

# 1 Three-dimensional structure of a molecule

## Purpose

In this chapter, you will learn that it is sometimes not sufficient to describe the structure of a molecule in a planar, two-dimensional way, which is usually used in textbooks, because the atoms that make up a molecule are arranged three-dimensionally in space.

The three-dimensional structures of organic compounds significantly depend on the shapes and characteristics of the hybridized atomic orbitals of the carbon atom. Here you learn about  $sp^3$ ,  $sp^2$  and  $sp$  hybridized orbitals, which are involved deeply in the structure of molecules.

Models are useful tools to conceptualize the shapes of molecules. The commercially available molecular models will be classified based on their features.

Sometimes a compound may have two or more names. Similarly, several nomenclatures are used in discussing the stereochemistry of organic compounds. The nomenclature based on the sequence rule will be introduced because this method corresponds to the systematic nomenclature that is most widely used.

## New terms and concepts

molecular formula  
 rational formula  
 structural formula  
 dihedral angle (Compare with torsion angle in Ch. 2)  
 carbon atomic orbital  
 $sp^3$  hybridization  
 tetrahedral structure  
 configurational isomer  
 enantiomer (enantio isomer)  
 Configuration (steric configuration)  
 $sp^2$  hybridization  
 $sp$  hybridization  
 molecular model  
 space filling model  
 skeletal model  
 ball and stick model  
 free rotation  
 restricted rotation  
 sequence rule  
 replica atom

## Goals of this chapter

After you master this chapter successfully, you will be able to do the following:

- 1 to understand that organic compounds are three-dimensional, and that you cannot properly draw these on a two-dimensional sheet of paper. To know their geometry depends on the hybridization states of their carbon atoms, and that there are three types of hybridization—  $sp^3$ ,  $sp^2$  and  $sp$ .
- 2 to know that such three-dimensional structures result in configurational isomers; that is, these are identical in their structural formulas but differ in the three-dimensional spatial arrangement of their atoms and that a pair of enantiomers (enantio isomers) is similar to the relation between the left hand and the right hand.
- 3 to learn that molecular models help greatly in comprehending the three-dimensional structure

of molecules and that there are several types of molecular models, and that each of these has its own characteristics.

4 to understand that the structure of molecules is not always fixed and that rotation about bonds can result in a change in their structures.

### 1.1 Isomerism, isomers

A compound, whether it is organic or inorganic, always has its own specific molecular formula. The reverse, however, is not always true. Thus one molecular formula can sometimes signify more than one compound. Molecules with identical molecular formulas and different structures are **isomers**, and such phenomena are called **isomerism**.

Isomerism can be divided into classes in accordance with how much those isomers resemble each other. In order to understand isomerism, it is necessary to determine and describe exactly the molecular structure of each molecule. The **molecular formula** provides the number and the type of atoms within a molecule.

#### Q1.1

There is a certain liquid compound **1** whose molecular formula is  $C_4H_{10}O$ . Does the molecular formula of **1** exactly describe its structure and properties?

A **rational formula** indicates the group that a compound belongs to by showing the functional groups (or units) that are the source of the properties of the compound (**functional group**). A **structural formula** connects each atom to another with the required number of bonds. It can completely describe molecular structures as far as the sequence of atoms is concerned.

#### Q1.2

When a piece of sodium was added to compound **1**, it dissolved while generating good deal of gas. Write the rational formula of **1**. Is only one compound possible for this rational formula?

#### A1.1

Both alcohols and ethers can correspond to the given formula. Besides, even several more isomers are possible for each of them.

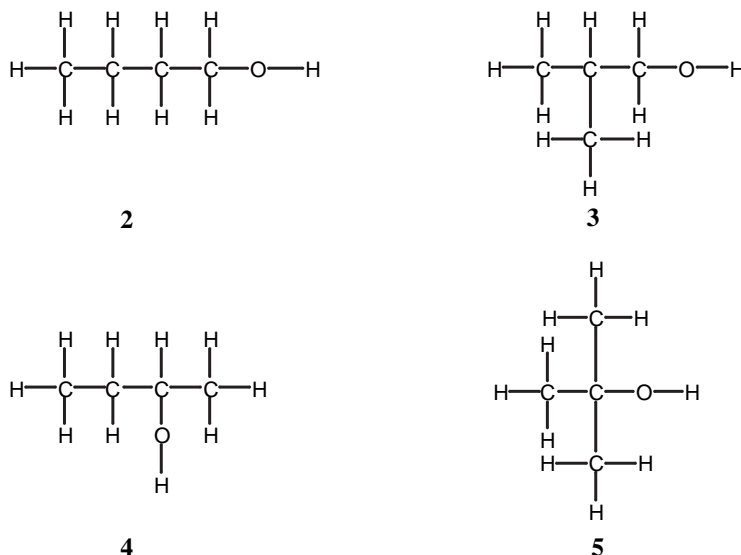
#### Q1.3

Draw all possible structural formula of **1**.

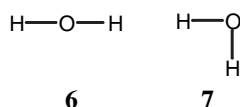
#### A1.2

The rational formula would be  $C_4H_9OH$  since it should be an alcohol. However, the rational formula  $C_4H_9OH$  does not specify a compound because there are various ways to arrange the atoms that form the  $C_4H_9-$  group.

## A1.3



It is not necessary to draw bonds so that they correspond to their actual lengths, even though the bond lengths of C-C, C-O and C-H bonds in structural formula 2~5 differ from each other. Actual bond angles between bonds are also not indicated in a structural formula. For example, the real bond angle for  $\angle\text{HOH}$  of water  $\text{H}_2\text{O}$  has been experimentally determined to be about  $104^\circ$ . However, the structural formula of water is usually drawn as 6 or 7. Thus, the dimension and direction of bonds in a structural formula may not precisely indicate the actual molecular structure.



### S1.1 molecular formula, rational formula, structural formula

molecular formula: describes only the number and kind of atoms contained in a molecule

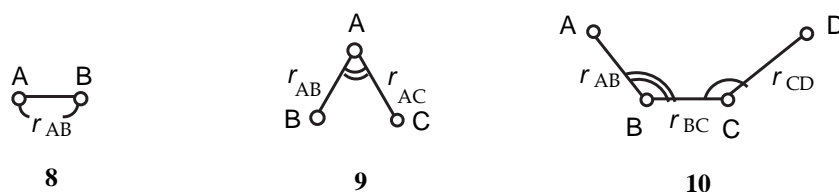
rational formula: simply describes the functional groups (including multiplex bonds) contained in a molecule

structural formula: exactly describes the order of atoms in a molecule by means of bonds.

## 1.2 Factors to determine molecular structures

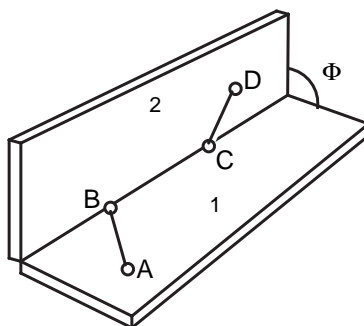
Even in the structural formula 2~5, these can not indicate the real structure of those molecules, since those formulas drawn on a sheet of paper can describe only the sequence of atoms in the molecules.

Then, what kind of parameters could define a molecular structure? It can be defined solely by the atomic distance  $r_{AB}$  for diatomic molecules A-B, and, by three parameters – two atomic distances  $r_{AB}$ ,  $r_{AC}$  and bond angle  $\angle\text{BAC}$  for triatomic molecules A-B-C. Both atomic distance and bond angle are the specific parameters for atoms that form the bonds, and they have values that can be predicted by chemical bond theory.



For tetra-atomic molecules A-B-C-D, the three atomic distances  $r_{AB}$ ,  $r_{BC}$ ,  $r_{CD}$  and two bond

angles  $\angle ABC$ ,  $\angle BCD$  are not enough to define the geometry of the molecule. Even though these parameters are specified, the geometry are not thereby defined. Thus, it is not yet certain whether or not those four atoms are located in an identical plane. If they are not in an identical plane, it must be determined which atom is not in that plane.



**Figure 1.1** Dihedral angle

The geometry of **10** can definitely be defined by a sixth parameter – the **dihedral angle**  $\phi$ . A dihedral angle is defined as an angle between plane 1 that includes atoms A, B and C and plane 2 that includes B, C and D. To determine the structure of a tetra-atomic molecule, it is necessary to introduce a new parameter, the dihedral angle, which is determined from neither by the atomic distance nor the bond angle

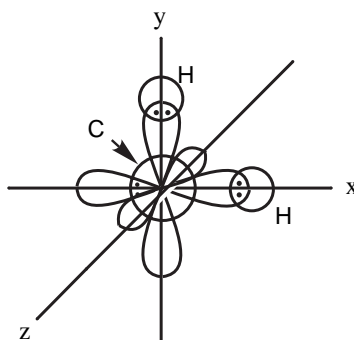
This fact suggests the following:

- 1) Molecules are three-dimensional, and may not always be represented on two-dimensional paper.
- 2) Molecular structures are not defined by atoms or by types of bonding in the molecules.

You will learn that bond angles play the main role in determining molecular structures. Therefore the atomic orbitals of a carbon atom, which is the factor that controls bond angles in organic compounds, should be carefully studied.

### 1.3 Atomic orbitals of carbon atoms; hybridization

The electron configuration of a carbon atom in its ground state is  $1s^2 2s^2 2p^2$ . Reasoning from the electron configuration and the direction of the atomic orbitals, the bonding electrons are only only two 2p electrons that occupy the 2p orbitals because 2s electrons are not involved in bond formation; these form an unshared electron pair. Thus, hydride of carbon would be expected to be  $\text{CH}_2$ , and its bond angle should be  $90^\circ$ , which is the angle between the two 2p orbitals.



**Figure 1.2** Hypothetical hydride of carbon;  $\text{CH}_2$

#### Q1.4

As is well known, however, the fact is that the stable hydride of carbon is methane  $\text{CH}_4$ , and it

has four covalent bonds, not two. Therefore, the electron configuration of the carbon atom should be  $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ . What kind of structure can indicate such an electron configuration? □

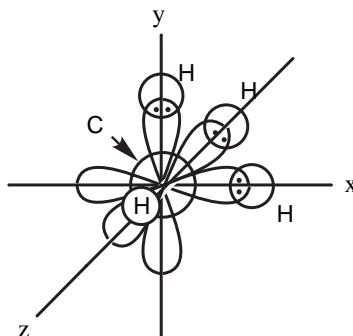
However, studies of methane and its substituted species (*e.g.* chloroform  $\text{CH}_3\text{Cl}$ ) reveal that those four hydrogen atoms in methane are identical. That fact means that a carbon atom must use four identical atomic orbitals with one unpaired electron in each orbital, but does not use an s orbital and the three p orbitals as such. It can be explained in term of hybridization, namely, mixing an s orbital and three p orbitals to make up four equivalent new orbitals, and the resulting orbital is called an  **$sp^3$  hybridized orbital**.

### Q1.5

If the four hydrogen atoms of methane are identical, what kind of structure we expect? Draw each of the expected structures. □

### A1.4

It is the same situation as Fig 1.2. Three C-H bonds are orthogonal to each other. Though the fourth C-H bond has no particular direction, it should be placed on the opposite side to the other three. In any case, one of the hydrogen atoms should be different from the other three hydrogen atoms (see Fig. below. This is the hypothetical hydride of carbon;  $\text{CH}_4$ ).



□

One may contend that it is impossible to decide which of those expected structures **11~13** can be the true structure of methane without some direct observations. However, if substituted methanes should have the same structure as methane, it is possible to deduce the structure of methane from the numbers of the isomers among the substituted methanes.

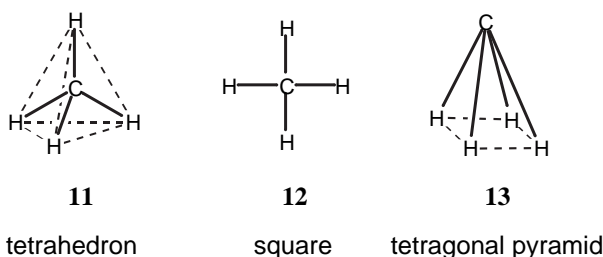
### Q1.6

How many isomers could be expected to each of the following compounds (a)-(d) if methane were arranged as **11** or **12**?

(a) methyl chloride; (b) methylene chloride; (c) chloroform; (d) carbon tetrachloride □

### A1.5

The following three structures may be possible. Here **12** can be considered as a special case of **13**.





Since some investigations have revealed that only one compound exists as methylene chloride, the tetrahedron should be the acceptable structure of methane. The atomic orbitals of an  $sp^3$  hybridized carbon atom that forms the tetrahedral structure are shown in Fig 1.4. Methane is made up of four  $\sigma$  bonds which are formed by the overlap of each  $sp^3$  orbital of a carbon atom with a  $1s$  orbital of a hydrogen atom. Therefore the direction of those atomic orbitals determines the geometry of the molecule.

In addition, the chemistry of a molecule that is formed by substituting for the three hydrogens of methane each with different atom or group (hereafter referred to as “**ligand**”), such as the comparatively simple molecule bromochlorofluoromethane  $CHBrClF$ , provides more critical evidence for the tetrahedral structure of methane.

### Q1.7

How many isomers of  $CHBrClF$  can exist, if the structure of methane is **11** or **12**?

### A1.6

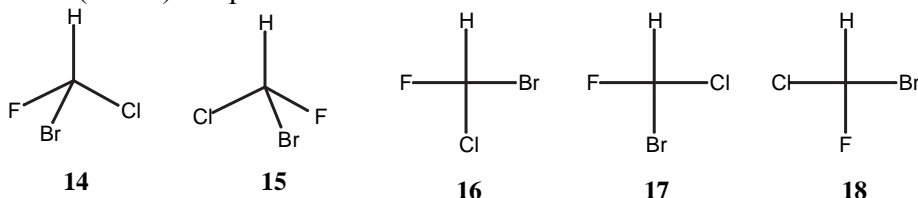
	<b>11</b>	<b>12</b>
(a) $CH_3Cl$	1	1
(b) $CH_2Cl_2$	1	2
(c) $CHCl_3$	1	1
(d) $CCl_4$	1	1



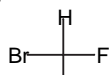
### A1.7

Two isomers (**14**, **15**) are possible for **11**

Three isomers (**16-18**) are possible for **12**



However, there are some stipulations with regard to the answer for **12**. For example, it is



supposed that  $CHBrClF$  could not be distinguished from **16**. This is equivalent to assuming that there is no front or back for an atom (thus a molecule).

You have learned that the pair of isomers **14** and **15** differ in the three-dimensional arrangement of their atoms, even though they seem to be similar on the two-dimensional plane. Generally, isomers that, though identical in their structural formulas, differ in the arrangement of their atoms in space are called **stereoisomers**. Some classes of stereoisomers, a pair of nonidentical images such as a right hand and a left hand or a real image and its mirror image, are called a pair of **enantio isomers** or simply a pair of **enantiomers**. Though the terms antipode and mirror image isomer are also used, the term enantiomer will be used exclusively in this textbook. **14** and **15** differ in their steric configurations around the carbon atom.

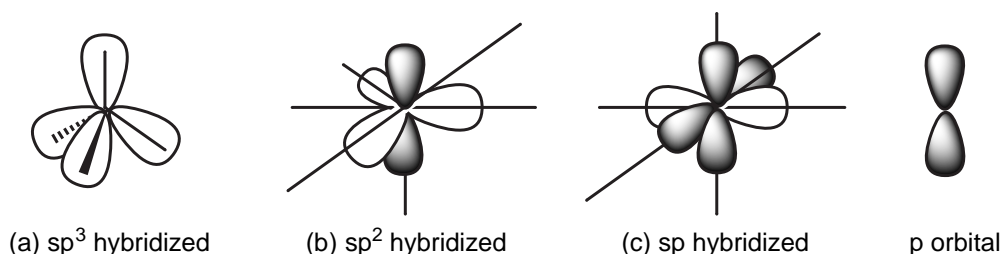
Next, we will discuss the relations between stereoisomers, including enantiomers. While it is clear that they are isomers with different structures, is there any difference in their properties or chemical reactivity? Stereochemistry is a branch of science that involves the study of the physical and chemical properties of various compounds, especially those associated with three-dimensional structures. Chemistry could not progress without stereochemistry. Stereochemistry is an essential part of chemistry. Then, is it necessary to separate the study of stereochemistry from the study of

chemistry?

There is a good reason for stereochemistry to be recognized as an important and independent field of chemistry. First of all, the physical and chemical properties of stereoisomers are sometimes so different that it is possible to gain a great deal of information about the relation between molecular structure and properties. In addition, a definite and considerably elaborate procedure is necessary to represent information about the three-dimensional structure of a molecule on a two-dimensional sheet of paper and then to reproduce the original three-dimensional information from that representation.

### 1.4 Multiple bonds

The carbon atom is not always connected to four different atoms. Carbon atoms involved in double or triple bonds combine three or two other atoms. First of all, you will consider carbon atoms that form a double bond. A carbon atom with the electron configuration  $2s^1 2p_x^1 2p_y^1 2p_z^1$  can form three hybridized orbitals of equal energy from three atomic orbitals, 2s and two of 2p orbitals. One of the 2p orbitals (*e.g.*  $2p_z$  orbital) remains unaffected. This hybridized orbital is called an  **$sp^2$  hybridized orbital** from its constitution. All of the  $sp^2$ -hybridized orbitals are on the same plane that includes the carbon atom, and the remaining 2p orbital is perpendicular to the plane. Fig 1.3(b) shows the atomic orbital of the  $sp^2$  hybridized carbon atom.



**Figure 1.3** Hybridized atomic orbitals of carbon

#### Q1.8

Predict the angles between each of the three  $sp^2$  orbitals. □

The skeleton of ethylene is formed when  $sp^2$  hybridized orbitals of each of two-carbon atoms overlap to form a  $\sigma$  bond. Overlap can take place when two p orbitals are placed parallel and the result is the formation of a  $\pi$  bond. Therefore, a double bond is made up from a  $\sigma$  bond and a  $\pi$  bond. Ethylene  $C_2H_4$  is completed when the hydrogen atoms are attached to each of the residual  $sp^2$  hybridized orbitals.

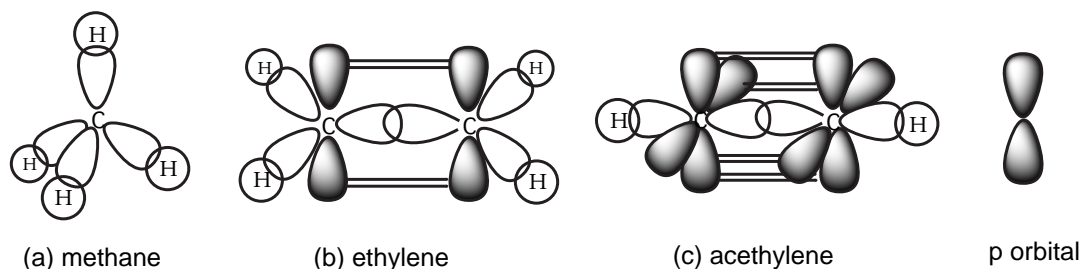
#### Q1.9

Explain the special arrangement of six atoms of ethylene—how are they arranged in the space? Describe the structure of ethylene by the overlap of atomic orbitals starting from Fig 1.4(b). □

#### A1.8

$120^\circ$ . These three should be arranged symmetrically since these are on the same plane and equivalent. □

If a carbon atom forms a triple bond, it can be connected to only two other atoms. In this case, the carbon in the  $2s^1 2p_x^1 2p_y^1 2p_z^1$  electron configuration forms two equivalent  $sp$  hybridized orbitals (Fig 1.4(c)) from a 2s and one of the 2p orbitals, two 2p orbitals are left over. The  $sp$  hybridized orbitals are in opposite directions. In other words, the angle between each of two  $sp$  hybridized orbitals is  $180^\circ$ . In acetylene  $C_2H_2$ , a  $\sigma$  bond is formed by the overlap of  $sp$  hybridized orbitals from each  $sp$  hybridized carbon, and two  $\pi$  bonds are also formed by the overlap of two pairs of p orbitals, and hydrogen atoms are bonded to the remaining two  $sp$  hybridized orbitals.



**Figure 1.4** The structure of basic organic compounds.

**Q1.10**

Explain the geometry of the four atoms of acetylene, and draw the bonding diagram for acetylene by using Fig 1.4(c). □

**A1.9**

The six atoms should be placed on the same plane. See Fig 1.4(b). □

Essential facts covered in this section are given below.

**S1.2 hybridization of carbon atom**

$sp^3$  hybridization: (s + p + p + p), tetrahedral (*e.g.* methane, ethane)

$sp^2$  hybridization: (s + p + p) + p; trigonal planar (*e.g.* ethylene, benzene)

$sp$  hybridization: (s + p) + p + p; linear (*e.g.* acetylene)

**A1.10**

The four atoms should be arranged in line. See Fig 1.4(c). □

There are two methods to represent multiple bonds by molecular models. In the first method, a multiple bond is represented by means of a bond with a bond length or a bond angle from among those for a single bond. The Dreiding model is one example. Another method is to represent in some way the multiple bond between atoms directly by some ways. The HGS model utilizes the first method. Its sets of balls and sticks is suitable for this way, but the model may also be used for the second way. For example, the ethylene molecule can be represented by connecting two balls for an  $sp^3$  hybridized carbon (designated as  $C^4$ ) by two curved bonds (Fig 1.7(a)). As for acetylene, three curved bonds can be applied.

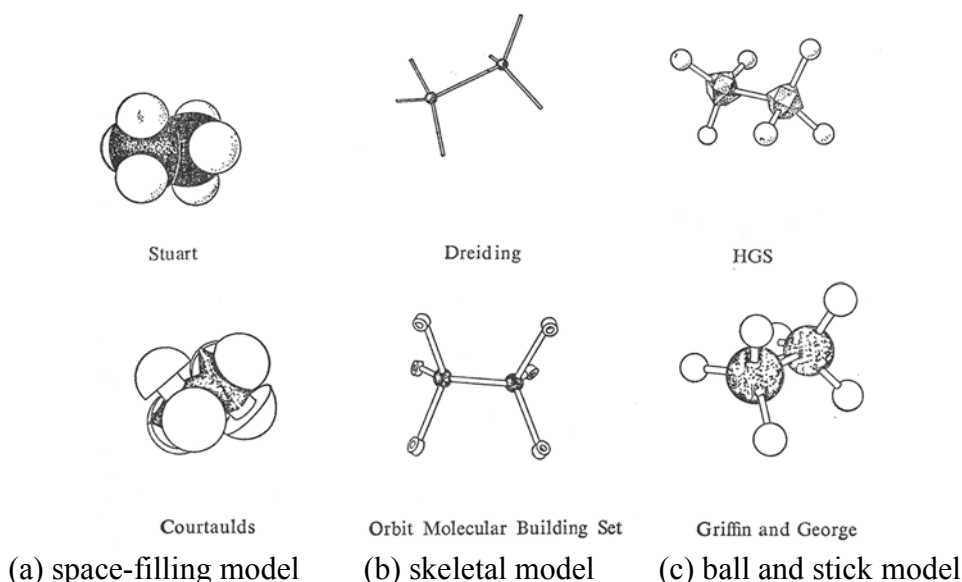
**1.5 Molecular models and geometry of molecules**

As is clear from the figures in the previous sections, it is not easy to draw arrangements of atoms that make up molecules on the two-dimensional plane of paper even for considerably simple molecules such as methane, ethane and acetylene.

Therefore, since the latter half of the 19<sup>th</sup> century, when the importance of stereochemistry was recognized, various molecular models were devised and some of them are now commercially available to assist chemists. However, previously the molecular models were used only for research, not for education, because stereochemistry was a limited field of science regarding which only some chemists were likely to be interested. In the 20<sup>th</sup> century, increased recognition for stereochemistry, especially among chemists studying organic chemistry, brought molecular models into education.

Fig. 1.5 illustrates typical molecular models now commercially available. Each is a model of ethane.





**Figure 1.5** Various molecular models

(a) Space filling models (*e.g.* Stuart model, Courtaulds model) represent the spread of electronic clouds. However, they fail to represent atoms inside a molecule clearly. It is not always easy to understand the arrangement of atoms in a complex molecule until one has had some experience.

(b) Skeletal models represent a molecule only with sticks proportional to the bond length. The utility of this type of model is that it is easier to have a good idea on the bond angles, bond lengths and the shape of the whole molecule, which is not so clear in the space filling model.

(c) Ball and stick models can be considered a variation of (b). The location of an atom (or rather the location of an atomic nucleus) is shown by a ball with several holes. Sticks of appropriate length represent the bonds. The angle of each hole on the ball is fitted to correspond to bond angles, and the length of each stick is also made proportional to the corresponding bond length. The utility of this model, from which it is often easy to understand the chemical structure of a molecule since the balls are colored as are the elements that they symbolize, can make it the most suitable one for education.

The HGS model is a domestic product, and it is easily available everywhere, and a set for students at a modest price is also available. It would be valuable to obtain a molecular model, because it is very important for learning stereochemistry.

The HGS model consists of balls (in fact polyhedrons) with four holes for  $sp^3$  hybridized carbon atoms, balls with five holes (two for p orbitals) for  $sp^2$  hybridized carbon atoms, multipurpose ones with many holes including those for  $sp$  hybridization, and plastic rods of various lengths. The balls are color-coded for differentiation. There are balls with many holes to be used to construct complex molecules.

### S1.3 Variety of molecular models

space filling model: emphasize electron clouds (*e.g.* Stuart model)

skeletal model: emphasize bond length and bond angle (*e.g.* Dreiding model)

ball and stick model: emphasize atoms (*e.g.* HGS model)

#### Q1.11

If you have a molecular model, try to assemble a model for the following molecules.

(a) water, (b) methane, (c) ethyl alcohol, (d) ethylene, (e) acetylene, (f) 1-butanol, (g) 2-methyl-2-propanol. □

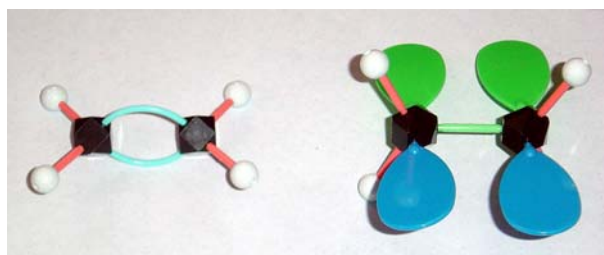
#### Q1.12

Which of these two methods to represent multiple bonds has greater utility? Describe the advantages and disadvantages of each method. □

### A1.11

Since the questions are straightforward, try by yourself. □

The HGS model provides the third method to solve the problem. A double bond can be represented by using balls with five holes (designated as  $C^5$ ) and hydrogen atoms and plates for p orbitals (fig 1.6 (b)). Since a molecule will be most stable when two pairs of p orbitals overlap most effectively, the most stable structure of ethylene can be achieved by fastening those plates.

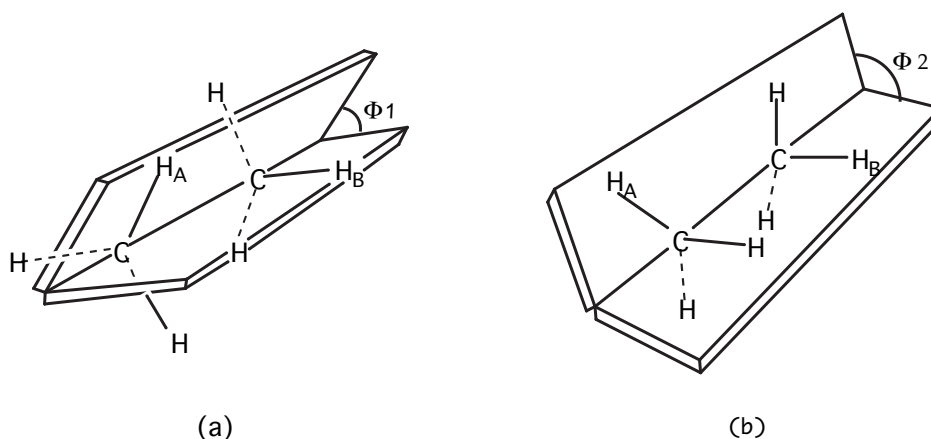


(a) the model with bent bonds    (b) the model with plates for p orbitals

**Figure 1.6** Molecular model of ethylene by HGS molecular model

There remains one important problem; rotation about a single bond. When you build up a molecular model of ethane, the geometry of two methyl groups is not fixed, whichever model is chosen. In molecular models, one of the methyl groups can be rotated about the C-C bond while holding the other methyl group. Thus, the shape of the whole molecule is changed continuously. However, even if the shape had changed, the bond angles and bond lengths would not have changed. What changed is the distance between hydrogen atoms of those two methyl groups.

Suppose you choose one of the hydrogen atoms of each methyl group and call these  $H_A$  and  $H_B$ , respectively. It is clear that the distance between  $H_A$  and  $H_B$  is changing during the rotation about the C-C bond, and this can be portrayed by the change in the dihedral angle defined by four atoms  $H_A-C-C-H_B$  (Fig. 1.7).



**Figure 1.7** The shape of ethane and the dihedral angle

But, does the change that takes place in molecular models correspond to the actual phenomenon? Or is it only the result of imperfection with models? That such a **free rotation** about a carbon-carbon single bond is possible was widely affirmed more than a hundred years ago. By the middle of the 20<sup>th</sup> century, however, further understanding had developed, and it was recognized

that such a rotation is not completely free but restricted to some extent – **restricted rotation**.

How are structure, character and reactivity of a molecule influenced by the rotation? This is also an interesting issue in stereochemistry.

### A1.12

The six atoms involved in an ethylene molecule are always placed on one plane, since the overlap between the p orbitals prevent the rotation around the double bond. However, the first method would fail to represent this planar nature since the model allows the free rotation around the C-C bond. On the other hand, the second way can represent the planar nature among the six atoms, while there is one disadvantage: the  $\angle\text{HCH}$  angle is incorrect (tetrahedral angle instead of the correct angle of  $120^\circ$ ). Furthermore, this method cannot represent the fact that a double bond is formed from two different bonds,  $\sigma$  and  $\pi$  bonds. □

## 1.6 Nomenclature of stereochemistry

The nomenclature of compounds should play an important role because sometimes there are more than one molecules present in single molecular formula. First of all, a name must specify only one compound (though two or more names are possible for one compound). Secondly, it should be able to deduce the structure of a compound unambiguously from its name. After the age of Lavoisier, chemists took great pains to devise reasonable, universal and simple rules for the nomenclature of compounds. As a result, even beginners can easily understand and use the established rules of nomenclature to deduce simple compounds. For example,  $\text{C}_4\text{H}_9\text{OH}$  **2~5** is named as follows.

	(A) trivial names	(B) systematic names
<b>2</b>	2-butyl alcohol	1-butanol
<b>3</b>	isobutyl alcohol	2-methyl-1-propanol
<b>4</b>	<i>sec</i> -butyl alcohol	2-butanol
<b>5</b>	<i>tert</i> -butyl alcohol	2-methyl-2-propanol

The first nomenclature (A) is traditional which has been used since the 19<sup>th</sup> century, while the second nomenclature (B) is more regular or systematic. Once you understand its general rules, it will be more useful.

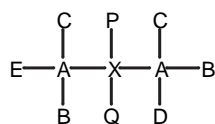
Structural isomers, which have the same molecular formula but differ in the sequence of atoms with which the atoms are arranged in space, also require a nomenclature system by which one name will correspond to only one compound. It should also be possible to reconstitute the structure from the name. Although the nomenclature based on stereochemistry of a molecule – **stereochemical nomenclature** -- is much more recent than nomenclature for compounds, they share common ways of development. This means that stereochemical nomenclature for certain group of compounds (*e.g.* alkenes or oxime *etc.*) was established first, and subsequently systematic nomenclature applicable to every group of compounds was devised.

Although systematic nomenclature will become the standard, the former system still plays some role. Indeed, both nomenclatures are actually used, and the need to read past literature written with old-fashioned nomenclature still exists. Therefore, you will be taught both nomenclatures in this textbook.

### The sequence rule

The systematic nomenclature is based on the **sequence rule**. The sequence rule decides the priority sequence among ligands. The stereochemistry of a compound is described by the order ranked according to the sequence rule and several additional rules about each compounds.

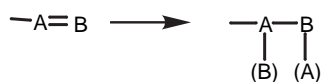
Now, let us take a look at the compound **19** and rank the ligands that are bonded to the atom X in order of priority.



19

**Determination of the priority**

- 1) Generally, the greater the atomic number, the higher the priority.
- 2) In the case of isotopes, the larger is the mass number, the higher is priority.
- 3) First of all, the priority depends on the atoms that directly attached to the atom X.
- 4) In the case of a tie in the 1<sup>st</sup> atom (*i.e.* A, A), the ligands that are attached to each of the atoms, the 2<sup>nd</sup> atom, (*i.e.* B, C, D, and B, C, E, respectively) must be considered.
- 5) Even if there are still tie atoms remaining, the procedure must be repeated till the priority is determined.
- 6) If an atom is doubly or triply bonded to another atom, the priority system treats it as if it were bonded to two or three of those atoms. Thus, in a A=B double bond, the atom A is considered to be bonded to two of atom B, the atom B is to be bonded to two of atom A, and the sequence rules (1)~(5) are to be applied.



These atoms (A) or (B) are called **replica atoms**.

**S1.4 Sequence rules**

- (1) If the atom of the ligand that is directly bonded to the central atom (the first atom) has a greater atomic number than that of other ligands, the ligand has a higher priority.
- (2) In the case of a tie of atomic numbers between the atoms attached to the first atom, the second atom must be considered. If the priority is not determined at this stage, the third or fourth atoms must be taken into account in turn.
- (3) For a multiple bond, the sequence rule splits double and triple bonds into two and three single bonds, respectively. This is done by duplicating or triplicating the doubly or triply bonded atoms. The duplicated and triplicated atoms are called replica atoms.

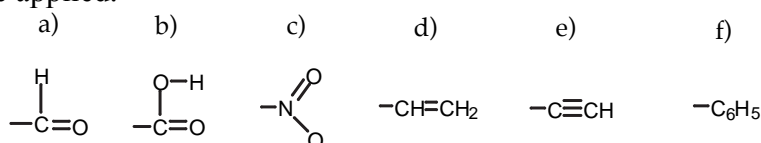
**Q1.13**

Rank the following ligands in the order of their priority.

- a) hydrogen, iodine, fluorine, bromine.
- b)  $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{Cl}$ ,  $-\text{OH}$
- c)  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{OH}$ ,  $-\text{ONa}$
- d)  $-\text{OCH}_3$ ,  $-\text{NHCH}_3$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{Cl}$
- e)  $-\text{OCH}_2\text{C}(\text{CH}_3)_3$ ,  $-\text{OCH}_2\text{CH}_2\text{Cl}$ ,  $-\text{OCH}_3$ ,  $-\text{H}$

**Q1.14**

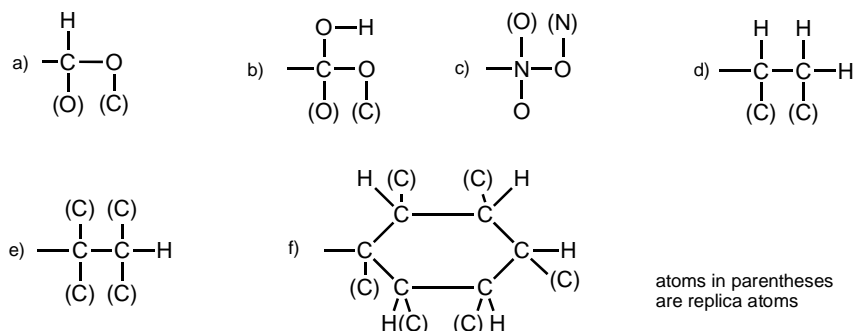
Supply appropriate replica atoms for the following ligands and modify these so that the sequence rule can be applied.

**A1.13**

- a)  $\text{I} > \text{Br} > \text{Cl} > \text{F} > \text{H}$ , b)  $\text{Cl} > \text{OCH}_3 > \text{OH} > \text{CH}_3$ , c)  $\text{ONa} > \text{OH} > \text{C}_2\text{H}_5 > \text{CH}_3$ ,  
d)  $\text{Cl} > \text{SO}_3\text{H} > \text{NHCH}_3 > \text{OCH}_3$ , e)  $\text{OCH}_2\text{CH}_2\text{Cl} > \text{OCH}_2\text{C}(\text{CH}_3)_3 > \text{OCH}_3 > \text{H}$

**Q1.15**

Assign priority to the ligands a)~f) in Q 1.14. □

**A1.14****A1.15**

	a)	b)	c)	d)	e)	f)
ligand	$\begin{array}{c} \text{H} \\   \\ \text{---C=O} \end{array}$	$\begin{array}{c} \text{O---H} \\   \\ \text{---C=O} \end{array}$	$\begin{array}{c} \text{O} \\ // \\ \text{---N} \\ \backslash \\ \text{O} \end{array}$	$\text{---CH=CH}_2$	$\text{---C}\equiv\text{CH}$	$\text{---C}_6\text{H}_5$
1st atom	C <sub>1</sub>	C <sub>2</sub>	N <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
2nd atom	O <sub>11</sub> O <sub>12</sub> H <sub>13</sub>	O <sub>21</sub> O <sub>22</sub> O <sub>23</sub>		C <sub>41</sub> C <sub>42</sub> H <sub>43</sub>	C <sub>51</sub> C <sub>52</sub> C <sub>53</sub>	C <sub>61</sub> C <sub>62</sub> C <sub>63</sub>
3rd atom					C <sub>511</sub> C <sub>512</sub> H <sub>513</sub>	$\begin{cases} \text{C}_{611}\text{C}_{612}\text{H}_{613} \\ \text{C}_{621}\text{C}_{622}\text{H}_{623} \end{cases}$
priority	3	2	1	6	5	4

The priorities of common ligands are listed in S1.5. It may be called your attention to the fact that the order can easily be changed by substitution. For example, the methyl group is ranked lower than the ethyl group in the list. However fluoromethyl CH<sub>2</sub>F- has a higher priority than the ethyl.

**S1.5 Priority of representative ligands (lower to higher)**

1 Hydrogen	20 Isopropenyl	39 Methoxycarbonyl <sup>a</sup>	58 Methoxy
2 Methyl	21 Acetylenyl	40 Ethoxycarbonyl <sup>b</sup>	59 Ethoxy
3 Ethyl	22 Phenyl	41 Benzyloxycarbonyl <sup>b</sup>	60 Benzyloxy
4 <i>n</i> -Propyl	23 <i>p</i> -Tolyl	42 <i>tert</i> -Butoxycarbonyl <sup>b</sup>	61 Phenoxy
5 <i>n</i> -Butyl	24 <i>p</i> -Nitrophenyl	43 Amino	62 Glycosyloxy
6 <i>n</i> -Pentyl	25 <i>m</i> -Tolyl	44 Ammonio <sup>+</sup> H <sub>2</sub> N-	63 Formyloxy
7 <i>n</i> -Hexyl	26 3,5-Xylyl	45 Methylamino	64 Acetoxy
8 Isopentyl	27 <i>m</i> -Nitrophenyl	46 Ethylamino	65 Benzoyloxy
9 Isobutyl	28 3,5-Dinitrophenyl	47 Phenylamino	66 Methylsulfinyloxy
10 Allyl	29 1-Propynyl	48 Acetylamino	67 Methylsulfonyloxy
11 Neopentyl	30 <i>o</i> -Tolyl	49 Benzoylamino	68 Fluoro
12 2-Propynyl	31 2,6-Xylyl	50 Benzyloxycarbonylamino	69 Mercapto HS-
13 Benzyl	32 Trityl	51 Dimethylamino	70 Methylthio CH <sub>3</sub> S-
14 Isopropyl	33 <i>o</i> -Nitrophenyl	52 Diethylamino	71 Methylsulfinyl
15 Vinyl	34 2,4-Dinitrophenyl	53 Trimethylammonio	72 Methylsulfonyl
16 <i>sec</i> -Butyl	35 Formyl	54 Phenylazo	73 Sulfo HO <sub>2</sub> S-
17 Cyclohexyl	36 Acetyl	55 Nitroso	74 Chloro
18 1-Propenyl	37 Benzoyl	56 Nitro	75 Bromo
19 <i>tert</i> -Butyl	38 Carboxyl	57 Hydroxy	76 Iodo

<sup>a</sup> ANY alteration to structure, or substitution, etc., may alter the order of preference.

<sup>b</sup> These groups are ROC(=O)-.