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Organic Chemistry

Chapter 2

Introduction to Organic Nomenclature and Functional Groups

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Chapter Outline

Objectives

- ✔ Know how to draw the structure of an organic molecule
- ✔ Know how to draw the structure of an alkane from its name or to name an alkane from its structure
- ✔ Know how to draw and name cycloalkanes
- ✔ Recognize a functional group
- ✔ Know how to draw and name alkenes and alkynes
- ✔ Know how to draw and name alkyl substituted arenes
- ✔ Know how to name organohalogen compounds

The Naming of Cats is a difficult matter,
It isn't just one of your holiday games;
At first you may think I'm as mad as a hatter
When I tell you a cat must have THREE DIFFERENT NAMES.
—T. S. Eliot

As the nineteenth century progressed, chemists discovered and synthesized more and more different compounds. The names they gave the compounds reflected their source or some property of the compound. Because of the difficulty of remembering the name of all these compounds, chemists knew they needed a systematic method for naming the compounds they were working with. The International Union of Pure and Applied Chemistry (IUPAC) committee took over the task of developing systematic rules of nomenclature. The first report of the IUPAC committee was presented in 1889. Since then, the IUPAC committee has continued studying nomenclature and releasing new rules as required. By using these rules, chemists, or you, can look at the name of a compound and draw its structure or look at the structure of a compound and write its name. Learning how to name and draw the structure of the various compounds is the first step in learning to speak the language of organic chemistry.

Heteroatoms are atoms other than carbon or hydrogen.

A functional group is the atom, or atoms, that are the center of reactivity of a molecule.

Chapter 1 presented organic chemistry as the chemistry of the carbon atom. However, many organic compounds contain other atoms besides carbon that contribute significantly to the physical and chemical properties of the compound. Chemists call these atoms **heteroatoms**, and the groups they form, **functional groups**. This chapter provides an overview of the rules for naming organic

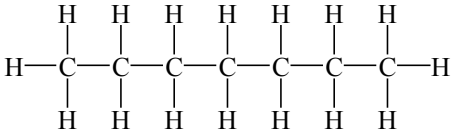
compounds. It also introduces the major functional groups that you will encounter as you study organic chemistry along with the rules of how to name them and draw their structures. The presence of heteroatoms radically changes the physical and chemical properties of the compounds to which they are bonded. In fact, the carbon—heteroatom bonds and the carbon—carbon multiple bonds are the main sites where chemical reactions take place.

Organic compounds are arranged into classes according to the particular functional groups that they contain. Members of each class of compounds share common chemical and physical characteristics. The names of organic compounds are assigned according to the class of the compound as determined by the functional groups. This chapter also shows how to draw the structural representations of these compounds.

2.1 Drawing Organic Structures

Molecules are actual, three-dimensional entities. Their structure is a major factor that determines their physical properties and the way one molecule interacts with another molecule. Because molecules are normally too small to see, chemists have devised ways to visually represent molecules. One way is by using a **two-dimensional structural formula** like that of the hydrocarbon heptane.

A two-dimensional structural formula of a hydrocarbon shows all of the atoms with all of their bonds in the plane of the page.



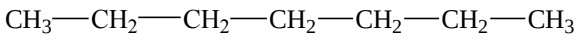
Heptane

Hydrocarbons are compounds composed only of carbon and hydrogen atoms.

Hydrocarbons provide the backbone of all organic compounds. Each carbon atom in a hydrocarbon forms a total of four bonds. These bonds are combinations of single bonds with hydrogen atoms and single or multiple bonds with other carbon atoms.

For molecules that contain a large number of atoms or complex structures, drawing every bond and every atom is time and space consuming. A common notation developed to abbreviate the drawing without sacrificing the clarity of the structure is the **condensed structural formula** shown below for heptane:

A condensed structural formula includes all of the atoms but uses line bonds to emphasize the main structural characteristics of the molecule.



Heptane

Taking out the lines representing the carbon—carbon bonds condenses this formula still more:

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

Heptane

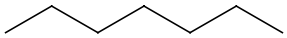
Heptane has five repeating —CH_2— groups, called methylene groups. Because many organic molecules have such repetitive groups, an even more condensed notation shows these repeating units. Using this notation, the formula for heptane is as follows:

$CH_3(CH_2)_5CH_3$

Heptane

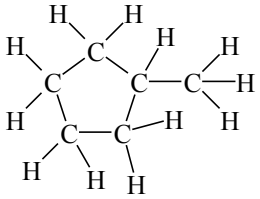
Bond-line formulas represent the carbon atoms as the intersection of lines and as line ends. You assume all the hydrogens needed to complete carbon's valences.

The **bond-line structural formula** is the notation that most organic chemists prefer to use. Bond-line formulas are easy to draw and quickly convey the essential structure of a molecule. Both the ends and the angles of the structure represent the carbon atoms. C—H bonds are not shown, but you should assume that the appropriate number of hydrogen atoms is present to complete the four bonds required by carbon to have its octet of electrons. The bond-line formula for heptane looks like this:



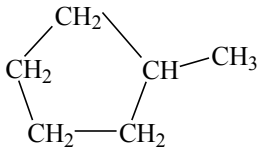
Heptane

Not all hydrocarbons are straight chains; many are rings. Chemists use the same structural formulas for them. Because the illustration of the two-dimensional structural formula of methylcyclopentane is so cluttered, it does not clearly show the ring.



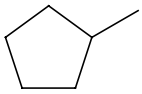
Methylcyclopentane

The condensed structural formula is clearer.



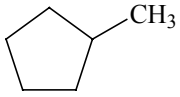
Methylcyclopentane

The bond-line structural formula is even clearer. Thus, chemists use it most frequently.



Methylcyclopentane

Often, chemists combine the bond-line and condensed notations to clarify a structure or emphasize specific features. This formula also represents methylcyclopentane.



Methylcyclopentane

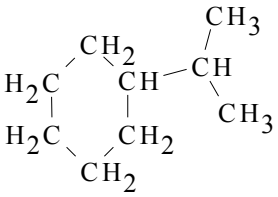
Exercise 2.1

Redraw each of the following condensed structural formulas using the bond-line notation.

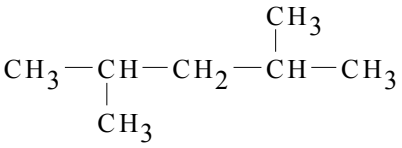
a) $CH_3CH_2CH_2CH_2CH_2CH_3$

b) $(CH_3)_2CH(CH_2)_4CH_3$

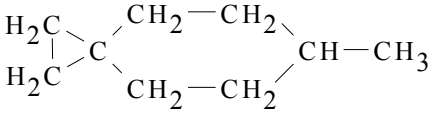
c)



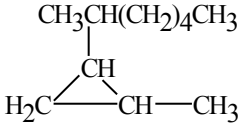
d)



e)

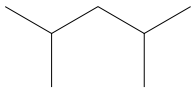


f)

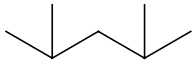


Sample solution

d)



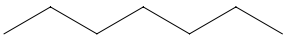
Chemists usually write the bond-line structural formula as shown above because this structure closely represents the actual structure of the molecule. In the molecule the carbons are sp^3 hybridized with 109.5° bond angles. The following notation is also a correct bond-line structural formula, but few chemists draw it this way because the bond angles are too small to represent the actual molecule.



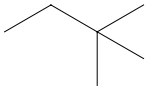
Exercise 2.2

Redraw each of the following bond-line structural formulas as condensed structures.

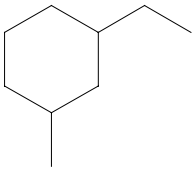
a)



b)



c)



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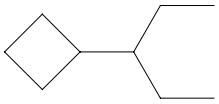

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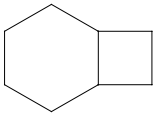

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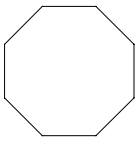


Sample solution

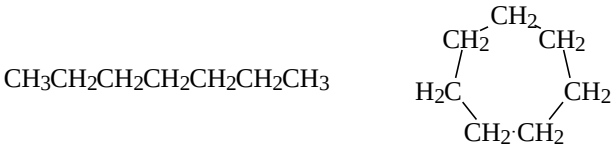
b) $CH_3CH_2C(CH_3)_3$

2.2 Alkanes

Each carbon atom in a saturated alkane forms bonds to four other atoms.

Of the various groups of organic compounds, alkanes have the simplest structure. Alkanes are hydrocarbons in which all the carbons form sp^3 hybridized bonds; thus, each carbon atom bonds with four other atoms in the tetrahedral shape. Because each carbon atom in an alkane bonds to four other atoms, chemists say they are **saturated hydrocarbons**. Beginning in Chapter 13, you will study **unsaturated hydrocarbons**. Saturated hydrocarbons fall into two general types: alkanes and cycloalkanes. Alkanes have the general molecular formula C_nH_{2n+2}, and cycloalkanes have the general molecular formula C_nH_{2n}. The molecular formula for the seven-carbon alkane, heptane, is C_7H_{16}. The molecular formula for the seven-carbon cycloalkane, cycloheptane, is C_7H_{14}.

An unsaturated molecule has multiple bonds between some pairs of atoms in the molecule.



Heptane Cycloheptane

Chemists call alkanes with all the carbon atoms connected in a single continuous sequence normal alkanes. Other names for normal alkanes are linear and straight chain alkanes. However, don't let these names mislead you because, as you will learn in Chapter 3, carbon chains are actually twisted and kinked.

A series of molecules that differ by one carbon atom, but that are otherwise identical, is called a homologous series.

A succession of hydrocarbons that differ from each other by one methylene group (—CH_2—) is a **homologous series**. For example, the first three alkanes, methane (CH_3—H), ethane (CH_3CH_2—H), and propane ($CH_3CH_2CH_2$—H), are all members of a homologous series. Chemists often call each compound in a homologous series a homolog.

2.3 Structural Isomerism

Alkanes that contain up to three carbons form only the straight chain arrangement because that is the only way they can bond together. Alkanes that consist of more than three carbons have more than one possible molecular structure. For example, the molecular formula C_4H_{10} has two possible structural formulas.

Isomers are compounds with the same molecular formula but different molecular structures.

Stereoisomers have different three-dimensional structures, and constitutional isomers have different bond sequences.

Compounds with the same molecular formula but different molecular structures are called **isomers**. There are two categories of isomers: **stereoisomers** and **constitutional isomers**. The atoms that make up stereoisomers bond in the same order but differ in the spatial arrangement of those atoms. The only way you can distinguish between some stereoisomers is by examining their structures in three dimensions. Portions of Chapters 3 and 14, as well as all of Chapter 11, discuss stereoisomers in greater detail.

Constitutional isomers also contain the same atoms, but the order in which the atoms bond together is different in each isomer. The two structural formulas of C_4H_{10} are constitutional isomers. These two structural formulas represent completely different organic compounds—not only are their atoms bonded differently, but they have different physical properties. For example, the boiling point of $CH_3CH_2CH_2CH_3$ is –0.6°C, whereas the boiling point of $CH(CH_3)_3$ is –10.2°C.

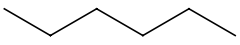
As the number of carbons in a compound increases, so does the number of possible isomers. For the molecular formula C_5H_{12} there are three possible isomers and for C_6H_{14} there are five. For $C_{10}H_{22}$, however, there are a total of 75 isomers, for $C_{20}H_{42}$ there are over 300,000, and for $C_{40}H_{82}$ there are 6.35×10^{13}.

Exercise 2.3

Draw structural formulas for all isomers of the alkane C_6H_{14} using both the condensed and bond-line notations.

Sample solution

When drawing a set of structures for a particular molecular formula, it is important to follow an organized method. First draw the longest chain possible for the structure:

$CH_3CH_2CH_2CH_2CH_2CH_3$ 

Hexane

Once you've done this, shorten the chain by one carbon and draw a methyl branch on C2.

2-Methylpentane

Continue with this process, constantly double-checking for duplicates until there are no more structures to draw.

2.4 IUPAC Nomenclature

The development of a systematic approach to the naming of chemical compounds did not begin until near the end of the nineteenth century. Before that time, the names given to compounds reflected such things as their source or some property of the compound. Formic acid was distilled from some species of ants; thus, its name comes from the Latin word for ants, *formicae*. Ethyl alcohol was called grain alcohol because it was obtained from the fermentation of grains. Pure acetic acid was called *glacial* acetic acid because the laboratories of chemists were cold (glacier-like?) in the winter and pure acetic acid freezes just below room temperature. Thus, if the acid was pure, it was solid—glacial—in the winter.

Chemists still use these older, or common, names. In fact, many of the frequently used chemicals are known best by their common names. To help you become familiar with these common names, this book sometimes uses them. However, it is more important that you learn the systematized (IUPAC) rules of nomenclature.

The fundamental rule of chemical nomenclature is that *each different compound must have its own unique name*. The IUPAC system provides a unique name for each of the nearly 10 million known organic compounds, as well as the thousands of new compounds discovered or synthesized each year. The IUPAC rules are simple to learn and easy to use. With these rules you can readily write the name of any compound you might encounter or derive the structure of any given compound from its name.

Chemists adopted the IUPAC system of nomenclature for several reasons. First, chemists everywhere understand it. Second, they can readily adapt it to the indexing methods used for the chemical literature. Third, they can easily use it for computerized literature searching operations.

2.5 Naming Alkanes

The IUPAC method for naming a straight chain or unbranched alkane is as follows:

Step 1 Start with the prefix that indicates the number of carbons in the compound. The following compound has 8 carbons. The prefix for 8 carbons is oct–.

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

Step 2 Add the *–ane* ending. The name of the compound is octane.

The prefixes for most alkanes larger than four carbons come from Greek and Latin origin. Learning these prefixes is like learning to count in another language: one, two, three, four, five, six becomes meth–, eth–, prop–, but–, pent–, hex–. Table 2.1 lists the names for unbranched, sometimes-called normal, alkanes.

Name	Number of Carbon Atoms	Structure
Methane	1	CH_4
Ethane	2	CH_3CH_3
Propane	3	$CH_3CH_2CH_3$
Butane	4	$CH_3CH_2CH_2CH_3$
Pentane	5	$CH_3CH_2CH_2CH_2CH_3$ [or $CH_3(CH_2)_3CH_3$]
Hexane	6	$CH_3(CH_2)_4CH_3$
Heptane	7	$CH_3(CH_2)_5CH_3$
Octane	8	$CH_3(CH_2)_6CH_3$
Nonane	9	$CH_3(CH_2)_7CH_3$
Decane	10	$CH_3(CH_2)_8CH_3$
Undecane	11	$CH_3(CH_2)_9CH_3$
Dodecane	12	$CH_3(CH_2)_{10}CH_3$
Tridecane	13	$CH_3(CH_2)_{11}CH_3$
Tetradecane	14	$CH_3(CH_2)_{12}CH_3$
Pentadecane	15	$CH_3(CH_2)_{13}CH_3$
Hexadecane	16	$CH_3(CH_2)_{14}CH_3$
Heptadecane	17	$CH_3(CH_2)_{15}CH_3$
Octadecane	18	$CH_3(CH_2)_{16}CH_3$
Nonadecane	19	$CH_3(CH_2)_{17}CH_3$
Eicosane	20	$CH_3(CH_2)_{18}CH_3$
Heneicosane	21	$CH_3(CH_2)_{19}CH_3$
Doeicosane	22	$CH_3(CH_2)_{20}CH_3$
Trieicosane	23	$CH_3(CH_2)_{21}CH_3$
Triacontane	30	$CH_3(CH_2)_{28}CH_3$
Hentriacontane	31	$CH_3(CH_2)_{29}CH_3$
Dotriacontane	32	$CH_3(CH_2)_{30}CH_3$
Tritriacontane	33	$CH_3(CH_2)_{31}CH_3$
Tetracontane	40	$CH_3(CH_2)_{38}CH_3$

Name	Number of Carbon Atoms	Structure
Pentacontane	50	$CH_3(CH_2)_{48}CH_3$
Hexacontane	60	$CH_3(CH_2)_{58}CH_3$
Hectane	100	$CH_3(CH_2)_{98}CH_3$

Table 2.1. The names and structures of some unbranched alkanes.

Exercise 2.4

Name the following alkanes.

a) $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ b) $CH_3(CH_2)_9CH_3$
c) $CH_3(CH_2)_6CH_3$ d) $CH_3(CH_2)_{41}CH_3$

Sample solution

b) $CH_3(CH_2)_9CH_3$ has nine CH_2 groups and two CH_3 groups for a total of eleven carbons. The alkane chain with eleven carbons is undecane.

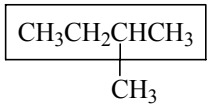
In a branched alkane the longest continuous chain of carbon atoms does not include all of the carbon atoms in the molecule.

Not all alkanes are unbranched; in fact, most are **branched**. Except for the shorter alkanes, which have only one or two different possible structures, branched alkanes have many different possible structures. Fortunately, the IUPAC system for naming branched alkanes makes it possible to distinguish between the many different structures. The following step-by-step description is used for naming branched alkanes:

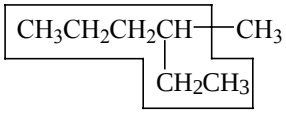
Step 1 Locate the longest continuous chain of carbon atoms.

a. This chain determines the compound's parent name. The parent name for the following compound is butane because the longest continuous chain contains four carbons. The box indicates the longest chain. The carbon—hydrogen group that is not a part of the parent chain is called a **substituent**.

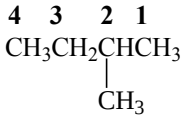
A substituent is some group, other than hydrogen, attached to the longest chain of carbon atoms in a molecule.



b. The longest continuous chain is not always immediately obvious from the way the formula is written. For example, the following structure represents hexane because the longest chain contains six carbons. So, count the carbons carefully.



Step 2 Number the carbons in the parent chain beginning with the end of the chain nearest the substituent.



An alkyl group is any single carbon or carbon chain, along with their hydrogens, attached to the parent chain.

Step 3 Use these numbers to designate the position of the substituent, called an **alkyl group**, in the name of the compound.

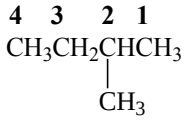
An alkyl group is an unbranched alkane with a hydrogen atom removed from the terminal, or end, carbon. To name the alkyl group, replace the *–ane* ending of the unbranched alkane with *–yl*. Thus, if you take one hydrogen from CH_4, it becomes —CH_3, and the name changes from methane to methyl. Table 2.2 illustrates this process with several additional examples.

Alkane	Name	Alkyl Group	Name
CH_3—H	Methane	CH_3—	Methyl
CH_3CH_2—H	Ethane	CH_3CH_2—	Ethyl
$CH_3CH_2CH_2$—H	Propane	$CH_3CH_2CH_2$—	Propyl
$CH_3CH_2CH_2CH_2$—H	Butane	$CH_3CH_2CH_2CH_2$—	Butyl
$CH_3CH_2CH_2CH_2CH_2$—H	Pentane	$CH_3CH_2CH_2CH_2CH_2$—	Pentyl

Table 2.2. Naming of alkyl groups.

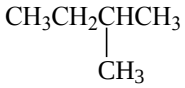
Step 4 Now you have all the parts of the compound's name. Put them together in the following way.

a. Write down the number of the carbon from which the alkyl group branches. In the example it is carbon 2.



b. Add a hyphen.
c. After the hyphen, place the name of the alkyl group. In this example, it is a methyl group.

d. Finally, add the name of the parent compound. In this example, the parent compound is butane. So the complete name is 2-methylbutane.

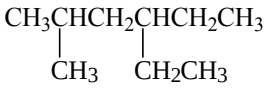


2-Methylbutane

When naming a compound with two or more alkyl groups, follow the above steps with these additions:

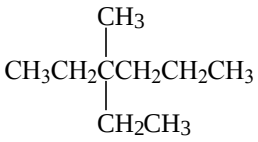
Step 5 To name a molecule with multiple substituents use the following rules:

a. When numbering the parent chain, give each substituent a number that corresponds to its location on the longest chain by listing the groups alphabetically[1]. If a compound contains both an ethyl and a methyl group, list the ethyl before the methyl. The general form of such a name is #-alkyl-#-alkylalkane. As a specific example, the name of the following compound is 4-ethyl-2-methylhexane:



4-Ethyl-2-methylhexane

b. If the two alkyl groups are on the same carbon, use the number of that carbon twice. For example, the following compound is called 3-ethyl-3-methylhexane:

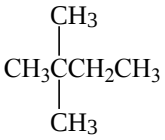


3-Ethyl-3-methylhexane

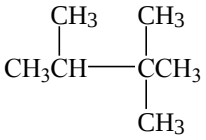
c. When multiple alkyl groups are identical, indicate this by the use of prefixes di–, tri–, tetra–, penta–, and so on with the alkyl group name. Also, every identical group must have a number with commas separating those numbers.

[1] Some handbooks also list groups by increasing size or complexity. For example, methyl would be listed before ethyl. However, alphabetical listing is the most commonly used system.

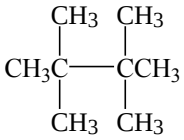
The general forms are #,#-dialkylalkane and #,#,#-trialkylalkane. When naming compounds with the prefixes of di–, tri–, and so on, do *not* alphabetize the prefixes. Thus, dimethyl follows triethyl. The following compounds are 2,2-dimethylbutane, 2,2,3-trimethylbutane, and 2,2,3,3-tetramethylbutane.



2,2-Dimethylbutane



2,2,3-Trimethylbutane



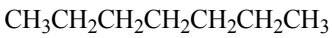
2,2,3,3-Tetramethylbutane

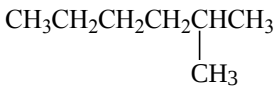
Exercise 2.5

Write the structural formulas and the IUPAC names for the nine isomers of C_7H_{16}. (*Hint*: It is helpful to name them as you go, to quickly eliminate duplication.)

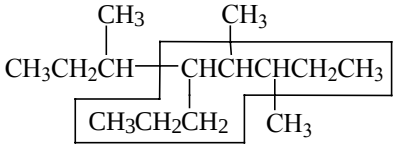
Sample solution

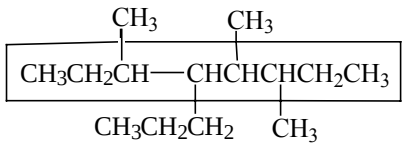
Starting with the simplest structures and working toward the more complex, the first two structures would be heptane and 2-methylhexane.





Step 6 If two or more chains compete for selection as the parent chain, choose the one with the smaller or simpler alkyl groups attached. This often means the greatest number of alkyl groups. For example, for the following structure, the lower chain has more and simpler attached groups than the upper chain even though the chains are both the same lengths:

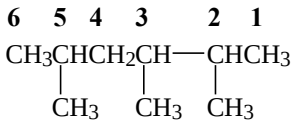




3,4,6-Trimethyl-5-propyloctane

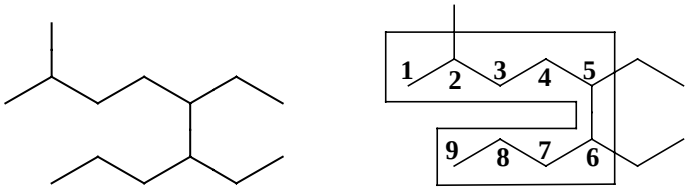
Thus, the correct name for the structure is 3,4,6-trimethyl-5-propyloctane.

Step 7 When branching occurs an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference. Looking again at the previous structure, its name cannot be 3,5,6-trimethyl-4-propyloctane as it would give a higher number at the first point of difference. In the following structure numbering from the right end gives lower numbers than when numbered from the left end. Thus, the structure's name is 2,3,5-trimethylhexane and not 2,4,5-trimethylhexane.

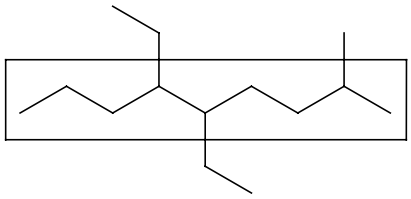


2,3,5-Trimethylhexane

The same principles apply to naming a compound when its bond-line formula is given. The colored screen on the right indicates the longest chain for the following compound.



The colored screen covers nine carbons. To simplify the way the drawing looks, redraw the longest chain straightened and number the carbon atoms as shown below.



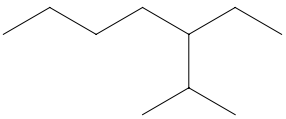
5,6-Diethyl-2-methylnonane

The name of this compound is 5,6-diethyl-2-methylnonane.

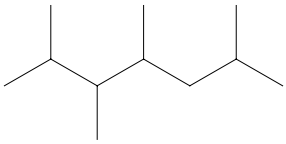
Exercise 2.6

Name each of the following alkanes using the IUPAC system.

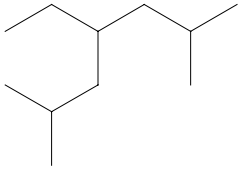
a)



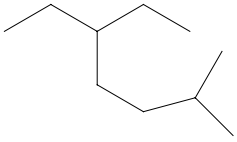
b)



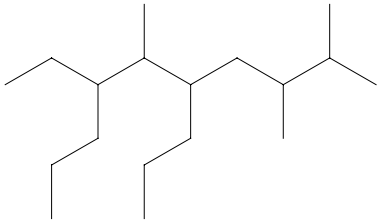
c)



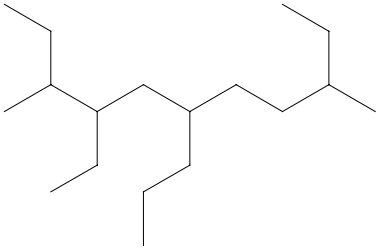
d)



e)

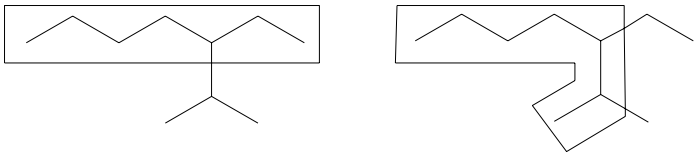


f)



Sample Solution

a) The longest chain has seven carbons, but there are two ways of counting them. The second way, shown on the right, is the preferred way because it has the smaller or simpler of attached groups. Thus, the compound is 3-ethyl-2-methylheptane.



A Summary of the Steps Used to Name an Alkane:

Step 1 Find the longest possible chain of carbon atoms. Name this chain based on the number of carbons in this chain. If there is more than one chain of the same length, choose the one with the simpler substituents.

Step 2 Number the carbons on the longest chain. Begin numbering from the end closest to a substituent on the chain.

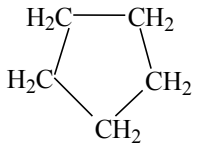
Step 3 Name any substituents using the alkane name for the number of carbons in the chain, changing the *–ane* suffix to *–yl*.

Step 4 List the names of the substituents alphabetically. Precede each substituent with a number and a dash. Immediately follow the last substituent by the name of the longest chain.

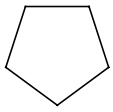
Step 5 If there are multiple instances of a substituent, list the substituent name with the prefix di–, tri–, etc., indicating the number of identical substituents. Number each substituent and separate the numbers with commas.

2.6 Naming Cycloalkanes

Cycloalkanes are hydrocarbons that have the general molecular formula C_nH_{2n} and in which some, or all, of the carbon atoms form a ring. The condensed structural and bond-line formulas for cyclopentane are as follows:



Condensed formula



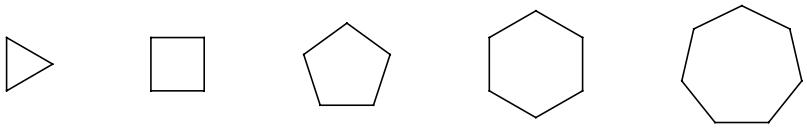
Bond-line formula

To name cycloalkanes, use the following steps.

Step 1 Determine the parent name of the compound by counting the number of carbons in the ring. Use the same parent name

for the ring that you would use for the normal alkane containing that number of carbons.

Step 2 Add the prefix *cyclo*– to the parent name.

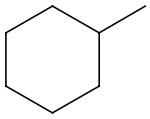


Cyclopropane Cyclobutane Cyclopentane Cyclohexane Cycloheptane

Step 3 Name any alkyl group substituents the same way that you name any other alkyl group.

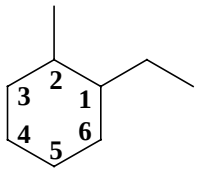
Step 4 Determine the position of the alkyl group or groups on the ring.

a. For a ring with only one alkyl group attached, you do not need a number to designate the group's position. The carbon bearing a single group is always carbon number 1. For example, the following compound is methylcyclohexane:



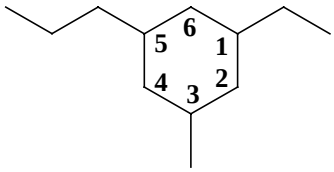
Methylcyclohexane

b. When a ring has more than one alkyl group attached, number the ring to give the lowest sum of numbers. If there are two groups, assign the number one to the first alkyl group alphabetically. Then count the shortest distance to the second substituent. With three or more substituents, determine a set of numbers to give the lowest sum of numbers. For example, the following compound is 1-ethyl-2-methylcyclohexane, not 1-ethyl-6-methylcyclohexane:



1-Ethyl-2-methylcyclohexane

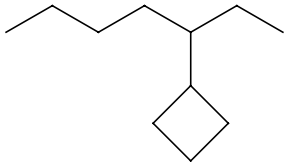
c. If the sum of numbers is identical either direction around the ring, then count towards the second group alphabetically on the ring. The following compound is 1-ethyl-3-methyl-5-propylcyclohexane:



1-Ethyl-3-methyl-5-propylcyclohexane

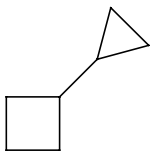
The more complex ring-containing alkanes need the following additional steps to name the compound.

Step 5 When the alkane chain is complex or has more carbons than the ring, name the ring as a substituent on the alkane chain. Follow the above steps for naming a normal alkane and for naming a cycloalkane. Call the ring a cycloalkyl group.



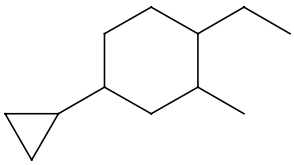
3-Cyclobutylheptane

Step 6 When one ring is attached to another ring, call the larger ring the parent compound. Use the above steps for naming the cycloalkane and cycloalkyl portions of the compound.



Cyclopropylcyclobutane

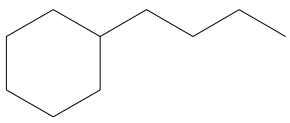
When naming molecules with a cycloalkyl substituent, consider the prefix *cyclo*– when alphabetizing.

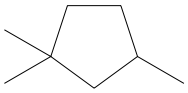


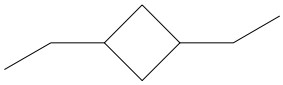
4-Cyclopropyl-1-ethyl-2-methylcyclohexane

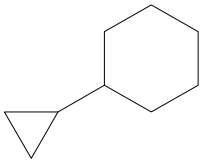
Exercise 2.7

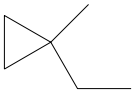
Name the following cycloalkanes using the IUPAC system.

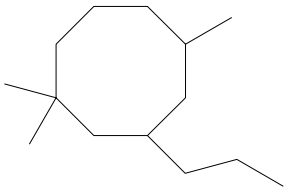
a) 

b) 

c) 

d) 

e) 

f) 

Sample solution

a) To name the compound go through the steps covered in this section using only the ones that apply to this particular compound.

Step 1 Count the number of carbons in the ring. There are six. The parent name is hexane.

Step 2 Add the prefix *cyclo–* to the parent chain. This gives cyclohexane.

Step 3 Determine the name of the alkyl group. It has four carbons, so it is a butyl group.

Step 4 a) Determine the position of the substituent alkyl group on the ring. As there is only one, no number is required in the name.

These steps cover all the features of this compound. Its IUPAC name is butylcyclohexane.

2.7 Naming Complex Alkyl Groups

Because of the complexity of some alkyl groups, they are inconvenient to name following the steps covered in Sections 2.4 and 2.5. To name some of the simpler of these complex side chains, use the prefixes *n–*, iso, *sec–*, and *tert–*. While these prefixes are not a part of the IUPAC system, chemists commonly use them.

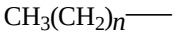
When using this system to name one of these complex alkyl groups, follow these steps.

Step 1 Use the IUPAC system to name the rest of the compound and to determine the position of the alkyl group.

Step 2 Count the number of carbons in the complex alkyl group to determine its name and use the appropriate prefix to show its arrangement.

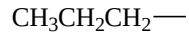
a. The prefix *n*–

An alkyl group with one or two carbons forms only one possible isomer, so call it a methyl or ethyl group. An alkyl group with three or more carbons can form two or more possible isomers; thus, you need a way to show that the group is the straight chain isomer. The following structure illustrates the generalized structure of a straight chain alkyl group isomer. The values of *n* are 2 or more.



The prefix n– *is derived from the word* normal*, meaning an unbranched chain.*

Use the prefix ***n***– to name a straight chain isomer that contains three or more carbons. When naming molecules with the prefix *n*–, ignore the prefix when alphabetizing the name of the group. Two specific examples are the *n*-propyl and *n*-butyl groups.



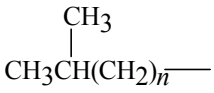
n-Propyl group

n-Butyl group

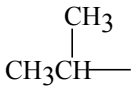
b. The iso prefix

The iso prefix is not italicized because it is not separated from the name by a dash. The other prefixes are separated from the name by a dash and are italicized.

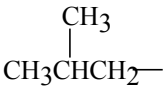
The prefix iso indicates a structure in which two methyl groups are bonded to the end of an alkyl side chain farthest from the point where the side chain bonds to the parent chain. The following structure illustrates a generalized structure for an isoalkyl group. The value of *n* is 0, 1, 2, or occasionally 3.



Two specific examples of the iso structure are the isopropyl and the isobutyl groups. When naming molecules with an iso alkyl group, consider the prefix when alphabetizing the name of the group.



Isopropyl group

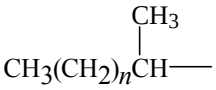


Isobutyl group

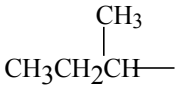
A secondary carbon bears two carbon—carbon bonds and is the carbon at the point where the group attaches to the main chain.

c. The prefix *sec*–

The prefix *sec*– indicates a structure in which the carbon that bonds the alkyl side chain to the parent chain bears a methyl group branch, making that carbon a **secondary** carbon. Following is the generalized structure of a *sec*-alkyl group. The value of *n* is 1, 2, or occasionally 3.



A specific example is the *sec*-butyl group.



sec-Butyl group

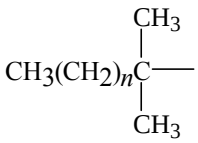
To name a molecule with a *sec*-alkyl group, ignore the prefix when alphabetizing the name of the group.

An exception to the use of the prefix *sec*– is when n=0. According to this system the name of the group should be *sec*-propyl. However, *sec*-propyl is not the accepted name for this group. Call the group isopropyl instead.

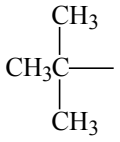
A tertiary carbon is the carbon at the point where the group attached to the main chain bears three carbon—carbon bonds.

d. The prefix *tert*–

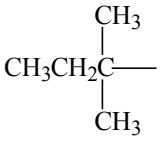
The prefix *tert*– describes a structure in which the carbon that bonds the alkyl side chain to the parent chain bears two methyl group branches, making it a **tertiary** carbon. Below is the generalized structure for a *tert*-alkyl group. The value of *n* is 0, 1, or 2.



Specific examples are the *tert*-butyl and *tert*-pentyl groups. As with the *n*– and *sec*– prefixes, ignore the *tert*– prefix when alphabetizing the name of the group.



tert-Butyl group



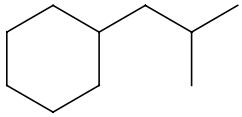
tert-Pentyl group
(Sometimes called a
tert-Amyl group)

Step 3 Write the name of the compound following this format:

#-prefix-alkylalkane

The following two step-by-step examples illustrate how to use this nomenclature system.

Step 1 Determine the parent chain. In this case the parent chain is a cyclohexane.

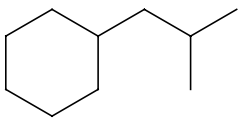


Step 2 Determine the position of the side chain. Because there is only one substituent on the ring its position number is 1. When writing the name of the compound, the position number is understood.

Step 3 Determine the side chain type. It is an iso group, because it has two methyl groups at the end of the side chain opposite the end bonded to the parent chain.

Step 4 Determine the name of the alkyl group by counting the number of carbons in the group. There are four, so it is a butyl group.

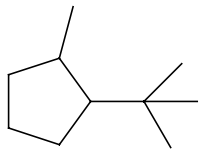
Step 5 Put all the parts of the name together in the following order: alkyl group prefix, alkyl group name, name of parent group. The name of this compound is isobutylcyclohexane.



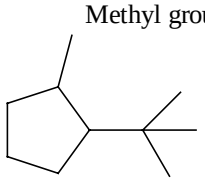
Isobutylcyclohexane

Example two is more complicated, but you follow the same steps.

Step 1 Determine the name of the parent chain. It is a ring structure that contains five carbons; thus, its name is cyclopentane.

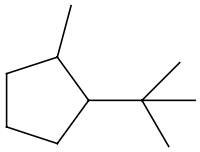


Step 2 Determine the names of the side chains. Because this compound contains two side chains, you must first know their names to alphabetize them so you can determine their positions. One is a methyl group; the other is a complex alkyl group. The complex alkyl group has four carbons and two methyl side groups attached to the carbon that is bonded to the ring, thus, it is a *tert*-butyl group.



Step 3 Determine the position of the two alkyl groups on the parent chain. Alphabetize the groups ignoring the prefix: *tert*–. The *tert*-butyl group comes first, and the methyl group comes next. Thus, the *tert*-butyl group's position is number 1, and the methyl group's position is number 2.

Step 4 Put all the names of parts together to get the name 1-*tert*-butyl-2-methylcyclopentane.

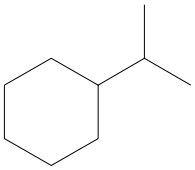


1-*tert*-Butyl-2-methylcyclopentane

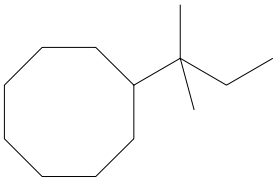
Exercise 2.8

Name the following compounds using the prefixes *n*–, iso, *sec*–, and *tert*–.

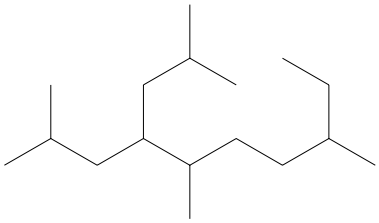
a)



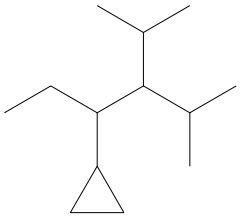
b)



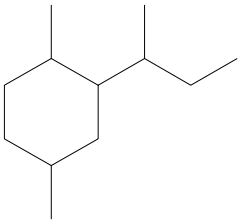
c)



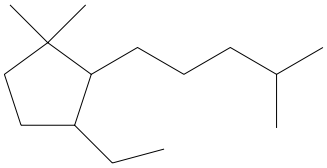
d)



e)



f)



Sample solution

b) To name this compound, follow these steps.

Step 1 Determine the name of the parent chain. In this case the parent chain is an eight-carbon ring, so the parent name is cyclooctane.

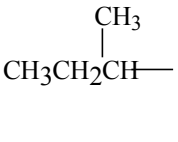
Step 2 Determine the name of the alkyl group side group. It has two methyl groups on the carbon bonding the group to the parent chain, thus, it is a *tert*– group. It has a total of five carbons, making the group a *tert*-pentyl group.

Step 3 When you put the names of all the parts of the compound together, you get the name *tert*-pentylcyclooctane.

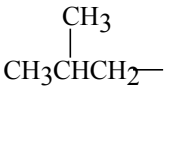
Even though chemists use the *n*–, iso, *sec*–, and *tert*– prefixes, remember that they are not really a part of the IUPAC system. For these, and for even more complicated branched side chains, the

IUPAC nomenclature is the proper terminology. To name branched side chains using IUPAC system follow these steps.

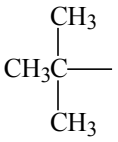
Step 1 Find the longest chain of carbons starting with the carbon that bonds the alkyl chain to the parent chain.
Step 2 Number the carbons of the longest chain, beginning with C1 for the carbon at the point of attachment to the parent chain.
Step 3 Name and number any branches attached to the numbered side chain.
Step 4 When including the name of the branched side chain in the complete name of the compound, enclose the side chain name in parentheses. For example, the IUPAC name for the *sec*-butyl group is 1-methylpropyl and, when writing it as part of the name of the compound, enclose it in parentheses.



(1-Methylpropyl) group
(*sec*-Butyl group)

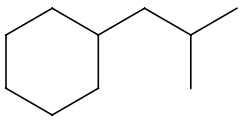


(2-Methylpropyl) group
(Isobutyl group)

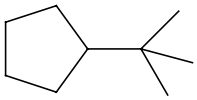


(1,1-Dimethylethyl) group
(*tert*-Butyl group)

Two examples using this nomenclature are as follows.



(2-Methylpropyl)cyclohexane



(1,1-Dimethylethyl)cyclopentane

Exercise 2.9

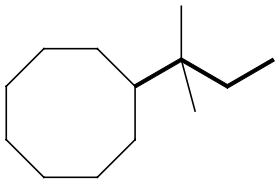
Name the structures in Exercise 2.8 using the IUPAC system.

Sample solution

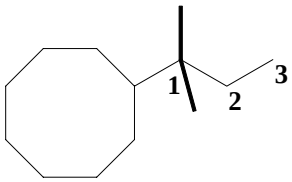
b) Name this compound the same way that you did when working Exercise 2.8, except substitute the following step for Step 2.

Step 2 Determine the name of the alkyl side chain.

a) Find the longest chain that begins with the carbon bonded to the ring. That chain includes three carbons, so it is a propyl group.



b) Number the chain. C1 is the carbon that bonds the alkyl group to the parent chain.
c) Name and number any groups attached to the longest chain. There are two methyl groups, and they are both bonded to C1.



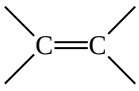
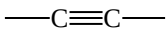
When you put the name together, you get (1,1-dimethylpropyl)cyclooctane.

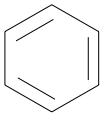
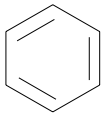
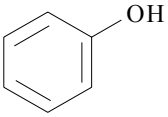
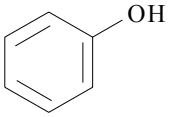
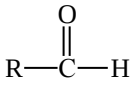
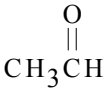
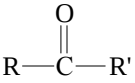
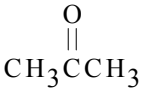
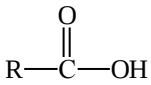
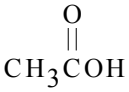
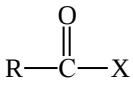
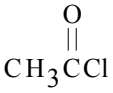
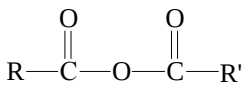
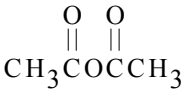
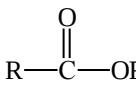
2.8 Functional Groups

The site of a functional group is the center of reactivity in a molecule. A functional group generally contains double or triple bonds and/or heteroatoms.

Alkanes are the simplest type of organic molecules, and they provide the backbone for many of the more complicated organic molecules, however, they are generally very unreactive. Possessing a **functional group** usually makes a molecule more reactive. Functional groups determine the types of chemical reactions that molecules will undergo and, to a large extent, the physical properties of the molecules to which they are attached.

Functional groups consist of carbon—carbon multiple bonds and/or carbon—heteroatom single and multiple bonds. Heteroatoms most commonly found in organic compounds are nitrogen, oxygen, sulfur, phosphorus, and the halogens. Table 2.3 lists the main functional groups with examples and their names. Subsequent sections in this and later chapters examine the nomenclature of the functional groups in detail.

Functional Group	Structure	Example	Name of Example
Double bond		$CH_2=CH_2$	Ethene or ethylene
Triple bond		$CH\equiv CH$	Ethyne or acetylene

Functional Group	Structure	Example	Name of Example
Arene			Benzene
Organohalogen or alkyl halide	R—X (X = F, Cl, Br, or I)	CH_3CH_2Br	Bromoethane or ethyl bromide
Alcohol	R—OH	CH_3CH_2OH	Ethanol or ethyl alcohol
Thiol	R—SH	CH_3CH_2SH	Ethanethiol
Phenol			Phenol
Ether	R—O—R'	$CH_3CH_2OCH_2CH_3$	Ethoxyethane or diethyl ether
Epoxide			Epoxyethane or ethylene oxide or oxirane
Sulfide (or Thio ether)	R—S—R'	$CH_3CH_2SCH_2CH_3$	Diethyl sulfide
Amine	RNR'R" (R' and R" = H, alkyl, or aryl)	$CH_3CH_2NHCH_3$	N-Methylethanamine or ethyl methyl amine
Aldehyde			Ethanal or acetaldehyde
Ketone			Propanone or acetone
Carboxylic acid			Ethanoic acid or acetic acid
Acyl halide	 (X = Cl or Br)		Ethanoyl chloride or acetyl chloride
Anhydride			Ethanoic anhydride or acetic anhydride
Ester			Ethyl ethanoate or ethyl acetate

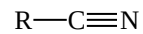
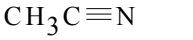
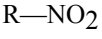
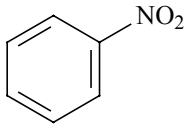
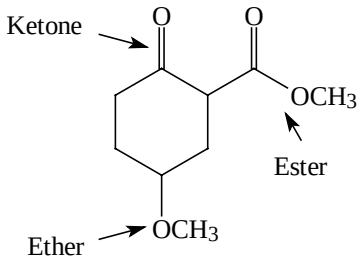
Functional Group	Structure	Example	Name of Example
Amide	 (R' and R" = H, alkyl, or aryl)		N-Ethyl ethanamide or N-ethylacetamide
Nitrile			Ethanenitrile or acetonitrile
Nitro			Nitrobenzene

Table 2.3. The main functional groups in organic chemistry. The R stands for an alkyl group. An R' or R" stands for some alkyl group different than R.

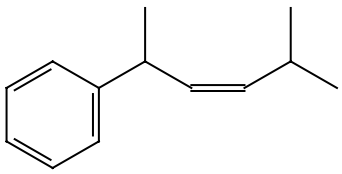
Consider the following example. It contains ether, ketone, and ester functional groups. Note that an ester contains portions that look like both the ether and the ketone. A common error that students make when learning functional group names is to call an ester a ketone-ether group.



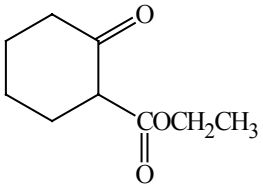
Exercise 2.10

Identify the functional groups present in each of the following molecules.

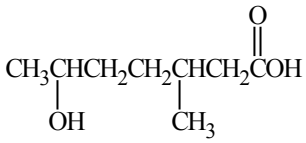
a)



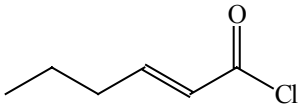
b)



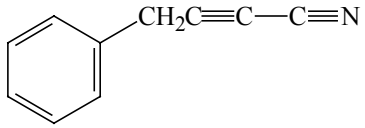
c)



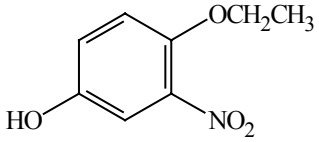
d)



e)

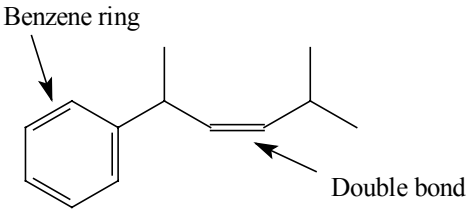


f)



Sample solution

a)



2.9 Naming Alkenes and Alkynes

Alkenes and cycloalkenes are hydrocarbons that have one or more carbon—carbon double bonds. The generalized molecular formula for alkenes is C_nH_{2n}. This formula is the same as the molecular formula for a cycloalkane; therefore, alkenes and cycloalkanes are constitutional, or structural, isomers.

Alkenes are occasionally referred to as olefins. Olefin is an old term meaning "oil forming" and comes from the fact that ethene, a gas, reacts with chlorine, a gas, to form an "oily" liquid product.

The way you name alkenes is quite similar to the way you name alkanes.

Step 1 Find the longest continuous chain of carbon atoms containing the double bond. This is the parent chain.

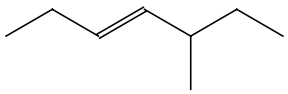
Step 2 Name this chain by replacing the —*ane* ending of the name of the alkane chain of the same length with —*ene*.

Step 3 Indicate the position of the double bond by numbering the parent chain from the end that gives the first carbon of the double bond the lowest number. Here are two examples that show how to number.

$CH_3CH_2CH{=}CH_2$
1-Butene
(not 3--butene)

$CH_3CH_2CH{=}CHCH_3$
2-Pentene
(not 3-pentene)

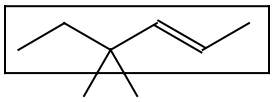
Because the double bond takes priority over other substituents in an alkene, sometimes the atoms of side chains and other functional groups must receive higher numbers than they otherwise would. For example, 5-methyl-3-heptene is the correct name for the following compound, not 3-methyl-4-heptene, even though the latter has a lower number for the methyl group.



5-Methyl-3-heptene

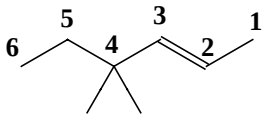
The following example shows step-by-step how to name an alkene.

Step 1 Find the longest chain of carbons containing the double bond. It contains six carbons.



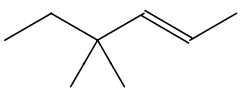
Step 2 Name the parent chain. Its name is hexene.

Step 3 Determine the position of the double bond in the parent chain. In this case, you number the parent chain from right to left because that gives the first carbon of the double bond the lowest number. The parent name is 2-hexene.



Step 4 Number and name the substituents. The compound has two methyl groups bonded to C4.

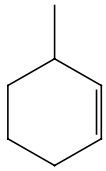
Step 5 Put together all the pieces of the name. The compound's complete name is 4,4-dimethyl-2-hexene.



4,4-Dimethyl-2-hexene

Naming cycloalkenes is similar to naming alkenes, except that you number the ring so that the double bond is *between* C1 and C2.

For example, the following compound is 3-methylcyclohexene, *not* 2-methylcyclohexene.



3-Methylcyclohexene

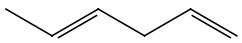
Polyene is the generalized name for a molecule that has more than one double bond. A diene is a molecule with two double bonds. A triene is a molecule with three.

A type of organic compounds, called **polyenes**, contains two or more double bonds. For example, **dienes** have two double bonds, and **trienes** have three. To name a diene or a triene, follow the same steps for naming an alkene with these exceptions.

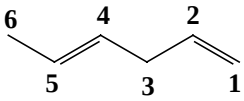
Step 1 Write the numbers indicating the locations of the double bonds separated by commas and followed by a hyphen.

Step 2 After the hyphen, write the parent name of the compound, changing the ending from —*ene* to —*diene*, if there are two double bonds, or —*triene*, if there are three, etc.

The following example demonstrates how to name a polyene.

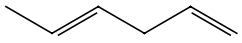


Step 1 Determine the length of the parent chain and the positions of the double bonds. The parent chain is six carbons long. There are two double bonds, and their positions are C1 and C4.



Step 2 Write the numbers of the locations of the double bonds followed by a hyphen: 1,4–.

Step 3 After the hyphen write the name of the parent chain with the –*diene* ending. The name of the compound is 1,4-hexadiene.



1,4-Hexadiene

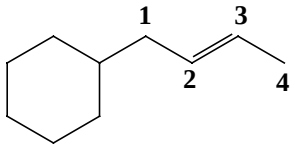
Special Types of Dienes

Two special types of dienes are the conjugated diene and the cumulated diene. In a conjugated diene, the double bonds are separated by only one single bond. In a cumulated diene, the double bonds share a carbon. Conjugated dienes are important because their chemical properties differ greatly from simple alkenes. Chapter 16 introduces conjugated dienes and their properties. Chapters 17 and 18 continue this study with benzene. The simplest conjugated diene is 1,3-butadiene, CH_2=CH—CH=CH_2. The simplest cumulated diene is 1,2-propadiene, CH_2=C=CH_2. 1,2-Propadiene is sometimes called allene.

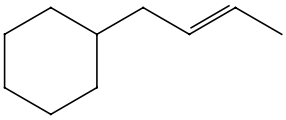
An alkenyl group is a side chain containing a double bond.

The generalized name for a side chain containing a double bond is **alkenyl**. Alkenyl side chain names are used when another name, especially a ring, would name a larger number of carbons in the molecule. To name an alkenyl side chain, use the same procedure that you use for naming an alkene with the following exceptions.

Step 1 Start numbering from the carbon that bonds the side chain to the parent chain.

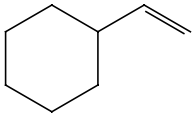


Step 2 When naming the side chain, use the —*enyl* suffix instead of —*ene*. Parentheses are often required so that you know the number belongs with the side chain.

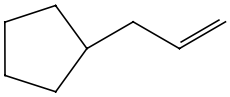


(2-Butenyl)cyclohexane

Many alkenyl side chains are better known by their common names than by their IUPAC names. Two of these are the ethenyl (CH_2=CH—) and 2-propenyl (CH_2=$CHCH_2$—) groups. Their common names are vinyl and allyl.



Vinylcyclohexane

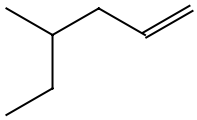


Allylcyclopentane

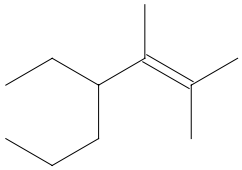
Exercise 2.11

Name each of the following molecules.

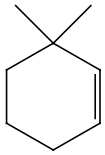
a)



b)

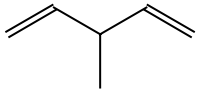


c)

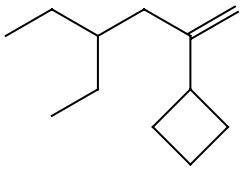


d) $CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3$

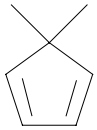
e)



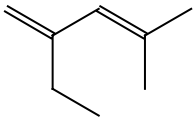
f)



g)



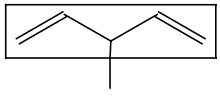
h)



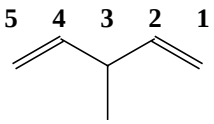
Sample solution

e) The following step-by-step process yields the correct answer.

Step 1 Determine which carbons make up the parent chain. There are five carbons with two double bonds, so the parent chain is a pentadiene.

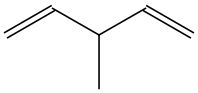


Step 2 Determine the positions of the double bonds. They are on C1 and C4.



Step 3 Determine the name and position of the side chain. It is a methyl group on C3.

Step 4 Put together all the parts. The name of the compound is 3-methyl-1,4-pentadiene.



3-Methyl-1,4-pentadiene

Alkynes are hydrocarbons that contain one or more carbon—carbon triple bonds.

Chemists often refer to **alkynes** as acetylenes from the common name of the simplest compound of this type, ethyne (HC≡CH), which is usually called acetylene. Follow these steps to determine the IUPAC name of an alkyne.

Step 1 Find the parent chain. As with alkenes, it must contain the triple bond. The parent chain contains five carbons.

$$CH_3CH_2C{\equiv}CCH_3$$

Step 2 Name the parent chain by substituting the —*yne* ending for the —*ane* ending of the parent carbon chain. The name of the parent chain is pentyne.

Step 3 Indicate the position of the triple bond by numbering the parent chain from the end that gives the first carbon of the triple bond the lowest number. The position of the triple bond is C2.

Step 4 Place the number of the position of the triple bond first, followed by a hyphen followed by the name of the parent chain. The name of the compound is 2-pentyne.

$$CH_3CH_2C{\equiv}CCH_3$$

2-Pentyne

Sometimes the parent chain of a molecule contains both a double bond and a triple bond. To name such a compound use the same procedure as you do for determining the parent chain. Then determine the position and name of each multiple bond with the following steps.

Step 1 Find the longest continuous chain containing both the double and triple bonds.

Step 2 Number the chain so that the multiple bonds get the lowest possible numbers.

Step 3 Number the position of the double bond on the parent chain. In the following example that is C1.

$$CH_2{=}CHCH_2C{\equiv}CCH_3$$

Step 4 Use the *—en* ending to indicate the name of the parent chain. The parent chain contains six carbons, so that gives the name hexen—.

Step 5 For the triple bond, use the *—yne* ending along with the number identifying the triple bond's position on the parent chain. Number the parent chain so that either the double or triple bond takes precedence over any other substituent, irrespective of whether the *—en* or *—yne* gets the lowest number. The name of the example compound is 1-hexen-4-yne.

$$CH_2{=}CHCH_2C{\equiv}CCH_3$$

1-Hexen-4-yne

However, when both groups could get the same number, the *–en* takes priority and receives the lower number.

$$CH_3CH{=}CHCH_2C{\equiv}CCH_3$$

2-Hepten-5-yne

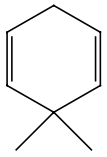
(*not* 5-Hepten-2-yne)

Exercise 2.12

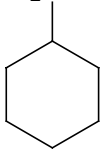
Provide either the IUPAC name or a structural formula for the following compounds.

a) 5-methylcyclo-octyne

b) 3-ethyl-2,4,4-trimethyl-2-octen-5-yne

c) 

d) $H_2C{=}CHCH_2CHC{\equiv}CCH_3$



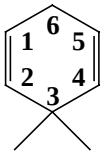
e) $CH_3C{\equiv}C{-}C{\equiv}C{-}C{\equiv}CCH_2CH_3$

Sample solution

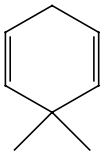
c) The following step-by-step process yields the name for this compound.

Step 1 Determine and name the parent chain. The parent chain is a ring with six carbons. It also contains two double bonds. Thus, the name of the parent chain is cyclohexadiene.

Step 2 Determine the positions of the double bonds. Remember that you want to number in such a way as to give the methyl groups their lowest possible number, too.



Step 3 Put the various parts together with commas separating the numbers and hyphens separating the numbers and words. The name of this compound is 3,3-dimethyl-1,4-cyclohexadiene.

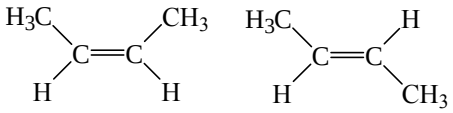


3,3-Dimethyl-1,4-cyclohexadiene

2.10 Naming Alkenes, Part II

Cis *comes from a Latin word meaning "on the same side" and* trans *from the Latin word meaning "across".*

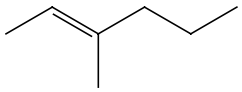
Because alkenes do not rotate about the double bond they can exhibit ***cis-trans*** isomerism. For example, 2-butene has two possible stereoisomers. In one, both methyl groups are on the same side of the double bond; in the other, the methyl groups are on opposite sides of the double bond.



cis *trans*

The names for the two isomers of 2-butene are *trans*-2-butene and *cis*-2-butene.

For more complex structures, the *cis* or *trans* designation refers to the parts of the main carbon chain in which the double bond is found. For example, the following compound is *trans*-3-methyl-2-hexene because the substituents on the main chain have a *trans* relationship to each other.

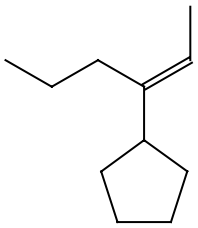


trans-3-Methyl-2-hexene

Exercise 2.13

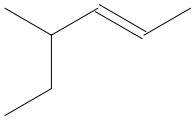
Name each of the following molecules using IUPAC rules.

a)

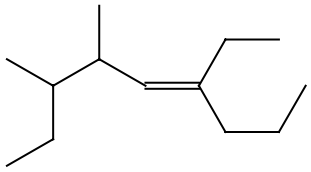


b)

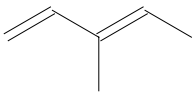
c)



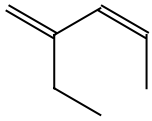
d)



e)



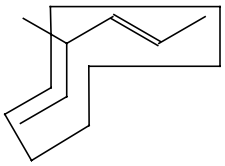
f)



Sample solution

c) To name this compound, follow these steps.

Step 1 Determine the parent chain. The longest chain that contains the double bond has six carbon atoms with the position of the double bond at C2. Thus, the parent chain is 2-hexene.



Step 2 The substituent is a methyl group on C4.

Step 3 The two substituents attached to the double bond are on opposite sides of the double bond and thus are *trans* to each other.

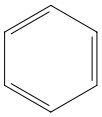
The name of this compound is *trans*-4-methyl-2-hexene.

2.11 Arenes

Arenes are cyclic hydrocarbons with alternating single and double bonds.

Aromatic hydrocarbons are arenes based on benzene.

Arenes are cyclic hydrocarbons that contain three single bonds and three double bonds conjugated in a six-carbon ring. Arenes are usually derived from benzene. Another commonly used name for arenes is **aromatic hydrocarbons**.



Benzene

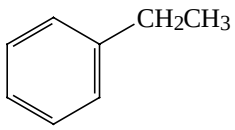
During the late 19th century, chemists isolated a number of other compounds similar to benzene. Among the similarities of these compounds was a distinctive pleasant odor. Because of this odor, chemists called this class of polyenes aromatic hydrocarbons. In time, aromatic hydrocarbons, or arenes, came to include all compounds that have the six-carbon ring structure drawn with alternating single and double bonds—whether or not they have the distinctive pleasant odor. Although arenes have double bonds, they are distinctly different from the common alkenes. Chemists call the chemical properties that are associated with the type of conjugation of double bonds found in arenes **aromaticity**.

Aromaticity refers to the special stability of benzene and benzene-like compounds. Chapter 17 explains this special stability.

The following steps are used for naming aromatic hydrocarbons.

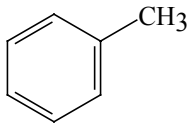
A derivative of benzene is a benzene ring with one or more other groups bonded to it.

Step 1 Name aromatic hydrocarbons as **derivatives** of benzene. For example, ethylbenzene is a benzene ring with an ethyl group attached.



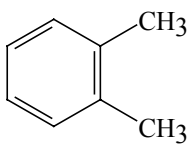
Ethylbenzene

Step 2 Not all benzene derivatives have the word benzene in their names. A number of these derivatives have their own unique names. For example, methylbenzene is more frequently known as toluene. Most of these unique names will be covered in more detail in Chapter 17.

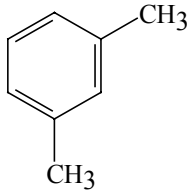


Toluene
(or Methylbenzene)

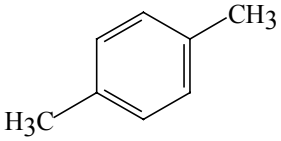
Step 3 When a benzene ring bears two side chains or groups, indicate their positions by numbering them or, as is more common, by using the prefixes *ortho–*, *meta–*, and *para–*, abbreviated as *o–*, *m–*, and *p–*. *Ortho–* indicates a 1,2-disubstituted benzene ring, *meta–* indicates 1,3, and *para–* names a 1,4 arrangement. Ignore the positions of the double bonds in the benzene ring when numbering the chains or groups. Number the ring so as to have the lowest sum of numbers, giving the first substituent the number 1.



1,2-Dimethylbenzene
or *o*-Dimethylbenzene
or *o*-Xylene



1,3-Dimethylbenzene
or *m*-Dimethylbenzene
or *m*-Xylene



1,4-Dimethylbenzene
or *p*-Dimethylbenzene
or *p*-Xylene

A benzene ring can be a functional group of a larger molecule. Its molecular formula is (C_6H_5—).

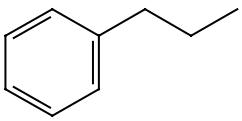
A phenyl group is a benzene ring substituent attached to the parent molecule.

Step 4 To name a benzene group as a side chain, call it a **phenyl group**. (Do not call a benzene ring functional group a benzyl group as would seem likely from the naming of the previous substituent groups. There is a benzyl substituent group, but its formula is $C_6H_5CH_2$—.)

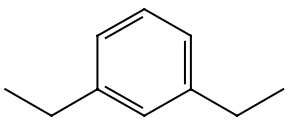
Exercise 2.14

Name each of the following aromatic hydrocarbons.

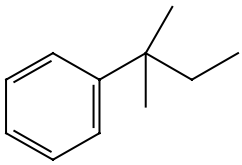
a)



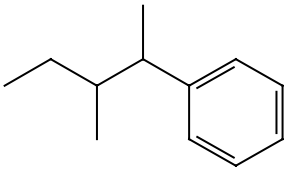
b)



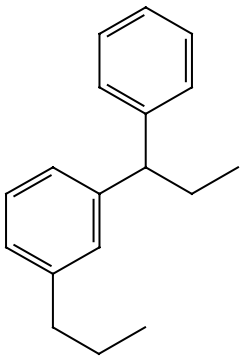
c)



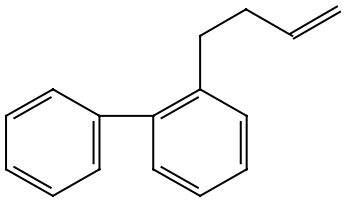
d)



e)



f)



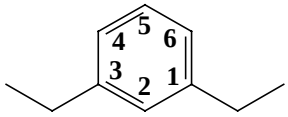
Sample solution

b) The following step-by-step process names this compound.

Step 1 Name the compound as a derivative of benzene. Thus, the parent name of the compound is benzene.

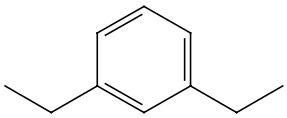
Step 2 Number the positions of the side chains to get the smallest total. Both are ethyl groups, so both are alphabetically the same, and either could receive the number one. Start with the

ethyl on the right and number to the left to give the smaller total.



Step 3 Because the compound is a 1, 3 substituted benzene, you can call it by the *meta* prefix.

Step 4 Put the name together. The name is 1,3-diethylbenzene or *m*-diethylbenzene.



1,3-Diethylbenzene
or *m*-Diethylbenzene

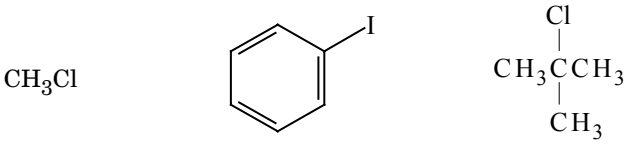
2.12 Organohalogens

Except for Section 2.8, which presented a table listing the various functional groups important in organic chemistry, the preceding sections covered the naming of hydrocarbons, or organic compounds that contain only carbon and hydrogen. Section 2.12 introduces the nomenclature of those compounds that contain heteroatoms. Remember a heteroatom is any atom other than carbon or hydrogen in an organic molecule. Compounds with one or more halogen atoms are organohalogens. The halogens include fluorine (F), chlorine (Cl), bromine (Br), and iodine (I), with chlorine and bromine being the most common.

To name organohalogens, follow these steps.

Step 1 Consider organohalogens as substituted hydrocarbons. They have the same priority as alkyl groups in naming. Use the prefixes *bromo–*, *chloro–, fluoro–*, and *iodo–*.

Step 2 List any halogens alphabetically, along with any alkyl groups:



Chloromethane	Iodobenzene	2-Chloro-2-methylpropane

The rules are found in Section 2.5, page 000.

Common Names for Some Organohalogen Compounds

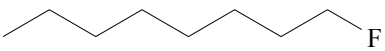
Most organohalogen compounds are named according to the standard IUPAC rules of nomenclature. The general form of the common name for many of these compounds is alkyl halide. Some examples are methyl chloride, isopropyl iodide, *sec*-butyl chloride, and *tert*-butyl bromide. There are a few compounds that do not follow this form. In most chemistry laboratories, the following names are used more often than the IUPAC names.

CH_2Cl_2	$CHCl_3$	CCl_4
Methylene chloride	Chloroform	Carbon tetrachloride

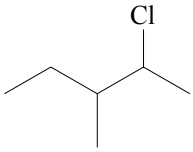
Exercise 2.15

Write a name for each of the following organohalogens.

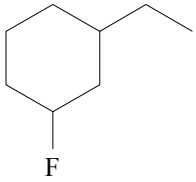
a)



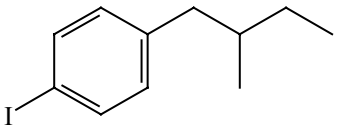
b)



c)

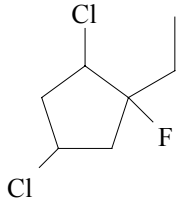


d)



e) $Br(CH_2)_3CH{=}CHCH_2CH_2CH_3$

f)

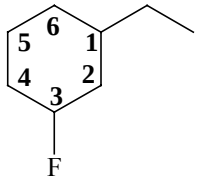


Sample solution

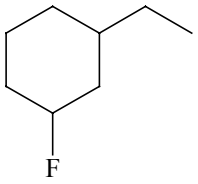
c) The following step-by-step analysis names this compound:

Step 1 Find the parent chain. The parent chain is a six-membered hydrocarbon. Its name is cyclohexane.

Step 2 Number the side chains. There are two, an ethyl group and a fluorine. Alphabetically ethyl comes first, so it gets the number one. Give the fluorine the number 3, not the number 5.



Step 3 Put the name together. The name of the compound is 1-ethyl-3-fluorocyclohexane.



1-Ethyl-3-fluorocyclohexane

2.13 Using Molecular Formulas

The molecular formula of a compound includes the chemical symbols of the various elements contained in one molecule of that compound and numbers that tell how many atoms of each element is present. However, using a molecular formula to draw a structural formula is not easy, as the molecular formula does not tell you what types of bonds are present or their locations. The generalized molecular formula for straight chain, or **acyclic**, alkanes is C_nH_{2n+2}. When the molecular formula for a compound differs from the alkane molecular formula having the same number of carbons, then you must account for the deviations. The most common deviations are a reduction in the number of hydrogen atoms or the addition of heteroatoms.

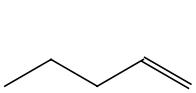
An acyclic structure has no rings.

When a compound deviates from the parent molecular formula, consider first whether or not the compound is saturated. Remember a saturated hydrocarbon is one that has only single bonds and an unsaturated hydrocarbon is one that contains double or triple bonds. A special case is a compound that contains a ring. Although a

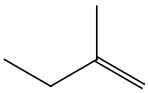
Two fewer hydrogens than are present in the parent formula indicate a unit of unsaturation.

cycloalkane is saturated, a compound with one ring has the same molecular formula as an acyclic compound with one double bond. A molecule with two fewer hydrogens than are found in its parent molecular formula has one **unit of unsaturation**. For example, one unit of unsaturation may correspond to a double bond between two atoms or to a ring. Two units of unsaturation may correspond to a triple bond between two atoms, two double bonds, two rings, or one ring and one double bond.

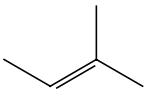
Pentane has the molecular formula C_5H_{12}. It is a saturated compound with no rings or double bonds. Another compound, with the formula C_5H_{10}, has the same number of carbons but two fewer hydrogens; thus, it has one unit of unsaturation. This means that it could contain one double bond or one ring. If the compound C_5H_{10} contains a double bond, it could be 1-pentene, 2-methyl-1-butene, 2-methyl-2-butene, or other possibilities.



1-Pentene



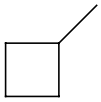
2-Methyl-1-butene



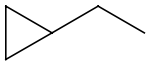
2-Methyl-2-butene

If it has a ring, it could be cyclopentane, methylcyclobutane, ethylcyclopropane, or other possibilities.

Cyclopentane



Methylcyclobutane



Ethylcyclopropane

As you can see, the molecular formula alone is not sufficient to determine whether or not a compound with a unit of unsaturation has a ring or a multiple bond. To make such a determination, you must obtain experimental evidence. You could get this evidence from chemical reactions or spectroscopy. In most cases, you need both types of additional data before you can assign the structure.

Exercise 2.16

Draw all possible structures having the molecular formula C_5H_{10}. Name them using the IUPAC system.

The presence of oxygen or sulfur in a molecular formula does not affect the determination of units of unsaturation. If a halogen is present, count it as equivalent to a hydrogen atom. A generalization

that you can make is—compounds with four or more units of unsaturation are usually aromatic. However, for each nitrogen or phosphorus present, subtract one hydrogen before calculating the number of units of unsaturation. For example, to find the number of units of unsaturation the molecular formula C_4H_9N first subtract one hydrogen from the nine listed to yield eight. With four carbons, a saturated alkane has ten hydrogens. Thus, this molecule has one unit of unsaturation.

Exercise 2.17

How many units of unsaturation are present in each of the following molecular formulas?

a) C_8H_{14} b) $C_6H_{13}N$
c) $C_5H_6Cl_2$ d) $C_6H_{12}O_6$

Sample solution

a) An acyclic alkane with eight carbons has 18 hydrogens ($2n + 2$ where $n = 8$). Since this formula has 14 hydrogens, it is "missing" 4 hydrogens so it has two units of unsaturation.

Key Ideas from Chapter 2

- ❑ Organic molecules have a skeleton of carbon atoms, often with functional groups attached.

- ❑ Hydrocarbons include only carbons and hydrogens. There are two classes of hydrocarbons: saturated and unsaturated. Saturated hydrocarbons are called alkanes and contain only single bonds. Unsaturated hydrocarbons are called alkenes, alkynes, or arenes and include both single and double or triple bonds.

- ❑ Homologs are hydrocarbons that differ from one another only in the number of methylene groups (—CH_2—) present.

- ❑ To name a saturated hydrocarbon:
  1. Find the longest chain of carbon atoms. This is the parent chain. Name it.
  2. Identify and alphabetize all the alkyl groups attached to the parent chain.

3. Number the carbon atoms in the parent chain so that the attached groups get the lowest possible numbers.

- ❑ A functional group is an atom or group of atoms bonded to a hydrocarbon that plays a major role in determining the physical and chemical properties of the compound.

- ❑ To name a molecule with a functional group:
  1. Find the longest chain that includes the functional group.
  2. Number that chain so that the functional group gets the lowest possible number.
  3. Name all other groups alphabetically.

- ❑ A molecular formula gives information about the number of units of unsaturation in an organic compound. Use this information to assist you in determining the number of multiple bonds and/or rings in the molecule.