

1.3: Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.
- To give basic properties of alkanes.
- To name linear and branched alkanes using the IUPAC naming system.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

The three simplest alkanes—methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) are shown in Figure 1.3.1.

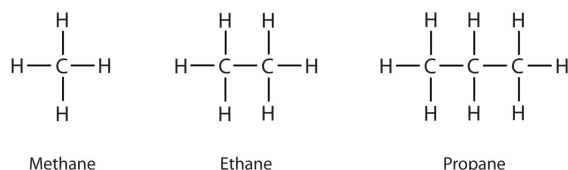


Figure 1.3.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 1.3.2).

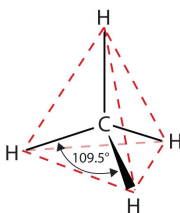


Figure 1.3.2: The Tetrahedral Methane Molecule

Methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH₂ unit. The first 10 members of this series are given in Table 1.3.1.

Table 1.3.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C _n H _{2n+2})	Condensed Structural Formula
methane	CH ₄	CH ₄
ethane	C ₂ H ₆	CH ₃ CH ₃
propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃
butane	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃
pentane	C ₅ H ₁₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Consider the series in Figure 1.3.3. The sequence starts with C_3H_8 , and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

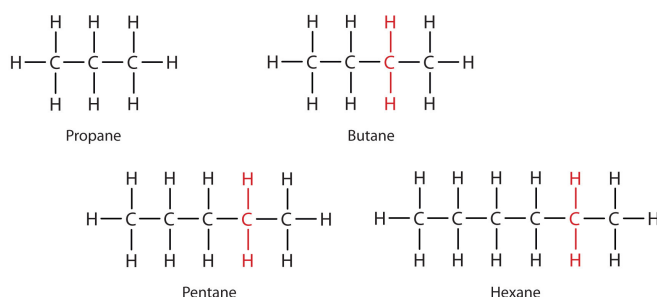


Figure 1.3.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

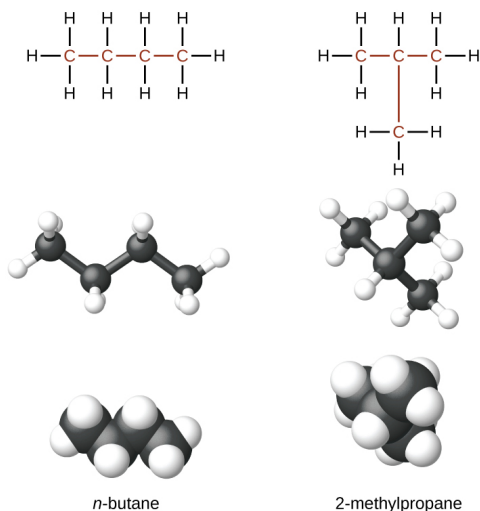
The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2} . Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 1.3.2) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table 1.3.2: Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point ($^{\circ}C$)	Boiling Point ($^{\circ}C$)	Phase at STP ⁴	Number of Structural Isomers
methane	CH_4	-182.5	-161.5	gas	1
ethane	C_2H_6	-183.3	-88.6	gas	1
propane	C_3H_8	-187.7	-42.1	gas	1
butane	C_4H_{10}	-138.3	-0.5	gas	2
pentane	C_5H_{12}	-129.7	36.1	liquid	3
hexane	C_6H_{14}	-95.3	68.7	liquid	5
heptane	C_7H_{16}	-90.6	98.4	liquid	9
octane	C_8H_{18}	-56.8	125.7	liquid	18
nonane	C_9H_{20}	-53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	-29.7	174.0	liquid	75

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP ⁴	Number of Structural Isomers
tetradecane	C ₁₄ H ₃₀	5.9	253.5	solid	1858
octadecane	C ₁₈ H ₃₈	28.2	316.1	solid	60,523

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C₄H₁₀: They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:



The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2-methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms).

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 1.3.4 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms. We will discuss isomers in more detail later in this chapter.

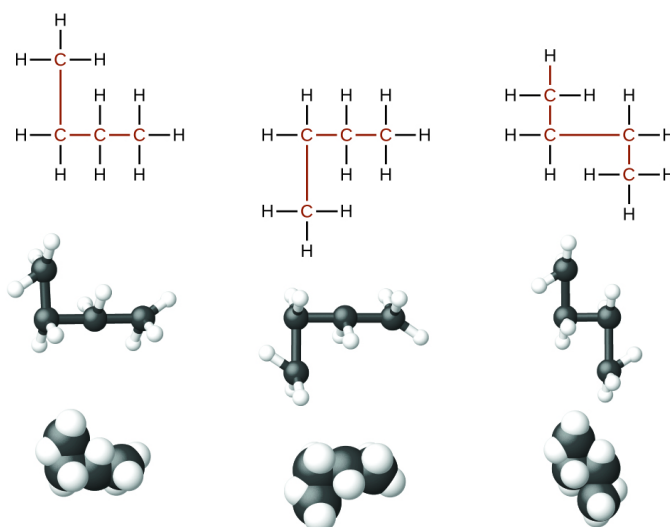
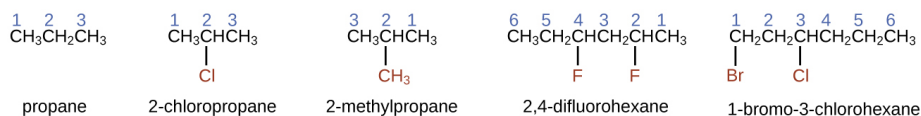


Figure 1.3.4: These three representations of the structure of *n*-butane are not isomers because they all contain the same arrangement of atoms and bonds.

The Basics of Organic Nomenclature: Naming Alkanes

The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

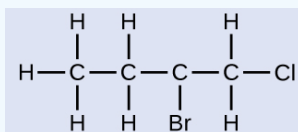
1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in Table 1.3.1.
2. Add prefixes to the name of the longest chain to indicate the positions and names of substituents. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.
- 3.



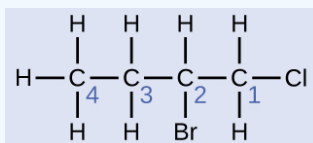
When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

✓ Example 1.3.1: Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



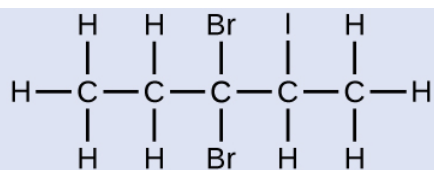
Solution



The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

? Exercise 1.3.1

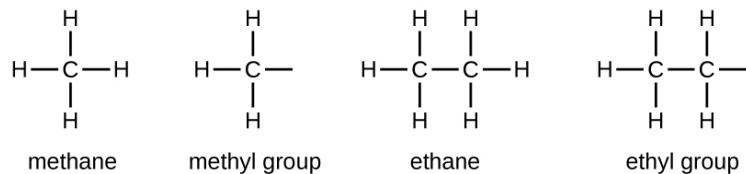
Name the following molecule:



Answer

3,3-dibromo-2-iodopentane

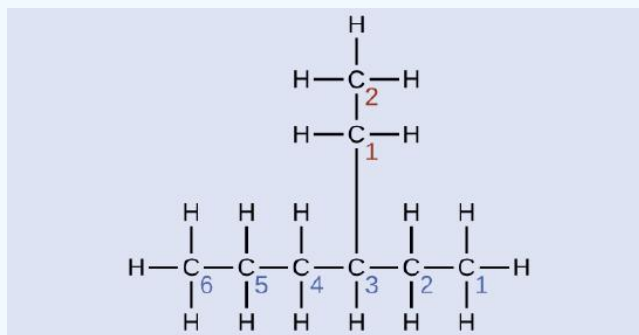
We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an alkyl group is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:



The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

✓ Example 1.3.2 Naming Substituted Alkanes

Name the molecule whose structure is shown here:

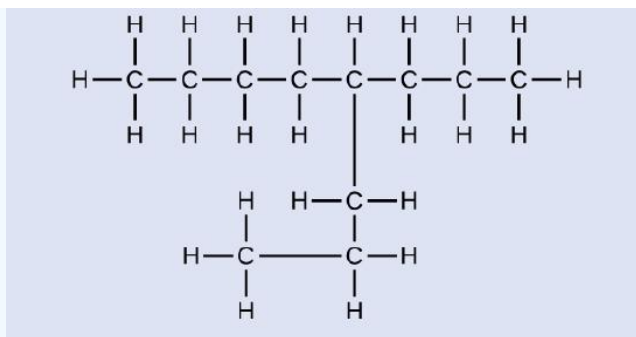


Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

? Exercise 1.3.2

Name the following molecule:



Answer

4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in Figure 1.3.4. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2-methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:

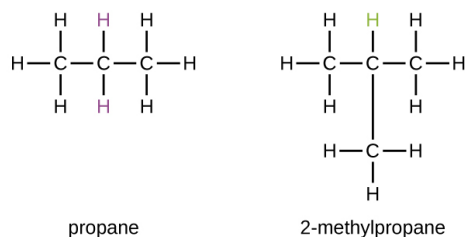
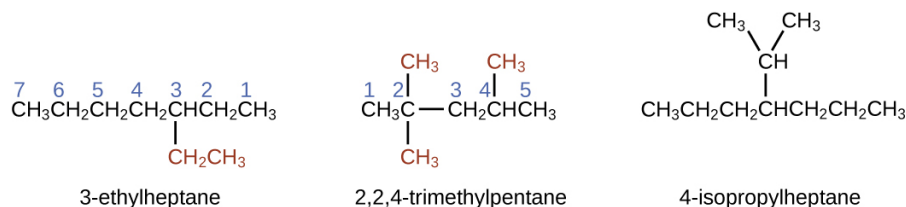


Figure 1.3.5.

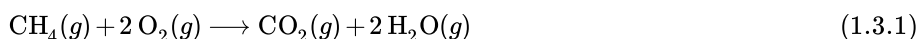
Alkyl Group	Structure
methyl	$\text{CH}_3\text{—}$
ethyl	$\text{CH}_3\text{CH}_2\text{—}$
<i>n</i> -propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$
isopropyl	$\begin{array}{c} \\ \text{CH}_3\text{CHCH}_3 \end{array}$
<i>n</i> -butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
sec-butyl	$\begin{array}{c} \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$
isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$
<i>tert</i> -butyl	$\begin{array}{c} \\ \text{CH}_3\text{CCH}_3 \\ \\ \text{CH}_3 \end{array}$

Figure 1.3.6: This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:



Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4 , is the principal component of natural gas. Butane, C_4H_{10} , used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure 1.3.7). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

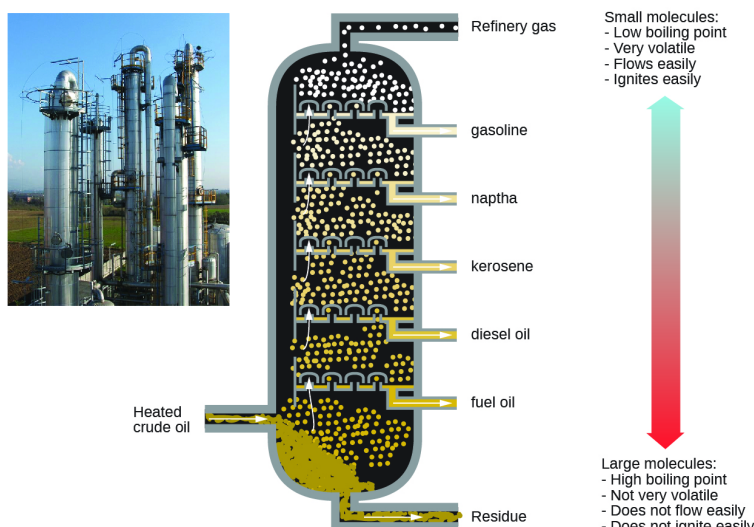


Figure 1.3.7: In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

Key Takeaways

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.
- Alkanes have low boiling points, are flammable, and are not soluble in water.
- The IUPAC naming system can distinguish between different isomers for a family of alkanes.

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