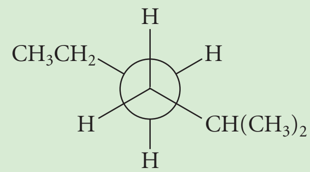
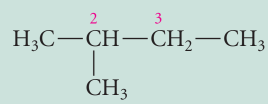


2-methylhexane
anti conformation about C3–C4 bond

Remember that Newman projections are used to examine conformations about *a particular bond.* If we want to examine the conformations about several different bonds, we must draw a different set of Newman projections for each bond.

PROBLEMS

2.3 (a) Draw a Newman projection for each conformation about the C2—C3 bond of isopentane, a compound containing a branched carbon chain.



isopentane

Show both staggered and eclipsed conformations.

(b) Sketch a curve of potential energy versus dihedral angle for isopentane, similar to that of butane in Fig. 2.5. Label each energy maximum and minimum with one of the conformations you drew in part (a).

(c) Which conformations are likely to be present in greatest amount in a sample of isopentane? Explain.

2.4 Repeat the analysis in Problem 2.3 for either one of the terminal bonds of butane.

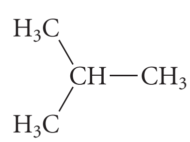
2.4 CONSTITUTIONAL ISOMERS AND NOMENCLATURE

A. Isomers

When a carbon atom in an alkane is bound to more than two other carbon atoms, a branch in the carbon chain occurs at that position. The smallest branched alkane has four carbon atoms. As a result, there are two four-carbon alkanes; one is *butane,* and the other is *isobutane*.

$$H_3C—CH_2—CH_2—CH_3$$

butane
bp −0.5°



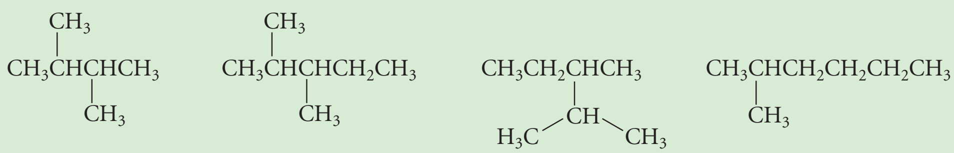
isobutane
bp −11.7°

These are different compounds with different properties. For example, the boiling point of butane is −0.5 °C, whereas that of isobutane is −11.7 °C. Yet both have the same molecular formula, C_4H_{10}. Different compounds that have the same molecular formula are said to be **isomers** or **isomeric compounds.**

There are different types of isomers. Isomers that differ in the connectivity of their atoms, such as butane and isobutane, are called **constitutional isomers** or **structural isomers**. Recall (Sec. 1.3) that *connectivity* is the order in which the atoms of the molecule are bonded.The atomic connectivities of butane and isobutane differ because in isobutane a carbon is attached to three other carbons, whereas in butane no carbon is attached to more than two other carbons.

Study Problem 2.2

Which of the following four structures represent constitutional isomers, which represent the same molecule, and which one is neither isomeric nor identical to the others? Explain your answers.



A *B* *C* *D*

Solution Compounds must have the same molecular formula to be either identical or isomeric. Structure *A* has a different molecular formula (C_6H_{14}) from the other structures (C_7H_{16}), and hence structure *A* represents a molecule that is neither identical nor isomeric to the others. To solve the rest of the problem, we must understand that *Lewis structures show connectivity only.* They do not represent the actual shapes of molecules unless we start adding spatial elements such as wedges and dashed wedges. This means that *we can draw a given structure many different ways.* Have you ever heard the old spiritual, "The foot-bone's connected to the ankle-bone . . . "? That's a song about connectivity of the typical human body. If the description fits you, its validity doesn't change whether you are sitting down, standing up, standing on your head, or doing yoga. Similarly, the connectivity of a molecule doesn't change whether it is drawn forwards, backwards, or upside-down. With that in mind, let's trace the connectivity of each structure above. Consider structures *B* and *C*. Each has two CH_3 groups connected to a CH, and that CH is connected to another CH, which in turn is connected to both a CH_3 group and a CH_2CH_3 group. In *B,* this connectivity pattern starts on the left; in *C,* it starts on the bottom. But it's the same in both. Because both structures have identical connectivities, they represent the same molecule.

Structures *D* and *B* (or *D* and *C*) have the same molecular formula C_7H_{16}, but, as you should verify, their connectivities are different, so they are constitutional isomers.

Butane and isobutane are the only constitutional isomers with the formula C_4H_{10}. However, more constitutional isomers are possible for alkanes with more carbon atoms. There are nine constitutional isomers of the heptanes (C_7H_{16}), 75 constitutional isomers of the decanes ($C_{10}H_{22}$) and 366,319 constitutional isomers of the eicosanes ($C_{20}H_{42}$)! From these few examples, it is easy to understand that millions of organic compounds are known and millions more are conceivable. It follows that organizing the body of chemical knowledge requires a system of nomenclature that can provide an unambiguous name for each compound.

B. Organic Nomenclature

An organized effort to standardize organic nomenclature dates from proposals made at Geneva in 1892. From those proposals the International Union of Pure and Applied Chemistry

(IUPAC), a professional association of chemists, developed and sanctioned several accepted systems of nomenclature. The most widely applied system in use today is called **substitutive nomenclature.**

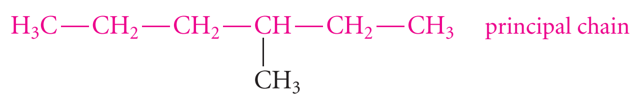
The IUPAC rules for the nomenclature of alkanes form the basis for the substitutive nomenclature of most other compound classes. Hence, it is important to learn these rules and be able to apply them.

C. Substitutive Nomenclature of Alkanes

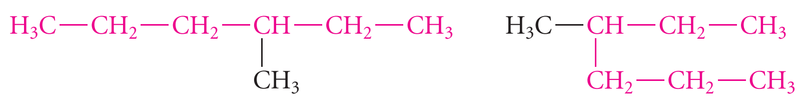
Alkanes are named by applying the following 10 rules *in order*. This means that if one rule doesn't unambiguously determine the name of a compound of interest, we proceed down the list *in order* until we find a rule that does.

1. *The unbranched alkanes are named according to the number of carbons, as shown in Table 2.1.*
2. *For alkanes containing branched carbon chains, determine the principal chain.*

The **principal chain** is the longest continuous carbon chain in the molecule. To illustrate:



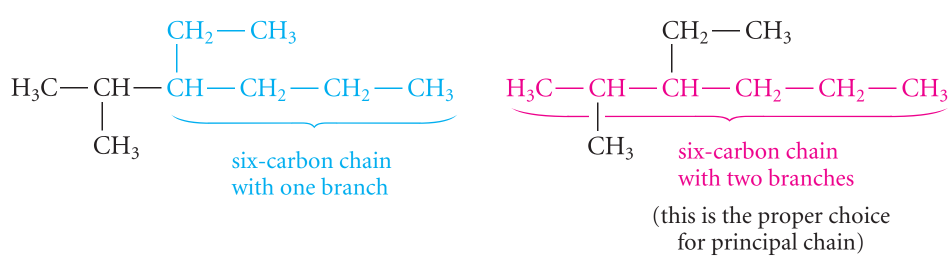
When identifying the principal chain, take into account that *the condensed structure of a given molecule may be drawn in several different ways* (Study Problem 2.2). Thus, the following structures represent the *same molecule,* with the principal chain shown in red:



(Be sure to verify that these structures have identical connectivities and thus represent the same molecule.)

3. *If two or more chains within a structure have the same length, choose as the principal chain the one with the greater number of branches.*

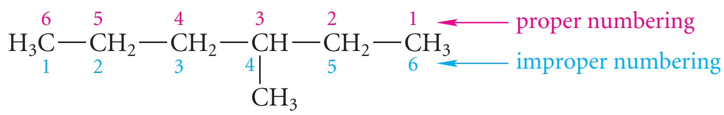
The following structure is an example of such a situation:



The correct choice of principal chain is the one on the right, because it has two branches; the choice on the left has only one. (It makes no difference that the branch on the left is larger or that it has additional branching within itself.)

4. *Number the carbons of the principal chain consecutively from one end to the other in the direction that gives the lower number to the first branching point.*

In the following structure, the carbons of the principal chain are numbered consecutively from one end to give the lower number to the carbon at the —CH_3 branch.



5. *Name each branch and identify the carbon number of the principal chain at which it occurs.*

In the previous example, the branching group is a —CH_3 group. This group, called a *methyl group,* is located at carbon-3 of the principal chain.

Branching groups are in general called **substituents,** and substituents derived from alkanes are called **alkyl groups.** An alkyl group may contain any number of carbons. The name of an unbranched alkyl group is derived from the name of the unbranched alkane with the same number of carbons by dropping the final *ane* and adding *yl*.

—CH_3			methyl (= meth~~ane~~ + yl)
—CH_2CH_3	or	—C_2H_5	ethyl (= eth~~ane~~ + yl)
—$CH_2CH_2CH_3$			propyl

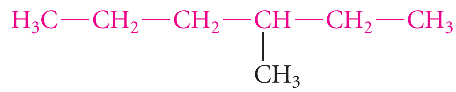
STUDY GUIDE LINK 2.1
Nomenclature of Simple Branched Compounds

Alkyl substituents themselves may be branched. The most common branched alkyl groups have special names, given in Table 2.2. These should be learned because they will be encountered frequently. Notice that the "iso" prefix is used for substituents containing two methyl groups at the end of a carbon chain. Also notice carefully the difference between an isobutyl group and a *sec*-butyl group; these two groups are frequently confused.

TABLE 2.2 Nomenclature of Some Short Branched-Chain Alkyl Groups

Group structure	Condensed structure	Written name	Pronounced name
H_3C CH— H_3C	$(CH_3)_2CH$—	isopropyl	isopropyl
H_3C $CHCH_2$— H_3C	$(CH_3)_2CHCH_2$—	isobutyl	isobutyl
CH_3CH_2CH— | CH_3	—	*sec*-butyl	secondary butyl or "sec-butyl"
CH_3 | H_3C—C— | CH_3	$(CH_3)_3C$—	*tert*-butyl (or *t*-butyl)	tertiary butyl or "tert-butyl"
CH_3 | H_3C—C—CH_2— | CH_3	$(CH_3)_3CCH_2$—	neopentyl	neopentyl

6. *Construct the name by writing the carbon number of the principal chain at which the substituent occurs, a hyphen, the name of the branch, and the name of the alkane corresponding to the principal chain.*



name: **3-methylhexane**

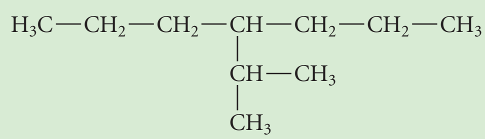
name of principal chain

number and name of alkyl substituent

Notice that the name of the branch and the name of the principal chain are written together as one word. Notice also that the name itself has *no* relationship to the name of the isomeric unbranched alkane; that is, the preceding compound is a *constitutional isomer of heptane* because it has seven carbon atoms, but it is named as a *derivative of hexane,* because its principal chain contains six carbon atoms.

Study Problem 2.3

Name the following compound, and give the name of the unbranched alkane of which it is a constitutional isomer.



Solution Because the principal chain has seven carbons, the compound is named as a substituted heptane. The branch is at carbon-4, and the substituent group at this branch is

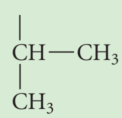
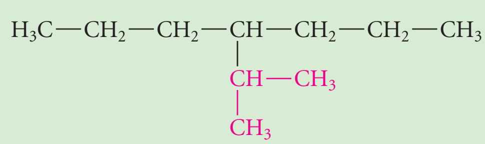


Table 2.2 shows that this group is an *isopropyl group*. Thus, the name of the compound is 4-isopropylheptane:

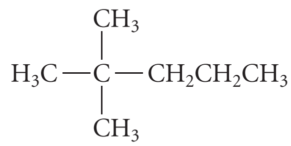


4-isopropylheptane

alkyl group name from Table 2.2

Because this compound has the molecular formula $C_{10}H_{22}$, it is a constitutional isomer of the unbranched alkane *decane*.

7. *If the principal chain contains multiple substituent groups, each substituent receives its own number. The prefixes di, tri, tetra, and so on, are used to indicate the number of identical substituents.*



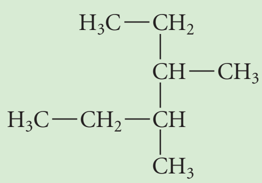
2,2-dimethylpentane

two methyl substituents

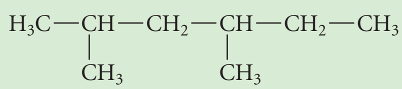
shows that both methyl branches are at carbon-2 of the principal chain

Study Problem 2.4

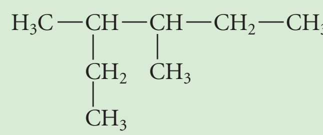
Which two of the following structures represent the same compound? Name the compound.



A



B

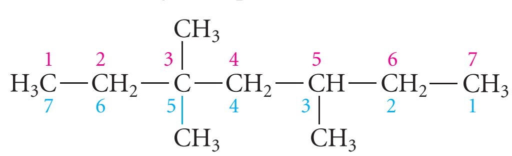


C

Solution The connectivities of both *A* and *C* are the same: [CH_3, CH_2, (CH connected to CH_3), (CH connected to CH_3), CH_2, CH_3]. The compound represented by these structures has six carbons in its principal chain and is therefore named as a hexane. There are methyl branches at carbons 3 and 4. Hence the name is 3,4-dimethylhexane. (You should name compound *B* after you study the next rule.)

8. *If substituent groups occur at more than one carbon of the principal chain, alternative numbering schemes are compared number by number, and the one is chosen that gives the smaller number* at the first point of difference.

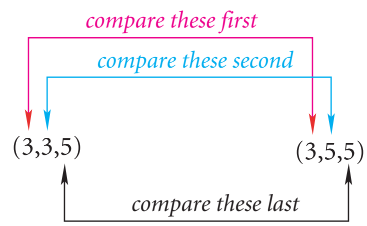
This is one of the trickiest nomenclature rules, but it is easy to handle if we are systematic. To apply this rule, write the two possible numbering schemes derived by numbering from either end of the chain. In the following example, the two schemes are 3,3,5- and 3,5,5-.



possible names:
3,3,5-trimethylheptane (correct)
3,5,5-trimethylheptane (incorrect)

A decision between the two numbering schemes is made by a *pairwise comparison* of the number sets (3,3,5) and (3,5,5).

How to do a pairwise comparison:

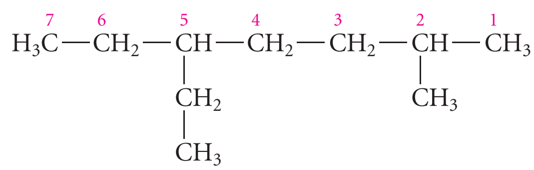


Because the *first point of difference* in these sets occurs at the second pair—3 versus 5—the decision is made at this point, and the first scheme is chosen, because 3 is smaller than 5. If there are differences in the remaining numbers, they are ignored. The sum of the numbers is also irrelevant. Finally, it makes no difference whether the names of the substituents are the same or different; only the numerical locations are used.

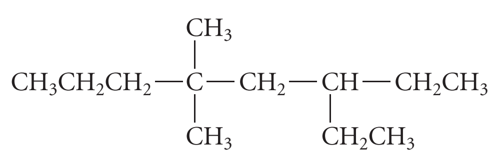
The next rule deals with the order in which substituents are listed, or "cited," in the name. Don't confuse the citation order of a substituent with its numerical prefix; they aren't necessarily the same.

9. *Substituent groups are cited in alphabetical order in the name regardless of their location in the principal chain. The numerical prefixes di, tri, and so on, as well as the hyphenated prefixes* tert- *and* sec-, *are ignored in alphabetizing, but the prefixes iso, neo, and cyclo are considered in alphabetizing substituent groups.*

The following compounds illustrate the application of this rule:



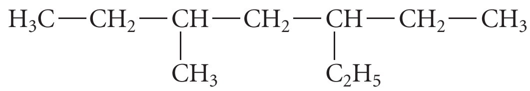
5-ethyl-2-methylheptane
(*ethyl* is cited before *methyl* even though it has a higher number)



3-ethyl-5,5-dimethyloctane
(note that *dimethyl* begins with the letter *m* for purposes of citation)

10. *If the numbering of different groups is not resolved by the other rules, the first-cited group receives the lowest number.*

In the following compound, rules 1–9 do not dictate a choice between the names 3-ethyl-5-methylheptane and 5-ethyl-3-methylheptane. Because the ethyl group is cited first in the name (rule 9), it receives the lower number, by rule 10.



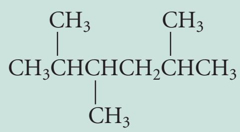
3-ethyl-5-methylheptane

Some situations of greater complexity are not covered by these 10 rules; however, these rules will suffice for most cases.

PROBLEM

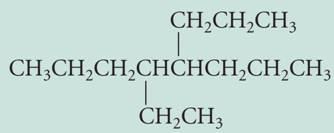
2.5 Name the following compounds.

(a)

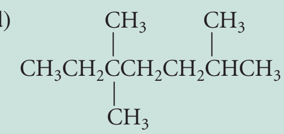


(b) compound *B* in Study Problem 2.4 on p. 62

(c)



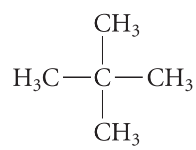
(d)



D. Highly Condensed Structures

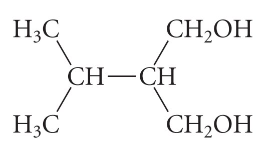
When space is at a premium, parentheses are sometimes used to form highly condensed structures that can be written on one line, as in the following example.

$(CH_3)_4C$ or $C(CH_3)_4$ means



When such structures are complex, it is sometimes not immediately obvious, particularly to the beginner, which atom inside the parentheses is connected to the atom outside the parentheses, but a little analysis will generally solve the problem. Usually the structure is drawn so that one of the parentheses intervenes between the atoms that are connected (except for attached hydrogens). However, if in doubt, look for the atom within the parentheses that is missing its usual number of bonds. When the group inside the parentheses is CH_3, as in the previous example, the carbon has only three bonds (to the H's). Hence, it must be bound to the atom outside the parentheses. Consider as another example the CH_2OH groups in the following structure.

$(CH_3)_2CH{-}CH(CH_2OH)_2$ means



Because the oxygen is bound to a carbon and to a hydrogen, it has its full complement of two bonds (the two unshared pairs are understood). The carbon of each CH_2OH group, however, is bound to only three groups (two H's and the O); hence, it is the atom that is connected to the carbon outside the parentheses.

If the meaning of a condensed structure is not immediately clear, *write it out in less condensed form*. If you will take the time to do this in a few cases, it should not be long before the interpretation of condensed structures becomes more routine.

Research in student learning strategies has shown that student success in organic chemistry is *highly correlated* with whether a student takes the time to *write out* intermediate steps in a problem. Such steps in many cases involve writing structures and partial structures. Students may be tempted to skip such steps because they see their professors working things out quickly in their heads and perhaps feel that they are expected to do the same. Professors can do this because they have years of experience. Most of them probably gained their expertise through step-by-step problem solving. In some cases, the temptation to skip steps may be a consequence of time pressure. If you are tempted in this direction, remember that a step-by-step approach applied to relatively few problems is a better expenditure of time than rushing through many problems. Study Problem 2.5 illustrates a step-by-step approach to a nomenclature problem.

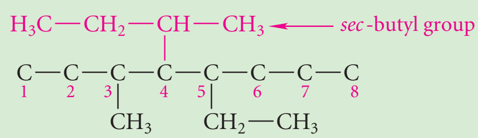
Study Problem 2.5

Write the Lewis structure of 4-*sec*-butyl-5-ethyl-3-methyloctane. Then write the structure in a condensed form.

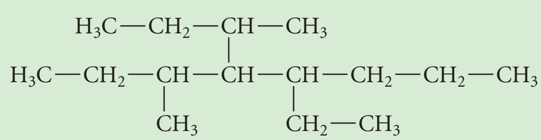
Solution To this point, we've been giving names to structures. This problem now requires that we work "in reverse" and construct a structure from a name. Don't try to write out the structure immediately; rather, take a systematic, stepwise approach involving intermediate structures. First, write the principal chain. Because the name ends in *octane,* the principal chain contains eight carbons. Draw the principal chain without its hydrogen atoms:

C—C—C—C—C—C—C—C

Next, number the chain from either end and attach the branches indicated in the name at the appropriate positions: a *sec*-butyl group at carbon-4, an ethyl group at carbon-5, and a methyl group at carbon-3. (Use Table 2.2 to learn or relearn the structure of a *sec*-butyl group, if necessary.)

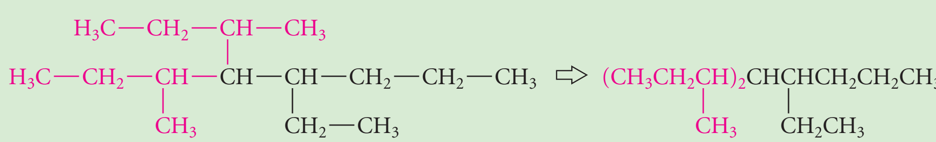


Finally, fill in the proper number of hydrogens at each carbon of the principal chain so that each carbon has a total of four bonds:



4-*sec*-butyl-5-ethyl-3-methyloctane

To write the structure in condensed form, put like groups attached to the same carbon within parentheses. Notice that the structure contains within it two *sec*-butyl groups (red in the following structure), even though only one is mentioned in the name; the other consists of a methyl branch and part of the principal chain.



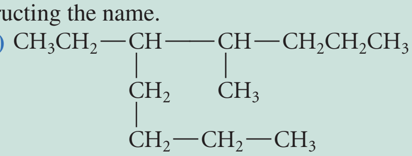
Nomenclature and Chemical Indexing

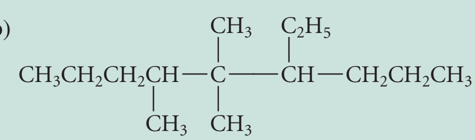
The world's chemical knowledge is housed in the **chemical literature,** which is the collection of books, journals, patents, technical reports, and reviews that constitute the published record of chemical research. To find out what, if anything, is known about an organic compound of interest, we have to search the entire chemical literature. To carry out such a search, organic chemists rely on two major indexes. One is *Chemical Abstracts,* published by the Chemical Abstracts Service of the American Chemical Society, which has been the major index of the entire chemical literature since 1907. The second index is *Beilstein's Handbook of Organic Chemistry,* known to all chemists simply as *Beilstein,* which has published detailed information on organic compounds since 1881. Initially, a search of these indexes was a laborious manual process that could require hours or days in the library. Today, however, both *Chemical Abstracts* and *Beilstein* have efficient search engines that enable chemists to search for chemical information from a personal computer. Nomenclature plays a key role in locating chemical compounds, particularly in *Chemical Abstracts*, but it is also possible to search for a compound of interest by submitting its structure. A search of *Chemical Abstracts* yields a short summary, called an *abstract*, of every article that references the compound of interest, along with a detailed reference to each article. *Beilstein* yields not only the appropriate references but also detailed summaries of compound properties.

PROBLEMS

2.6 Draw structures for all isomers of **(a)** heptane and (b) hexane. Give their systematic names.

2.7 Name the following compounds. Be sure to designate the principal chain properly before constructing the name.

(a) 

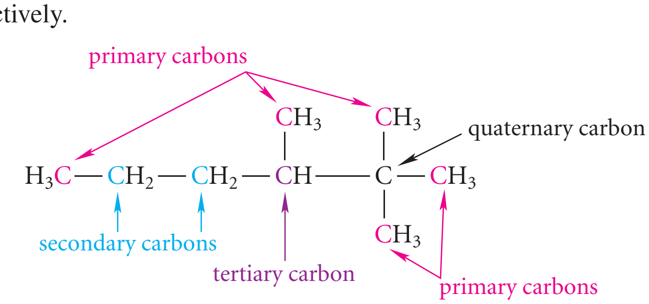
(b) 

2.8 Draw a structure for $(CH_3CH_2CH_2)_2CHCH(CH_2CH_3)_2$ in which all carbon–carbon bonds are shown explicitly; then name the compound.

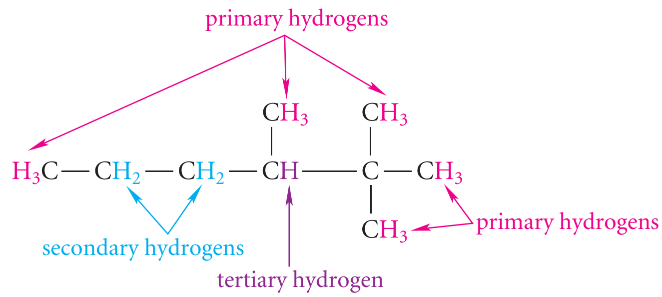
2.9 Draw the structure of 4-isopropyl-2,4,5-trimethylheptane.

E. Classification of Carbon Substitution

When we begin our study of chemical reactions, it will be important to recognize different types of carbon substitution in branched compounds. A carbon is said to be **primary, secondary, tertiary,** or **quaternary** when it is bonded to one, two, three, or four other carbons, respectively.



Likewise, the hydrogens bonded to each type of carbon are called primary, secondary, or tertiary hydrogens, respectively.



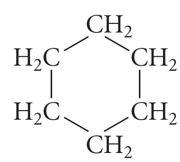
PROBLEMS

2.10 In the structure of 4-isopropyl-2,4,5-trimethylheptane (Problem 2.9)
(a) Identify the primary, secondary, tertiary, and quaternary carbons.
(b) Identify the primary, secondary, and tertiary hydrogens.
(c) Circle one example of each of the following groups: a methyl group; an ethyl group; an isopropyl group; a *sec*-butyl group; an isobutyl group.

2.11 Identify the ethyl groups and the methyl groups in the structure of 4-*sec*-butyl-5-ethyl-3-methyloctane, the compound discussed in Study Problem 2.5. Note that these groups are not necessarily confined to those specifically mentioned in the name.

2.5 CYCLOALKANES AND SKELETAL STRUCTURES

Some alkane contain carbon chains in closed loops, or rings; these are called **cycloalkanes.** Cycloalkanes are named by adding the prefix *cyclo* to the name of the alkane. Thus, the six-membered cycloalkane is called *cyclohexane*.



cyclohexane

The names and some physical properties of the simple cycloalkanes are given in Table 2.3. The general formula for an alkane containing a single ring has two fewer hydrogens than that of the open-chain alkane with the same number of carbon atoms. For example, cyclohexane has the formula C_6H_{12}, whereas hexane has the formula C_6H_{14}. The general formula for the cycloalkanes with one ring is C_nH_{2n}.

Because of the tetrahedral configuration of carbon in the cycloalkanes, the carbon skeletons of the cycloalkanes (except for cyclopropane) are not planar. We'll study the conformations of cycloalkanes in Chapter 7. For now, remember only that planar condensed structures for the cycloalkanes convey no information about their conformations.

Skeletal Structures An important structure-drawing convention is the use of **skeletal structures,** which are structures that show only the carbon–carbon bonds. In this notation, a cycloalkane is drawn as a closed geometric figure. In a skeletal structure, it is understood that