

STRUCTURAL ORGANIC CHEMISTRY. THE SHAPES OF MOLECULES. FUNCTIONAL GROUPS

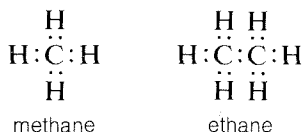
In this chapter we first briefly review the most important types of covalent bonds encountered in organic substances and the ways in which these bonds are represented in structural formulas. Next we consider the sizes and shapes of organic molecules and how structural formulas written in two dimensions can be translated into three-dimensional models that show the relative positions of the atoms in space. We also discuss models that reflect the relative sizes of the atoms and the way in which the atoms may interfere with each other when in close quarters (steric hindrance). Then we go on to further important aspects of structure—the functional group concept and position isomerism.

Our aim is to have you become more familiar with the various kinds of organic compounds and begin to see how the practicing organic chemist visualizes molecules and correlates the diverse kinds of structures that he has to deal with in his work.

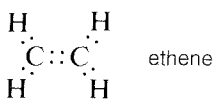
2-1 STRUCTURAL FORMULAS

The building block of structural organic chemistry is the tetravalent carbon atom. With few exceptions, carbon compounds can be formulated with four

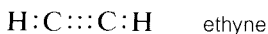
covalent bonds to each carbon, regardless of whether the combination is with carbon or some other element. The two-electron bond, which is illustrated by the carbon–hydrogen bonds in methane or ethane and the carbon–carbon bond in ethane, is called a **single bond**. In these and many related substances, each carbon is attached to four other atoms:



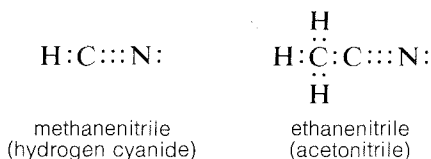
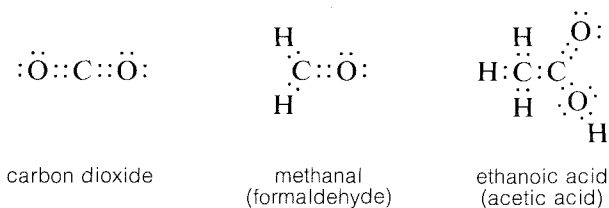
There exist, however, compounds such as ethene (ethylene), C_2H_4 , in which two electrons from each of the carbon atoms are mutually shared, thereby producing *two* two-electron bonds, an arrangement which is called a **double bond**. Each carbon in ethene is attached to only three other atoms:



Similarly, in ethyne (acetylene), C_2H_2 , three electrons from each carbon atom are mutually shared, producing *three* two-electron bonds, called a **triple bond**, in which each carbon is attached to only two other atoms:

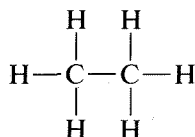


Of course, in all cases each carbon has a full octet of electrons. Carbon also forms double and triple bonds with several other elements that can exhibit a covalence of two or three. The carbon–oxygen (or carbonyl) double bond appears in carbon dioxide and many important organic compounds such as methanal (formaldehyde) and ethanoic acid (acetic acid). Similarly, a carbon–nitrogen triple bond appears in methanenitrile (hydrogen cyanide) and ethanenitrile (acetonitrile).

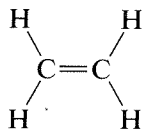


By convention, a single straight line connecting the atomic symbols is used to represent a single (two-electron) bond, two such lines to represent a

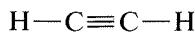
double (four-electron) bond, and three lines a triple (six-electron) bond. Representations of compounds by these symbols are called **structural formulas**; some examples are



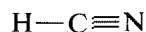
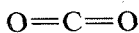
ethane



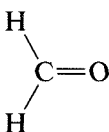
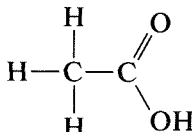
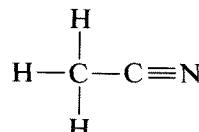
ethene



ethyne

methanenitrile
(hydrogen cyanide)

carbon dioxide

methanal
(formaldehyde)ethanoic acid
(acetic acid)ethanenitrile
(acetonitrile)

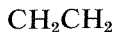
A point worth noting is that structural formulas usually do not indicate the *nonbonding* electron pairs. This is perhaps unfortunate because they play as much a part in the chemistry of organic molecules as do the bonding electrons and their omission may lead the unwary reader to overlook them. However, when it is important to represent them, this can be done best with pairs of dots, although a few authors use lines:



To save space and time in the representation of organic structures, it is common practice to use "condensed formulas" in which the bonds are not shown explicitly. In using condensed formulas, normal atomic valences are understood throughout. Examples of condensed formulas are



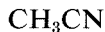
ethane



ethene

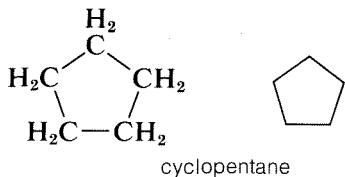


ethyne

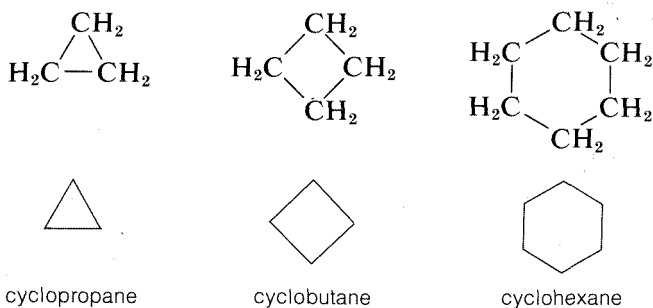
methanal
(formaldehyde)ethanoic acid
(acetic acid)methanenitrile
(hydrogen cyanide)ethanenitrile
(acetonitrile)

Another type of abbreviation that often is used, particularly for ring compounds, dispenses with the symbols for carbon and hydrogen atoms and leaves only the lines in a structural formula. For instance, cyclopentane, C_5H_{10} , often is represented as a regular pentagon in which it is understood that each apex represents a carbon atom with the requisite number of hydro-

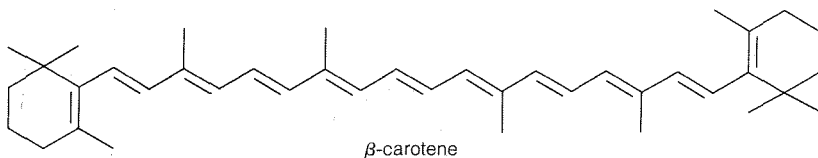
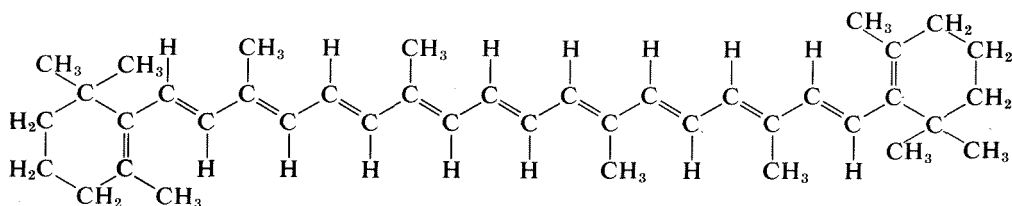
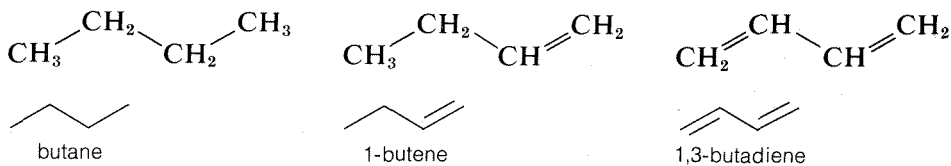
gens to satisfy the tetravalence of carbon:



Likewise, cyclopropane, C_3H_6 ; cyclobutane, C_4H_8 ; and cyclohexane, C_6H_{12} , are drawn as regular polygons:



Although this type of line drawing is employed most commonly for cyclic structures, its use for open chain (acyclic) structures is becoming increasingly widespread. There is no special merit to this abbreviation for simple structures such as butane, C_4H_{10} ; 1-butene, C_4H_8 ; or 1,3-butadiene, C_4H_6 , but it is of value in representing more complex molecules such as β -carotene, $C_{40}H_{56}$:



Line structures also can be modified to represent the three-dimensional *shapes* of molecules, and the way that this is done will be discussed in detail in Chapter 5. At the onset of your study of organic chemistry, you should write out the formulas rather completely until you are thoroughly familiar with what these abbreviations stand for.

2-2 THE SIZES AND SHAPES OF ORGANIC MOLECULES. MOLECULAR MODELS

The size and shape of molecules are as much a part of molecular structure as is the order in which the component atoms are bonded. Contrary to the impression you may get from structural formulas, complex molecules are not flat and formless, but have well-defined spatial arrangements that are determined by the lengths and directional character of their chemical bonds. It is not easy to visualize the possible arrangements of the bonds in space and it is very helpful to have some kind of mechanical model that reflects the molecular geometry, including at least an approximation to the relative lengths of the bonds. "Ball-and-stick" models such as the ones used by Paterno (Section 1-1D) fill this purpose admirably.

2-2A Bond Angles and Ball-and-Stick Models

It is well established that the normal carbon atom forms its four single bonds in compounds of the type CX_4 so that the four attached atoms lie at the corners of a regular tetrahedron. The bond angles $X-C-X$ are 109.5° and this value is the "normal" valence angle of carbon. For many purposes, ball-and-stick models of organic compounds give useful information about the spatial relationships of the atoms, and for CX_4 the angles between the sticks are set at 109.5° (Figure 2-1). Organic molecules strongly resist deformation forces that alter their valence angles from normal values. Therefore ball-and-stick models correspond better to the behavior of actual molecules if the connectors representing single bonds are made to be rather stiff.

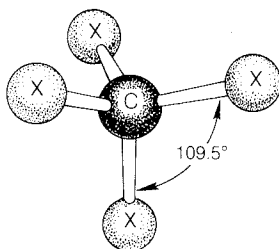


Figure 2-1 Ball-and-stick model of CX_4

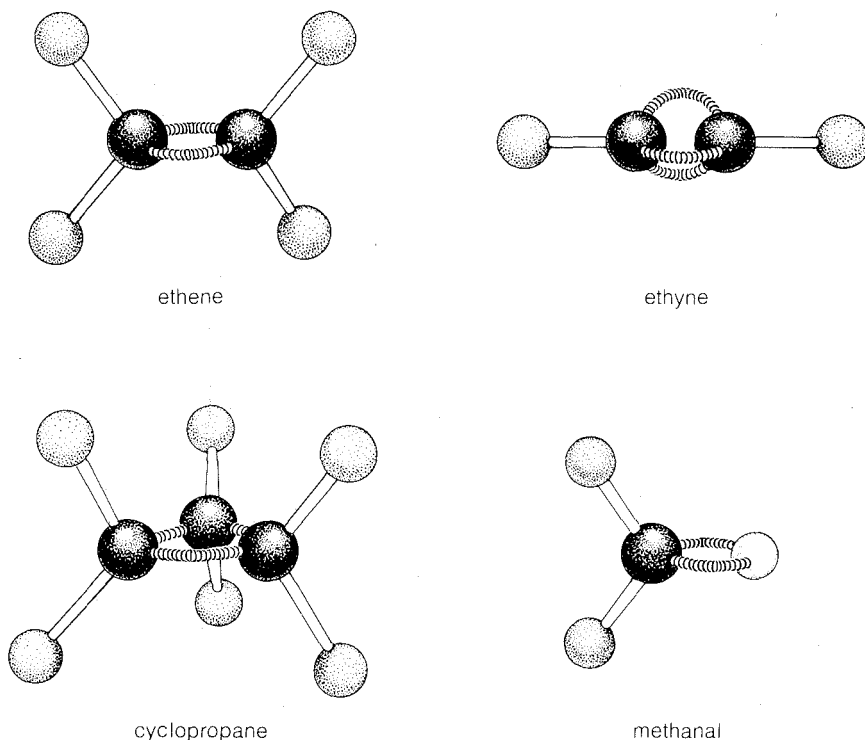
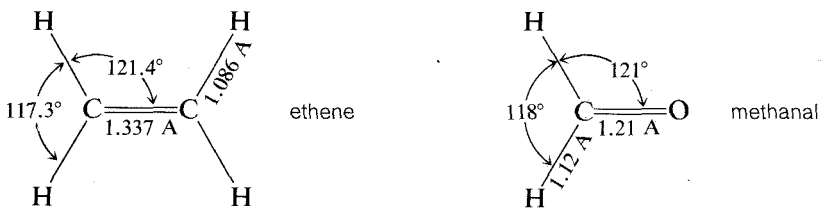


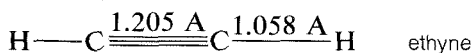
Figure 2-2 Ball-and-stick models of some simple organic molecules

Whereas methane, CH₄, is tetrahedral, ethene, C₂H₄, is not. According to the best available physical measurements, all six atoms of ethene lie in a single plane and the H—C—H bond angles are 117.3°. Methanal (formaldehyde) also is a planar molecule with an H—C—H bond angle of 118°.



Models of ethene and methanal can be built with ball-and-stick models by using flexible couplings or bent sticks to form the double bonds (Figure 2-2), but the H—C—H angles are inaccurate because they are 109.5° rather than the observed 117° to 118°.

Ethyne, C₂H₂, has been established experimentally to be a linear molecule; that is, the H—C—C bond angle is 180°:



This geometry also results with ball-and-stick models, if the triple bond is constructed of three flexible couplings or bent sticks as shown in Figure 2-2.

Structural units that have C—C—C valence angles substantially less than the tetrahedral value include double and triple bonds, and small rings such as cyclopropane. Several bent bonds are required to construct models of compounds containing these units. Interestingly, such compounds are much less stable and more reactive than otherwise similar molecules for which models can be constructed with straight sticks at tetrahedral angles.

2-2B Bond Lengths and Space-Filling Models

The length of a chemical bond is the average distance between the nuclei of two bonded atoms, regardless of where the bonding electrons happen to be. The customary unit of length is the angstrom¹ ($\text{A} = 10^{-10} \text{ m}$), and measurements often can be made with an accuracy of 0.001 A by using the techniques of molecular spectroscopy, x-ray diffraction (for crystalline solids), and electron diffraction (for volatile compounds). Bond lengths vary considerably with structure and depend on the identity of both atoms, the type of bonding (single, double, or triple), and the nature of other atoms or groups bonded to the two atoms in question. These effects are apparent in the data of Table 2-1, which lists the bond lengths in several simple organic compounds. Multiple bonds, double or triple, clearly are shorter than single bonds, and it can be stated as a general observation that the more bonding electrons in a given bond, the shorter (and stronger) the bond. The lengths of single C—C bonds also vary significantly depending on what other atoms or groups are attached to the carbons. Thus Table 2-1 shows that single C—C bonds become progressively shorter as the number of multiple bonds or electronegative atoms attached to the carbons increases.

Although molecular models cannot represent the subtle variations in bond lengths and bond angles that actual molecules exhibit, most kinds of commercially available molecular models do attempt to reproduce relative bond lengths with some degree of reality. In the ball-and-stick type, the sticks usually come in various lengths to simulate different kinds of bonds; C—H bonds typically are scaled to represent 1.1 A, C—C bonds to be 1.54 A, and C=C and C≡C to be correspondingly shorter. In some model sets the bonds can be cut to any desired length.

While ball-and-stick models of molecules are very useful for visualizing the relative positions of the atoms in space, they are unsatisfactory whenever we also want to show how large the atoms are. Actually, atomic radii are so large relative to the lengths of chemical bonds that when a model of a molecule such as methyl chloride is constructed with atomic radii and bond lengths, both to scale, the bonds connecting the atoms are not clearly evident. None-

¹The angstrom unit likely will be replaced eventually by the nanometer ($1 \text{ nm} = 10^{-9} \text{ m} = 10 \text{ A}$).

Table 2-1
Bond Lengths in Simple Organic Molecules^a

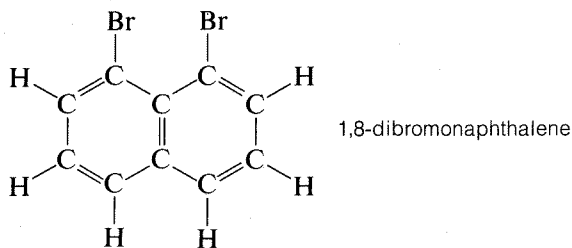
Compound	Formula	Bond length, Å				
		C—C	C=C	C≡C	C—H	C—Cl
ethane	CH ₃ —CH ₃	1.534			1.093	
ethene	H ₂ C=CH ₂		1.339		1.086	
ethyne	HC≡CH			1.205	1.058	
butane	CH ₃ —CH ₂ —CH ₂ —CH ₃	1.539			1.100	
2-butene	CH ₃ —CH=CH—CH ₃	1.520	1.339			
2-butyne	CH ₃ —C≡C—CH ₃	1.47		1.20	1.09	
1,3-butadiene	CH ₂ =CH—CH=CH ₂	1.483	1.337		1.08 ^b	
1-buten-3-yne	CH≡C—CH=CH ₂	1.448	1.34	1.20	1.07 ^b	
chloroethane	CH ₃ —CH ₂ Cl	1.595			1.101 ^c	1.779
1,1-dichloroethane	CH ₃ —CHCl ₂	1.55				1.79
1,1,1-trichloroethane	CH ₃ —CCl ₃	1.54			1.09	1.76
hexachloroethane	CCl ₃ —CCl ₃	1.49				1.76

^aFrom "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Special Publication Nos. 11 and 18*, The Chemical Society, London, 1958 and 1965.

^bRefers to C—H of terminal CH₂ group.

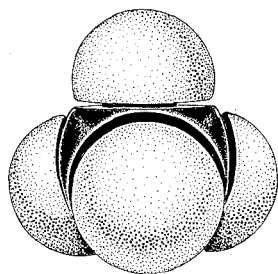
^cRefers to C—H of CH₂Cl group.

theless, such "space-filling" models made with truncated balls held together with snap fasteners are used widely to determine the possible closeness of approach of groups to each other and the degree of crowding of atoms in various arrangements (see Figure 2-3). Especially excellent, but expensive, models used for this purpose are the Corey-Pauling-Kolton (CPK) models. Figure 2-3 shows how the CPK models can indicate intense molecular crowding, as between the bromines in 1,8-dibromonaphthalene, a close relative of 1,2-dibromobenzene mentioned in Section 1-1G:

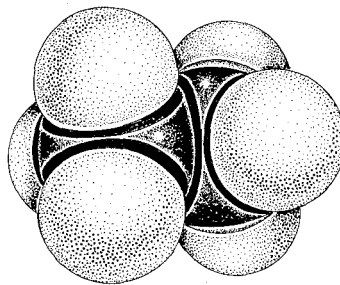


As we shall see, such crowding has many chemical consequences.

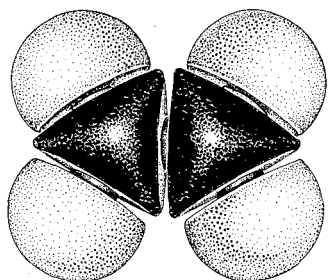
Ideally, a model should reflect not only the size and shape of the molecule it represents but also the flexibility of the molecule. By this we mean that



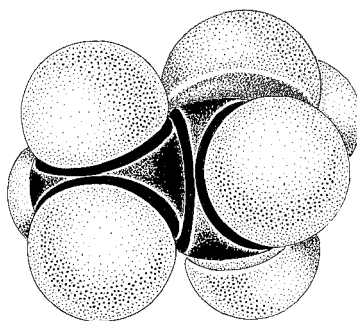
methane



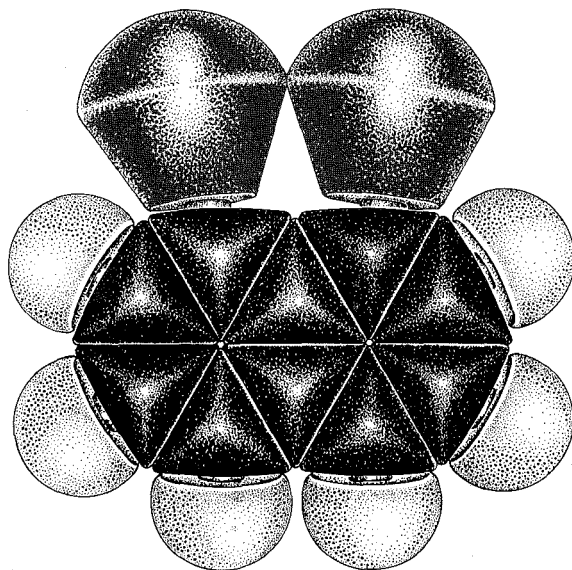
ethane



ethene



ethanol



1,8-dibromonaphthalene

Figure 2-3 CPK space-filling models of organic compounds

it should simulate the type of motions available to the molecule, particularly bond rotation. For example, it is known that rotation normally occurs about single bonds in open-chain compounds but is restricted about double bonds. Motions of this kind are demonstrated easily with ball-and-stick models, but are not at all obvious with the space-filling type. For this reason, ball-and-stick models or their equivalent are more generally useful than the space-filling models for visualizing structures and the positions of the atoms relative to one another.

2-3 CLASSIFICATION OF ORGANIC COMPOUNDS BY FUNCTIONAL GROUPS

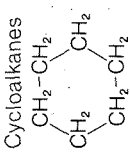
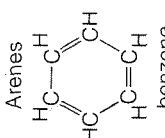
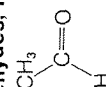
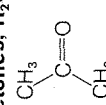
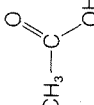
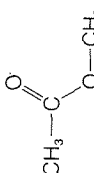
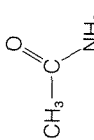
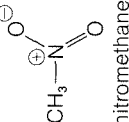
There are a number of recurring types of structural features in organic compounds that commonly are known as **functional groups**. In fact, a traditional approach to the subject of organic chemistry involves the classification of compounds according to their functional groups. Thus the structural features $C=C$, $C\equiv C$, $C=O$, OH , NH_2 , and $C\equiv N$ are the functional groups of alkenes, alkynes, carbonyl compounds, alcohols, amines, and nitriles, respectively. It will be helpful to look at the structural features of some of the major types of organic compounds even though the details of their chemistry will not be discussed until later chapters. Examples of structures arranged in accord with their functional groups are given in Table 2-2. The examples chosen are representative of compounds containing carbon and hydrogen (**hydrocarbons**) as well as compounds containing halogens, oxygen, nitrogen, and sulfur. We do not expect you to memorize this table. In time you will become familiar with all of the types of structures in it.

In Table 2-2 we generally have used **systematic names** as first-choice names because these names emphasize the relationships between the compounds and ease the burden of the beginning student in having to remember many special names. We have little hope that systematic names such as methanal, 2-propanone, and ethanoic acid soon will replace the commonly used nonsystematic names formaldehyde, acetone, and acetic acid. But there is no question that every organic chemist knows what compounds the names methanal, 2-propanone, and ethanoic acid represent, so the beginner can communicate with these names and later become familiar with and use the special names. We will have more to say on this subject in Chapter 3.

Exercise 2-1 Draw the Lewis electron-pair structure of 2-propanone (acetone) clearly showing the bonding and nonbonding electron pairs in the valence shell of each atom. Draw structural formulas for other compounds having the composition C_3H_6O that possess

- a. an aldehyde function.
 - b. an ether function in a ring.
 - c. an alcohol function and a double bond.
 - d. an alcohol function and a ring.
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Table 2-2
Types and Examples of Organic Compounds Arranged According to Functional Groups

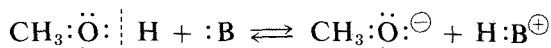
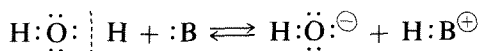
Hydrocarbons, R—H^a Alkanes $\text{CH}_3\text{CH}_2\text{CH}_3$ propane	Alkenes $\text{CH}_3\text{CH}=\text{CH}_2$ propene	Alkynes $\text{CH}_3\text{C}\equiv\text{CH}$ propyne	Cycloalkanes  cyclohexane	Arenes  benzene
Alcohols, R—OH $\text{CH}_3\text{CH}_2\text{—OH}$ ethanol (ethyl alcohol)	Ethers, R—O—R $\text{CH}_3\text{CH}_2\text{—O—CH}_2\text{CH}_3$ ethoxyethane (diethyl ether)	Halides, R—X $\text{CH}_3\text{CH}_2\text{—Br}$ bromoethane (ethyl bromide)	Aldehydes, RCHO  ethanal (acetaldehyde)	Ketones, R₂CO  2-propanone (acetone)
Carboxylic Acids, R—CO₂H  ethanoic acid (acetic acid)	Esters, R—CO₂R  methyl ethanoate (methyl acetate)	Amides, R—CONH₂  ethanamide (acetamide)		
Amines, R—NH₂ $\text{CH}_3\text{CH}_2\text{—NH}_2$ ethanamine (ethylamine)	Nitro Compounds, R—NO₂  nitromethane	Nitriles, RC≡N $\text{CH}_3\text{C}\equiv\text{N}$ ethanenitrile (acetonitrile)	Thiols, RSH $\text{CH}_3\text{CH}_2\text{—SH}$ ethanethiol	

^aThe symbol R represents a hydrocarbon group.

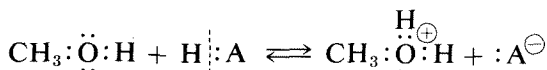
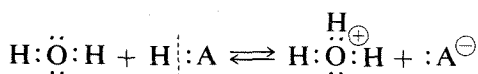
2-3A How Are Functional-Group Classifications Useful?

One of the main reasons for classifying compounds by their functional groups is that it also classifies their chemical behavior. By this we mean that the reactions of compounds and, to some extent, their physical properties are influenced profoundly by the nature of the functional groups present. Indeed, many organic reactions involve transformations of the functional group that do not affect the rest of the molecule. For instance, alcohols, $R-OH$, can be transformed into a number of other compounds, such as organic halides, $R-Cl$ or $R-Br$; ethers, $R-O-R$; and amines, $R-NH_2$ without changing the structure of the hydrocarbon group R . Furthermore, any compound possessing a particular functional group may be expected to exhibit reactions characteristic of that group and, to some extent at least, of inorganic compounds with similar functional groups.

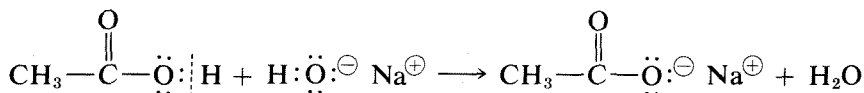
A good example of the use of the functional-group concept is for acid-base properties. Alcohols, ROH , are structurally related to water, HOH , in that both possess a hydroxyl function. We may then expect the chemistry of alcohols to be similar to that of water. In fact, both are weak *acids* because the OH group has a reactive proton that it can donate to a sufficiently strongly basic substance, written as $:B$ here:



Water and alcohols both are weak *bases* because the oxygens of their OH groups have unshared electron pairs to use in bonding with a proton donated by an acid, HA :

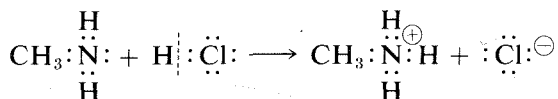
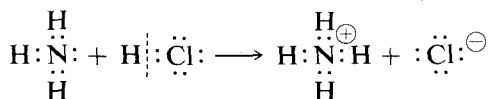


We can carry the analogy further to include carboxylic acids, RCO_2H , which also have a hydroxyl function. They also should possess acidic and basic properties. They do have these properties and they are, in fact, stronger acids than either water or alcohols and form salts with bases:



Amines, RNH_2 , are structurally related to ammonia, NH_3 , and we therefore may predict that they will have similar properties. A property of ammonia that you probably will have encountered earlier is that it acts as a

base and forms salts with acids. Amines behave likewise:

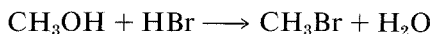
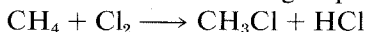


It is with logic of this kind—inferring chemical behavior from structural analogies—that much of organic chemistry can be understood. There are other logical classification schemes, however, and one of these depends more on *types* of reactions than on functional groups.

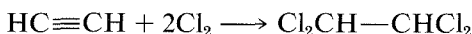
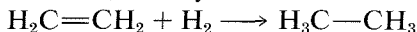
2-3B Classifications by Reaction Types

The rationale of classification by reaction types is that different functional groups may show the same kinds of reactions. Thus, as we have just seen, alcohols, carboxylic acids, and amines all can accept a proton from a suitably strong acid. Fortunately, there are very few different types of organic reactions—at least as far as the overall result that they produce. The most important are acid-base, substitution, addition, elimination, and rearrangement reactions. Some examples of these are given below, and you should understand that these are descriptive of the overall chemical change and nothing is implied as to *how* or *why* the reaction occurs (also see Section 1-II).

Substitution of one atom or group of atoms for another:



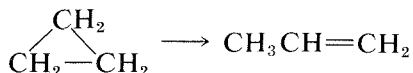
Addition, usually to a double or triple bond:



Elimination, which is the reverse of addition:

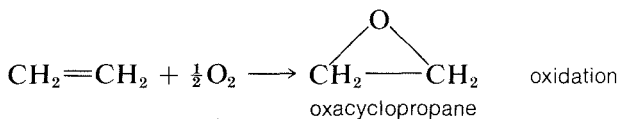
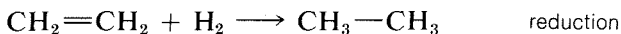


Rearrangement where one structure is converted to an isomeric structure:

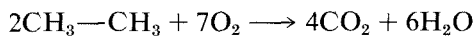


Certain reactions commonly are described as either *oxidation* or *reduction* reactions and most simply can be thought of as reactions that result in changes in the oxygen or hydrogen content of a molecule by direct or indirect

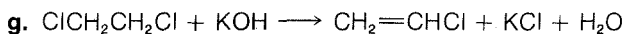
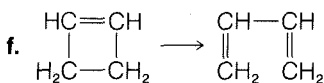
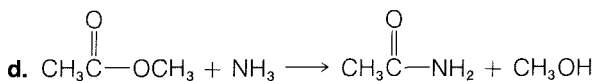
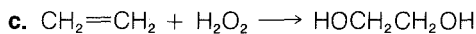
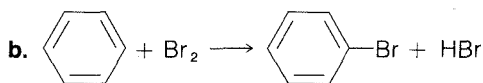
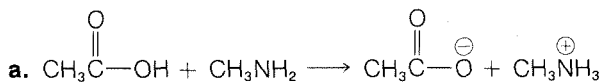
reactions with oxygen or hydrogen, respectively. They frequently fall into one of the categories already mentioned. Reduction of ethene to ethane is clearly *addition*, as is oxidation of ethene to oxacyclopropane:

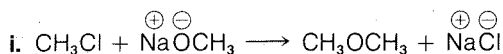
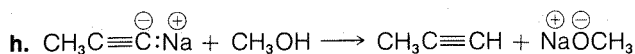


Reactions that lead to substantial degradation of molecules into smaller fragments are more difficult to classify. An example is the combustion of ethane to carbon dioxide and water. All of the chemical bonds in the reactants are broken in this reaction. It seems pointless to try to classify this as anything but a complete combustion or oxidation reaction:



Exercise 2-2 Classify each of the following reactions as a substitution, addition, elimination, rearrangement, oxidation–reduction, or acid–base proton–transfer reaction:





Exercise 2-3 Write a balanced equation for the complete combustion of benzene, C_6H_6 , to CO_2 and H_2O , and for the incomplete combustion of benzene to CO and H_2O .

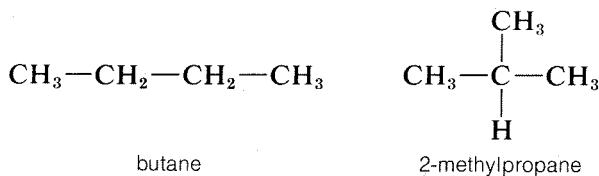
Exercise 2-4 How many grams of bromine will react by addition with (a) 20 g of ethene (b) 20 g of ethyne?

Exercise 2-5 Write balanced equations for the reactions of (a) metallic sodium with water, (b) metallic sodium with methanol, (c) sodium hydride with water, and (d) sodium hydride with ethanol.

Exercise 2-6 Write balanced equations for the reactions of (a) ammonia with sulfuric acid, (b) $\text{CH}_3\text{CH}_2\text{NH}_2$ with sulfuric acid, (c) sodium hydroxide with ammonium chloride, and (d) sodium hydroxide with $\text{CH}_3\text{CH}_2\text{NH}_3\overset{\oplus}{\text{Cl}}\overset{\ominus}$.

2-4 ISOMERISM IN ORGANIC COMPOUNDS

More than one stable substance can correspond to a given molecular formula. Examples are butane and 2-methylpropane (isobutane), each of which has the molecular formula C_4H_{10} . Similarly, methoxymethane (dimethyl ether) and ethanol have the same formula, $\text{C}_2\text{H}_6\text{O}$:



methoxymethane
(dimethyl ether)

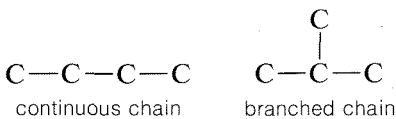
ethanol



Compounds having the same number and kind of atoms are called **isomers**.² Whereas only one stable substance is known corresponding to the formula CH_4 , thirty-five stable isomers have been prepared of the formula C_9H_{20} . From this one may begin to sense the rich variety of organic chemistry, which leads to many problems—in telling one compound from another, in determining structures, and also in finding suitable names for compounds. In the rest of this chapter we will describe one type of isomer—the position isomer—and in later chapters we will discuss another type of isomer—the stereoisomer—and the experimental approaches that are used to establish the purity, identity, structure, and stereochemistry of organic compounds.

2-4A Position Isomers

Compounds having the same number and kind of atoms but having different bonding arrangements between the atoms are called **position isomers**. Butane and 2-methylpropane are examples of position isomers. The atoms are connected differently in the two structures because the carbon chain in butane is a straight or continuous chain, whereas in 2-methylpropane it is branched:



Therefore these two molecules are structurally different and, accordingly, do not have the same chemical and physical properties. They cannot be converted one into the other without breaking and remaking C—C and C—H bonds. Methoxymethane and ethanol are also position isomers because the oxygen clearly is connected differently in the two molecules:



The term *position isomer* means the same as *constitutional isomer*. The designation *structural isomer* also is used, but this term is taken by some to include both position isomers and stereoisomers; that is, “structure” can mean both the way in which atoms are connected and their different arrangements in space.

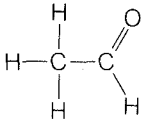
The number of position isomers possible for a given formula rapidly increases with the increasing number of carbon atoms, as can be seen from the number of theoretically possible structures of formula $\text{C}_n\text{H}_{2n+2}$ up to $n = 10$ given in Table 2-3. In 1946, it was reported that all of the 75 compounds with values of $n = 1$ to $n = 9$ had been prepared in the laboratory. Before we can begin to discuss the chemistry of these compounds it is necessary to know how

²The prefix *iso* is from the Greek word meaning the same or alike.

Table 2-3
Alkanes (C_nH_{2n+2})

No. of carbons (n)	Name	No. of isomers
1	methane	1
2	ethane	1
3	propane	1
4	butane	2
5	pentane	3
6	hexane	5
7	heptane	9
8	octane	18
9	nonane	35
10	decane	75
20	eicosane	366,319
30	triacontane	4.11×10^9

to name them; without convenient and systematic rules for nomenclature that are adopted universally, catastrophic confusion would result. We shall tackle this problem in the next chapter.

Exercise 2-7 Draw structural formulas of the type  representing each

of the required number of isomers for the following formulas. Be sure to use the normal valences for all of the atoms. Table 2-2 will be helpful to indicate possible structural types of various isomers.

- | | |
|-------------------------------|-------------------------------------------------------------------|
| a. C_5H_{12} (three) | f. C_3H_5Cl (at least three) |
| b. $C_3H_4Br_2$ (four) | g. C_6H_6 (at least five; more than 100 can be written!) |
| c. C_2H_4O (three) | h. $C_2H_4O_2$ (at least four) |
| d. C_4H_8 (four) | i. C_3H_4O (at least three) |
| e. C_3H_5N (four) | j. C_2H_3N (at least three) |

Supplementary Exercises

2-8 Draw Lewis electron-pair structures for the following substances whose structural formulas are given. Use distinct, correctly placed dots for the electrons and show

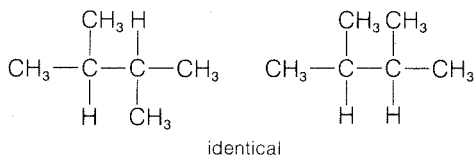
both the bonding and nonbonding pairs. Mark all atoms that are not neutral with charges of the proper sign.

- | | |
|---------------------------------------------------------------|-----------------------------------------------------------------------------|
| a. propane, $\text{CH}_3\text{CH}_2\text{CH}_3$ | g. methoxymethane, CH_3OCH_3 |
| b. methylcyclopropane, $(\text{CH}_2)_2\text{CHCH}_3$ | h. ethanal, CH_3CHO |
| c. propadiene, $\text{CH}_2=\text{C}=\text{CH}_2$ | i. ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$ |
| d. propyne, $\text{HC}\equiv\text{CCH}_3$ | j. benzenamine, $\text{C}_6\text{H}_5\text{NH}_2$ |
| e. benzene, C_6H_6 | k. nitromethane, CH_3NO_2 |
| f. tetrafluoroethene, $\text{F}_2\text{C}=\text{CF}_2$ | l. benzenecarbonitrile, $\text{C}_6\text{H}_5\text{C}\equiv\text{N}$ |

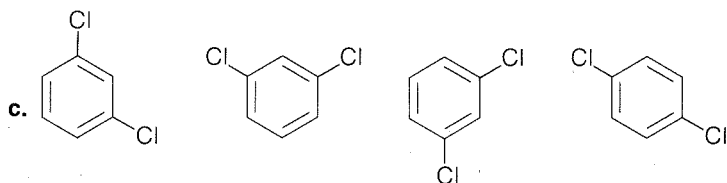
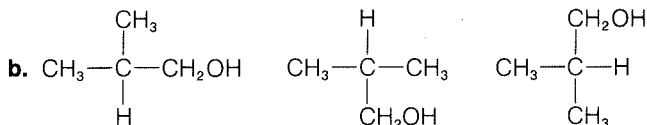
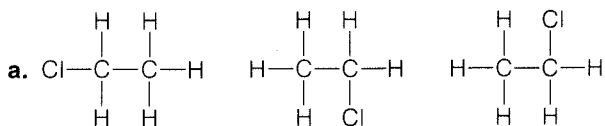
2-9 Write an expanded structural formula with a line for each bond (like the formulas on p. 32) for each of the following substances which are represented by a condensed formula:

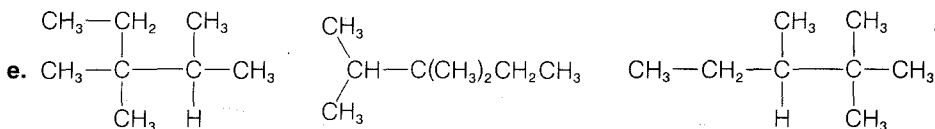
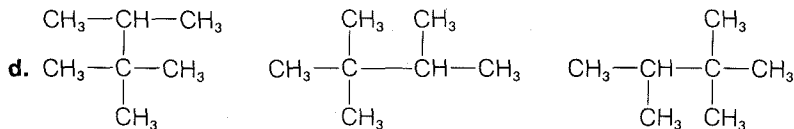
- | | |
|-------------------------------------------------|--------------------------------------------------------|
| a. $\text{CH}_3\text{CH}(\text{CH}_3)_2$ | f. $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ |
| b. CH_3CCCH_3 | g. CH_2CHCHO |
| c. $(\text{CH}_2)_4$ | h. $\text{C}_6\text{H}_5\text{NO}_2$ |
| d. CH_2CHCCH | i. $\text{C}_2\text{H}_5\text{CN}$ |
| e. $\text{CH}_3\text{CONHCH}_3$ | j. $(\text{CH}_3\text{O})_2\text{CO}$ |

2-10 Free rotation generally occurs around $\text{C}-\text{C}$ *single* bonds (see Section 1-1E). Thus the following structural formulas are of the same compound, 2,3-dimethylbutane, because rotation about the central $\text{C}-\text{C}$ bond makes the structures identical:



For the following structural formulas, determine which represent the same compound and which do not.





2-11 Write all the structural formulas you can for the different covalent isomers of the following molecular formulas. All the atoms should have their normal valences (i.e., monovalent for hydrogen and halogens, divalent for oxygen, trivalent for nitrogen, and tetravalent for carbon).

- a. C_3H_6 (two) d. $\text{C}_2\text{H}_4\text{ClF}$ (two)
 b. C_3H_4 (three) e. $\text{C}_3\text{H}_9\text{N}$ (four)
 c. $\text{C}_2\text{H}_4\text{O}$ (three) f. $\text{C}_4\text{H}_9\text{Cl}$ (four)

2-12 With reference to Table 2-2 if necessary, draw structural formulas that satisfy the following descriptions:

- a. three position isomers of $\text{C}_2\text{H}_4\text{O}_2$ with a carbonyl group ($\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$).
- b. four position isomers of $\text{C}_4\text{H}_{10}\text{O}$ with a hydroxyl group ($-\text{OH}$).
- c. a compound of formula C_5H_{12} that would have all its hydrogens located in chemically *identical* positions. (Chemically identical means that if one were to substitute a bromine for any one of the hydrogens, the same monobromo compound would be formed.)
- d. a compound of formula $\text{C}_3\text{H}_7\text{ON}$ with two chemically different methyl groups and an amide function.
- e. two compounds of formula $\text{C}_4\text{H}_8\text{O}$, one of which is an aldehyde, the other a ketone.
- f. two compounds of formula $\text{C}_3\text{H}_6\text{O}_2$, one of which is a carboxylic acid, the other a carboxylic ester.
- g. two compounds of formula $\text{C}_3\text{H}_4\text{O}$, both with $\text{C}=\text{O}$ groups.
- h. a compound of formula $\text{C}_9\text{H}_{12}\text{N}_2$ in which all the hydrogens are located in chemically identical positions and both nitrogens are present as nitrile functions.