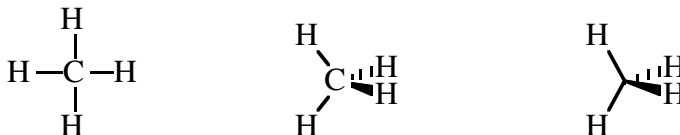**Simplest Organic Molecules**: The carbon atoms in organic molecules covalently bind to each other as well as to atoms of other elements. The most common of these other atoms is hydrogen. Organic compounds that contain ONLY carbon and hydrogen are called hydrocarbons. The simplest one is methane (aka "swamp gas"), CH_4, which has the structure:

All three of these represent the same molecule. The first one is the Lewis structure. It clearly shows that the central carbon atom is bound to four hydrogen atoms. The second one shows the relative spatial arrangements of the atoms. The third one is the same as the second except that the carbon atom is not explicitly written. Since organic compounds can contain many carbon atoms, chemists use the short hand notation of omitting carbon atoms. As we will see, there are usually a lot of hydrogen atoms as well, so these are often omitted as well. The implication, however, is that each carbon has a total of 4 covalent bonds. All other atoms (referred to as "hetero-atoms", meaning different that carbon [but excluding hydrogen]) are always explicitly included.

Types of Hydrocarbons: Two carbon atoms can form up to three covalent bonds to each other. Therefore, when forming chains of bound carbon atoms, we can come across multiply bound carbon atoms. To distinguish between these hydrocarbons, we use the following names: **Saturated** and **Unsaturated**. The saturated hydrocarbons, also called **alkanes**, contain only singly bonded carbon atoms. The unsaturated hydrocarbons have multiple bonds.

We can further distinguish between the unsaturated hydrocarbons:
   • **Alkenes** - hydrocarbons containing one of more double bonds (no triple bonds).
   • **Alkynes** - hydrocarbons containing at least one triple bond.
   • **Aromatics** - ringed hydrocarbons containing double bonds in a specific order.

The alkanes, alkenes, and alkynes together form the **aliphatic** group. This name is somewhat archaic, but is still used. Other archaic names are: **paraffins** = alkanes, **vinyls** and **olefins** = alkenes.

Alkanes: Names and Isomers - Instead of just delving into the plethora of organic molecules and their reactions, we need to establish a "language". That is, we need to be able to describe, in words, the structures of the molecules of interest. There are two schools of thought on this. One says, give each molecule a name, and we will learn the names. For example,

is called norbornane. It is just a name.

The second school of thought, championed by the International Union of Pure and Applied Chemists (IUPAC), is more systematic. In this system of nomenclature, there is a basis name describing a chain length or general shape, and everything else is based on these. For example, the structure above would be [2,2,1]bicycloheptane. Right now, both names are equally obscure, but, as time goes on, you will see how the second name has more "meaning".

There are a few names that remain "meaningless", but are so often used that they have been accepted. For example, benzene does not really fit the systematic naming, but it is almost exclusively used to refer to the structure:
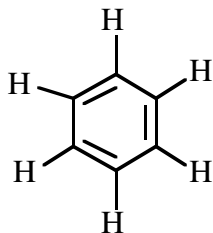

Thus, there are several of these you will learn (as we get to them), but we will focus on the IUPAC naming instead.

Straight Chain Alkanes - The IUPAC naming system starts by finding the longest straight chain of carbons, and using that as the "basis" or parent name. Therefore, we will first "define" the names of the first 11 straight chain alkanes. The first, methane, CH_4, has already been mentioned. The next ten are actually a bit more interesting, because the root names will be used in naming the alkenes and alkynes. They are:

C_2H_6	Ethane	C_7H_{16}	Heptane
C_3H_8	Propane	C_8H_{18}	Octane
C_4H_{10}	Butane	C_9H_{20}	Nonane
C_5H_{12}	Pentane	$C_{10}H_{22}$	Decane
C_6H_{14}	Hexane	$C_{11}H_{24}$	Unedecane

The first thing to notice is that all the names listed above end with "ane". This indicates that they are all alkanes. The second thing to notice is that starting from 5, the names are based on the Greek words for the number. The names for the 1, 2, 3, and 4 are archaic, but are so commonly used that no one wants to change them (except for the hard-core IUPAC people, but they are a definite minority). You will NEED TO KNOW THESE!!!

Branched Chain Alkanes: Once we have the basis names clear, we can now describe how to name the constitutional isomers for a given molecular formulae. Using butane as an example, we can draw the formula C_4H_{10} in two distinct ways:
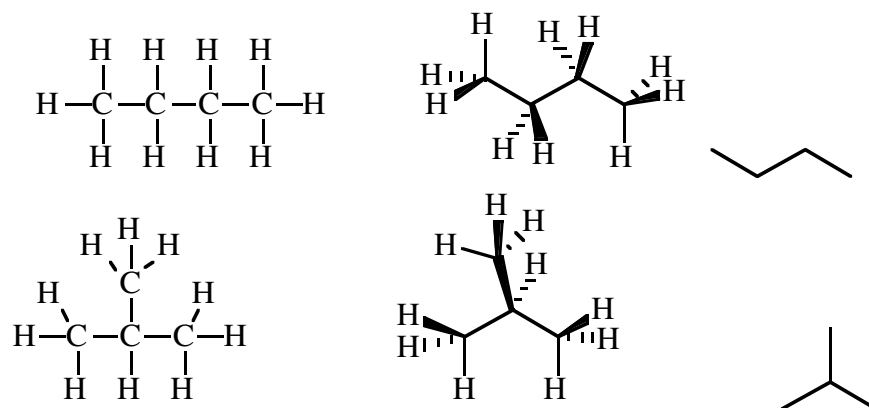
For review note that the Lewis structures clearly show the connectivity, while the <u>wire frame</u> structures (i.e. the right-most drawings) are the cleanest looking. Based on the formula, C_4H_{10}, there would be no way for us to know which structure is the correct one.

To avoid this, most organic chemists write their formulae in a slightly different way. They treat the CH_3 and CH_2 groupings as unique entities. Thus, the straight butane would have the formula: $CH_3CH_2CH_2CH_3$. The branched butane would be $CH_3CH(CH_3)_2$. Of course, this helps on paper, but when speaking about them, there is no easy way to say those two formulae. This is where we will begin our description of the IUPAC naming.

The straight chain molecule is butane. The second molecule has as its longest chain a three membered molecule, i.e. the base name is propane (shown in the wire frame below with dark lines). The "side chain" or substituent is a one-carbon entity, like methane. However, to describe that it is a side chain, not the main chain, we call it a **methyl group**. In fact, all alkanes that exist as side chains get they "yl" suffix, replacing the "ane" (i.e. they are called <u>alkyl</u> side chains).
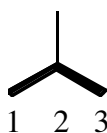

The next step is to decide where on the main chain of the molecule is the methyl group. On the diagram above, numbers have been assigned to the main chain carbons. The side chain methyl group is attached to the second (number 2) carbon. Therefore, the IUPAC name for this molecule is: **2-methylpropane**.

Larger Molecules - We have just shown that C_4H_{10} can represent two different molecules. As the number of carbons increases, so do the number of possible molecules. This is because there are more positions for side chains, as well as the possibility for multiple side chains and longer side chains. For example, the following three wire frame representations all correspond to C_5H_{12}:

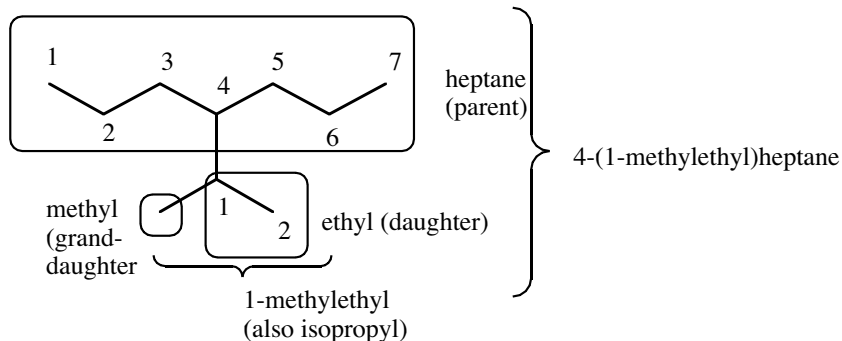pentane   2-methylbutane   2,2-dimethylpropane
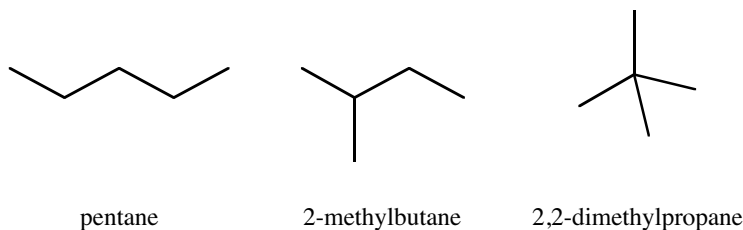
Notice, the last structure is a propane chain with two methyl side chains, both on the second carbon. The IUPAC name expresses this by first showing us where the substituents are (2,2), then telling us how many there are (di), and finally, what they are (methyl). For C_6H_{14}, there are even more possibilities:
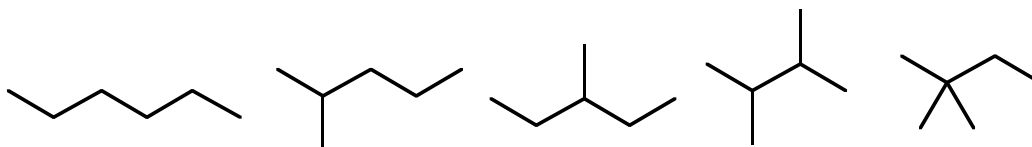
As the number of carbons increase, the possibilities become astronomical! That is why there are so many more organic molecules than inorganic ones. A group of molecules that have the same molecular formula, but different molecular structures is called a collection of constitutional **isomers**.

When naming molecules with long and complicated side chains, the rules of nomenclature become a little trickier. Recently, the IUPAC has made a few changes to the naming system. The molecule's base name is the longest straight chain (but, as we will see later, this may be superceded by something called a **priority group**). The side (daughter) chains are counted from the point (carbon) at which they connect to the main (parent) chain. These side chains can themselves have side chains (grand-daughter chains?), and must be numbered according to where they connect to the side chain. An example of this is given below:

1   3   5   7   heptane
       4   (parent)
2   6
                                        4-(1-methylethyl)heptane
methyl   1
(grand-   2   ethyl (daughter)
daughter
                1-methylethyl
                (also isopropyl)

Note that the side chains of the daughter are put into a parenthesis with the daughter chain to imply that the parenthetical group, as a whole, is a side chain of the parent group. The number prior to the parenthesis indicates that the entire side chain occurs at the fourth carbon of the parent chain.

Conformations of Cycloalkanes: Because carbons bind readily to one another, it is not too surprising to find out that the chains of carbons can come full circle. Of course, there has to be a minimum number of carbons (namely three) to accomplish this. These cyclic alkanes are given names corresponding to the straight-chain counterparts, with the prefix **cyclo** placed in front of the name. Thus, we have:

etc.
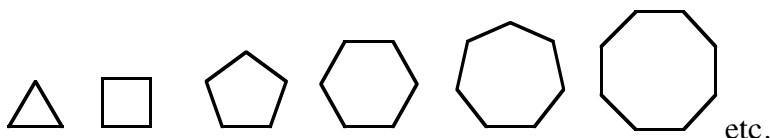
We know that the angle between the two adjacent bonds in a tetrahedral carbon is about 109.5˚. And, we know that rotation about the single bond is easy. The question that arises is as follows: What do the cycloalkanes really look like? Clearly, drawing them like we did above does not comply with the 109.5˚ bond angle! How can we represent them (on paper) so that the actual angles are visible?

The simplest, and most important, ring (i.e. cycloalkane) to study turns out to be the six membered cyclohexane ring. The three membered (cyclopropane) and four membered (cyclobutane) are unusual, and we will talk about them later.

If we were to "build" a cyclohexane molecule using tetrahedral carbon atoms, we could make three distinctly shaped molecules, all with the correct bond angles. They could be drawn as follows:

"chair"   "boat"   "twist"
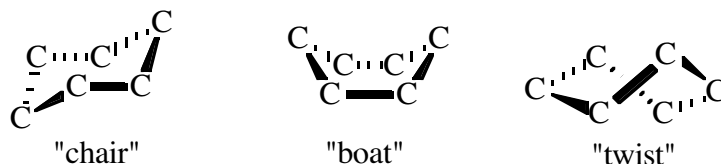
The carbon atoms were included for clarity. The three structures are, of course, **conformational isomers**. The cyclohexane molecule can switch between these structures simply by partial rotations around the bonds. The three names given below the drawings are commonly used to refer to the specific shape we are referring to.

The wire frame versions of these three conformers are:
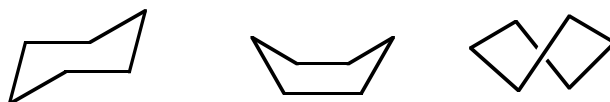
The most common form happens to be the "chair" conformation, and we will talk about why that is in the next section. However, we should draw a few of the other cycloalkanes as well:
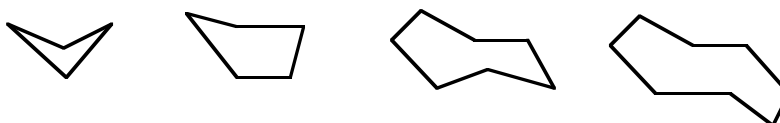
Generally speaking, we do not have to worry about the conformation of these (non-6-membered) rings. In fact, more often than not, we represent them using the normal, geometric pictures at the very beginning of this discussion.

Ring Strain and Steric Hindrance: Earlier we mentioned that cyclopropane and cyclobutane were "unusual". What this meant is that there is no way to form these rings while preserving the 109.5° angles. In fact, cyclopropane MUST have 60° angles! This deviation from 109.5° is referred to as **ring strain**. You can imagine that the bonds are being forced closer to each other than they would normally be, causing a strained system. These rings (especially cyclobutane) are very reactive due to their <u>instability</u> caused by this strain.

Cyclopropane would seem to be even more strained since the bonds are even closer together than in cyclobutane. However, cyclopropane is one of these "exceptions" that we love talking about in chemistry. Without going into too much detail, the bonding between the atoms in cyclopropane is different than any other carbon-containing ring. We will not spend any more time talking about this.

Of all the ring structures, cyclohexane has the least ring strain. This might not seem to make sense, especially compared to the larger rings. However, there is another factor that goes into the determination of ring strain besides the bond angles. This factor is called **steric hindrance**. This is the same effect that makes methane a tetrahedron, namely:

> <u>Atoms in the same molecule that are NOT bound to each other tend to stay way from each other</u>.

This is easily visualized by comparing the "chair" and "boat" conformations of cyclohexane. To help in the illustration, we will include four hydrogen atoms. That being said, here are the two structures:

Nomenclature of Alkyl Halides - When faced with task of naming an alkyl halide IUPAC came up with the following rule:
- Find the name of the non-halogenated hydrocarbon.
- Determine the numerical position of the carbon or carbons that are halogenated, and with which halogens are present.
- Name the molecule by stating the position, amount, and type of halogen (using the name **halo**), along with the rest of the alkane's name.

So, for the examples above, assuming X=Cl, we have CH_3CH_2Cl = chloroethane, and $CH_3CH_2CCl(CH_3)_2$ = 2-chloro-2methylbutane.

Alkenes and Alkynes: Until now, we have only focused on organic molecules containing only single bonds between the carbons. Once we allow for double and triple bonds, the number of possible structures increases dramatically. We will have to learn how to name these new structures, how to make them, and, of course, what can be done to them.

IUPAC Nomenclature - The names of these molecules, just like the alkanes, are governed by a set of rules put forth by the IUPAC. And, as implied earlier, the names of the longest straight chains (or rings) will have the same "root" name as the alkane names, with the final "ane" being replaced by "ene", "yne", or some combination, depending on the structure. Note, carbon-carbon double bonds take precedence over triple bonds.

The general rules are as follows:
1. Find the longest chain containing the multiple bonds.
2. Start numbering the carbons from the end closest to the first double bond. If there are two of the same multiple bonds equally spaced from the ends, start counting from the side closest to the first branch.
3. Determine the kinds of branches and where they are (i.e. which carbon in the chain).
4. Name the molecule, specifying what kind and where the multiple bond(s) is (are), and how many of them are present. (Generally, the position label is placed before the root name, except when there are both double and triple bonds present, in which case the numbers appear after the root name).

The easiest way to understand this is to do an example. To make it really tricky, let's use:

$$CH_3$$
$$H_2C=CHC=CHCH_2C\equiv CH$$
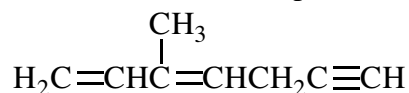
This has 2 double bonds and one triple bond. The longest chain has seven (hepta-) carbon atoms. Thus, we need to start numbering from the side closest to the first double bond:

$$CH_3$$
$$H_2C=CHC=CHCH_2C\equiv CH$$
$$1234567$$
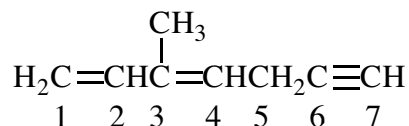
Next, we find what the side chain is and where it is located. In this case it is a methyl group at point number 3. Now, all that is left is the naming:

$$3\text{-methyl-hepta-6-yne-1,3-diene}$$

If the side chains have multiple bonds as well, they are named in the same way, but the "ene" or "yne" is replaced by "enyl" or "ynyl" (i.e. they are alkenyl or alkynyl groups). Of course, the side chain should NOT be multiply bound to the main chain.

Cis-Trans Isomers: Last week we discussed geometric isomers. Again using 2-butene as an example:

$$CH_3CH=CHCH_3$$
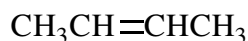
If we wanted to draw this using the wire structures, we would have to choose between:

and
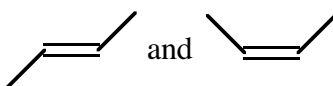
To distinguish between them, we refer to the one on the left as ***trans***-2-butene, and the one on the right as ***cis***-2-butene. "Trans" refers to the fact that the (largest) carbon containing groups connected to the double bond are "diametrically opposed". "Cis" means they are both on the same side. Compare this to 2-methylpropene.

It should be pointed out that *cis* and *trans* are not IUPAC names. However, most people do use these designations. The IUPAC names are E (instead of trans) and Z (instead of cis) from German words that mean "opposite" and "together", respectively. More specific rules exist to define these labels.

In naming molecules with double bonds, if there are different isomers possible, each double must be described as either *cis* or *trans*. For example, in the molecule below, the double bond at carbon four can either be *cis* or *trans*, whereas the one at carbon 6 cannot. Therefore, the structure on the left is *trans*-5-methyl-hepta-4,6-diene-1-yne, and the one on the right is the *cis* isomer.


and
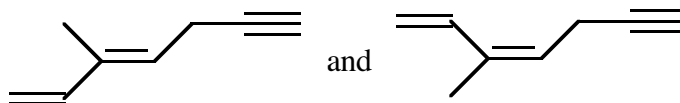
Aromaticity: Another curious class of conjugated polyenes are cyclic polyenes. In particular, if we look at 1,3,5-cyclohexatriene we would see:

or
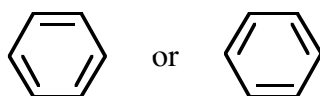
The resonance stabilization of this molecule is incredible. In fact, the common reactions of alkenes are virtually impossible to do on this molecule. We describe this particular brand of stability as **aromaticity**, and the general class of compounds as **arenes** (or **aromatic compounds**). This molecule has been known for many years, and is given the name **benzene**. Kekulé determined the structure of the molecule, and the two structures above are referred to as the **Kekulé structures**. To show that both are reasonable structures, and to demonstrate that there is resonance stability, we often draw benzene in the form:
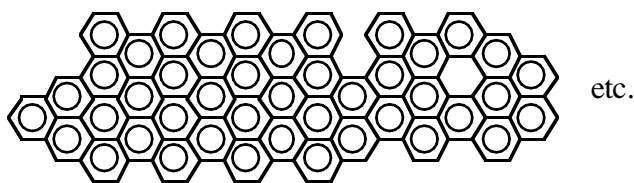

Besides benzene, there are compounds composed of fused benzene rings, for example naphthalene (old fashioned moth balls):

and graphite:

etc.
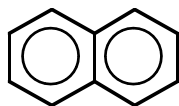
Generally, the names of these molecules use their common names as the base name, and then follow IUPAC rules as usual. Molecules that have a benzene ring as a side chain of a long alkane (or several rings on a shorter chain), tend to be named after the straight chain. The benzene group is called either a **phenyl** group. For some reason the name **benzyl** is used to describe a phenyl with a **methylene**, CH_2, group on it.

Ortho, Meta, Para: Certain well known compounds contain benzene rings. Certain ones are so common that they are known by "common" names. For instance, the molecule
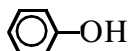
made by putting an -OH group on a benzene ring, is called **phenol**. These compounds can have other things coming off the ring, and the numbering is started from the main side chain (in this case the -OH). However, for commonly named compounds that have only one extra side chain, the prefixes "ortho", "meta", and "para" are used in lieu of the numbers. The positions, using phenol as the example, are: