Chemical Background for Spring 2010 BIO 311C – Brand
Part II

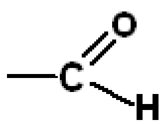
Discussion Period 2: Jan. 29 & Feb 1

Functional Groups of Organic Molecules

Many large biological molecules have several or many different functions, and each different function is associated with a specific region of the molecule. It is difficult to focus on, or even identify, a specific portion of a large biological molecule when observing a chemical or structural formula of the entire molecule. Fortunately, the atoms in organic molecules occur as small clusters, each with a characteristic structural formula and with characteristic chemical properties. It is often possible to focus on individual small clusters of atoms without considering the entire molecule.

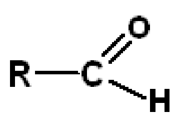
Each kind of small cluster of atoms in an organic molecule has a characteristic set of chemical properties, and is called a **functional group**.

For example a cluster of atoms in the structural formula shown below is called an **aldehyde** functional group.



Note that in this illustration one of the covalent bonds of the carbon atom does not show any atom connected to the other end of the bond. It is implied that another carbon atom is connected to the other end of the bond, and that carbon atom is connected to the rest of the molecule.

Sometimes the unspecified end of the covalent bond attached to carbon is shown as “R” (see structure illustrated below), which can be thought of as representing the “remainder” of the molecule:

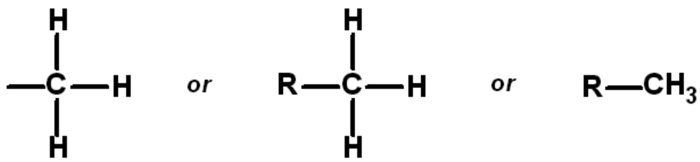


This functional group can be shown in the more abbreviated form shown below:

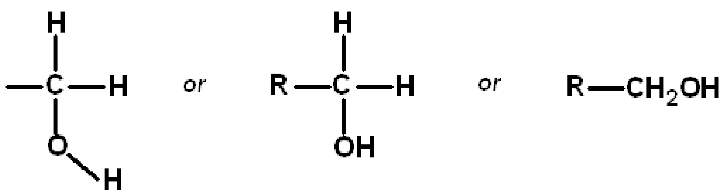
R —CHO

The names and structural formulas of functional groups that are especially important in biological molecules are shown below. Each functional group is shown in three different standard formats, separated by “or”.

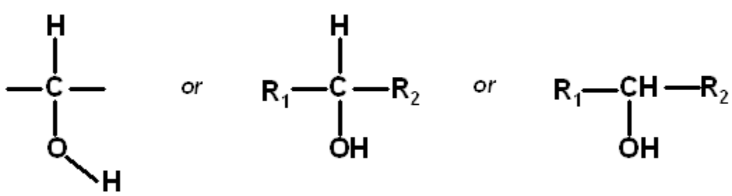
methyl:



primary alcohol:

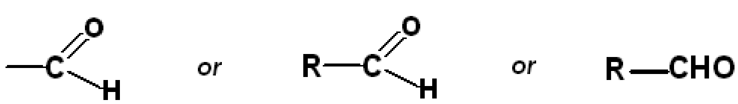


secondary alcohol:

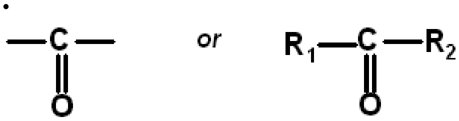


The subscripts "1" and "2" mean that the two unspecified molecular components (R-groups) attached to the alcohol functional group may be different from each other.

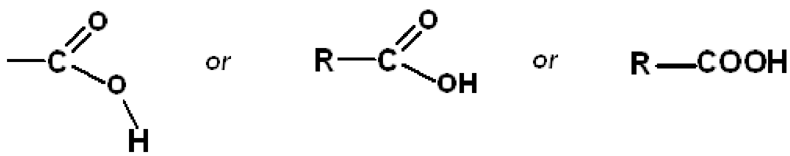
aldehyde:



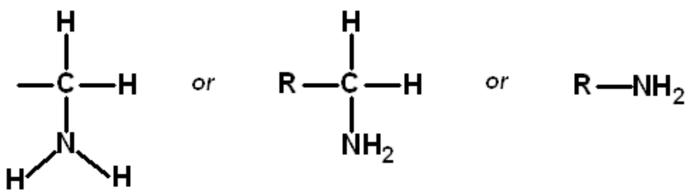
ketone:



carboxylic acid:

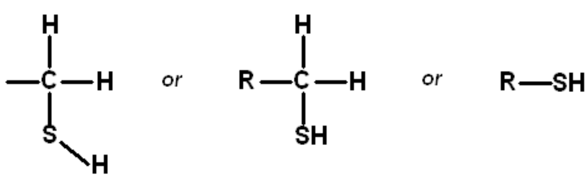


amine:

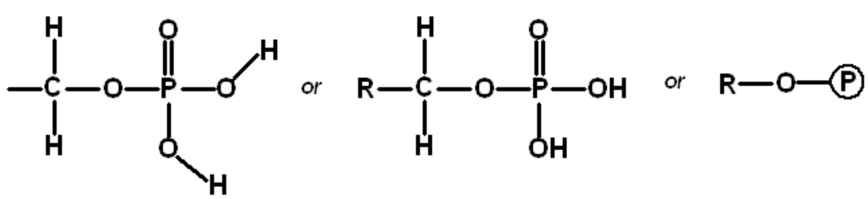


Compounds containing an amine functional group are called amines or “amino compounds”. The compound shown here is a “primary” amine. Secondary amines have structures homlogous to the structures of “secondary” alcohols.

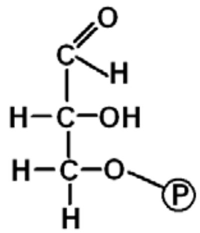
sulfhydryl:



organic phosphoric acid :



Organic molecules in living organisms can be characterized by their functional groups and can be examined one functional group at a time. For example, the organic molecule whose structure is shown below (glyceraldehyde) can be characterized by its three functional groups: an aldehyde, a secondary alcohol and a phosphoric acid.

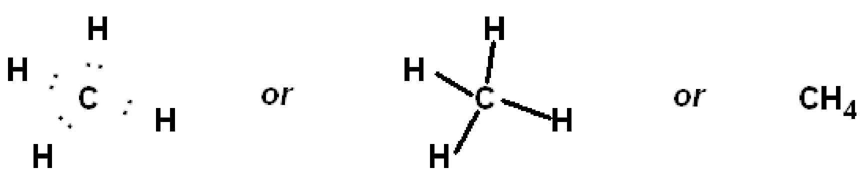


Covalent Bond Length, Strength and Angle

A covalent bond between two atoms holds the two atoms in a rather precise spatial arrangement with respect to each other. The distance between the centers of the two atoms in a covalent bond is called the **bond length**. The precise bond length between two atoms held together by a covalent bond depends on which kinds of atoms are bonded together and what other atoms are in close proximity to the two bonding atoms. However, the covalent bond length of most covalent bonds is approximately 1 angstrom (abbreviated as Å). An angstrom is one-ten billionth of a meter (10^{-10} m).

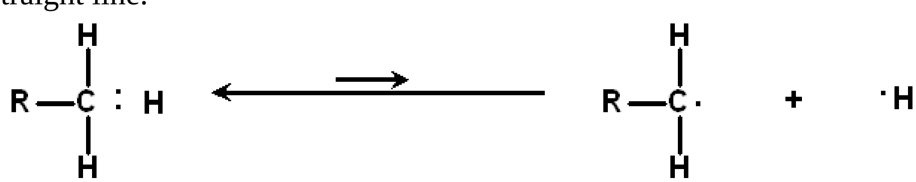
A covalent bond between two atoms is sometimes best illustrated with a pair of dots representing the pair of shared electrons, instead of a single straight line. One electron of the pair may be considered to have been contributed by each atom that participates in the bond.

Ex: **Methane**, also known as swamp gas, can be illustrated as shown below.



It is very difficult to separate a hydrogen atom from the methane molecule, because the covalency of neither the carbon atom nor the hydrogen atom would be satisfied in the separated components.

A chemical process showing a hypothetical separation and reuniting of atoms of a methane molecule is illustrated below. Note that all of the covalent bonds except one are shown in the customary way, as a single straight line.

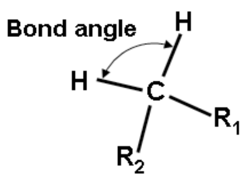


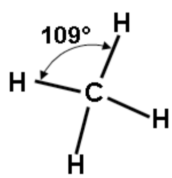
The long arrow pointing to the left in contrast to the shorter arrow pointing to the right indicates that the atoms are far more stable in the form of a methane molecule than as separated components. This is expressed by stating that the carbon-hydrogen covalent bonds of methane are strong (have large **bond strength)**.

Since covalent bonds in general have large bond strengths, molecules held together by covalent bonds are quite stable and not easily broken apart. The bond strength is given in units of energy, usually kilojoules (kJ). It is customary to determine the covalent bond energy for a specific bond of a molecule summed for a mole of identical molecules. Recall that a **mole** of molecules is approximately **6×10^{23} molecules**. Bond strengths for covalent bonds in biological molecules are typically **~ 400 kJ/mole**.

An atom with a covalency of 2 or higher can simultaneously covalently bond to two or more other atoms. For example, in methane a central carbon atom bonds simultaneously to 4 hydrogen atoms. The shape of the methane molecule is determined by the directions at which its hydrogen atoms project from the central carbon atom. Those directions can be expressed quantitative as bond angles. A **bond angle** of an atom that is bonded covalently to two (or more) other atoms is defined as the angle which the atom makes with respect to two other atoms.

Carbon has a covalency of 4 and therefore bonds simultaneously to four different atoms. A carbon atom belonging to a larger molecule is shown at left below. Two hydrogen atoms are shown bonded to the carbon, but the structure of the remainder of the molecule remains unspecified as **R_1** and **R_2**. The bond angle formed between the central carbon atom and the two hydrogen atoms will depend on the chemical and physical characteristics of R_1 and R_2. The structural formula as illustrated on a flat sheet of paper does not reflect the actual shape of the molecule. The two hydrogen atoms, R_1 and R_2 actually project away from the central carbon atom in three dimensions.





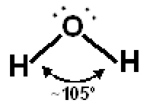
The angle formed by any two of the hydrogen atoms bonded to the central carbon atom in methane (shown at right above) is exactly 109 degrees (the tetrahedral angle).

Covalent bonds that have carbon as the central atom often have bond angles near to 109°. In the molecule shown at left above, if R_1 and R_2 are big and bulky components of the molecule, they might take up a lot of space around the central carbon atom and push the hydrogen atoms slightly closer together, thereby forming a bond angle somewhat less than 109°.

Methane, whose structural formula is shown above right, contains four identical hydrogen atoms bonded covalently to a central carbon atom. All bond angles in methane are exactly 109°.

Various methods are used to illustrate 3-dimensional projections on a flat sheet of paper. Figure 4.3 (p. 60) and Figure 5.4b (p. 71) of Campbell & Reece (7^{th} Edition) show examples of how the 3-dimensional orientation of the atoms in organic molecules may be represented in 2 dimensions.

The structural formula of water is illustrated below. Two pairs of electrons are shown above the oxygen atom. These pairs of electrons occur in an orbital of oxygen that projects out broadly from the oxygen atom, repelling each other and forcing the covalently-bonded hydrogen atoms into a bond angle of somewhat less than the tetrahedral angle (109°).



Also in primary amine functional groups the bond angle between the two hydrogen atoms attached to the central nitrogen atom is generally somewhat less than 109º.

As indicated in the preceding paragraphs and illustrations, covalent bonds can be characterized by three criteria: bond length, bond angle and bond strength. These qualities are very important for organic molecules of biological importance because they determine, respectively, the size, the shape, and the stability of the molecule.

<u>Polarity of Covalent Bonds</u>

If the two atoms that participate in the covalent bond are identical and are equally influenced by nearby molecules and atoms, then they share the pair of electrons equally.

Example: **molecular hydrogen**, our best hope as a clean-burning fuel to replace gasoline.

H : H

The pair of electrons in molecular hydrogen is shown an equal distance from the two atoms, indicating that the electrons are shared equally between the atoms.

If two <u>different</u> <u>kinds</u> of atoms contribute to the covalent bond, then they may have very different affinities for the pair of shared electrons.

Atoms that have a strong pull on the pair of electrons contributing to the covalent bond are called **electronegative** atoms, or atoms of **high electronegativity**).

Atoms that have a relatively weak pull on the pair of electrons contributing to the covalent bond are called **electropositive** atoms or atoms of **low electronegativity**.

Of the 6 kinds of atoms of primary importance in biological molecules, oxygen is the most electronegative and nitrogen is the next-most electronegative. Phosphorous is the most electropositive.
.
The order of decreasing electronegativity is:

O > N > S > C ≈ H > P

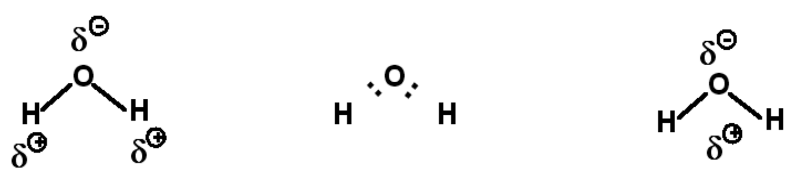
Carbon and hydrogen have almost the same electronegativity. Because of the differing electronegativities of oxygen and hydrogen, the shared pair of electrons in a covalent bond between an oxygen atom and a hydrogen atom remains closest to the oxygen and farthest from the hydrogen. Thus, there is a slight net negative charge on the oxygen side of the bond and a slight net positive charge on the hydrogen side of the bond. This is illustrated in two ways below for an alcohol functional group.

The symbol “delta” (δ) of the Greek alphabet is read as “partial”. Thus, the oxygen atom is said to have a **partial negative charge** while the hydrogen atom is said to have a **partial positive charge**. We often write circles abound positive or negative electrical charges shown on molecules.

A covalent bond between two atoms of very different electronegativities is called a **polar covalent bond.**

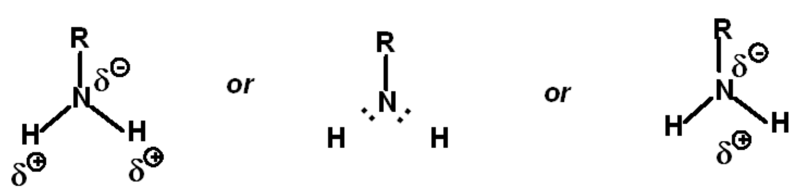
A covalent bond connecting an oxygen atom or a nitrogen atom to a carbon, hydrogen or phosphorus atom is a polar covalent bond. In contrast, a covalent bond between two carbon atoms, or between a carbon atom and a hydrogen atom, is not a polar covalent bond since the pair of electrons is shared almost equally between the two atoms. A covalent bond between a sulfur atom and either a carbon atom or a hydrogen atom is a weakly polar bond.

Three ways of showing the polar covalent bonds in a molecule of water are shown below. The illustration shown at right indicates that the hydrogen end of water has a partial positive charge while the oxygen end has a partial negative charge. Thus, a molecule of water has a somewhat positive end and a somewhat negative end



Molecules such as water, in which one region of the molecule has a negative charge, while another region of the molecule has a positive charge, are called **polar molecules**. Thus, water is a polar molecule.

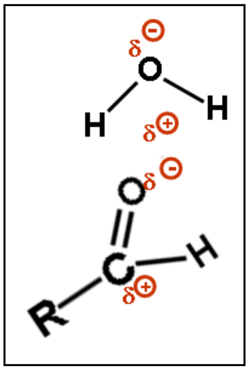
Amines also contain polar covalent bonds, as illustrated below. Thus, a molecule that contains an amine functional group is expected to be a polar molecule.



Polar Bonding Between Molecules

Since opposite charges attract, a partially positively charged region of one molecule will be attracted to a partially negatively charged region of another molecule.

In the illustration at right the positively-charged end of a water molecule is shown next to the oxygen atom of an aldehyde functional group. This kind of electrical interaction between a partially-positively-charged region of one molecule and a partially-negatively-charged region of another molecule is called **polar bonding**. Polar bonds between biological molecules are much weaker than are covalent bonds, and do not have characteristic bond lengths, bond angles or bond strengths.

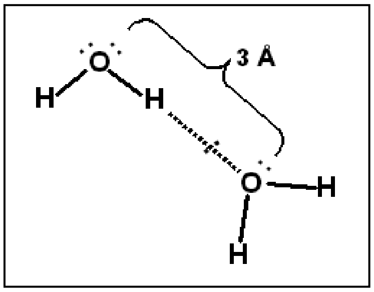


Hydrogen Bonds

A more structured arrangement of strongly electronegative atoms with respect to a partially-positively-charged hydrogen atom is called a **hydrogen bond**. Hydrogen bonds are very important in stabilizing 3-dimensional shapes of biological molecules, and in stabilizing interactions between various kinds of biological molecules.

As with covalent bonds, there are bonding rules for hydrogen bonds. Only certain combinations of pairs of atoms can interact to form a hydrogen bond. One of the atoms in the pair must be a very electronegative atom, an oxygen atom or else a nitrogen atom in the case of biological molecules. The other atom of the pair must be a hydrogen atom that is bonded covalently to an oxygen atom or else to a nitrogen atom.

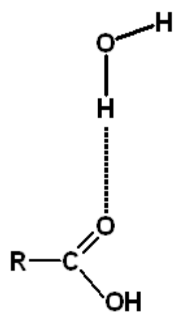
An example of a hydrogen bond between two water molecules is shown at right. Note that the hydrogen atom is aligned between two oxygen atoms. The **hydrogen bond length** is measured as the distance between the two electronegative atoms, in this case two oxygen atoms. Bond lengths of hydrogen bonds are approximately 3 Å.

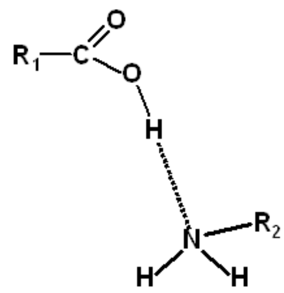


A hydrogen bond angle can be defined by treating the hydrogen atom as a central atom and measuring the angle that the two participating electronegative atoms (in this case two oxygen atoms) make with the hydrogen atom. The **hydrogen bond angle** is approximately 180 degrees.

Hydrogen bonds are well-structured but are much weaker than covalent bonds. The exact strength of hydrogen bonds varies, depending on what other atoms are covalently attached to the hydrogen-bonding atoms. A typical **hydrogen bond strength** is approximately 40 kJ/mole. Thus, 40 kJ of energy would be required to break a specific hydrogen bond between two molecules, summed for a mole of identical bonds.

Two examples of hydrogen bonds that can be formed using functional groups of importance in biological molecules are shown below.





When a diagram of a molecule is rotated, its functional groups may be shown projecting in various directions. It is important to be able to identify specific functional groups, regardless of which direction they project.

In addition to oxygen and nitrogen, fluorine (F) atoms can also form hydrogen bonds. However, fluorine does not occur in molecules of biological importance and need not be considered here.

Important features of covalent bonds and hydrogen bonds are summarized in the table below.

	covalent bond	**hydrogen bond**
typical bond length	**1 Å**	**3 Å**
typical bond angle	**109º**	**180º**
typical bond strength	**400 kJ/mole**	**40 kJ/mole**