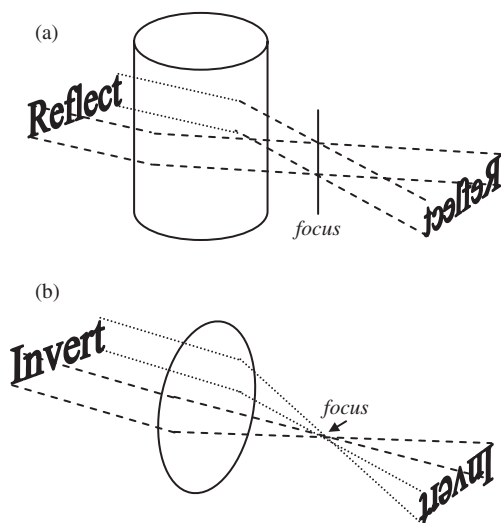
In two dimensions, we can illustrate the difference between the inversion centre and a simple reflection using lens optics. In Figure 1.17a, a drinking glass is used as a cylindrical lens behind which a piece of paper carries the word 'Reflect' and is backlit in the set-up shown in Figure 1.17a. When viewed through the glass at a distance beyond the focus of the cylindrical lens the word is reversed, as shown in Figure 1.17b. This result is the same as if we had reflected the word through a plane perpendicular to the paper. The optical quality of the drinking glass is low, so distortion of the letters is also apparent. If we use a small pocket lens in a similar set-up (Figure 1.17c), then the result is not only the reversal of the word, but also the top and bottom of the letters are swapped over, as shown in Figure 1.17d. Figure 1.18 shows ray diagrams of the optics for the cylindrical and normal lens. In the cylindrical case (Figure 1.18a) the rays from the object (the word 'Reflect' in this case) are brought to a line focus because the lens has no curvature in the vertical direction. When the viewer is placed beyond the focus, rays from the left of the object appear to the right and *vice versa*, leading to the observed reversal. For the hand lens (Figure 1.18b) the focus is a point and so, in addition to left and right reversing, top and bottom are also swapped.

These are two-dimensional examples, because the words are planar; in fact, the third dimension, perpendicular to the paper, is used to carry out the operation using the optics. A square planar species, such as the  $[\text{PtCl}_4]^{2-}$  ion shown in Figure 1.19a, has a centre of inversion, and the operation seems to act much like our optics example. On inversion, the chlorine atoms *trans* to each other in the original molecule are interchanged.

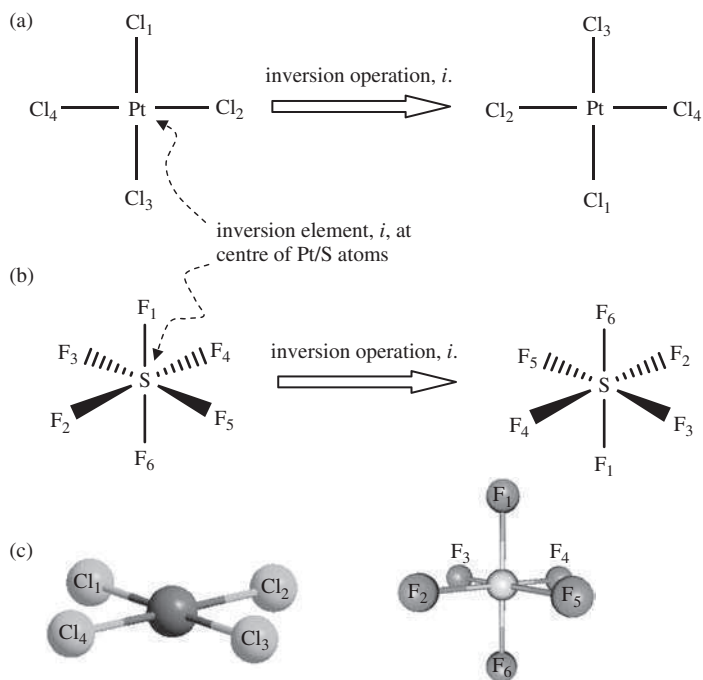


**Figure 1.17** A two-dimensional illustration of the difference between reflection and inversion operations. (a) The set-up used and (b) the result of viewing the word 'Reflect' through a cylindrical lens. (c) The set-up and (d) result of viewing the word 'invert' beyond the focal point of a hand lens.

However, in three dimensions the inversion operation will swap left with right, top with bottom and back with front simultaneously. For this to be a symmetry operation which leaves the molecule unchanged, the centre of inversion symmetry element will always be at the centre of the structure. So the Pt atom in  $[\text{PtCl}_4]^{2-}$  remains in the same position after the operation. Figure 1.19b shows the three-dimensional example  $\text{SF}_6$ ; here, the central S atom is on the inversion centre and so remains in the same place after inversion, but, with the F atoms labelled, it can be seen that atoms *trans* to one another are again swapped over. The molecular models of these two structures in Figure 1.19c should help to visualize the process.



**Figure 1.18** Ray tracing diagrams for (a) the reflection and (b) the inversion operations presented in Figure 1.17.



**Figure 1.19** The inversion element and operation for (a) a chemical complex  $[\text{PtCl}_4]^{2-}$  and (b) the molecule  $\text{SF}_6$ . (c) Ball and stick representations of the two structures used in (a) and (b).

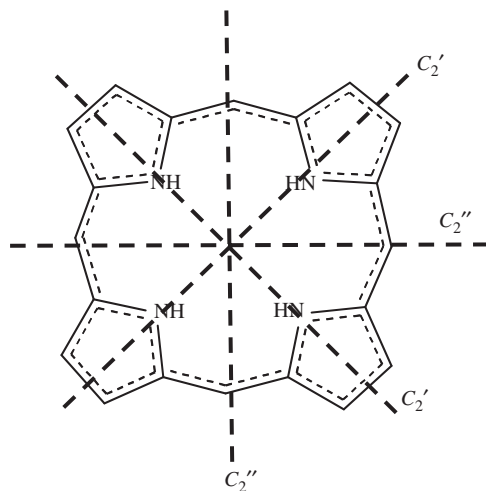
**Problem 1.2:** Square planar complexes have five planes of symmetry; using the structure of  $[\text{PtCl}_4]^{2-}$  from Figure 1.19a, find these planes and sketch out the result of each associated operation on the positions of the Cl atoms. Hence, confirm that no mirror plane gives the arrangement shown after the inversion operation in Figure 1.19a.

### 1.3 Examples of the Impact of Geometric Symmetry on Chemistry

So far, we have only considered some of the geometric factors involved with symmetry. Even so, the use of symmetry to identify equivalent atoms or groups in molecules already allows some insight to be gained into the way symmetry can be used to interpret the chemical behaviour of molecules possessing, or lacking, the symmetry elements introduced so far. We can also start to explore how symmetry helps deduce chemical structure from experimental data.

#### 1.3.1 Oxygen Transfer via Metal Porphyrins

Rotation axes and mirror planes are very common symmetry elements in molecules and can lend important properties to the structure. For example, in biology, the porphyrin ring (Figure 1.20) is the basic structure of an important class of tetra-dentate ligands. The idealized unsubstituted ring has a  $C_4$  principal axis at its centre perpendicular to the plane of the ring. This will give rise to two  $C_4$  ( $C_4$  and  $C_4^3$ ) and one  $C_2$  ( $C_4^2$ ) operations. Figure 1.20 also shows that there are four  $C_2$  axes in the plane of the ring: two  $C_2'$  and two  $C_2''$ . Each of these axes can be used to turn the planar molecule over so that the upper and lower faces are interchanged. Since this is achieved through symmetry operations, it implies



**Figure 1.20** The porphyrin ring structure. A  $C_4$  axis passes through the centre of the ligand perpendicular to the molecular plane; this is also a  $C_2$  axis, since  $C_2^1 = C_4^2$ . The four  $C_2$  axes shown in the molecular plane form two sets of two, labelled  $C_2'$  and  $C_2''$ .

that the two faces of the ring are identical. This does have important consequences for the biological processes involving porphyrin rings. In particular, complexes of  $\text{Fe}^{2+}$  with more elaborate porphyrin ligands are essential for the function of haem, which is involved in oxygen storage in the haemoglobin component of blood. When it is oxygenated, the central Fe atom carries a single oxygen atom which sits above the plane of the ring and it is coordinated by part of the host protein structure from below. Since the two faces of the porphyrin ligand are linked by symmetry operations, it does not matter ‘which way up’ the porphyrin is orientated as it is incorporated into the protein.

### 1.3.2 Nuclear Magnetic Resonance: Chemical Equivalence

An important use of symmetry is as an aid in the determination of molecular structure from spectroscopic data. We often know the molecular formula of a new compound, but this does not tell us the molecular structure. In a nuclear magnetic resonance (NMR) experiment, a macroscopic sample of an unknown compound is exposed to a strong magnetic field. Magnetic nuclei in the sample will have different energies depending on the orientation of their magnetic moment with respect to the external field. According to quantum mechanics, the magnetic moment of a nucleus is dependent on its spin. For nuclei with a spin of  $1/2$ , such as  $^1\text{H}$  or  $^{13}\text{C}$ , two states will be possible: one with the spin aligned with the external field and one with the spin aligned opposite to the external field. The energy difference between these two states is small, of the same order of magnitude as the energy of a photon of radio-frequency electromagnetic radiation. This means that, if the sample is probed using radio-frequency waves, we will see an absorption when the photon energy exactly matches the energy difference between the two magnetic states of the nucleus.

In NMR spectroscopy, the probe frequency of the radio waves is actually held fixed and in the original approach the magnetic field applied was scanned through a range of values. The energy difference between the two spin states will be altered as the field is scanned, and a strong absorption will be observed when the energy difference exactly matches the probe radio-frequency. In most modern machines the ‘scanning’ process has been replaced by a pulsed approach, which allows all environments of a given nucleus to be analysed simultaneously.

In addition to the magnetic field applied in the experiment, the nuclei also experience the magnetic field created by the electrons and other magnetic nuclei in the molecule. The electronic effect tends to be larger than the nuclear influence on the local magnetic field at a given nucleus and so the nuclear effects are only resolved in high-resolution spectra. In the following examples we will only consider low-resolution spectra, and so will ignore the magnetic coupling between nuclei. The magnitude of the electronic contribution to the local magnetic field depends on how the electron density is distributed in the molecule; in particular, the field from the valence electrons will depend on the other elements present and the types of bonding holding the structure together. So, the energy separation between the spin states depends not just on the applied field from the NMR machine, but also on the local chemical environment of the nucleus being probed. This makes NMR an extremely useful technique in chemistry, because the positions of the NMR bands provide information on the molecular structure of the sample.

Generally, NMR spectra are plotted in terms of chemical shifts, which are the absorption frequency differences between the sample nuclei and the same element in a laboratory



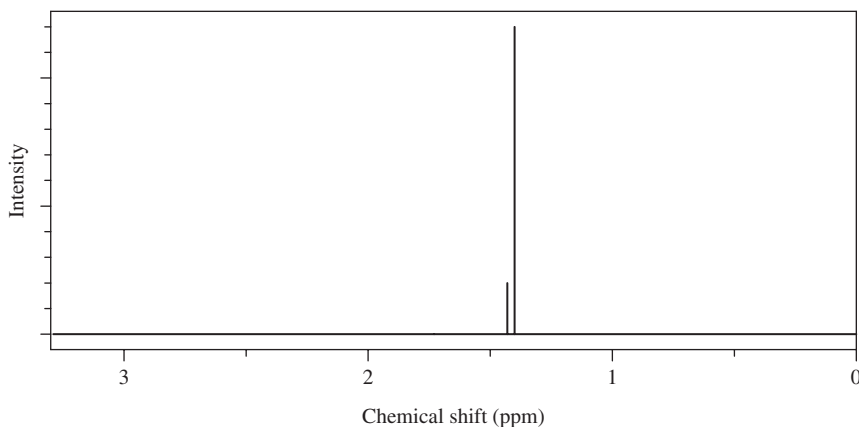
standard. For carbon ( $^{13}\text{C}$ ) and hydrogen ( $^1\text{H}$ ) NMR experiments, a commonly used standard is tetramethylsilane (TMS). The chemical shift  $\delta$  is defined as

$$\delta = \frac{\nu - \nu_{\text{TMS}}}{\nu_{\text{TMS}}} \times 10^6 \quad (1.1)$$

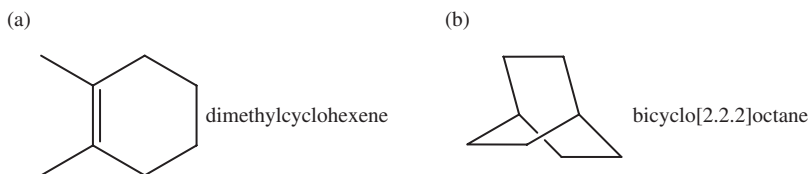
where  $\nu$  is the absorption frequency of the sample atoms and  $\nu_{\text{TMS}}$  is the absorption of the corresponding element ( $^{13}\text{C}$  or  $^1\text{H}$ ) in the standard. This chemical shift is dimensionless, since the reference absorption frequency appears in the denominator; this ensures that experiments on spectrometers with different probe frequencies give the same chemical shift values for a given sample. The difference in frequencies observed between samples and the standard is typically only a few kilohertz, whereas the probe frequency will be in the 200–1000 MHz range. Hence, the factor of  $10^6$  is introduced to give chemical shifts that can be quoted using simple numbers, typically 0–12 for  $^1\text{H}$  NMR, and the shifts are quoted as parts per million (ppm).

The chemical shifts from a  $^1\text{H}$  NMR spectrum are used as an indication of the chemical environment of each proton in the molecule of the sample. If two hydrogen atoms are linked by a symmetry operation, then they will have the same environment and are referred to as chemically equivalent. The line in the  $^1\text{H}$  NMR spectrum for each will occur at exactly the same position, and so the intensity of the peak at this chemical shift will be twice that of a hydrogen atom in a unique environment, i.e. not linked to any other hydrogen atoms by symmetry operations. This allows us to use the intensity of the peaks as an indication of the number of equivalent hydrogen atoms in a molecule and so may help to determine the sample's molecular structure.

As an example, Figure 1.21 shows a computer-generated  $^1\text{H}$  NMR spectrum for a compound with the chemical formula  $\text{C}_8\text{H}_{14}$ . There are several possibilities for the molecular structure of this sample, two of which are given in Figure 1.22. The spectrum shows two peaks with the lower chemical shift having a height six times that of the other signal.

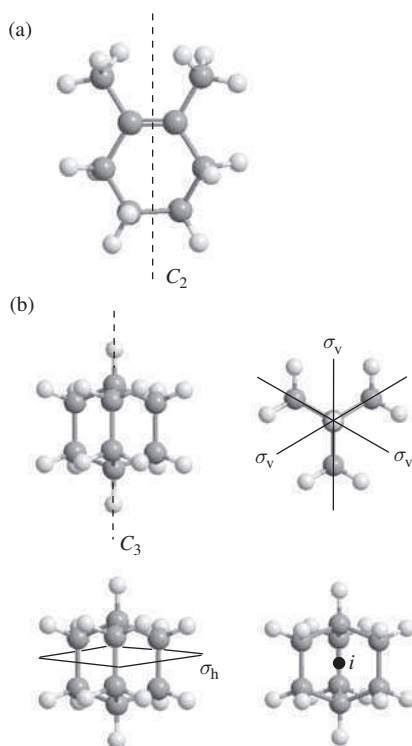


**Figure 1.21** A  $^1\text{H}$  NMR spectrum for a compound with the chemical formula  $\text{C}_8\text{H}_{14}$  generated using the ChemDraw package.



**Figure 1.22** Two possible molecular structures for the chemical formula  $C_8H_{14}$ .

This implies that there are only two environments for the 14 hydrogen atoms and they are divided into a set of 2 and a set of 12. Three-dimensional structures of the two alternatives are shown in Figure 1.23, along with examples of the rotation axes and mirror planes that are symmetry elements of the structures.



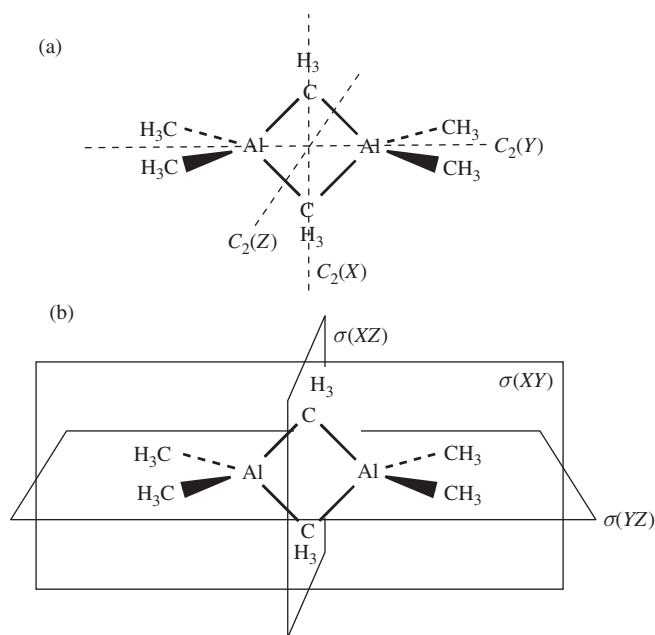
**Figure 1.23** (a) The  $C_2$  axis in dimethylcyclohexene and (b) the principal  $C_3$  axis and example symmetry planes for bicyclo[2.2.2]octane.

Only bicyclo[2.2.2]octane has a structure consistent with the spectrum, since the two hydrogen atoms that lie on the principal axis ( $C_3$ ) are linked by  $\sigma_h$  and by  $i$  and all of the other 12 hydrogen atoms are linked by combinations of  $\sigma_h$ ,  $\sigma_v$ ,  $C_3$  and  $i$  operations. None of the symmetry operations would interchange the axial hydrogen atoms with any of the

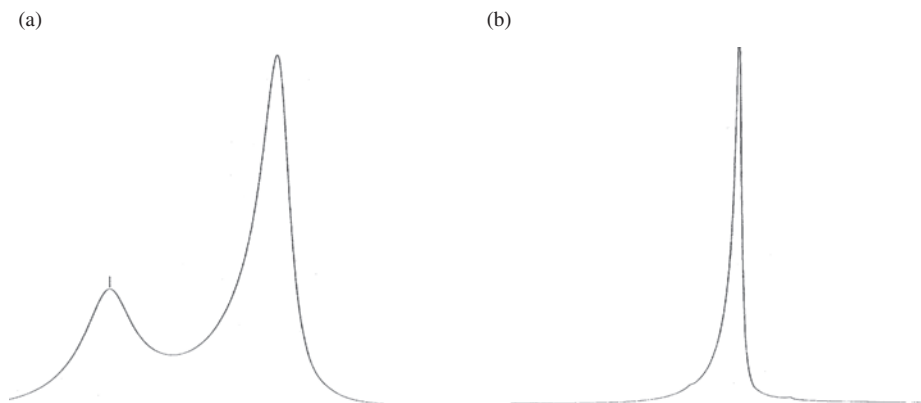
hydrogen atoms in the  $\text{CH}_2$  groups, and so there are two distinct sets of hydrogen atoms. This gives the same division of the hydrogen atoms between the two environments that was implied from the spectral data. The dimethylcyclohexene alternative has only a  $C_2$  axis and no other symmetry axes or planes. As we shall see below, this means that it has hydrogen atoms in at least three different environments, and so would be expected to give a more complex  $^1\text{H}$  NMR spectrum.

The absorption event in an NMR experiment takes a short, but finite, time. If the proton in a  $^1\text{H}$  NMR experiment is moving rapidly, then it may experience more than one environment on the time scale of the experiment and only the average chemical shift will be observed. For example, methyl groups are usually undergoing rapid rotation at room temperature, and so the three hydrogen atoms will appear equivalent even though they may not be linked by symmetry operations. In the spectrum of dimethylcyclohexene we would see only a single chemical shift for all six of the methyl protons, since the two methyl groups are linked by symmetry operations in the static structure. Similarly, molecular motion would be expected to cause the hydrogen atoms of each  $\text{CH}_2$  group in the ring to interchange rapidly from axial to equatorial as the ring changes its conformation. The  $C_2$  axis implies that the two  $\text{CH}_2$  groups adjacent to the methylated carbon atoms are equivalent and that the remaining  $\text{CH}_2$  groups are also equivalent to one another. This gives at least three distinct  $^1\text{H}$  NMR signals.

This type of analysis can also give some information on the dynamics of molecular motion. Figure 1.24 shows the structure of  $\text{Al}_2(\text{CH}_3)_6$ . The symmetry axes and mirror

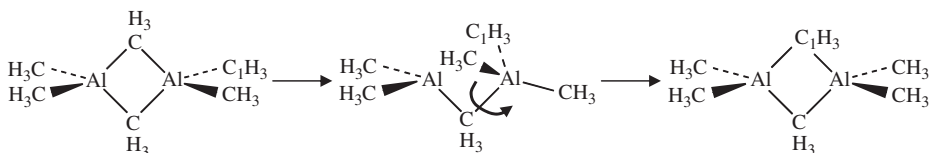


**Figure 1.24** The structure of  $\text{Al}_2(\text{CH}_3)_6$  showing (a) the rotation axes and (b) mirror planes assuming the structure of the methyl group can be ignored.



**Figure 1.25**  $^1\text{H}$  NMR spectra of  $\text{Al}_2(\text{CH}_3)_6$ : (a) at  $-40^\circ\text{C}$ ; (b) at  $20^\circ\text{C}$ .

planes for the structure are illustrated assuming that the internal structure of the methyl groups can be ignored due to the rapid rotation discussed above. Using the symmetry operations, we see that the methyl groups form two sets: The four methyl groups that have only one bond to an Al atom (terminal methyl groups) and the two methyl groups that bridge between Al atoms. Figure 1.25a shows the  $^1\text{H}$  NMR spectrum for  $\text{Al}_2(\text{CH}_3)_6$  taken at a temperature of  $-40^\circ\text{C}$ . As expected, we see two chemical shifts, with the signal for the terminal methyl hydrogen atoms more intense than that for the hydrogen atoms of the bridging methyl groups. However, a spectrum of the same sample taken at  $20^\circ\text{C}$  shows only a single peak, as illustrated in Figure 1.25b. This peak has a chemical shift in between the values found for the terminal and bridging methyl hydrogen atoms at lower temperature. This suggests that at  $20^\circ\text{C}$  there is a rapid interchange of the terminal and bridging methyl groups so that the hydrogen atoms sample both environments. A possible mechanism for this process is shown in Figure 1.26. Here, exchange is achieved without dissociation of the dimer, a bond between an Al and bridging methyl group is broken by thermal excitation and then a simple rotation converts the methyl group labelled  $\text{C}_1\text{H}_3$  from terminal to bridging.



**Figure 1.26** Possible mechanism for the rapid interchange of terminal and bridging methyl groups in  $\text{Al}_2(\text{CH}_3)_6$ .

## 1.4 Summary

*Symmetry elements* are imaginary geometrical entities that are the signature of symmetry properties in objects. So far, we have seen that a line of symmetry is required for a rotation

axis, a plane for a reflection and a single point for inversion. The symmetry element is the set of points that are not moved when the corresponding symmetry operation takes place.

*Symmetry operations* are the actions, such as rotations or reflections, that can be used to transform an object in such a way that, after the operation, it is indistinguishable from the starting point.

The symmetry elements and operations of a molecule are given standard symbols, including:

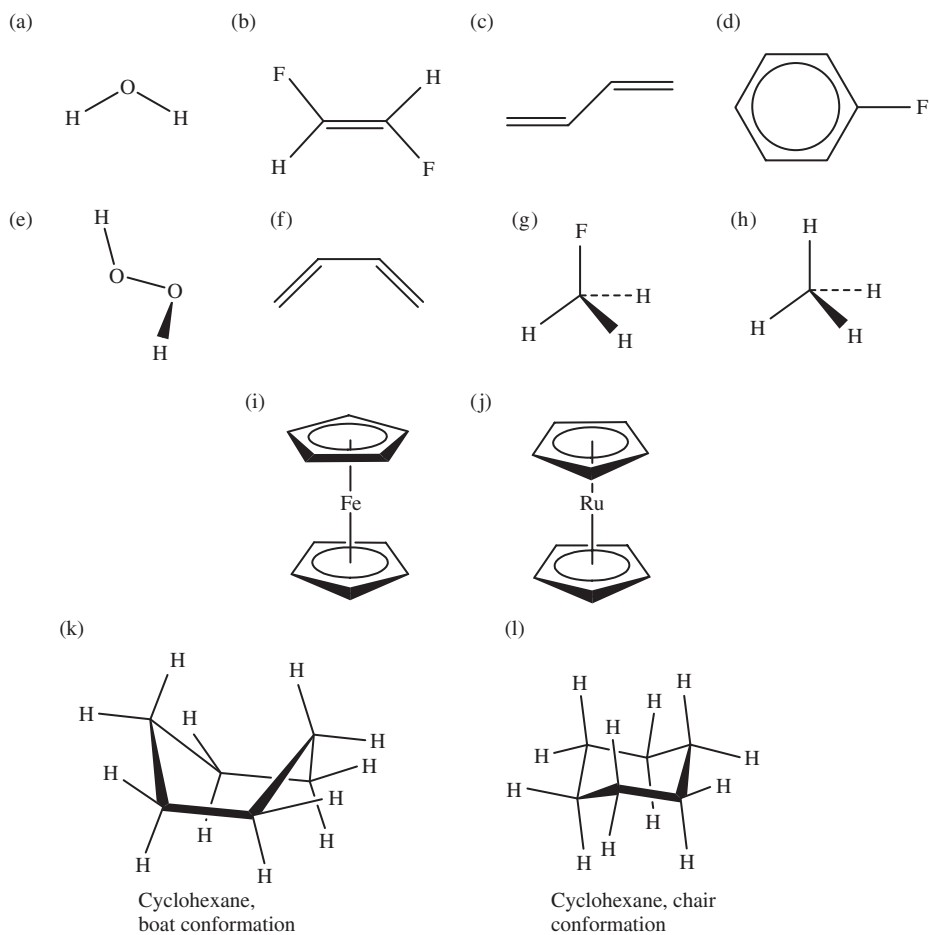
- *Proper rotation axes*, labelled  $C_n$ , where  $n$  is the axis order. The highest order axis present for a given molecule is called the principal axis and defines the vertical direction used to orientate the molecule in space.
- *Reflection planes*, labelled  $\sigma$ , with three possible subscripts:
  - $\sigma_v$ , a vertical mirror plane, contains the principal axis – if there are horizontal  $C_2$  axes, then  $\sigma_v$  will also contain those of highest priority;
  - $\sigma_d$ , a dihedral mirror plane, also contains the principal axis – if there are horizontal  $C_2$  axes, then  $\sigma_d$  will bisect the angle between those of highest priority;
  - $\sigma_h$ , a horizontal mirror plane, is perpendicular to the principal axis.
- *Inversion centre*, labelled  $i$ , has a single point as the symmetry element. Inversion requires each point in the molecule to have an equivalent point on the opposite side of the centre of symmetry and equidistant from it. A molecule may have at most one point of inversion.

Atoms in a molecule that are linked by symmetry operations have identical chemical environments, and so identical NMR chemical shifts.

## 1.5 Self-Test Questions

These questions are designed to give you practice at applying the concepts learned in this chapter. Most of the questions for this chapter require you to visualize the geometry of a molecule, and you may find it useful to construct models. In the illustrations here, as in the rest of the text, we continue to use the convention that C atoms are not explicitly labelled in organic molecules and hydrogen atoms are omitted unless the geometry is ambiguous without them. The ‘flying wedge’ convention is also used to indicate bonds above and below the plane of the paper.

1. For each of the molecules in Figure 1.27 identify all of the rotation axes present, giving the order of each axis and describing any that form a set of identical axes. You should make sketches of the molecules viewed from different directions to illustrate your answer.
2. Give the orders of the principal axes for the molecules illustrated in Figure 1.27.
3. Identify all the mirror planes present in the molecules of Figure 1.27 and use the rotation axes you have found to label them as  $\sigma_v$ ,  $\sigma_d$  or  $\sigma_h$ .



**Figure 1.27** Example molecules for symmetry analysis.

- How many distinct  $^1\text{H}$  NMR peaks would you expect for each molecule containing H atoms in Figure 1.27?
- Draw molecular structures of each of the isomers of difluorobenzene and identify all axes and mirror planes of symmetry for each case.

## Further Reading

Crystal symmetry is covered in several texts, including:

Senechal, M. (1990) *Crystalline Symmetries: An Informal Mathematical Introduction*. Adam Hilger (ISBN 0-7503-0041-8).

Franzen HF (1994) *Physical Chemistry of Solids, Basic Principles of Symmetry and Stability of Crystalline Solids*. World Scientific Publishing (ISBN 9-8102-1154-6).

# 2

## More Symmetry Operations and Products of Operations

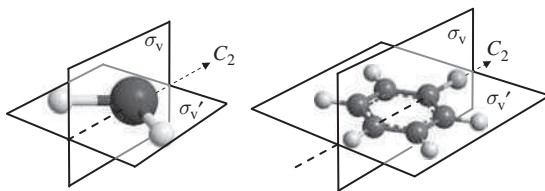
### 2.1 Introduction

In this chapter we will explore further the symmetry operations that are used to describe molecular structure. New operations are introduced to complete the set used in molecular symmetry. Particular sets of operations often recur, with many molecules having the same collection of operations. Once we establish how the properties of a molecule depend on the set of valid operations, this will mean that we can actually infer the properties of many related molecules of the same symmetry. The sets of operations are referred to as point groups, and our main task in this chapter is to introduce the concept of a point group. The formal construction of the point groups most commonly used in chemistry is carried out in Chapter 3. The properties of the point groups, and their application in vibrational spectroscopy and MO theory, are then the subject of the remainder of the book.

The definition of a point group comes from the general idea of a group in mathematics. For molecular point groups to take advantage of general group theory we require two additional symmetry operations to be defined: the identity and the improper rotation. These operations are introduced in the first half of the chapter through the idea of a group being *closed*.

### 2.2 Background to Point Groups

In Chapter 1 we covered three types of symmetry operation:  $m$  rotations about an axis of order  $n$ ,  $C_n^m$ ; reflection through a plane,  $\sigma_v$ ,  $\sigma_d$  or  $\sigma_h$ ; and inversion through a point,  $i$ . Point groups arise from the observation that a given set of operations is valid for more than one molecule. For example, Figure 2.1 shows that both water and fluorobenzene have a single



**Figure 2.1** The symmetry elements of water and fluorobenzene; in this case, each element has only one corresponding operation.

$C_2$  axis and two vertical mirror planes,  $\sigma_v$  and  $\sigma_v'$ . These molecules do not have any other rotation axes or mirror planes and do not have an inversion centre; so, according to the operations met so far, this set completely describes the symmetry of both molecules. The two molecules are said to belong to the same symmetry point group because they have exactly the same set of valid symmetry operations.

## 2.3 Closed Groups and New Operations

### 2.3.1 Products of Operations

In general, the idea of a point group is a mathematical abstraction that helps us classify molecular geometry. A point group is a list of all symmetry operations that an object which belongs to the group can undergo and remain apparently unchanged. The set of operations that form a group must be complete, in the sense that if any two members of the group are applied in succession the result must also be a single operation which is a member of the group. This means that the group is 'closed', i.e. it is not possible to generate a new symmetry operation by combining those in the group. This property of groups can be useful: ensuring that the group of operations is closed is one way of checking that all the operations that are possible have been identified. The requirement for a group to be closed also leads to further symmetry operations, as will be shown in the following sections.

#### *Multiplication Table for $H_2O$*

To check that a group is closed we form the product of each pair of operations within the group and find the single equivalent operation that achieves the same end point. The product of a pair of symmetry operations is defined as the result of applying them in succession. Taking  $H_2O$  as an example,  $C_2\sigma_v'$  is the product of a vertical reflection through the molecular plane and a  $180^\circ$  rotation and is achieved by carrying out the reflection followed by the rotation. This would be one possible combination of operations for the  $H_2O$  molecule; and if the group is closed, all such products should be equivalent to a single operation. A complication can arise in finding the single operation that is equivalent to the product. For the example of  $C_2\sigma_v'$  the hydrogen atoms would be swapped but either the  $C_2$  operation or the  $\sigma_v$  operation alone would also interchange them; so, by looking only at atom positions, it is impossible to tell which operation to choose. There is not enough information in just the atom positions to tell the operations apart; some way is needed to