12: INTRODUCTION TO ORGANIC CHEMISTRY - ALKANES

CHAPTER OVERVIEW

12: Introduction to Organic Chemistry - Alkanes

12.1: The Nature of Organic Molecules

Learning Objectives

- Describe the basic structural properties of simple organic molecules.

Organic chemistry is the study of the chemistry of carbon-containing compounds. Carbon is singled out because it has a chemical diversity unrivaled by any other chemical element. Its diversity is based on the following:

- Carbon atoms bond reasonably strongly with other carbon atoms.
- Carbon atoms bond reasonably strongly with atoms of other elements.
- Carbon atoms make a large number of covalent bonds (four).

Curiously, elemental carbon is not particularly abundant. It does not even appear in the list of the most common elements in Earth's crust. Nevertheless, all living things consist of organic compounds. Most organic chemicals are covalent compounds, which is why we introduce organic chemistry here. By convention, compounds containing carbonate ions and bicarbonate ions, as well as carbon dioxide and carbon monoxide, are not considered part of organic chemistry, even though they contain carbon.

Structural Properties of Carbon Compounds

A carbon atom has four valence electrons, it is **tetravalent**. Carbon can form four *covalent* bonds, or *share electrons with* up to four atoms in order to gain a complete octet. The simplest carbon compounds contain only carbon and hydrogen and are called **hydrocarbons**. Methane, the simplest hydrocarbon, contains a single carbon with four covalently bonded hydrogen atoms. Recalling what you have learned about molecular structures and VSEPR, we know that methane is **tetrahedral** (four electron groups and no lone pairs).

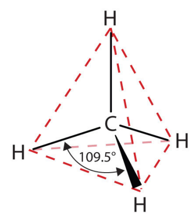


Figure 12.1.1: The Tetrahedral Methane Molecule

Carbon can also form **double bonds** by sharing *four electrons* with a neighboring carbon atom or **triple bonds** by sharing *six electrons* with a neighboring carbon atom. As shown in Figure 12.1.2 below, carbon with three electron groups attached will be **trigonal planar**, and carbon with two electron groups attached will be **linear**.

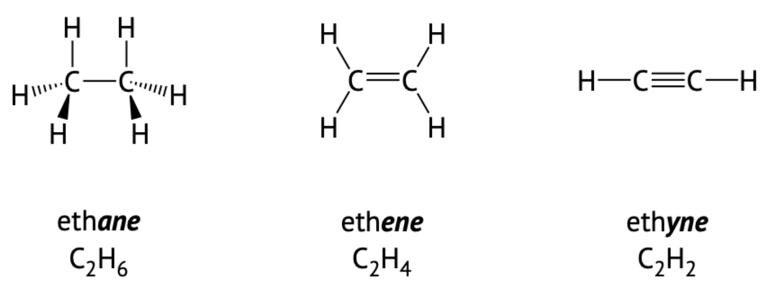


Figure 12.1.2: Two carbons can be attached together in single bond, a double bond, or a triple bond. Notice, in each example carbon makes four total bonds. The number of hydrogen atoms in each molecule decreases as the number of carbon–carbon bonds increase.

Simple hydrocarbon compounds are *nonpolar* due to the shape and the small electronegativity difference between carbon and hydrogen atoms. When carbon is bonded to a halogen or oxygen atom, the resulting bond is *polar*. It may be useful to review the section on electronegativity and polarity of bonds and molecules to be able to describe the properties of different organic compounds, specifically how they react and interact with other molecules.

Comparing Organic and Inorganic Compounds

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 12.1.1. Keep in mind, however, that there are exceptions to every category in this table.

Table 12.1.1: Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic Properties	**Example:** Hexane	**Inorganic Properties**	**Example:** NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

12.2: Families of Organic Molecules - Functional Groups

Learning Objectives

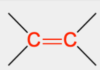
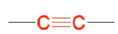
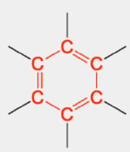
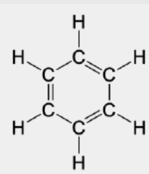
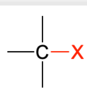
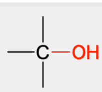
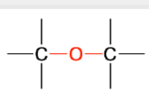
- Identify and describe functional groups in organic molecules.

Organic molecules can be classified into *families* based on structural similarities. Within a family, molecules have similar physical behavior and often have predictable chemical reactivity. The structural components differentiating different organic families involve specific arrangements of atoms or bonds, called **functional groups**. If you understand the behavior of a particular functional group, you can describe the general properties of that class of compounds.

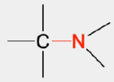
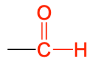
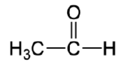
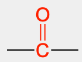
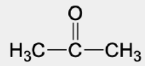
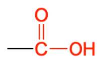
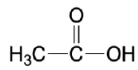
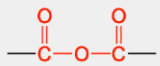
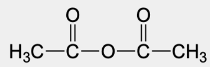
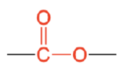
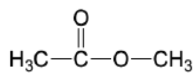
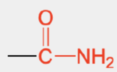
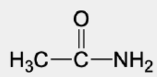
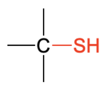
The simplest organic compounds are in the **alkane** family and contain only carbon–carbon and carbon–hydrogen *single* bonds but do not have any specific functional group. Hydrocarbons containing at least one carbon–carbon double bond, (denoted C=C), are in the **alkene** family. **Alkynes** have at least one carbon–carbon triple bond (C≡C). Both carbon–carbon double bonds and triple bonds chemically react in specific ways that differ from reactions of alkanes and each other, making these specific functional groups.

In the next few chapters, we will learn more about additional functional groups that are made up of atoms or groups of atoms attached to hydrocarbons. Being able to recognize different functional groups will help to understand and describe common medications and biomolecules such as amino acids, carbohydrates, and fats. Table 12.2.1 and Figure 12.2.1 below list several of the functional groups to become familiar with as you learn about organic chemistry.

Table 12.2.1: Organic Families and Functional Groups

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name	Name Suffix
alkane	none	$CH_3CH_2CH_3$	propane	-*ane*
alkene		$H_2C{=}CH_2$	ethene (ethylene)	-*ene*
alkyne		HC≡CH	ethyne (acetylene)	-*yne*
aromatic			benzene	none
alkyl halide	 (X = F, Cl, Br, I)	CH_3CH_2Cl	chloroethane	none
alcohol		CH_3CH_2OH	ethanol	-*ol*
ether		CH_3CH_2–O–CH_2CH_3	diethyl ether	none*

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hydrogens).
*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name	Name Suffix
amine		$CH_3CH_2NH_2$	ethylamine	*-amine*
aldehyde			ethanal	*-al*
ketone			propanone (acetone)	*-one*
carboxylic acid			ethanoic acid (acetic acid)	*-oic acid*
anhydride			acetic anhydride	none
ester			methyl ethanoate (methyl acetate)	*-ate*
amide			acetamide	*-amide*
thiol		CH_3CH_2SH	ethanethiol	*-thiol*
disulfide		$CH_3S–SCH_3$	dimethyl disulfide	none
sulfide		$CH_3CH_2SCH_3$	ethyl methyl sulfide	none

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hydrogens).
*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

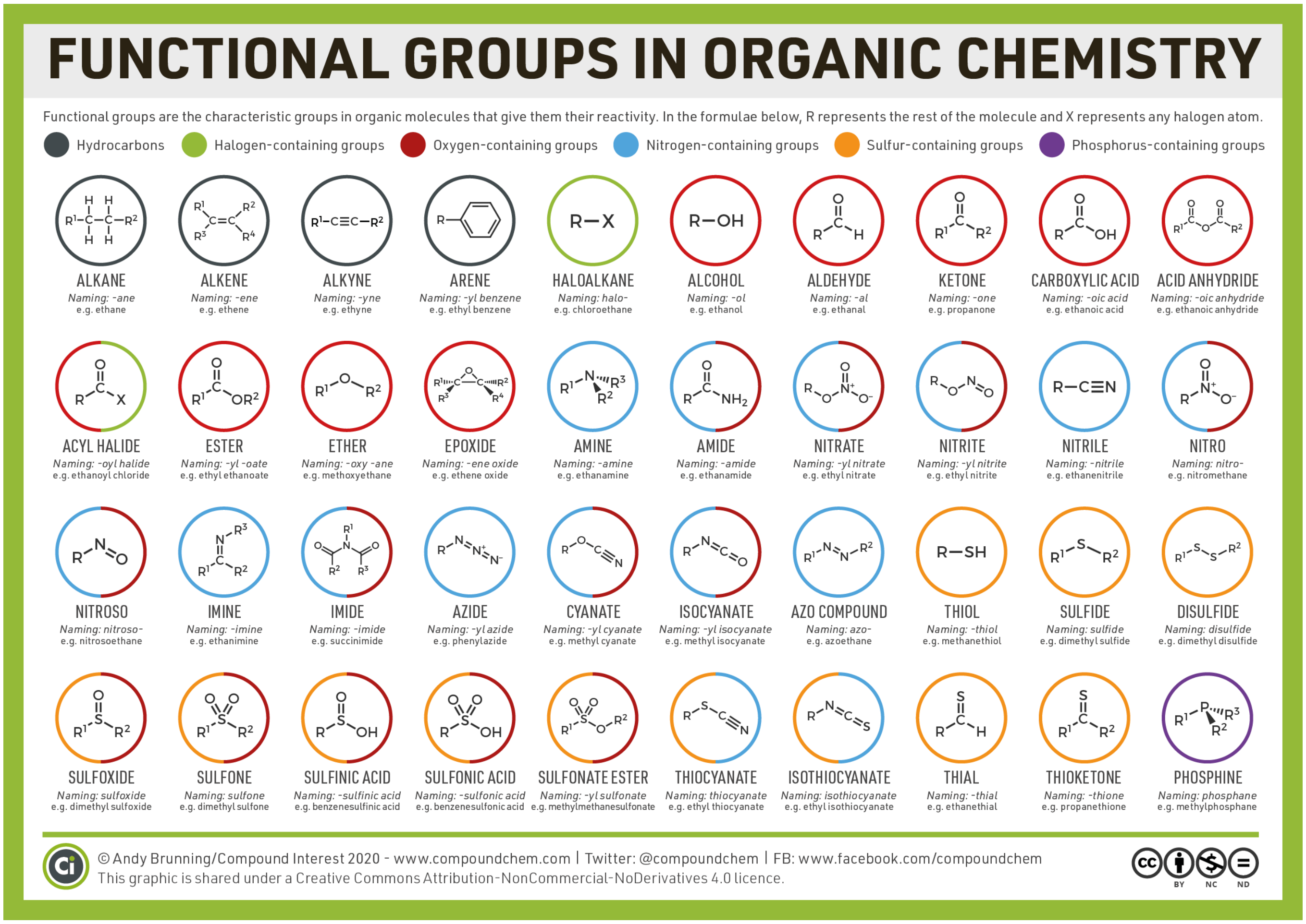


Figure 12.2.1: Functional groups in organic chemistry. (CC BY-NC-ND, CompoundChem.com).

12.3: The Structure of Organic Molecules - Alkanes and Their Isomers

Learning Objectives

- To identify simple alkanes as straight-chain or branched-chain.
- Describe and recognize structural and functional group isomers.

As you just learned, there is a wide variety of organic compounds containing different functional groups. However, all organic compounds are hydrocarbons, they contain hydrogen and carbon. The general rule for hydrocarbons is that any carbon must be bonded to at least one other carbon atom, except in the case of methane which only contains one carbon. The bonded carbons form the *backbone* of the molecule to which the hydrogen atoms (or other functional groups) are attached.

Hydrocarbons with only carbon-to-carbon single bonds (C–C) 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 these molecules.

> Saturated fats and oils are organic molecules that do not have carbon-to-carbon double bonds (C=C).

The three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) shown in Figure 12.3.1, 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 CH_2 unit (called methylene). Alkanes follow the general formula: 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 $C_8H_{(2 \times 8)+2} = C_8H_{18}$.

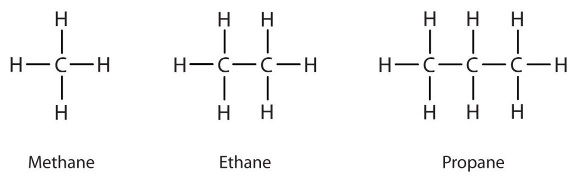
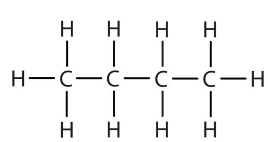


Figure 12.3.1: The Three Simplest Alkanes

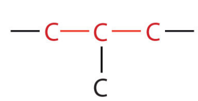
Isomers

Alkanes that contain one continuous chain of linked carbons are called **straight-chain** alkanes. As the number of carbons in a chain increases beyond three, the arrangement of atoms can expand to include **branched-chain** alkanes. In a branched chain, one or more hydrogen atoms along the chain is replaced by a carbon atom (or a separate chain of carbon atoms). It is important to note that while the structural arrangement of these chains are different, continuous versus branched, they both still follow the same general formula for alkanes as introduced above, C_nH_{2n+2}. In fact, alkane chains that have the same molecular formula (same number of carbon and hydrogen), but a different arrangement of atoms, are called **isomers**. Let's look at an example below:

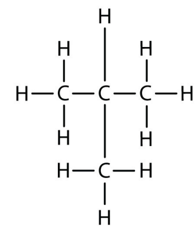
The structure of butane (C_4H_{10}) is written by stringing four carbon atoms in a row, and then adding enough hydrogen atoms to give each carbon atom four bonds:



Butane is a straight-chain alkane, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then *branch* the fourth carbon off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds:



The result is the isomer 2-methylpropane (also called isobutane), which is a branched-chain alkane with the same formula as butane, (C_4H_{10}). However, it is a *different* molecule with a *different* name and *different* chemical properties. A side-by-side comparison of these two molecules is shown in the below figure.

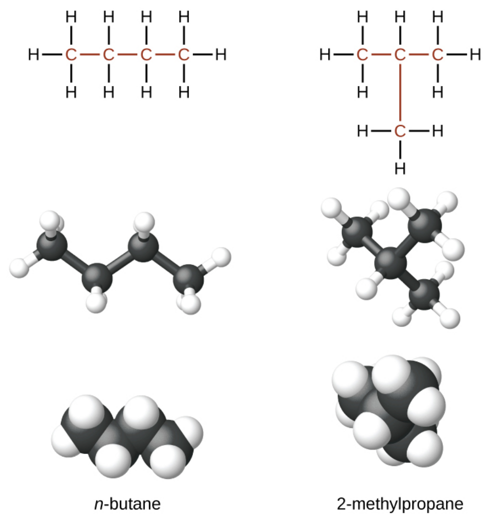


Figure 12.3.1: n-butane and 2-methylpropane. The compounds *n*-butane and 2-methylpropane are structural isomers, meaning they have the same molecular formula, C_4H_{10}, but different spatial arrangements of the atoms in their molecules. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching.

The four-carbon straight chain butane may be drawn with different bends or kinks in the backbone (Figure 12.3.2) because the groups can rotate freely about the C–C bonds. This rotation or bending of the carbon chain does *not* change the identity of the compound; all of the following structures represent the *same* compound, butane, with different bends in the chain:

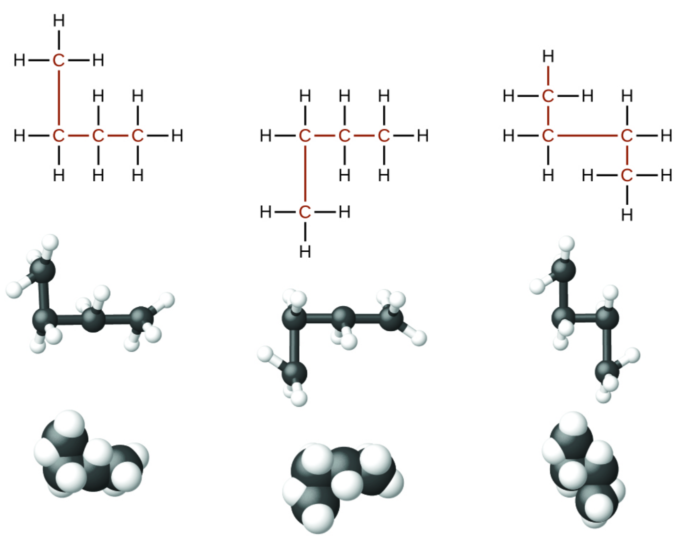
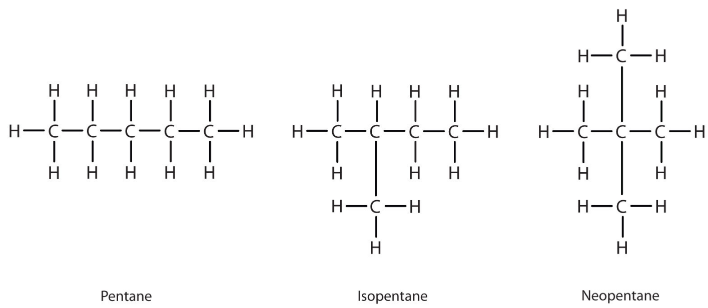


Figure 12.3.2: These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

When identifying isomers, it is useful to trace the carbon backbone with your finger or a pencil and count carbons until you need to lift your hand or pencil to get the another carbon. Try this with each of the above arrangements of four carbons, then do the same with 2-methylpropane. Butane has a continuous chain of four carbons no matter how the bonds are rotated – you can connect the carbons in a line without lifting your finger from the page. How many continuous carbons are in the 2-methylpropane backbone? You should be able to count a continuous chain of three carbon atoms only, with the fourth carbon attached as a branch, (compare the two structures in Figure $12.3.1$). In a later chapter, you will learn how to systematically name compounds by counting the number of carbons in the longest continuous chain and identifying any functional groups present.

Adding one more carbon to the butane chain gives pentane, which has the formula, C_5H_{12}. Pentane and its two branched-chain isomers are shown below. The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C. The names isopentane and neopentane are common names for these molecules. As mentioned above, we will learn the systematic rules for naming compounds in later chapters.



> A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

12.4: Drawing Organic Structures

Learning Objectives

- Draw condensed structures and line structures for simple compounds from the given molecular formulas.
- Convert between expanded, condensed and line structures.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the number and type of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and 2-methylpropane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them (**expanded structure**). This type of structure allows for easy identification of specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas that show the bonds between *all* atoms are sometimes difficult to type/write and take up a lot of space, especially when the number of atoms greatly increases. Chemists often use **condensed structures**, that show hydrogen atoms right next to the carbon atoms to which they are attached, to alleviate these problems. The ultimate condensed formula is a **line (or line-angle) structure**, in which carbon atoms are implied at the corners and ends of lines rather than written out, and each carbon atom is understood to be attached to the appropriate amount of hydrogen atoms to give each carbon atom four bonds. Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom. All three of these structure types are illustrated for butane and its isomer, 2-methylpropane in Figure 12.4.1 below.

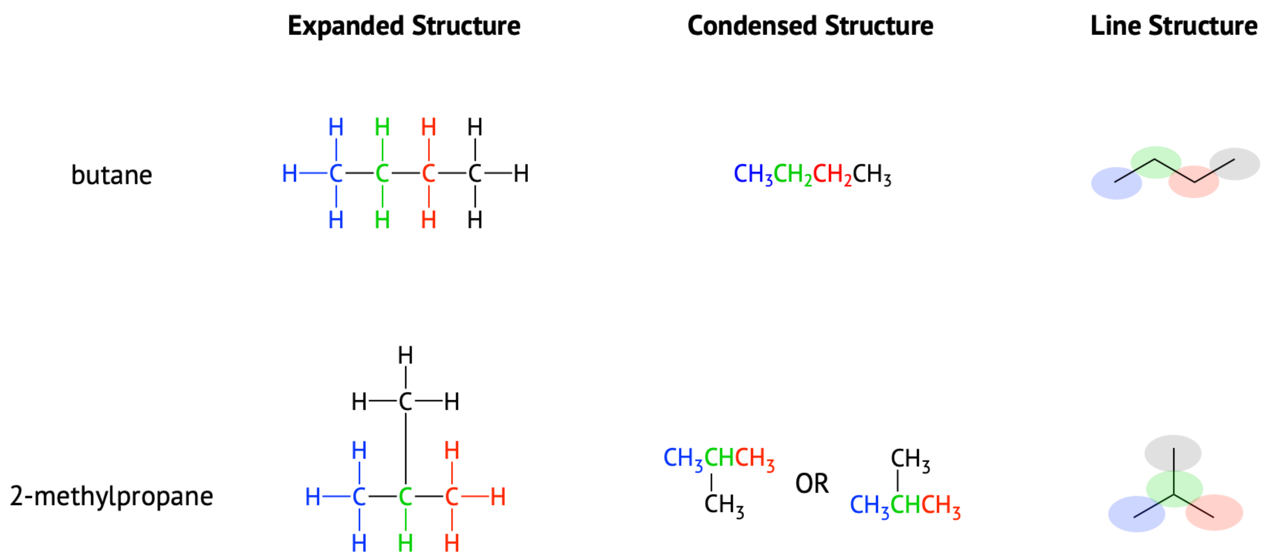


Figure 12.4.1: Structural representations for butane and its isomer, 2-methylpropane. (The colors are used to help identify carbons and do not represent any special properties.)

12.5: The Shapes of Organic Molecules

Maps take some time to build because we have to find or write matching materials. LibreTexts POV is that it is best to make available pages that we have finished rather than wait till the entire project is complete .This map is not completely finished, some pages are missing but we are workin' on it. . . (Public Domain ; Public Domain Pictures)

12.6: Naming Alkanes

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases: there are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes, etc. It would be difficult to assign each compound unique individual names that we could remember easily. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names mentioned earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.)

In the IUPAC system, a compound is named according to the number of carbons in the longest continuous chain (LCC) or parent chain and the family it belongs to. Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by a numerical prefix at the beginning of the name:

Prefix (substituent) – Parent (# carbons) – Suffix (family name)

2-methylpropane

(Table 12.6.1) below lists the IUPAC parent names that are used for charbon chains containing 1 to 10 carbons, along with straight-chain alkane examples for each. Notice that the suffix for each example in this table is *-ane*, which indicates these are members of the alk*ane* family.

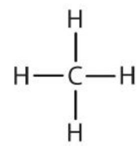
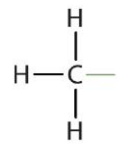
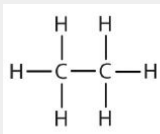
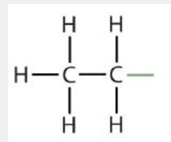
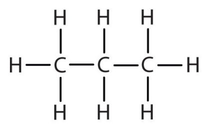
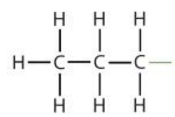
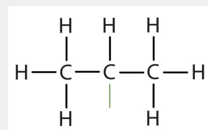
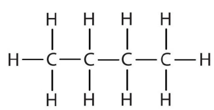
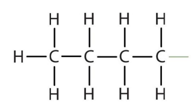
Table 12.6.1: Parent name for 1-10 carbons and Example Alkanes

Number of Carbons	Parent Chain (LCC) Name	Example Alkane Name	Example Condensed Structural Formula
1	*meth-*	methane	CH_4
2	*eth-*	ethane	CH_3CH_3
3	*prop-*	propane	$CH_3CH_2CH_3$
4	*but-*	butane	$CH_3CH_2CH_2CH_3$
5	*pent-*	pentane	$CH_3CH_2CH_2CH_2CH_3$
6	*hex-*	hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	*hept-*	heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	*oct-*	octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	*non-*	nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	*dec-*	decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Atoms or groups of atoms that branch off the parent chain are called **substituents**. When the substituent is a carbon or group of carbons, such as $–CH_3$ or $–CH_2CH_3$, it is called an **alkyl group**. Alkyl groups are alkanes that have had one hydrogen removed to allow for binding to a main chain carbon and are named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $–CH_3$ group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a **methyl group**. Removing a hydrogen from ethane, CH_3CH_3, gives $–CH_2CH_3$, or the **ethyl group**. The alkyl groups we will use most frequently are listed in Table 12.6.2 Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 12.6.2: Common Alkyl Groups

Parent Alkane	Alkyl Group	Condensed Structural Formula

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		CH_3–
ethane		ethyl		CH_3CH_2–
propane		propyl		$CH_3CH_2CH_2$–
		isopropyl		$(CH_3)_2CH$–
butane		butyl		$CH_3CH_2CH_2CH_2$–
		sec-butyl		
		isobutyl		
		tert-butyl (tBu)		

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 12.6.1).

Step 1: **Name the parent chain.** Find the longest continuous chain, (it may not always be the most obvious chain written in one line), and name according to the number of carbon atoms it contains. Add the suffix *-ane* to indicate that the molecule is an alkane. Use Table 12.6.1 as a reference to start, but it is a good idea to commit these to memory.

Step 2: **Number the carbon atoms in the parent chain,** giving carbons with any substituents attached the lowest number possible. These numbers are used to locate where substituents are attached to a main chain.

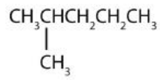
Step 3: **Name any substituents (including the location number).** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di*-, *tri*-, *tetra*-, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

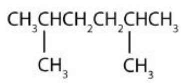
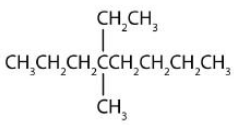
Step 4: **Write the name of the compound as a single word placing the substituent groups first (in alphabetical order), then the parent name, then the family name.** Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to practice it, not just memorize the rules. It's easier than it looks.

Example 12.6.1

Name each compound.

1. 

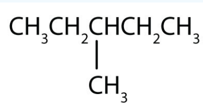
- 
- 

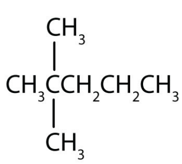
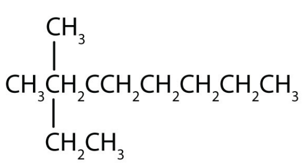
Solution

1. Step 1: The LCC has five carbon atoms, and so the parent compound name is pentane. Step 2: Number the carbons in the LCC from left to right. Step 3: There is a methyl group attached to carbon #2 of the pentane chain. Step 4: The name is 2-methylpentane.
2. Step 1: The LCC has six carbon atoms, so the parent compound is hexane. Step 2: Number the carbons in the LCC from left to right (or right to left, either way will be identical numbering). Step 3: There are two methyl groups attached to the second and fifth carbon atoms. Step 4: The name is 2,5-dimethylhexane.
3. Step 1: The LCC has eight carbon atoms, so the parent compound is octane. Step 2: Number the carbons in the LCC from left to right to give the *lower* number. Step 3: There are methyl and ethyl groups, both attached to the fourth carbon atom. Step 4: The correct name is thus 4-ethyl-4-methyloctane.

Exercise 12.6.1

Name each compound.

1. 

- 
- 

Example 12.6.2

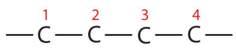
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

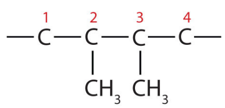
Solution

In drawing structures, always start with the parent chain.

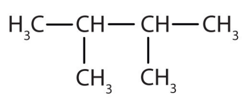
a. The parent chain is butane, indicating four carbon atoms in the LCC.



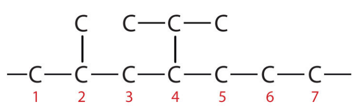
Then add the substituents at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (–CH_3) groups, one on the second carbon atom and one on the third.



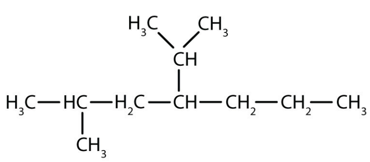
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds total.



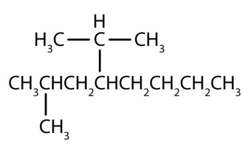
- Adding the substituents at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas (both are correct):



or



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 12.6.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

12.7: Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table 12.7.1 describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table 12.7.1: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.

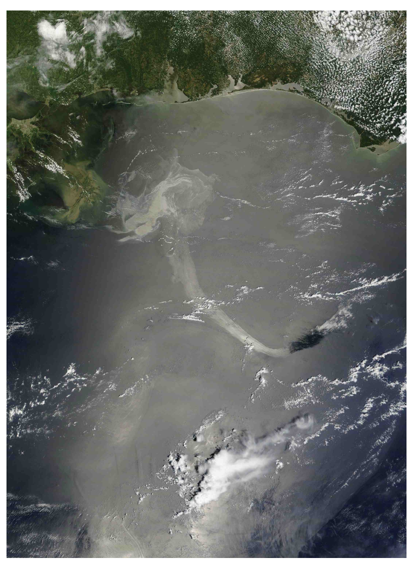


Figure 12.7.1: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, NASA.gov, Topics, Earth Features, Oil Spill(opens in new window) [www.nasa.gov].

Looking Closer: Gas Densities and Fire Hazards

Table 12.7.1 indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table 12.7.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called phospholipids and sphingolipids that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

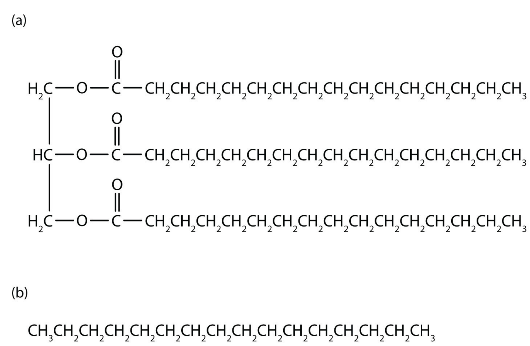


Figure 12.7.2: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

12.8: Reactions of Alkanes

Learning Objectives

- Understand the reactions of alkanes: combustion and halogenation.

Alkanes are relatively stable, nonpolar molecules, that will not react with acids, bases, or oxidizing or reducing reagents. Alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning “little affinity.”

However, heat or light can initiate the breaking of C–H or C–C single bonds in reactions called **combustion** and **halogenation**.

Combustion

Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the **combustion** reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{12.8.1}$$

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 straight- 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 12.8.1). You may recall that boiling point is a function of intermolecular interactions, which was discussed in an earlier chapter.

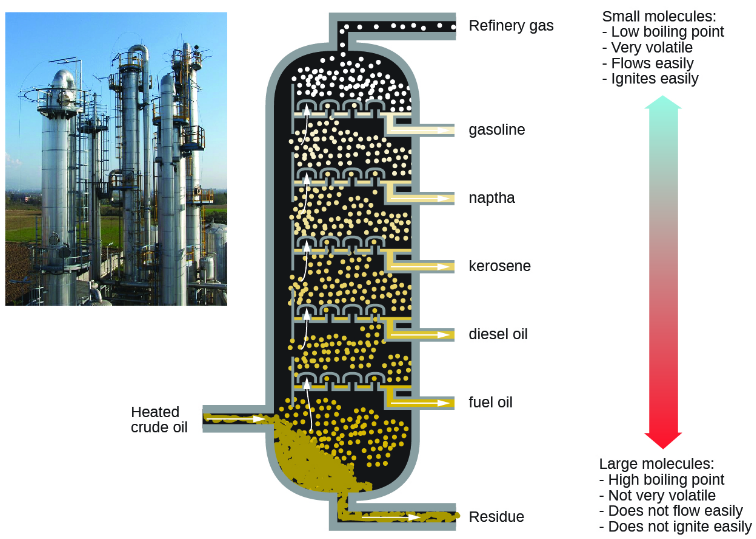


Figure 12.8.1:In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

If the reactants of combustion reactions are adequately mixed, and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and energy—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, other unwanted by-products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{12.8.2}$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Halogenation

In **halogenation** reactions, alkanes react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{12.8.3}$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table 12.8.1, along with some of their uses.

Table 12.8.1: Some Halogenated Hydrocarbons

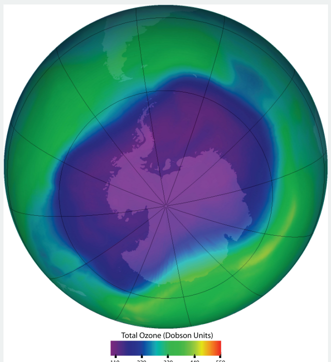
Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

Note To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

> **Note To Your Health: Chlorofluorocarbons and The Ozone Layer**
>
> Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table 12.8.2.
>
> Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O_3) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH_2FCF_3, which have no Cl or Br to form radicals, are one alternative. Another is hydrochlorofluorocarbons (HCFCs), such as $CHCl_2CF_3$. HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.
>
> 
>
>
> Figure 12.8.2: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, http://ozonewatch.gsfc.nasa.gov/daily.php?date=2006-09-24.

12.9: Cycloalkanes

Learning Objectives

- Identify the structures of cycloalkanes.

A **cyclic hydrocarbon** is a hydrocarbon in which the carbon chain joins to itself in a ring. A **cycloalkane** is a cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds and each carbon is bonded to two hydrogen atoms, they are saturated compounds. Cycloalkanes have the general formula C_nH_{2n}. The simplest of these cyclic hydrocarbons, cyclopropane, has the formula C_3H_6, which makes a three-carbon ring.

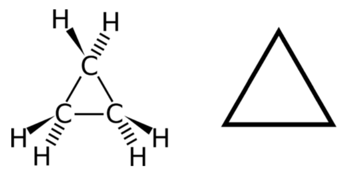
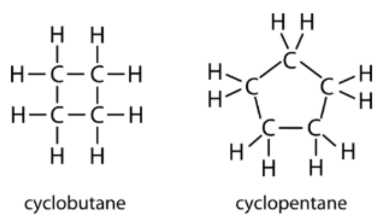


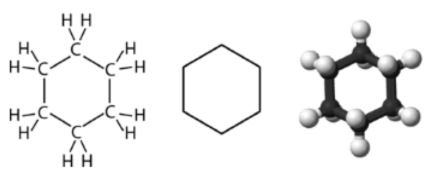
Figure 12.9.1: Cyclopropane is the simplest cycloalkane. Its highly strained geometry makes it rather unstable and highly reactive.

The structural formulas of cyclic hydrocarbons can be represented in multiple ways, two of which are shown above. Each atom can be shown as in the structure on the left from the figure above. A convenient shorthand is to omit the element symbols and only show the shape, as in the triangle on the right. Carbon atoms are understood to be the vertices of the triangle.

The carbon atoms in cycloalkanes have a bond angle of 109.5^o. However, an examination of the cyclopropane structure shows that the triangular structure results in a $C-C-C$ bond angle of 60°. This deviation from the ideal angle is called ring strain and makes cyclopropane a fairly unstable and reactive molecule. Ring strain is decreased for cyclobutane, with a bond angle of 90°, but is still significant. Cyclopentane has a bond angle of about 108^o. This minimal ring strain for cyclopentane makes it a more stable compound.



Cyclohexane is a six-carbon cycloalkane, shown below.



All three of the depictions of cyclohexane above are somewhat misleading, because the molecule is not planar. In order to reduce the ring strain and attain a bond angle of approximately 109.5^o, the molecule is actually puckered.

The ring structure in cycloalkanes also prevents rotation around the carbon–carbon bonds without breaking open the ring, thus they are more rigid and less flexible than acyclic alkanes. This property is called **restricted rotation**.

Note To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

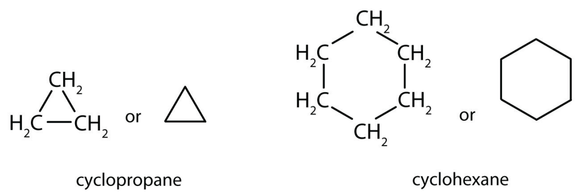
- **12.9: Cycloalkanes** by Anonymous is licensed CC BY-NC-SA 4.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.
- **25.6: Cyclic Hydrocarbons** by CK-12 Foundation is licensed CK-12. Original source: https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/.

12.10: Drawing and Naming Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example 12.10.1 interprets the name of a cycloalkane with a single substituent group.

Example 12.10.1

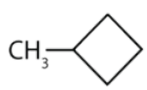
Draw the structure for each compound.

a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.

- The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



Exercise 12.10.1

Draw the structure for each compound.

a. cycloheptane
b. ethylcyclohexane