A review of some chemical concepts

If you took general chemistry you should know the fundamental physical concepts behind chemistry. Organic chemistry is still chemistry and we can apply the same fundamental ideas. This section will review some of these fundamentals that we will need to introduce organic chemistry. Mostly this is just to get your brain back in gear and refresh your memory with some essential vocabulary. After this introduction we will expand into concepts that are more specific to organic chemistry, items that you may have just touched upon in your previous chemical training.

Molecules, atoms, bonds

Molecules are made up of atoms of elements connect by bonds. Lets start with the idea of an atom. Every atom has a nucleus, which is surrounded by electrons. The number of protons in the nucleus of an atom determines which element it is. Change the number of protons and you have a different element. So an element is the fundamental unit in chemistry, since it cannot be broken down any further by chemical means.

Stepping outside of the nucleus we have electrons. Electrons arrange themselves in distinctive energy levels (termed shells, with shells consisting of orbitals). Using carbon (atomic number 6) as an example we seen that its electron configuration would be:

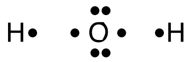
$$1s^2\ 2s^2\ 2p^2$$

A carbon atom has a total of six electrons (neutral charge is more stable) with four in its outer shell. These are the highest energy in the atom and are the most likely to interact with electrons from other atoms. These are termed valence electrons (making carbon tetravalent). You may remember that the 2p orbital can hold six electrons. Add two from the 2s and there is the potential to hold 8 electrons in the shell. If an atom has eight electrons in its outer shell it is said to have an octet, giving the atom additional stability. Nobel gasses (He, Ne, Ar, etc.) have this configuration and they are some of the least reactive elements known.

The carbon atom needs four electrons to achieve an octet. These electrons are not just going to jump in to the shell. This is where the idea of covalent bonding comes into play. Atoms with an incomplete octet can share their electrons with other atoms forming a bond. In reality the shared electrons spend their time between the atoms involved in the bond. This implies that each carbon atom has the ability (and desire) to form 4 covalent bonds. Each bond contributes another electron to the 2 shell of the carbon atom, giving a total of 8 for a full octet. Carbon is somewhat unique in that it readily forms bonds with other carbon atoms.

Lewis Structures

A common way to depict atoms and bonding is with Lewis Structures. In this system electrons are depicted as dots and bonds as two dots on top of each other or as a line. Let's consider water;



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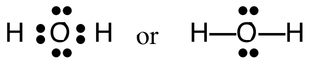

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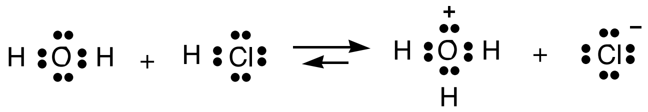


3

In **1** we see two hydrogen atoms and 1 oxygen atom depicted with their available valence electrons. Where did these numbers of electrons come from? In bonding these atoms together one obtains molecular water (**2**). Note that each of the atoms valence shell is not filled. Oxygen has an octet and hydrogen as 2 (filling the 1s orbital). Remember that electrons in a covalent bond are shared between atoms. A side point for naming structure depiction methods, when bonds are depicted as dots it is usually called a "Lewis Dot Structure". With bonds depicted as lines it is simply called a "Lewis Structure".

When considering a reaction as in **3,** one can use Lewis Structures to track electrons (essential when working with reaction equations). In the end all atoms must have octets (except of course for hydrogen which can not have more than two total electrons). Water is depicted as in **2** and hydrochloric acid (HCl) has its proper structure. In the reaction a hydrogen atom is transferred from the acid to the water, yielding hydronium (H_3O^+) and chloride ions. Note that in the ions all atoms have there required octets.

Why do the chlorine and oxygen atoms have charges? As an example, oxygen normally has 8 electrons (a neutral state). Let's count how many electrons the oxygen atom "owns" remembering that it contributes or gains one electron from each bone. We count 5 valence electrons (two nonbonded and one from each of the bonds with hydrogen) plus the two non-valence electrons, giving a total of 7. Seven is one less than 8, so the hydronium ion is considered to have a 1+ charge. For a similar reason the chloride ion has a 1– charge, one extra electron. When this type of methodology is used for find charge the amount is know as formal charge.

Connections and depictions

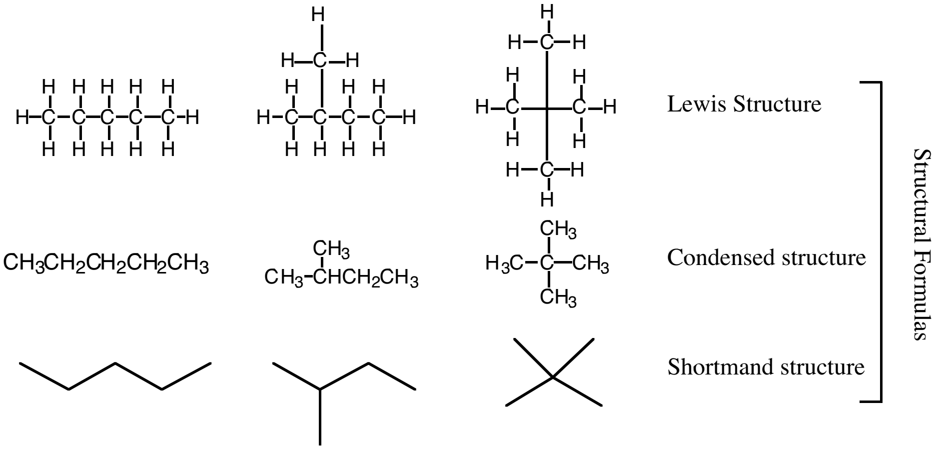
Saturated compounds (single bonds)

In general chemistry you learned about formulas, elemental symbols and numbers showing the relative (empirical formula) or absolute (molecular formula) numbers of those atoms. Sometimes these formulas are enough to tell what the actual connections between the atoms are. In organic chemistry this is seldom the case. Knowing that a carbon atom can easily bond with another carbon atom, you can see that we can have chains of many carbon atoms. Consider the molecular formula C_5H_{12}. If carbon atoms form bonds with other carbon and hydrogen atoms and hydrogen only bonds with carbon we have the following possibilities:

C_5C_{12} Molecular Formula

$CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2(CH_3)CH_2CH_3$ $CH_3C(CH_3)_2CH_3$ Condensed Formula

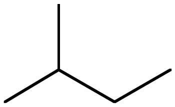
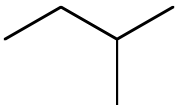
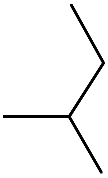
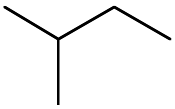
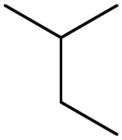
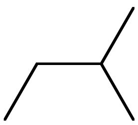
$CH_3(CH_2)_3CH_3$



In this case you can see that the molecular formula does not provide enough information to find the structure of the molecule. We have to write out how the different atoms are bonded together. The second row shows one type of short hand, sometimes called a condensed formula. The third depicts Lewis structures. In the forth a condensed structure is shown (note the similarities to the Lewis structures). The fifth row depicts a common short hand used in organic chemistry. In this style unlabeled junctions of lines are carbon atoms. Where there should be a bond to complete an octet on a carbon atom, but none is draw, it is assumed that this is bond with a hydrogen atom. As group the last three rows will also sometimes be called structural formulas. Until you have some practice and get the feel for drawing structures you should probably stick to Lewis and condensed structures.

As a group these compounds are called **constitutional isomers** — compounds having the same molecular formula but have different connection between their atoms (a different structure). Not only do these compound have different structure they have different physical properties as well (such as boiling and melting point).

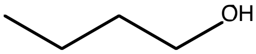
Are the following constitutional isomers?

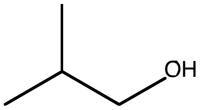







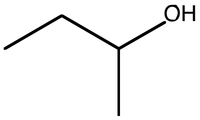
Of course not, they are just different ways of drawing the same molecule. In organic chemistry you have to be careful when looking at structures. It is important to focus on the bond connections, how the atoms are connected to each other. As we discuss naming of structures you will see how these problems are dealt with.

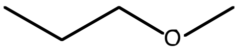
Here is another example with an oxygen atom thrown in the mix:

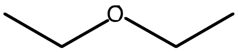
$C_4H_{10}O$

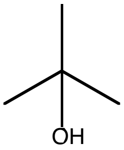










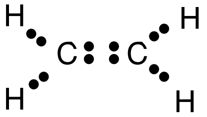


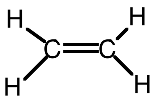
Again, all of these compounds are constitutional isomers with the molecular formula: $C_4H_{10}O$.

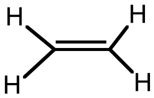
All of the compounds that we have mentioned in this section contain just single bonds between carbon atoms and other atoms (sometimes termed hetero atoms, except for hydrogen). The molecular formulas of compounds follow a pattern. For instance C_5H_{12} and $C_4H_{10}O$ follow the pattern C_nH_{2n+2}. When molecular formulas follow this pattern they usually only contain carbons and hydrogen (thus the term hydrocarbon). It tells us that the compounds contain only single bonds with no rings. These compounds are "saturated" with hydrogen, the carbons are bonded to all of the hydrogen atoms that they possibly can be. We will see other types of compounds in the next sections.

Unsaturated compounds (multiple bonds)

In the previous section we discussed saturated hydrocarbons. Here we will see that carbon atoms are not limited to forming just single bonds. To the carbon atom a bond is a bond, just one step closer to forming the desired octet. Consider a compound with the molecular formula C_2H_4. There is only one structure that this molecular formula can depict.



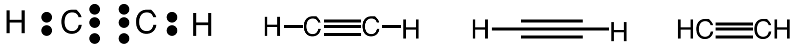




$H_2C{=}CH_2$

All of these structures represent the same compound. The same drawing standards that were used in the previous section apply here. Each atom has a filled valence shell. Note that the first structure is a Lewis dot structure. The double bond here is depicted as four dots, which in the following structures are just depicted as two lines.

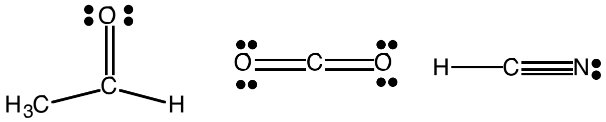
Lets add another bond between the carbons. Consider the formula: C_2H_2. Again there is really only one structure that matches this formula.



Again the same logic applies. This time we have a triple bond.

Reflecting on what we have done, it is seen that we have sequentially removed hydrogen atoms. When we remove hydrogen the compound becomes more unsaturated. We can even measure the degree of unsaturation. Each time a compound has two hydrogen atoms less then its saturated equivalent one-degree of unsaturation is seen. Compare C_2H_6 to C_2H_4 to C_2H_2. Each one has progressively more multiple bonding between carbons. The types of bonding that occur in a molecule are important to note, as they will have a major influence in the structure of a molecule. This is covered in the next section.

Carbon atoms can form multiple bonds with atom other than carbon:



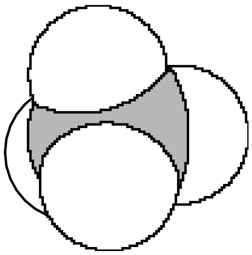
Make sure that you understand the bonding patterns that are present in these compounds.

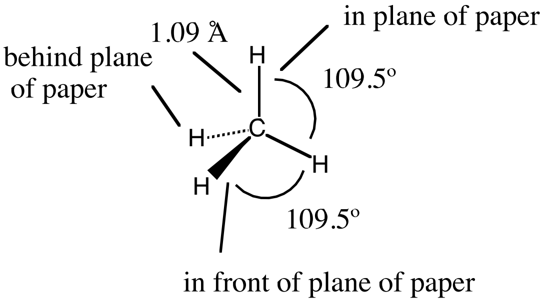
Structure

The tetrahedron

In general chemistry when you learned about ionic compounds you discussed the size of the ion and the distance between the atoms involved in the ionic bond. A big difference between covalent and ionic bonds is that covalent bonds have the property of direction. Covalent bonds have a direction in space. The two atoms involved in the bond are linked together like gumdrops at either end of a toothpick. No matter how you rotate them in three-dimensional space they will have the same position relative to each other. In ionic bonds the atoms can just circle around each other, remaining a certain distance from each other.

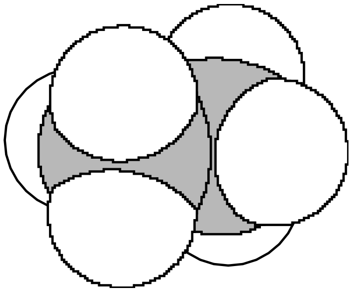
To describe the three-dimensional structure of a molecule we use the parameters **bond length** and **bond angle**. The bond length is the average distance between the nuclei of the two atoms involved in a covalent bond. Bond angle refers to the angle formed by two covalent bonds entering on a common atom. Experiments have shown the simplest hydrocarbon CH_4 to have the following structure.

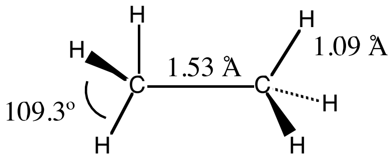




The structure on the left is called a space-filling model. It shows the atoms as spheres, with their radius being proportional to the atomic radius of the atom they depict (carbon is shaded and hydrogen is white). To the right is a more common perspective drawing showing some standards that allow us to depict three dimensions on a surface. A solid wedge depicts a bond coming out of the plane of the paper, a dotted line (sometimes a dashed wedge) is a bond behind the page, and the solid line is a bond in the plane of the paper.

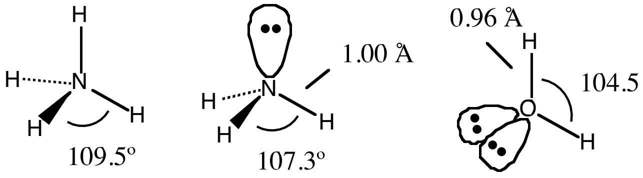
The shape of the molecule is a tetrahedron. There is a hydrogen atom a each corner and the carbon atom is at the center. We also see that the bond angle of the C–H bonds are each 109.5° and the bond length is 1.09Å (an ångstrom is 10^{-10} meters or 0.1 nm). Covalent bonds will differ in length depending on the atoms involved in the bond. If the atoms are singly bonded the bond angle will not change as much.





Where we have added a carbon atom and three more hydrogen atoms. Note that the C–H bond lengths have not changed and the H–C–H bond angle has changed little. The new C–C bond has a length of 1.53 Å. Like the C–H bond length, we observe that of C–C bond don't vary all that much.

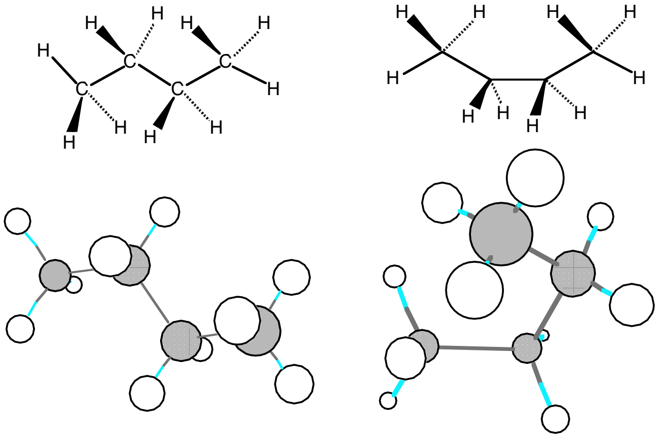
Other molecules also display tetrahedron like shapes. We also observe that unbonded electrons can occupy a corner of the tetrahedron, acting almost like an atom and a bond. Again the bond angles vary, but they are still close to 109°. Of course the observed bond distances vary much more.



Conformational Isomers

A property of carbon-carbon single bonds is that they are very non-rigid. The atoms at either end of the bonds have the ability to rotate, using the bond as the axis of rotation. Molecules that have the same molecular formulae, same connectivity, but whose atoms have different spatial positions due to rotations about a single bond are called **conformational isomers** (or **conformers**). The conformation refers to the spatial orientation of the atoms. We will not speak of these types of isomers too frequently. Physcially the atoms are rotating about each other very quickly and for most compounds (under normal conditions) this does not affect the chemistry of interest.

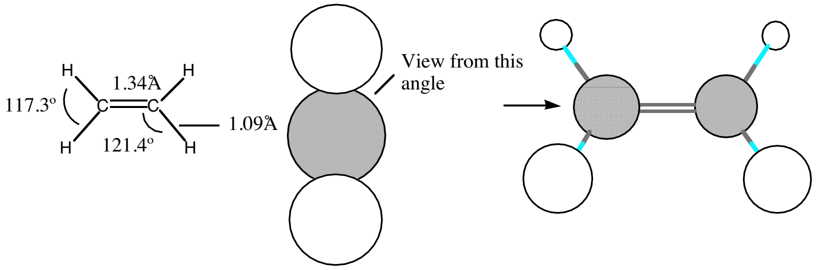
A simple example of a pair of conformational isomers is the following four-carbon hydrocarbon.



Both satisfy the formula C_4H_{10}, the connectivity $CH_3CH_2CH_2CH_3$, and the 109.5° bond angles. Therefore, they only differ from one another by a rotation about the middle carbon-carbon bond. Many other conformations of this molecule exist.

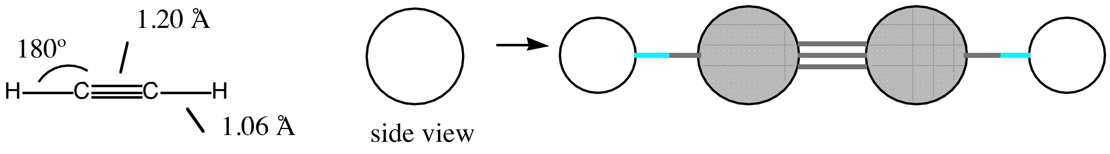
Planer molecules

Carbon-carbon double bonds are more rigid that single bonds. Thus compounds with double bonds (unsaturated compounds) will have a different structure that with those with just single bonds (saturated compounds). Consider our two carbon unsaturated compound with a double bond. We see that it has a bond length of 1.34 Å for the C=C compared to 1.52 Å for a C–C. The H–C–H bond angle of 117.3° is also different from the 109.3° observed previously. Because of the double bond this molecules is flat, completely in the plane of the paper. The middle view in the figure below is looking down the C–C double bond axis.



Linear Molecules

Continuing the trend, a triple bond between two carbons will be even more rigid that a double bond. The bond length is shorten to 1.2 Å and the bond angle is now 180° (making this a liner molecule). As before the middle view looks down the C–C triple bond axis.



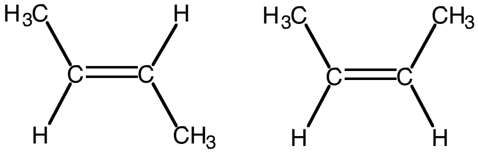
Shapes and Structures:

We have seen that the introduction of a double bond or triple bond changes the shape of the carbon atom relative to the tetrahedral alkane structure. Since the double bond only allows three "things" to surround the carbon, the structure about the carbon becomes **triangular** instead of tetrahedral. This means the bond angles are 120° instead of 109.5°. Similarly, the triple bond forces the bond angle to be 180°, and the structure becomes **linear** about the carbon with the triple bond. Given these restrictions, what other factors in the structure change?

Consider our four-carbon hydrocarbon and put a double bond between the middle two carbons.

$$H_3C{-}HC{=}CH{-}CH_3$$

Remembering that this will be a planer molecule. We could see that two forms of this molecule would be:



The presence of the double bond allows for a new type of isomer: **geometric**. These appear to be conformational isomers, since one can be made from the other by rotating about the double bond, *but* remember that double bonds are rigid! They do not allow for free rotation! So, to make one from the other, we would have to break the double bond, rotate the end, and then reform the double bond. In other words, we have to do a chemical reaction. This means that the two structures represent *different* molecules! They are geometric isomers. Like constitutional isomers, geometric isomers will have different physical properties. Unlike constitutional isomers, geometric isomers have the same bond connections. The following compound is a constitutional isomer (but not a geometric isomer) of the two above compounds.