Chapter 11: Organic Chemistry. Saturated Hydrocarbons

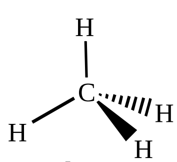
11.1 Organic and Inorganic Compounds

Historically, organic chemicals have been associated with living systems. This association originally derived from the belief that only living entities (i.e. plants and animals) could make organic chemicals. Indeed, until 1828 all attempts to prepare any organic chemical from exclusively inorganic reagents failed.

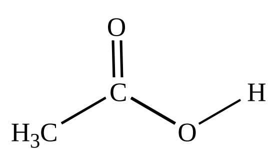
Before we go further, we need to define what an "organic" chemical is, as compared to an "inorganic" chemical. Unfortunately, there is no ironclad dividing line between these classes of chemicals. Nonetheless, we have a few guidelines that work for the vast majority of compounds. (You'll see few, if any, exceptions.)

1) Organic compounds always contain only *p*-block elements (Groups III-VII), at least one of which must be carbon.
2) Organic compounds almost always contain one or more C-H bonds.
3) Organic compounds are almost always molecules (as opposed to salts). Thus, all bonds are typically covalent in organic compounds.

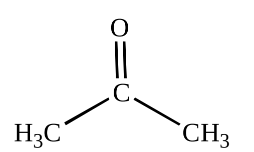
Methane (CH_4) is the prototypical organic molecule. Stick drawings of methane and some other organic molecules follow.



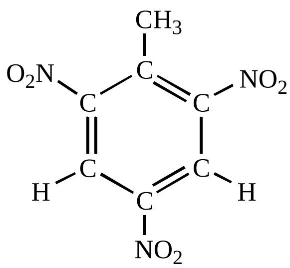
methane
(natural gas)



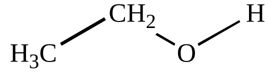
acetic acid
(vinegar)



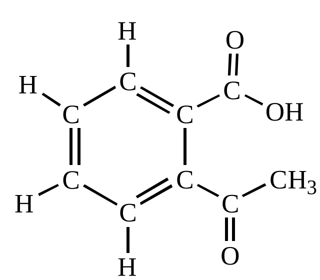
acetone
(nail polish remover)



2,4,6-trinitrotoluene
(TNT, explosive)



ethanol
(gasohol, beer)



2-acetylbenzoic acid
(acetylsalicylic acid,aspirin)

Although uncommon, there are organic compounds that don't contain a C-H bond. For example, CCl_4 is almost always classified as organic. There are two reasons for this. First, the series CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$ are all organic and CCl_4 is simply the final member of the series, and second, in nearly all respects it behaves chemically like the other compounds in this group. Likewise, although it is an ionic compound, $[(CH_3)_4N][CH_3CO_2]$ (tetramethylammonium acetate), would typically be considered an organic compound. (We will get to how to name organic compounds later.)

It is interesting that the very first "organic" compound prepared from exclusively inorganic reagents is now considered an inorganic compound. In 1828, Freidrich Wöhlers decomposed ammonium cyanate by boiling an aqueous solution of the chemical and obtained urea, a major constituent of urine.

$$NH_4NCO \xrightarrow[H_2O]{\Delta} H_2N\overset{\overset{\displaystyle O}{\|}}{C}NH_2$$

This experiment caused others to begin examining whether organic chemicals could generally be prepared from inorganic chemicals and it was quickly shown that there was nothing special about living systems in the synthesis of organic compounds.

Some general properties of organic compounds include:

1) Like all molecular compounds, organic molecules typically have low melting points (in fact many are liquids at room temperature). This is because London forces and dipole-dipole interactions are usually the forces acting between molecules (p. 161).
2) They tend to have low molecular polarities.
3) Poor water solubility. Few organic molecules are readily soluble in water. (Although the 3 oxygen containing molecules on p. 1 are quite water soluble. We'll see why later.)
4) Poor electrical conductivity. Few pure organic substances conduct electricity well. (There

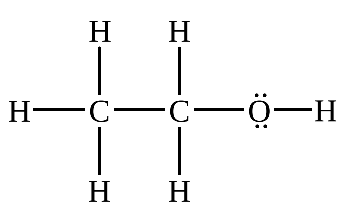
are no ions to help carry the charges.)

11.2 Some Structural Features of Organic Compounds

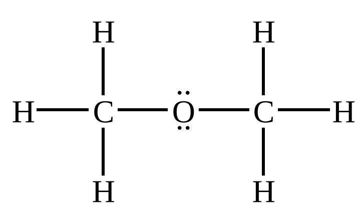
Communication is central to any field including chemistry. The structures you saw earlier have the advantage of conveying a large amount of information about the spatial arrangement of the atoms in a molecule. Each (except methane) contains some condensed structural information. The problem with these structures is that they take up a lot of space, which makes their use in normal text cumbersome. Furthermore, even when used to convey structural information, they take a good deal of effort to write out. In this section we will discuss a number of different ways to write out molecular formulas and see how they provide information to the reader.

Let's begin with methane, CH_4. You already know that hydrogen only forms 1 bond and that carbon tends to form 4 bonds. Thus the most reasonable structure is one in which you have 4 hydrogens, each connected to the carbon by a single bond. Furthermore, from Chapter 4.8, p. 105, you know that molecules with 4 bonds around a central atom with no lone pairs on the central atom are tetrahedral in shape. Because of this there is no good reason to draw a picture of methane, as opposed to simply writing out CH_4.

Ethanol is different however. If we simply write out C_2H_6O, it turns out there are <u>two</u> different structures that can drawn from this molecular formula:



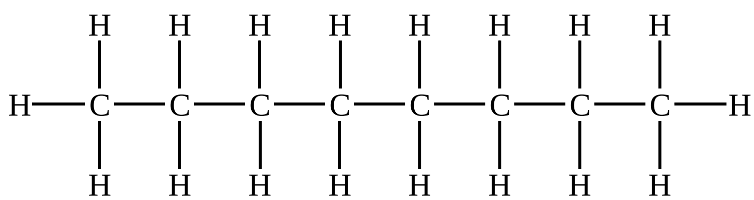
ethanol



dimethyl ether

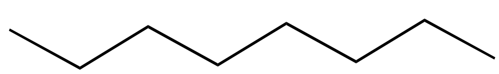
Thus a simple molecular formula isn't all that helpful in this situation. In fact, they are rarely useful in organic chemistry. We can use a slightly expanded molecular formula and still get a good deal of structural information, however. If we write ethanol as CH_3CH_2OH and dimethyl ether as CH_3OCH_3 we get the same information as in the pictures if we apply the rules for drawing Lewis structures to them and we do so using less space.

Another shortcut we can use involves repeating groups. Consider the molecule octane:

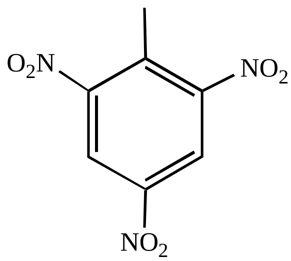


We could write this out as $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, but this too is cumbersome and is prone to either the writer or reader miscounting the number of CH_2 groups. These same types of problems exist when writing the formulae of cyclic molecules as text. We can shorten this long string to $CH_3(CH_2)_6CH_3$. Again, if we apply the rules of drawing Lewis structures, there is only one way to draw the structure of this molecule.

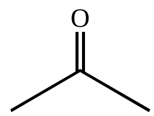
When drawing structural formulas, there is a different simplification organic chemists employ. We have already seen that organic compounds tend to have a lot of C-H bonds. Thus we simplify by assuming that carbon forms four bonds and that any bond to carbon that is not explicitly shown is a C-H bond. We simplify one step further by not bothering to actually draw in the letter C. In this case, octane becomes:



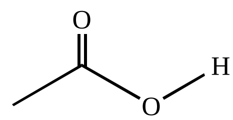
In this structure, each vertex is a carbon atom. The terminal carbons each have one C-C bond so they must have 3 C-H bonds as well. The middle carbons each have 2 C-C bonds, and so have 2 C-H bonds. Using this notation we can simplify some of the structures shown on the first page to



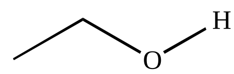
2,4,6-trinitrotoluene



acetone



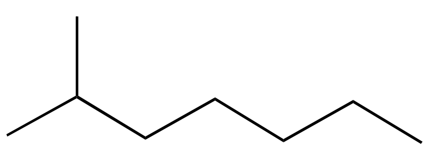
acetic acid



ethanol

Although you may find that it takes a little while to get used to drawing structures this way, you will find it makes your life much simpler in the long run.

We now turn to some odds-and-ends of discussing structures. First the octane molecule shown earlier is a <u>straight chain</u> structure. Don't take this as literal truth. In fact each carbon is tetrahedral, and if each CH_3 in octane were grasped and pulled apart, a structure much like the drawing above (for octane, with the zigzag line) would result. When C_xH_y groups appear off the "straight chain" a <u>branched chain</u> molecule results. Thus 2-methylheptane would look like:

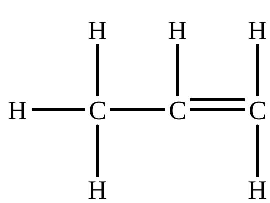


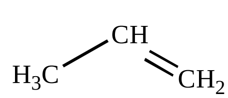
or
$$\begin{array}{l}\quad\;\; CH_3 \\ \quad\;\;\, | \\ CH_3CHCH_2CH_2CH_2CH_2CH_3\end{array}$$

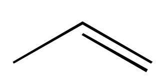
or
$$\begin{array}{l}\quad\;\; CH_3 \\ \quad\;\;\, | \\ CH_3CH(CH_2)_4CH_3\end{array}$$

or $(CH_3)_2CH(CH_2)_4CH_3$

Double and triple bonds are usually written explicitly. For example, propene can be written out in any of the following ways:







$CH_3CH{=}CH_2$

There exists free rotation about single bonds. In other words, if you had CH_3Cl and grasped the chlorine atom, the CH_3 group would spin like a propeller. What this means is that in a flask containing octane, all of the molecules aren't strung out like the picture, but rather they twist and coil and constantly reorient themselves. This will become important when we get to biochemistry.

11.3 Isomerism

Molecules possessing the same molecular formula but exhibiting different structures are called isomers. One of the reasons we use structural formulae is to show this explicitly. We have seen two examples of this so far. The first was shown explicitly, ethanol (CH_3CH_2OH) *vs*. dimethyl ether (CH_3OCH_3) (p. 3 of the notes). Can you figure out the other (answer next paragraph)?

There are actually several types of isomers but the only one we will be concerned with now are constitutional isomers. These are molecules that have the same numbers and types of atoms, but different atomic connectivities. We will see other types of isomers later. The other isomers are octane and 2-methylheptane (both are C_8H_{18}).

The properties of isomers may be very similar to one another (as is the case for octane & 2-methylheptane) or they may be quite different (see Table 11.1, p. 335 of your book for ethanol *vs*. dimethyl ether).

11.4 Functional Groups

The basic unit of organic chemistry is a molecule consisting of only carbon and hydrogen with only C-C and C-H single bonds. The variety found in organic chemicals largely derives from the replacement of hydrogen atoms with other groups, or the presence of C-C double and triple bonds. Collectively, these collections of atoms are called functional groups. A table (11.2) of important functional groups appears on p. 337 of your book. We will discuss most of these in Chapters 12 – 16 and all of them in the biochemistry chapters.

There are a few points worth mentioning here. Molecules possessing the same functional groups frequently exhibit similar properties. For example, amines are molecules possessing an $-NH_2$ group. Just like ammonia (NH_3) is water soluble, CH_3NH_2 (methyl amine) and $CH_3CH_2NH_2$ (ethyl amine) are water soluble. Both organic amines have unpleasant odors (actually worse than NH_3) and form basic solutions when dissolved in water just like ammonia.

Another feature of functional group chemistry is that the functional groups affect properties less as the molecules become larger. Let's look at the solubility of alcohols in water as the organic groups get larger:

Alcohol	Solubility (per 100 g of H_2O at 20 ºC)
CH_3OH	any amount
CH_3CH_2OH	any amount
$CH_3CH_2CH_2OH$	any amount
$CH_3CH_2CH_2CH_2OH$	7.9 g
$CH_3CH_2CH_2CH_2CH_2OH$	2.7 g
$CH_3CH_2CH_2CH_2CH_2CH_2OH$	0.6 g

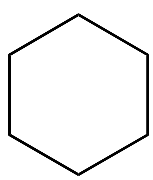
When a molecule contains more than one of the same functional group, the effect of the functional group on properties typically becomes more pronounced. Again let's look at a series of alcohols.

Compound	Boiling Point
CH_3CH_3	-88 ºC
CH_3CH_2OH	78 ºC
$HOCH_2CH_2OH$	197 ºC

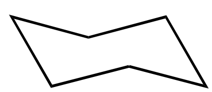
As we will see later in the semester, when a molecule contains two or more different functional groups the changes in physical properties may roughly average or unusual effects may occur.

11.5 Alkanes and Cycloalkanes

The simplest, most fundamental class of organic molecules is the alkanes. These are molecules consisting only of carbon and hydrogen with only C-H and C-C single bonds. Those alkanes that form rings are called cycloalkanes. Methane (CH_4) and ethane (CH_3CH_3) are alkanes. Cyclohexane (C_6H_{12}) is a cycloalkane. It can be represented by either of the two structures below. The second structure gives a more accurate picture of how the atoms are arranged in 3-dimensional space.



or



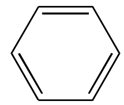
Alkanes are important as fuels (CH_4 = natural gas, C_3H_8 = propane (LPG), C_4H_{10} = butane (disposable cigarette lighters), C_5H_{12} – $C_{10}H_{22}$ = gasoline, higher order alkanes form kerosene and airplane fuel (as well as candle wax), and lubricating oils.

Alkanes and cycloalkanes are saturated hydrocarbons. By saturated we mean that each carbon atom is bound to the maximum possible number of hydrogen atoms. That is, there are no double or triple bonds in the molecule. Unsaturated hydrocarbons contain one or more double and/or triple bonds between two carbon atoms. In general, an unsaturated molecule contains one or more double and/or triple bonds between any atoms of two elements.

You may be familiar with these terms for dietary reasons. Fats are sometimes categorized as saturated, monounsaturated, or polyunsaturated. Saturated fats contain no C-C double bonds, monounsaturated fats contain 1, and polyunsaturated fats contain 2 or more C-C double bonds. Hydrogenated fats are mono- and polyunsaturated fats in which some or all of the double bonds have had hydrogen added. We'll see how this is done in the next chapter (p. 370). This is typically done for two reasons. First, double bonds are sites of reactivity. Reaction with oxygen and other species cause fats to become rancid. Thus, hydrogenating sites of unsaturation increases shelf life. The second reason is that saturated fats are usually solids, which makes them easier to store and transport. Sites of unsaturation raise melting points and most mono- and polyunsaturated fats are liquids.

Unfortunately, what is good for those who make and use fats is not good for those of us who eat them. The same sites of reactivity that lead to spoilage are sites our bodies use to get them out of the bloodstream. Also liquid fats are better for us because they won't form deposits. When enough saturated fat gets into our bloodstream (and it isn't all that much), it will deposit in our arteries and veins because it is not water soluble. Since there is no site of reactivity on it, once deposited it is difficult to remove saturated fats.

Alkanes and cycloalkanes are part of the aliphatic class of molecules. These are molecules that do not contain a benzene ring (see below). Aliphatic hydrocarbons may include double and triple bonds. Molecules containing a benzene ring (a 6 member ring with 3 C-C double bonds) are called aromatic. A stick diagram of benzene is shown below.



All hydrocarbons of any type are non-polar. In general, they mix well with one another and poorly with polar substances. (Aromatic hydrocarbons have a somewhat greater ability to mix with polar substances than do similar aliphatic compounds.)

11.6 Naming the Alkanes and Cycloalkanes

Your book has organized a set of rules nicely and all I'm going to do here is summarize them. These rules have been established by the International Union of Pure and Applied Chemistry (IUPAC).

1) All alkanes end in "–ane."
2) Pick out the longest continuous chain of carbon atoms in the molecule. Anything attached to that chain, including other hydrocarbon groups, is a substituent group. The alkane chain is named according to the following sequence:

   1 C = methane

   2 C = ethane

   3 C = propane

   4 C = butane

   all other compounds use Greek prefixes to indicated chain length

5 C = pentane	8 C = octane
6 C = hexane	9 C = nonane
7 C = heptane	10 C = decane

3) If the alkane has substituents, begin numbering choosing the side of the alkane with a

substituent closest to the end.

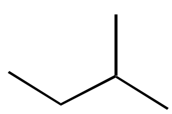
4) Hydrocarbon substituents begin with the same letters as the chains, but end in "–yl." (e.g. CH_3– = methyl).

5) If there is more than one group attached, list them in alphabetical order.

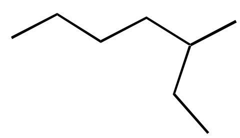
6) When two *identical* numbering schemes exist, the substituent coming first alphabetically should be assigned the lower number.

7) With cycloalkanes, no number is needed if there is only one substituent. If there are two or more substituents bound to the ring, the one which comes first alphabetically is assigned the lower number.

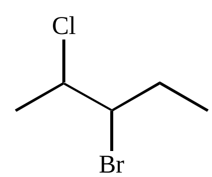
Examples: Name the following molecules:



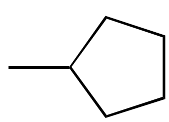
2-methylbutane



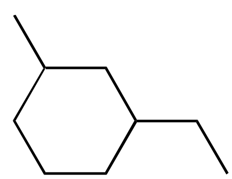
3-methylheptane



3-bromo-2-chloropentane

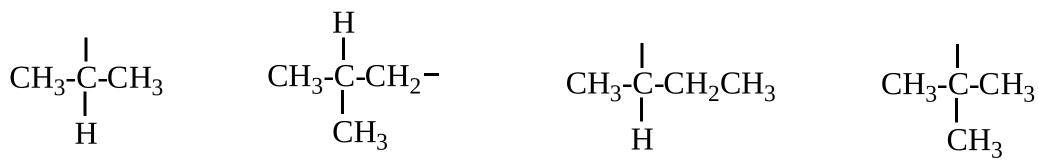


methylcyclopentane



1-ethyl-3-methylcyclohexane

There are also some common (or trivial) names used for organic chemicals. One type is the old systematic method. You won't encounter these names often in this course and from time to time you will do so outside of it. For example, rubbing alcohol is isopropyl alcohol using the old naming system and 2-propanol using the IUPAC method. The most important saturated hydrocarbon side chains with common names are:

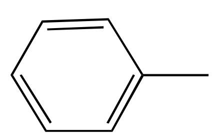


isopropyl isobutyl *sec*-butyl *tert*-butyl

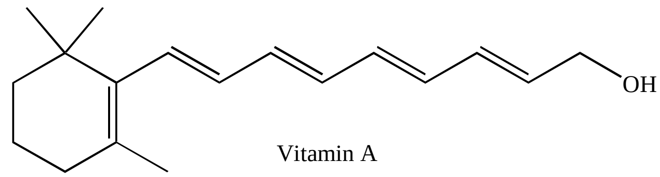
From what you've learned so far, you might have been able to guess that isopropyl alcohol is a molecule with an –OH group attached to propane. But where? The IUPAC name is 2-propanol so it is attached to the second (or middle) carbon. In general the prefix "iso" yields a group with the formula $(CH_3)_2CH(CH_2)_n$-, where n is a positive integer. Thus isopropyl has n = 0 and isobutyl has n = 1.

A second type is the unique name. Much like the systematic name for water would be dihydrogen oxide, but no one ever uses it, such names exist in organic chemistry too. (Indeed, if you look at the alkane prefixes beginning at 5 the prefixes are based on numbers, but 1 – 4 are based on unique names that later became part of the old and new systems.) An example from a later chapter will do nicely here.

Consider the molecule: $C_6H_5CH_3$. From its structure you might guess its name was either



methyl benzene or (as you'll learn later) phenyl methane. In reality, it is never called either of these names. It is always called toluene (airplane glue). As we progress through this course, we will encounter a number of molecules that go by common, rather than systematic names. In nearly all cases you will see that the systematic name is large and cumbersome, while the common name is short and frequently easy to remember (Vitamin A *vs*. 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8-nonatetraen-1-ol).


Vitamin A

11.7 Chemical Properties of Alkanes

In general alkanes are very non-reactive. They will also usually have the lowest melting and boiling points of any molecule with the same number of carbon atoms (replacing a hydrogen atom with any other group will increase molecular polarity and cause greater molecular attraction). They readily burn (one of the few reactions they engage in with gusto).

$$CH_{4\,(g)} + 3\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{\,(\ell)}$$

In the presence of high energy light and either chlorine or bromine, substitution of a hydrogen atom by a halogen atom can be effected. This reaction can be repeated until all hydrogen atoms have been replaced.

$$CH_{4\,(g)} + Cl_{2\,(g)} \xrightarrow{h\nu} CH_3Cl_{(g)} + HCl_{(g)}$$