
Electron
STOP

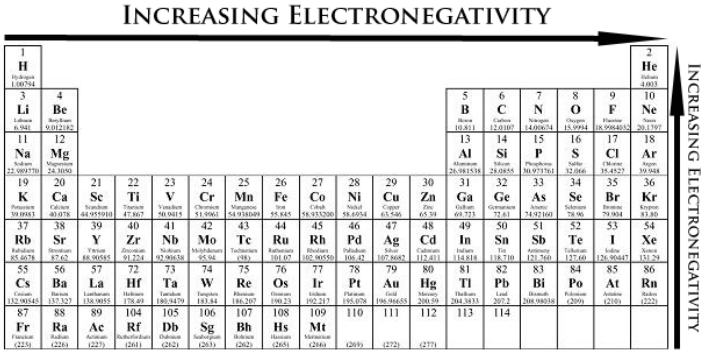
CHAPTER 1
INTRODUCTION TO ORGANIC CHEMISTRY

1.1 Review of chemical bonding fundamentals

Atoms try to achieve an s^2p^6 electron configuration (full outer valence shell, stable octet).

They can do this by forming
a) covalent bonds (sharing electrons equally),
b) polar covalent bonds (sharing electrons unequally) or
c) ionic bonds (losing or gaining electrons).

One can determine the type of bond formed between 2 atoms by comparing the electronegativity values of the 2 atoms. **Electronegativity** is a number between 1.0 and 4.0 that indicates how strongly an atom attracts electrons. Atoms on the left hand side of the periodic table have low values of electronegativity (less than 2.0) and atoms on the right hand side of the periodic table have higher values of electronegativity.



A difference more than or equal to 2.0 is an ionic bond
A difference between 0.4 and 2.0 is a polar covalent bond.
A difference in electronegativity less than or equal to 0.4 is a covalent bond.

The electronegativity of the atoms we will be dealing with this term:

H = 2.2; C = 2.6; O = 3.5; N = 3.1; F = 4.0; Cl = 3.2; S = 2.6; Br = 2.9; I=2.7

KNOW:
Covalent (non-polar): C-C, C-H, C-S, S-H
Moderately polar: C-Cl
Polar: O-H, N-H, C-N, C-O

Bonding in molecules is conveniently shown using Lewis dot diagrams which show the number of electrons in their outer shell.

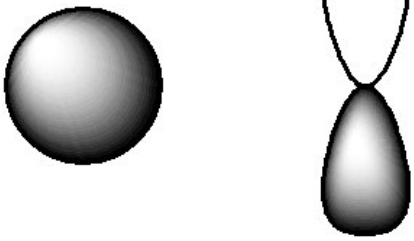
IA	IIA	IIIA	IVA	VA	VIA	VIIA	Noble Gases
H ·							**He :**
Li ·	**· Be ·**	**· B ·**	**· C ·**	**: N ·**	**: O ·**	**: F :**	**: Ne :**
Na ·	**· Mg ·**	**· Al ·**	**· Si ·**	**: P ·**	**: S ·**	**: Cl :**	**: Ar :**
K ·	**· Ca ·**					**: Br :**	**: Kr :**
Rb ·	**· Sr ·**					**: I :**	**: Xe :**
Cs ·	**· Ba ·**						

Know the Lewis dot structures of the highlighted atoms.

Bonding examples using Lewis dot:

2 F atoms $\quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}\cdot \quad + \cdot \underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: \longrightarrow \quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: \quad \text{or} \quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$

Review of s and p orbital shapes:



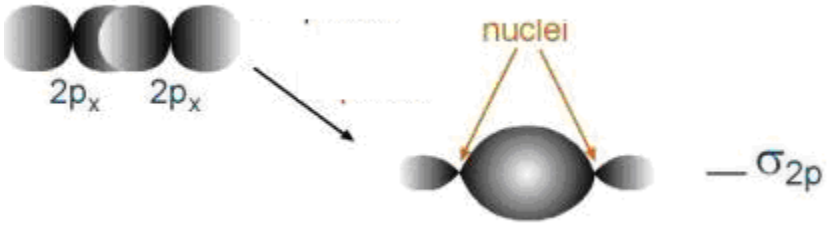
s orbital p orbital

Orbital overlap view:

F (atomic # 9) $1s^2 2s^2 2p^5$

F $1s^2 2s^2 2p^5$

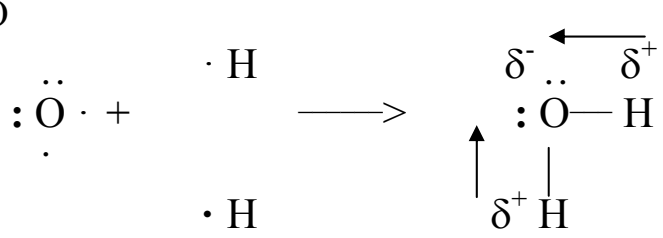
Each F atom is one electron short of a full outer shell. It can fill that unfilled p orbital by overlapping the unpaired electron of one F atom with the unpaired electron (with opposite spin) of a second F atom.



The resulting bond has its electron density concentrated on the line between the two F nuclei and is called a sigma bond.

Lewis dot notation for molecules containing O atoms:

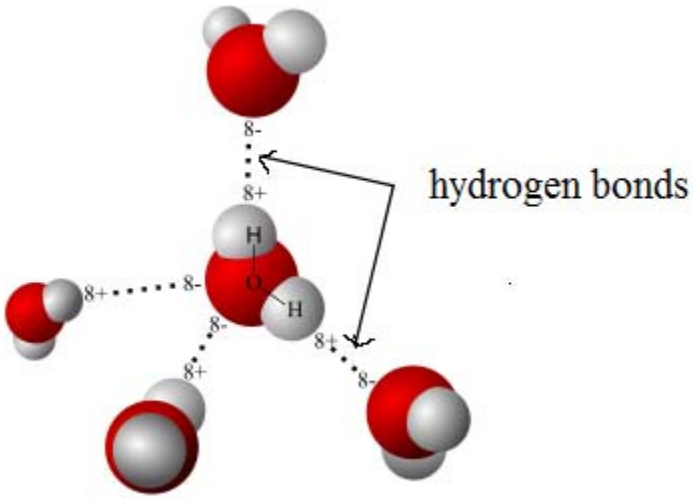
a)H_2O



The arrows indicate the dipoles: the direction in which the highest shared electron density occurs in the bond.

There are particularly strong attractions between the δ^- on the O of one water molecule and the δ^+ on the H atom of another water molecule. These attractions are called **hydrogen bonds.** They are very important attractions not only in water but in proteins,

carbohydrates, and nucleic acids. Hydrogen bonds are a specific type of polar attraction between a H with a δ^+ and a very electronegative atom F, O, or N.



Modified from Wikipedia

b) Do the Lewis dot diagram for H_2O_2.

loldamn.com

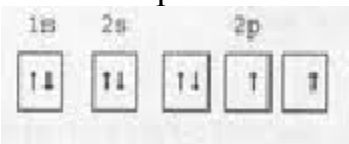
b) O_2

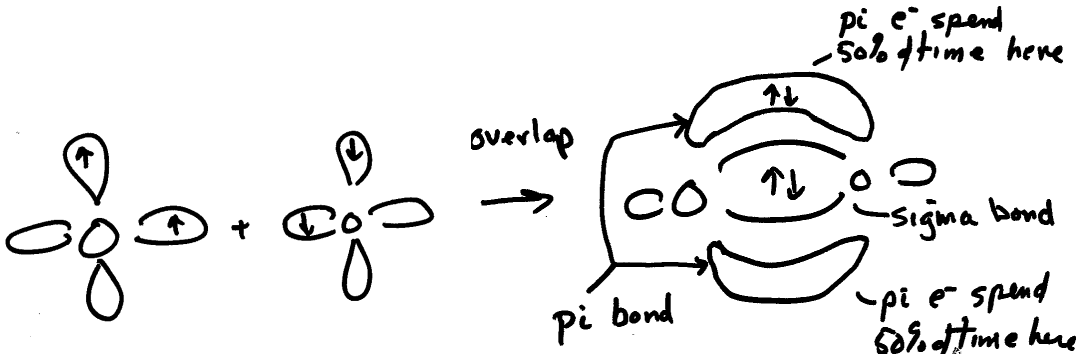
$$:\ddot{O}\cdot \quad + \quad \cdot\ddot{O}: \quad \longrightarrow \quad \ddot{O}=\ddot{O}$$

. . .. ..

The result is a double covalent bond with 4 shared electrons (2 pairs).

Orbital overlap representation of O_2 :
O: $1s^2 2s^2 2p^4$



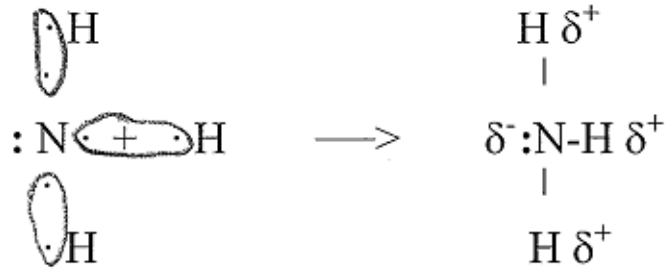


The 2 electrons in the pi orbital are not as close to the two positively charged O nuclei and can more easily react with another atom or especially a positively charged ion. In general pi electrons of a double bond will be more reactive than the sigma bond.

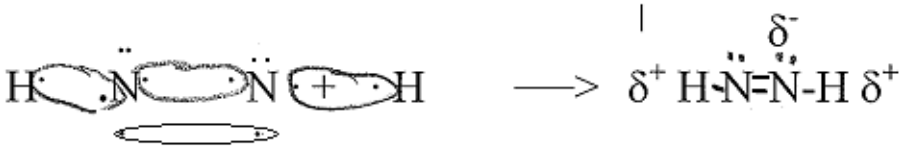
In both molecules above O atom forms two bonds, either two single bonds or one double bond

Lewis dot structures of molecules with N atoms

a)ammonia, NH_3

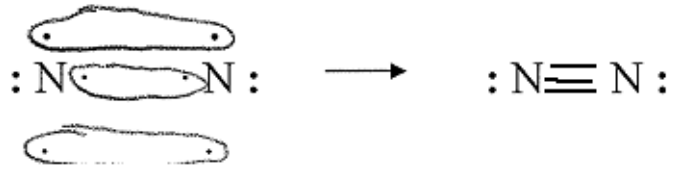


b) N_2H_2



In this molecule each N atom forms a double and a single bond.

c) N_2



This produces a triple covalent bond with 6 shared electrons (3 pairs).

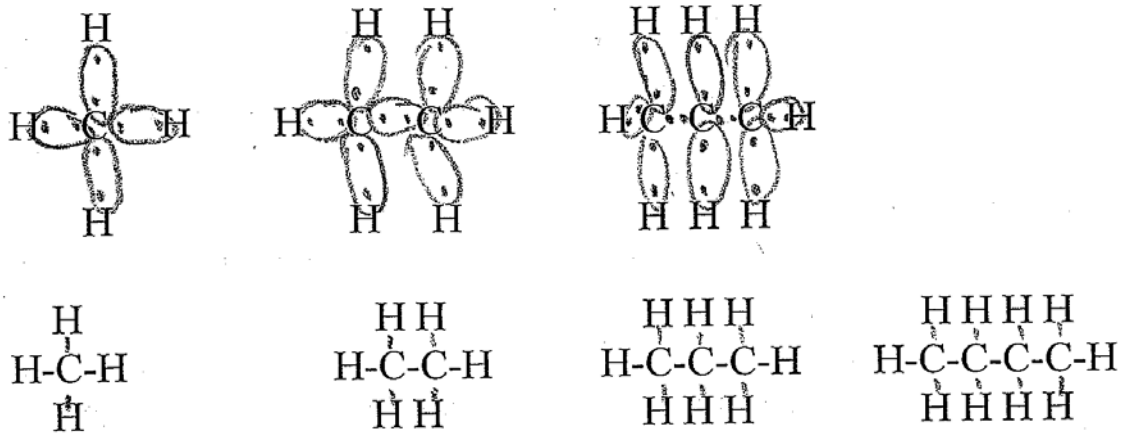
In all of the above molecules the 3 unpaired electrons of N form 3 bonds: 3 single bonds, a double and a single, or a triple bond.

What will the orbital overlap picture of N_2 look like?

Lewis dot structures for molecules with C atoms

C is in Group IV and it forms 4 bonds:

CH_4 C_2H_6 C_3H_8 C_4H_{10}



Since H is the most common atom found bonding with C we will sometimes simply show 4 bonds coming off of a C without explicitly showing the atom at the end of the bond. When we do this, it is assumed that H is the atom bonded. If some other atom beside H is bonded to C, we HAVE to show it explicitly.

These chains can be almost infinitely long and these long chains are what make the chemistry of carbon so extensive and so diverse.

1.2 Naming and Bonding of C chains

We will be working extensively with chains of one to ten C atoms and you should learn their names:

Number of C atoms	Name
1	Methane
2	Ethane
3	Propane
4	Butane

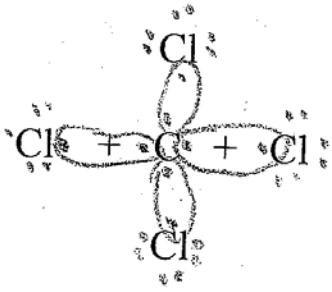
5	Pentane
6	Hexane
7	Heptane
8	Octane
9	Nonane
10	Decane

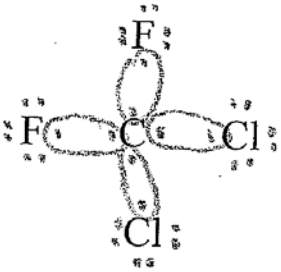
A couple of mnemonics developed by chemistry students may help you remember the order:
My Energetic Playful Beluga (whale) Pounces Hecka High on November Days.
or
Many Elephants Pop Barbiturates Producing Hellish Headaches On (the) Next Day.

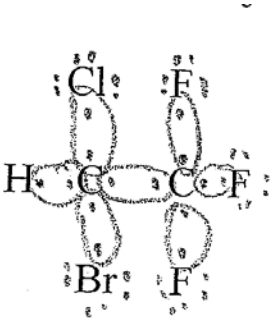
Carbon bonds to other atoms besides H. The halogens (F, Cl, Br, I) all have 7 electrons in their outer shell and form a single bond with C. They can substitute for H. For example:

Carbon tetrachloride Freon 12 Halothane

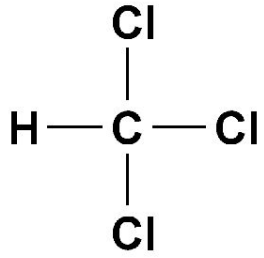
CCl_4 CF_2Cl_2 $C_2HClBrF_3$







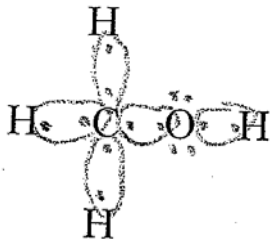
$CHCl_3$

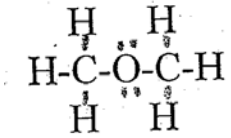


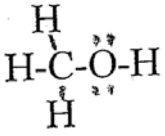
Common inhalation anesthetic until WWII

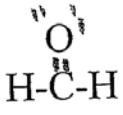
What sort of bonds (covalent, polar covalent, or ionic) are found in the above molecules?

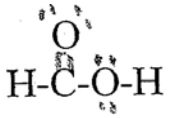
C atoms commonly bond to O atoms. A C atom needs a total of 4 bonds and O atom needs 2 bonds. For example:





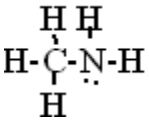


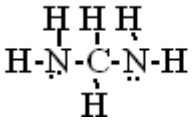


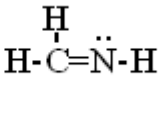


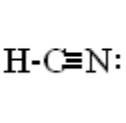
What type of bond is the C-H bond? O-H bond? C-O bond?

C atoms can also bond to N atoms. N atom is in Group V, has 3 unpaired electrons, and needs 3 bonds to obtain its full outer shell.







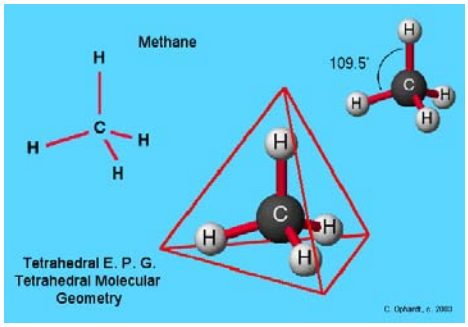


What type of bond (covalent, polar covalent, ionic) is the N-H bond? the C-N bond? Which of the 2 types of bonds is *more* polar?

1.3 Geometry of C compounds:Valence Shell Electron Pair Repulsion Model(VSEPR Model)

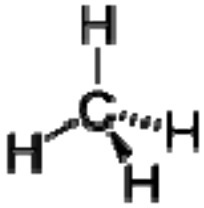
1.31 Geometry of C-C single bonds

Although we have drawn all the above molecules in 2 dimensions, they are in fact three dimensional molecules. The actual shape of methane (CH_4) is **tetrahedral** as shown in the model below.



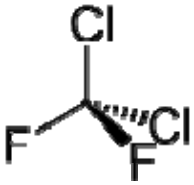
This shape can be justified on the basis that the 4 pairs of electrons in the C atom want to be as far apart as possible in 3 dimensional space because the negative charge of the outer valence electron pairs repel each other (hence the term valence shell electron pair repulsion model or VSEPR). This corresponds to a tetrahedral geometry with H-C-H bond angles of 109.5 ^{o}. Organic chemists frequently use a notation called wedge and dash notation to attempt to show the 3 dimensional tetrahedral shape in 2 dimensions.

Wedge and dash:

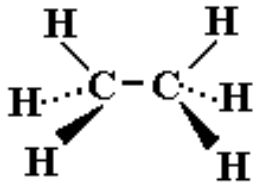


For methane one observes that two H atoms and one C atom can all be lined up in one plane. One remaining H atom sticks out towards the observer and its bond is represented with a wedge; the other H atom sticks out away from the observer and its direction is indicated with a series of dashes.

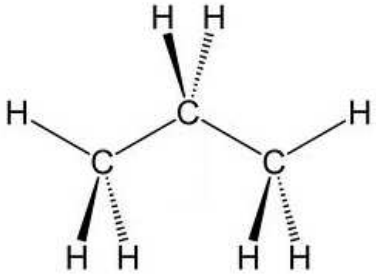
Exchanging H atoms for halogens, such as in Freon-12, $C_2Cl_2F_2$, still maintains the same basic tetrahedral geometry.



Similarly ethane has the following wedge and dash notation:

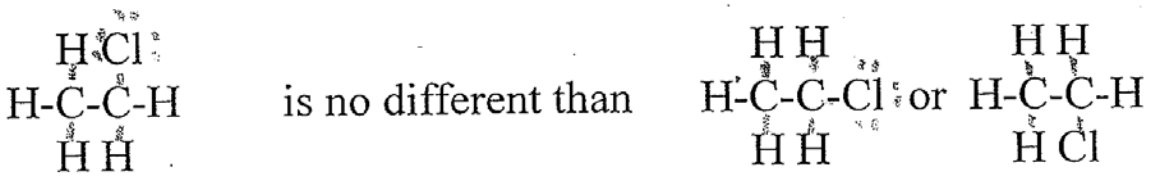


Likewise propane has the following wedge and dash notation:



Free rotation around C-C single bonds

C compounds are commonly drawn without using wedge and dash notation and the structures are drawn flat with bond angles that look like 90°, but one should always keep in mind that they are really 3 dimensional molecules. Another important property is that there is free rotation around the C-C single bonds. Thus the structure:



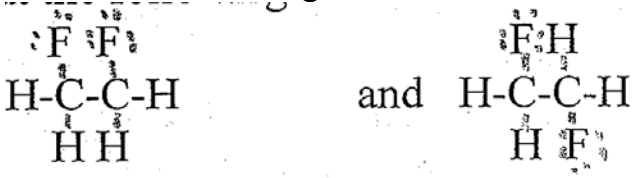
even though the structures may look different when drawn 2 dimensionally on paper.

Likewise the two structures:

are really the same because of free rotation found the second and third C atoms of the chain.

Whenever you are looking at chemical structures you always need to remember that these are really 3 dimensional molecules and that one can freely rotate around the single bonds.

Look at the following 2 structures. Are they the same molecule?



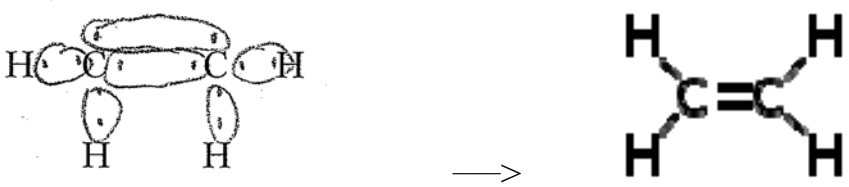
Are these 2 structures the same molecule?

They are, because one can simply flip the molecule on the left over to produce the structure on the right.

Are these 2 structures the same molecule?

1.32 Geometry of C-C double bonds

C can also form double bonds with other atoms. For example: ethylene(ethene),C_2H_4, has the structure

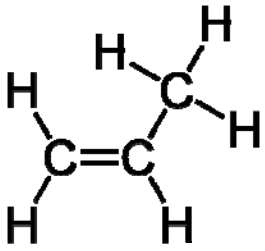


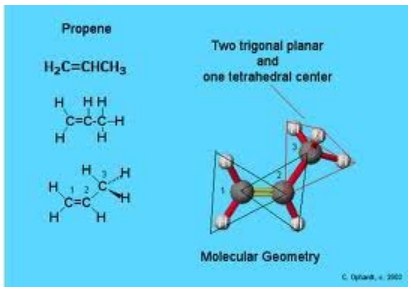
The actual geometry of the C=C in ethylene is **trigonal planar** (a flat planar structure with bond angles of 120^{o}) because the electrons in the C=C double bond and the two pairs of electrons in the C-H single bonds try to stay as far apart in space as possible. Unlike C-C single bonds there is **NO free rotation** around the C=C double bond. This will be important in future applications.

Ethylene is produced from crude oil and is the starting molecule for making the plastic material polyethylene. In rare instances vapors of ethylene from carbon deposits deep in the ground can rise to the surface along geological faults. Ethylene is a mild hallucinogen and it is thought that ethylene emanating into a cave at Delphi, Greece gave the oracles at Delphi their trances during which they made their predictions.

Wikimedia commons.This painting is by the Hon. John Collier and was painted in 1891. For more information on this artist, visit www.artmagick.com

One can have double bonds and single bonds in the same molecule, as in propene (propylene):



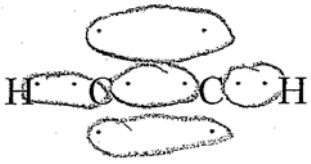


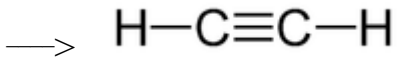
The geometry around the first two C atoms (from left to right) is **trigonal planar** with 120^o bond angle. The geometry of the H atoms around the third C atom is **tetrahedral** with 109.5^o bond angle.

1.33 Geometry around C-C triple bonds

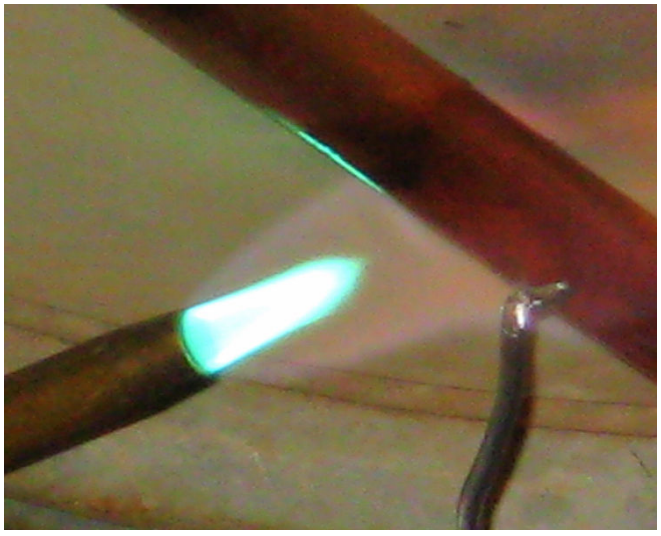
Carbon atoms can also form triple bonds with another atom

C_2H_2





Acetylene



Wikimedia commons: Authors: Paul Anderson and Sheila

The geometry of acetylene (ethyne) is **linear** (bond angle 180^{o}) because the C-C triple bond stays as far away from the C-H single bond as it can, namely 180^{o}. Acetylene is the fuel used by welders in oxy-acetylene torches.

ronnormansculpture.com

HCN

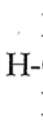
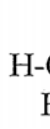
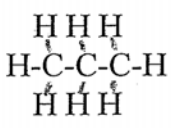
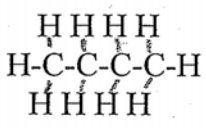
Hydrogen cyanide

Hydrogen cyanide was one of the gases the Nazis used to kill people in the gas chambers and was also used in the 1950's in the US for executing prisoners given the death penalty.

Wikimedia commons: Bunker #16 in Poznan (Poland); author: Radomil

1.4 Condensed notations

We will frequently use several types of condensed formulation for organic molecules, rather than writing the full structure that shows every bond:

	Methane	Ethane	Propane	Butane
Full structural formula:				

Condensed formula: CH_4 CH_3CH_3 $CH_3CH_2CH_3$ $CH_3(CH_2)_2CH_3$

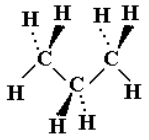
Likewise the condensed formula for pentane is $CH_3(CH_2)_3CH_3$
and hexane is $CH_3(CH_2)_4\,CH_3$

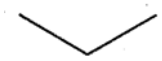
Practice problems. Write the condensed formula for
Heptane Octane Nonane Decane

A still more abbreviated notation, line-angle or line-bond notation, emphasizes the 109.5 tetrahedral bond angle of C-C single bonds and does not explicitly show any atoms at all! It is commonly used.

Thus propane, commonly written as 

can be drawn in wedge and dash notation as



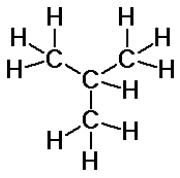
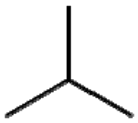
or in line-bond form as 

The end of each line as well as each "kink" is understood to be a C atom and the kink is made at approximately a 109.5^o tetrahedral bond angle. It is understood that enough H atoms are added to each C to meet the bonding rules.
The line bond notation for C chains containing 4-7 C atoms are shown below.

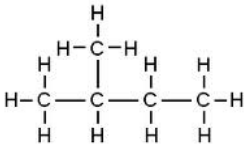
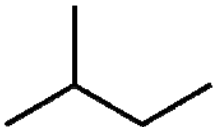
Butane  pentane 

Hexane  heptane 

Isobutane has the structural formula

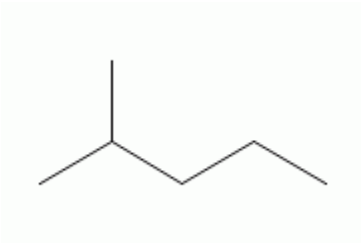
 and the line-bond notation: 

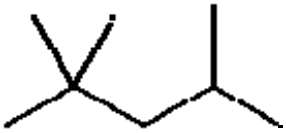
and similarly the structural formula

 has the line-bond notation 

Note that the structural formula makes the bond angles look like 90^{o}, but the line-bond notation must show the tetrahedral 109.5^{o} bond angle.

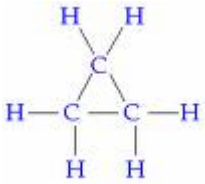
Write out the full structural formula for the following line-bond notations:



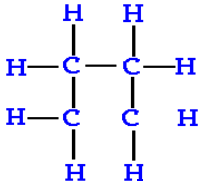


Carbon chains can also form rings as in the following examples:

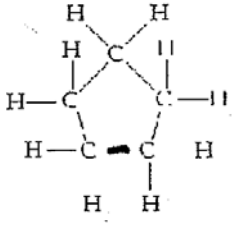
Cyclopropane



Cyclobutane

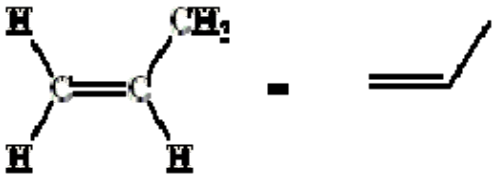


Cyclopentane



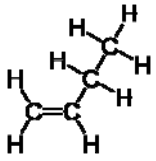
The shorthand notation similar to line-bond notation that we shall use for rings in the future is shown as follows:

The line-bond notation for double bonds is shown with the example of propene below:



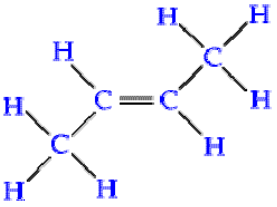
As in the previous examples of line-bond notation, all the atoms are left off and only the bond angles are shown, leaving the reader to supply just about everything!

Likewise



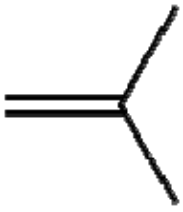
has the line-bond notation 

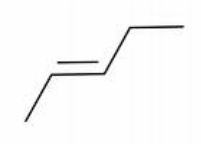
and

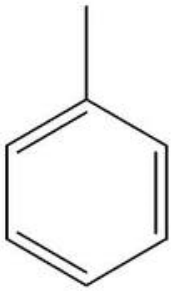


has the shorthand notation 

Try writing out the full structural formula for the following line-bond notations on a separate sheet of paper. Make sure your full structural formulas have the appropriate number of bonds on each atom!

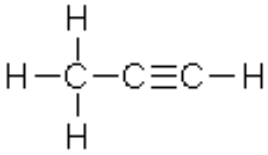





When you've done the full structures for each of the line-bond structures above, see if you can work backwards and draw the original the line-bond notation from the full structure!

The line-bond notation for C-C triple bonds is shown below

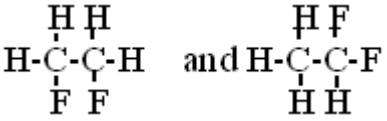


becomes

Write the full structural formula for each of the following line-bond notations:

1.5 Isomers

Let's look at the following 2 molecules:



Note that although these 2 structures have the same atomic composition ($C_2H_4F_2$), in the first molecule there is one F on each of the C atoms whereas on the second molecule both F atoms are on the same C atom. No matter how we rotate the molecule or turn it over or around, these 2 structures are fundamentally different molecules. We call these molecules **structural or constitutional isomers.**

Definition: Molecules which have the same formula, but which have a difference in structure (in what atoms are bonded to each other) are called **structural or constitutional isomers.**

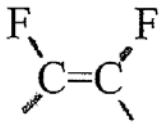
For each of the pairs of molecular structures shown below, are the pairs of molecules isomers or just different representations of the same molecule?

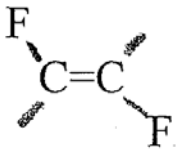
(Answer: These are different representations of the same structure because of free rotation around the C-Cl bonds. We can rotate the C-Cl bonds in any direction we want without creating a new structure.)

(Answer: These are structural isomers because the structure on the left has 2 Br atoms on one C atom and 1 Br atom on the other. The second structure has all 3 Br atoms on one C atom. We can't rotate or flip our way out of this one. These two structures have the same formula but different bonding and are hence structural isomers.)

(Answer: Each C atom has one F atom in the structure on the left, while the structure on the right has both F atoms on the same C atom. These are structural isomers.)

(Answer: Each C atom has one F atom in the structure on the left, while the structure on the right has both F atoms on the same C atom. These are structural isomers.)





This last pair of molecules is an example of a different type of isomer. All the atoms are bonded to the same atoms in both structures, but the F atoms are pointed the same direction (**cis or Z)** in the first structure and in opposite direction (**trans or E**) in the second structure. (In Latin cis means on the same side and trans means across. In German, Z stands for **zusammen** (same) and E stands for **entgegen**(opposite).

If there were a single bond between the 2 C atoms we could simply rotate around the C -C bond and make the F atoms point whichever direction we wanted, but remember there is NO free rotation in C=C bonds! If the 2 F atoms in a structure are pointing the same direction on a C=C they must stay that way and if the 2 F atoms are pointing opposite directions on a C=C double bond they will stay that way. Hence they are different molecules. Since they have the same formula we call these molecules isomers, but we do not call them structural isomers because both molecules have exactly the same atoms bonded to each other; they differ only in the direction in which atoms point. Since they differ only in geometry, we call them **geometric isomers**. We call the isomer in which both F atoms are pointing in the same direction the cis or Z isomer and the isomer in which the two F atoms are pointing in opposite directions the trans or E isomer.

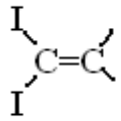
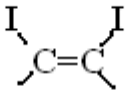
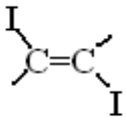
Geometric isomers

Definition: Molecules which have the same formula and the same atoms bonded to each other, and differ only in geometry, are called geometric isomers. Geometric isomers can only occur when there is no free rotation around bonds, either on a C=C double bond or on a ring.

Note that we cannot look at a single structure and say that it is a structural isomer or geometric isomer. We have to look and compare 2 different molecules.

Consider the following 3 molecules:

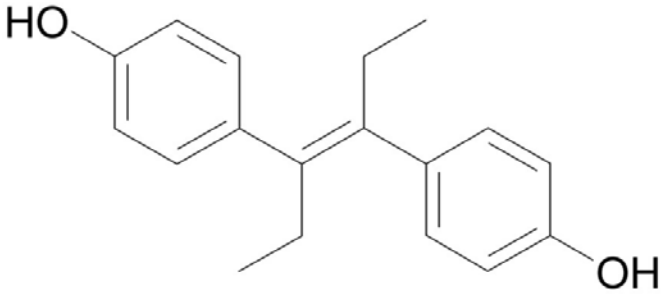
A B C

All three molecules have the same formula. Molecules B and C differ only in which direction the I atoms are pointing. Hence they are geometric isomers. Both B and C differ from A in the terms of which atoms are bonded to each other. Hence B and C are both structural isomers of isomer A. Thus molecule B(cis) is a geometric isomer of molecule C(trans) and a structural isomer of molecule A. A molecule can be both a geometric and structural isomer. Likewise molecule A is a structural isomer of both molecule B and C.

DES (Diethylstilbestrol)

An example of medically important cis-trans isomer is DES, diethylstilbestrol. Its structure is shown below. It can exist in both the cis and trans form. Which form is shown below? Draw the other form and label it.



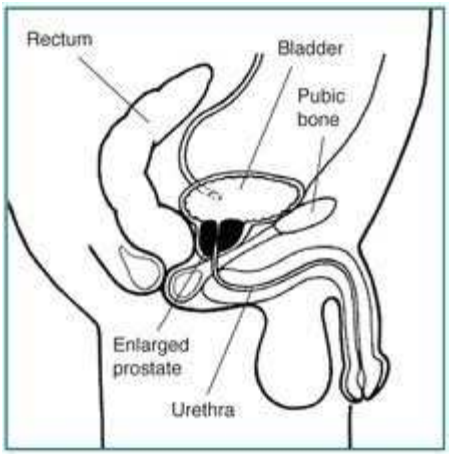
The other geometric isomer has only about 7% of the biological activity of the first form. This is because the DES binds to a receptor in the cell membranes which has a shape complementary to the one geometric isomer. The other geometric isomer does not fit nearly as well and has very little activity as a result.

The use of DES as a drug was first approved in the early 1940s to prevent miscarriages. Other approved uses included stopping milk flow in mothers who were not nursing, slowing down the spread of prostate cancer in men, as a "morning-after" pill, and several other uses. It is estimated that approximately 5-10 million people have taken DES.

Figure 2
Medical journal advertisement for prenatal tablets with vitamins and diethylstilbestrol

In 1953 a **double blind study** showed that DES was not actually any more effective than placebo for reducing the incidence of miscarriages , but this conclusion did not get adequate publicity among doctors and its use continued into the 1960's and an outright ban on prescribing it for this purpose did not occur until 1971.

No immediate adverse effects were noted with the babies born by mothers taking DES. However as the **DES daughters** reached puberty a variety of vaginal and cervical tissue abnormalities were noted. DES daughters are at increased risk of vaginal, cervical, and breast cancer. These women generally need to have Pap smears done on a regular basis to monitor whether these abnormal cells have become full blown cancer cells. They are also at increased risk for having difficulties in pregnancy and auto-immune disorders. In **DES sons** there appears to be an increased risk of epididymal cysts (in the testicles) and autoimmune diseases.



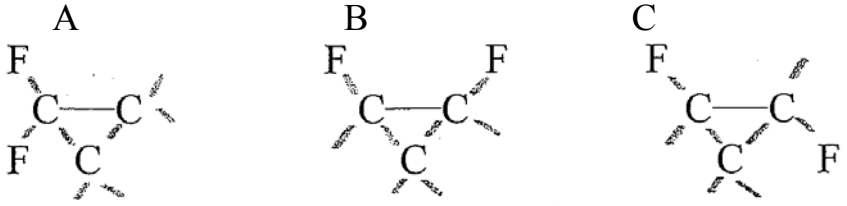
DES continued to be used to treat prostate cancer into the mid 1990's. Prostate cancer cells are dependent on male hormone for their continued growth and removal of male hormones will stop or at least greatly slow down the growth of prostate cancer cells. The original method for stopping testosterone production was a surgical orchiectomy(also spelled orchidectomy).

DES is an analog of female hormone which non-surgically reduces levels of male hormones, decreasing the rate of prostate cancer growth. Unfortunately, the prostate cancer cells eventually lose their requirement for male hormones and the cancer then progresses, frequently metastasizing to the bone. DES has been replaced with other **antiandrogens** and is rarely used on humans anymore, although veterinarians may still use it to treat female canine incontinence. (What is an antiandrogen?)

Geometric isomers in rings

As already indicated in the definition one can have geometric isomers only when one has restricted free rotation. This can occur on a double bond as in the previous example that we just looked at. It can also occur in ring structures. Consider the three molecules shown below.

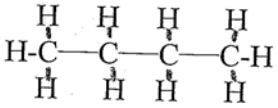
A B C

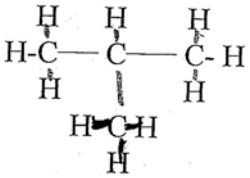


What is the relationship between molecules A and B?
What is the relationship between molecules B and C?
What is the relationship between molecule A and C?

Structural Isomers with Branching

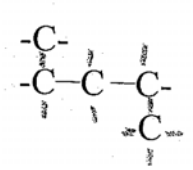
We can also have isomers by branching of a C chain. Consider the following two structures:

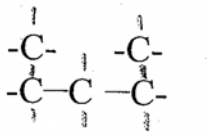




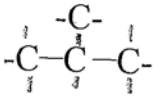
Observe that both structures have the same formula, C_4H_{10}, but that they do not have the same structure. The second structure has a C **branch** off the second C atom while the first molecule is an unbranched "straight" chain.

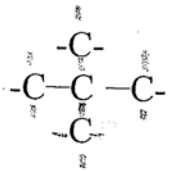
One has to be careful in determining whether a chain is branched or not. If one can put ones pencil down on one end of a carbon chain and trace all the C atoms in the structure without "backtracking" or lifting one's pencil, then the structure is not branched, even if one did several zig-zags. Thus the molecular structures shown below are **not** branched.





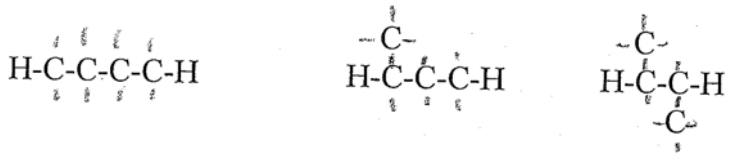
(These are different representations of the same structure, pentane.)
On the other hand, if one cannot trace all the C atoms in a single trace without backtracking, then there is a fundamental branch in the chain, as in the examples below.

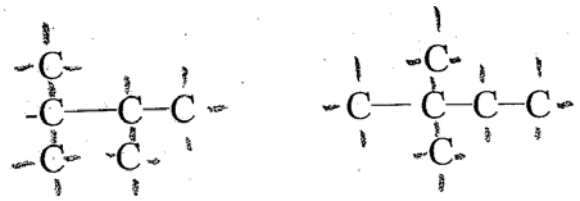




There is one branch in the first structure and two branches in the second structure.

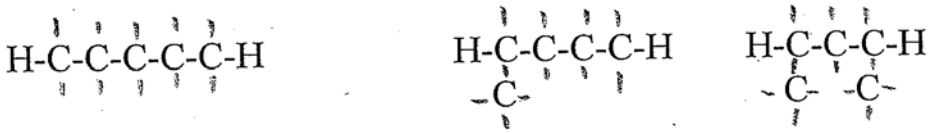
Study the structures shown below and decide whether they are structural isomers, geometric isomers, or the same molecule drawn differently.

1) 

2) 

Decide whether the following structures are structural isomers, geometric isomers, or the same molecule drawn differently

A B C

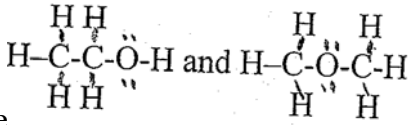
1) 

Using branches, find three isomers with the formula C_5H_{12}. (The first isomer is the straight chain that was mentioned earlier)

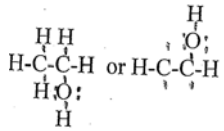
Using branches, find five isomers with the formula C_6H_{14}.

Isomers with O in the formula

Let's look at some isomers that contain O in the formula. Remember that O is in Group VI and has 6 electrons. Since it wants 8 total electrons it will tend to form 2 bonds, either 2 single bonds as in water (H_2O) or a double bond as in O_2.
Draw 2 isomers with the formula C_2H_6O.

Answer: The two isomers are  and

If you drew



note that free rotation of the OH off the C atoms makes all these the same molecule!

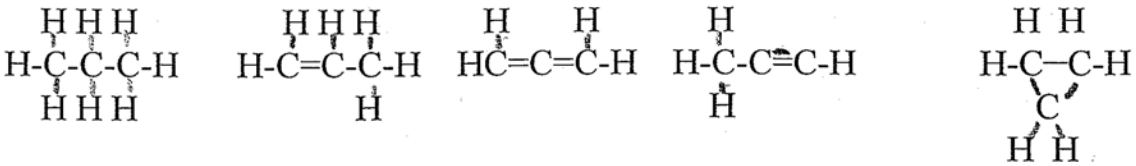
Draw the structure of 2 isomers with the formula C_2H_4O. This formula has 2 less hydrogen atoms than the C_2H_6O formula we just drew. In order to meet the bonding rules, all of the structures you draw will need to contain either a double bond or a ring.

Draw the structure of 3 isomers with the formula C_3H_8O.(No double bonds or rings needed.)

1.6 Predicting the Number of Double Bonds or Rings in a Formula

How do we decide whether we need any double bonds or rings when we are trying to draw structures? We will look at this in some detail and come up with an answer, because it will make life a lot simpler when we are drawing isomers with a given formula.

Compare the formulas for the following structures



C_3H_8 C_3H_6 C_3H_4 C_3H_4 C_3H_6

Note that the addition of a C=C results in a formula with 2 less H atoms than the saturated propane molecule with only single bonds. Putting two double bonds into a structure removes 4 H's. Introducing a triple bond in the structure removes 4 H atoms. The presence of a ring also removes 2 H atoms from the formula compared with the original propane molecule. These observations are true in general, not just for 3 C atoms. We can formulate the following generalizations.

A molecule with only single bonds, no double or triple bonds and no rings, is said to be **saturated**. It has the maximum number of H atoms (or equivalently halogen atoms) that is possible for that number of C atoms. Double bonds, triple bonds and rings all reduce the number of H atoms (or halogens) in the formula and a molecule with double bonds or rings is referred to as unsaturated. A **double bond** removes 2 H atoms and is said to be a **site of unsaturation (or degree of unsaturation)**. A **triple bond** removes 4 H atoms and constitutes **2 sites of unsaturation**. A **ring** removes 2 H atoms and also constitutes a **single site of unsaturation**.

How many H atoms are there in a **saturated** molecule?

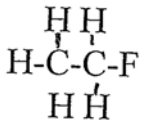
Let's look at the formulas for methane, ethane, propane, butane and pentane:

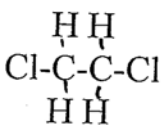
CH_4 C_2H_6 C_3H_8 C_4H_{10} C_5H_{12}

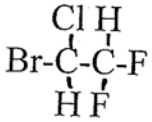
There is a relationship between the number of H atoms and the number of C atoms in each of these saturated molecules. Namely, if there are "n" C atoms in a formula, there will be (2n+2) H atoms in the saturated molecule.

How many H atoms are in a saturated molecule with
8 C atoms? _____ 10 C atoms? _____

Halogen atoms in a formula







C_2H_5F $C_2H_4Cl_2$ $C_2H_2F_2ClBr$

Note that all of these molecules are saturated (no double bonds, rings, or triple bonds) but they will not obey the 2n +2 rule unless we count the halogens (F, Cl, Br, I) in along with H atoms The halogens can substitute for H atoms 1 to 1, so we must include them in our counting along with H atoms. So include ***halogens*** along with ***hydrogen*** in counting the "H" actual molecular formula!

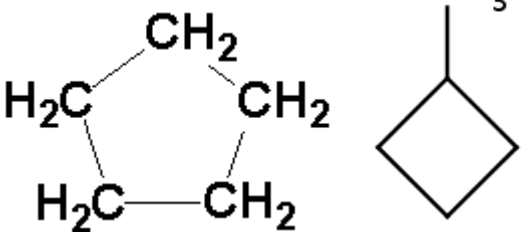
	C_2H_5F	$C_2H_4Cl_2$	$C_2H_2F_2ClBr$
	5H + 1 F 6 "H's"	4 H + 2 Cl 6 "H's	2 H + 2 F + 1 Cl + 1 Br 6 "H's"
Sites of unsatura-tion	0	0	0

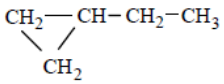
(Halogens were included with H in above calculations.)

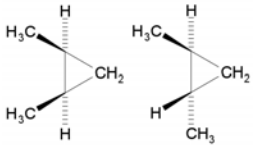
How many sites of unsaturation are in C_5H_{10}?

The 2n+2 rule predicts that a 5 C molecule should have 12 H atoms. The actual formula only has 10 H atoms, 2 short of saturation. Therefore there is one site of unsaturation. Any structure with this formula will need to have either a double bond or a ring.

Some of the many possibilities include:
1) a ring. (Ring can have any number of atoms within it.)

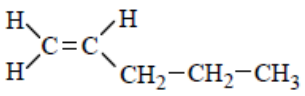
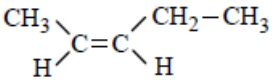
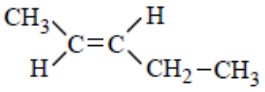
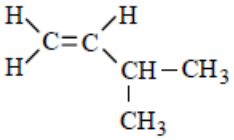
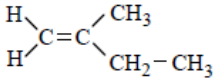
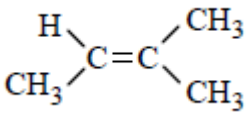






(What type of isomers are the above h molecule?)

2)Molecules with C=C

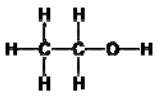
Predict how many sites of unsaturation will be found in the following formulas. Draw at least 3 isomers for each of the formulas.

a)C_6H_{10} b)$C_5H_{10}F_2$

How many sites of unsaturation in $C_3H_6Br_2$? Draw 4 isomers with the formula $C_3H_6Br_2$.

How many sites of unsaturation in $C_4H_8F_2$? Draw 5 isomers with the formula $C_4H_8F_2$:

Molecules with O in the formula

If we look at the structural formula for ethanol: 
we see that the formula is C_2H_6O and that there are 6 H atoms for 2 C atoms, just like in the case of ethane(C_2H_6) . Thus, the presence of O does NOT

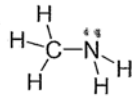
affect the "2n+2" rule and the O atom is NOT included with H atoms like we did with the halogen atoms when determining saturation.

Predict the number of sites of unsaturation in the following examples. Draw two isomers for the each formula.

C_2H_6O $C_2H_4F_2O$ C_2H_2O

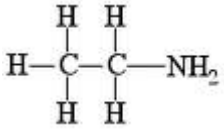
C_2F_2O $C_2H_2Cl_2O$ $C_2H_4F_2O$

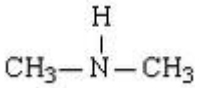
Molecules with N in the formula. Look at the saturated molecule:



If we apply the 2n+2 rule in the above molecule, we predict that we would have 4 H atoms for 1 C atom. The actual formula has 5 H atoms in the structure, 1 more H than predicted for a saturated molecule with 1 C atom We conclude that each N atom in a formula adds one more H atom to the saturated formula. To calculate the number of H atoms in the saturated molecule with N in the formula we have: 2n+2 + # of N atoms.

a) How many sites of unsaturation are there in C_2H_7N?
A saturated molecule with 2 C atoms and 1 N atom will have
2(2) + 2 + 1= 7 H atoms. Since the above formula has 7 H atoms, it is saturated.
Draw 2 isomers with the formula C_2H_7N.





b) How many sites of unsaturation are there in C_2H_5N?

As calculated above a saturated molecule with 2 C atoms and one N atom will have 7 H atoms. The actual formula has 5 H atoms, 2 H atoms(one site) short of saturation. There is one site of unsaturation: either a double bond or a ring.
Draw 3 isomers with the formula C_2H_5N.

[put in hyperlink with answers here]

c) How many sites of unsaturation are there in C_2H_3N?
Draw 3 isomers with the formula C_2H_3N.

d) How many sites of unsaturation are in C_3H_9N? Draw 4 isomers with formula C_3H_9N

e) How many sites of unsaturation are in C_3H_7N? Draw 4 isomers with formula C_3H_7N.

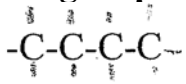
f) How many sites of unsaturation are in C_3H_5N? Draw 4 isomers with formula C_3H_5N.

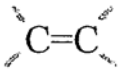
g) How many sites of unsaturation are in C_3H_3N? Draw 4 isomers with formula C_3H_3N.

1.7 FUNCTIONAL GROUPS

Certain combinations of bonds show up repeatedly in organic chemistry and organic chemists give those bonding combinations specific names. It is very useful to know the names of those specific types of bonds. Examples are shown below and you should make flash cards and learn them by heart. There can be (and frequently are) multiple functional groups in one organic molecule.

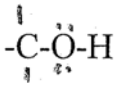
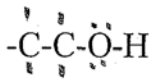
1.61 Functional groups containing only C atoms:

Alkane 

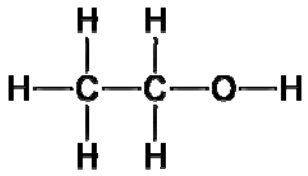
Alkene (Olefin) 

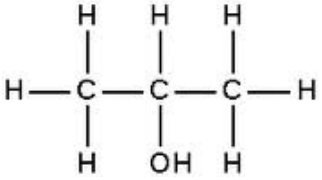
Alkyne 

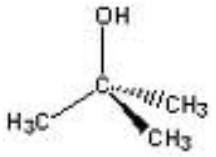
1.62 Functional groups containing one (or more) single bonded O atoms

a) Alcohol:   R-O-H

We can write a more generalized formula for a molecule with an alcohol functional group as R-O-H where R is the symbol organic chemists commonly use to indicate a C chain without specifying the exact length. Alcohols are often labeled more specifically based on the number of C atoms bonded to the C with the O-H.



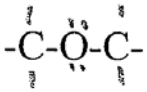


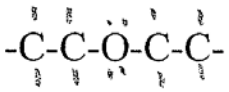


Primary alcohol Secondary alcohol Tertiary alcohol

Primary alcohols have 1 C bonded to the C with the OH group. Secondary alcohols have 2 C atoms bonded to the C with the OH. Tertiary alcohols have 3 C atoms bonded to the C atom with the OH.

b) Ether:

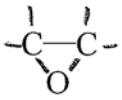




R-O-R

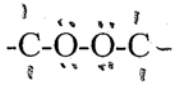
We might also write R_1-O-R_2 to indicate that R_1 and R_2 are not the same

c) Epoxide:

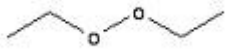


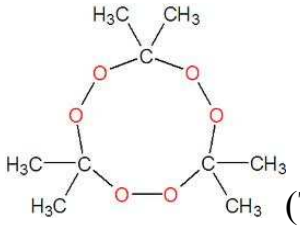
An epoxide is a special type of ether functional group in a 3-membered ring.

d) Peroxide:



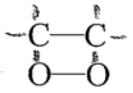
R-O-O-R

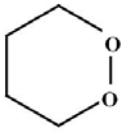




(TATP explosive)

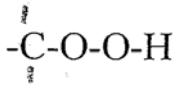
e) Endoperoxide:



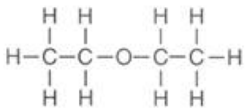


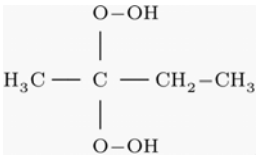
A peroxide group within a ring is called an endoperoxide.

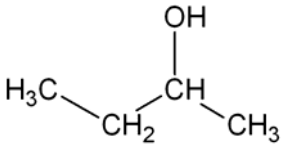
f) Hydroperoxide:

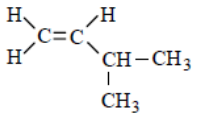


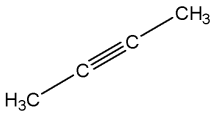
Circle and label the functional groups in the following molecules:

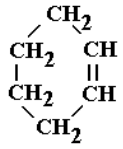


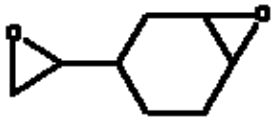


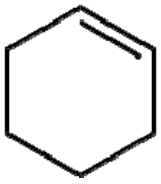


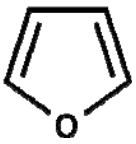


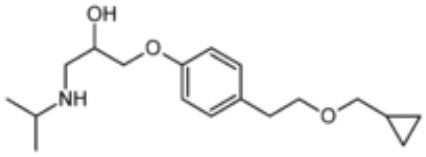


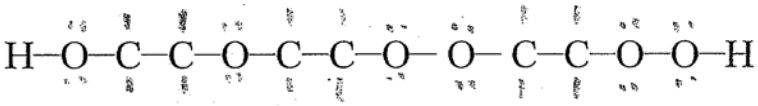


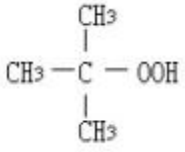


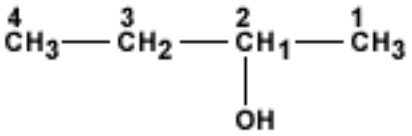


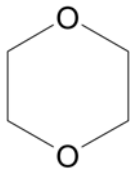
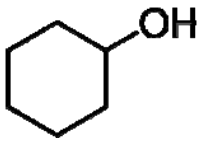
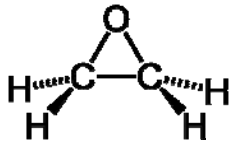
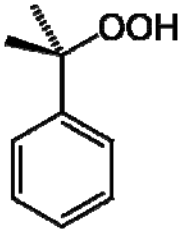
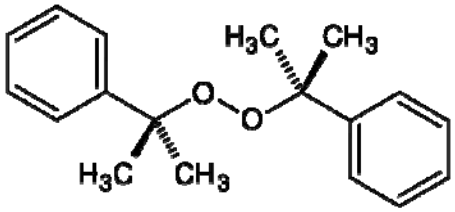




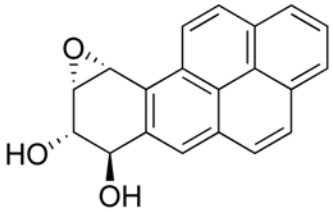
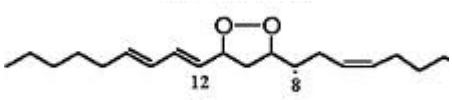






(6-membered rings containing 3 alternating double bonds are very common in organic chemistry and are called benzene rings.)

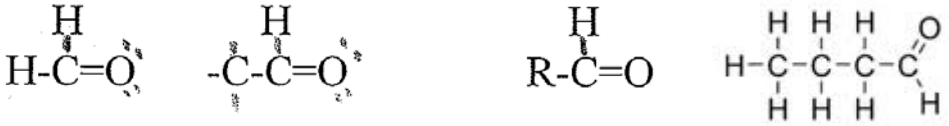



In the above structure explain the significance of the wedges and dashes.

1.63 Functional groups containing a C=O (carbonyl) group

1)An **aldehyde** has a **carbonyl group (C=O)** bonded to (at least) one H atom, as shown below

Aldehyde:



2)In a **ketone** the two additional bonds of the C of the **carbonyl group (C=O)** are both bonded to C atoms

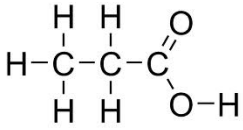
Ketone:

3) A **carboxylic acid** has the C atom of the **carbonyl group (C=O)** bonded to an OH group, as shown below. Even though you would be tempted to label the OH on the carbonyl group as an alcohol, the presence of the C=O

completely changes the chemical properties of the OH and it does not have the properties of an alcohol group and is not labeled as such.

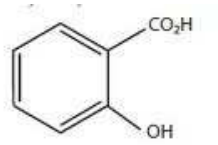
Carboxylic Acid 

The carboxylic acid group is often abbreviated COOH or CO_2H when shorthand notation is being used. Example:

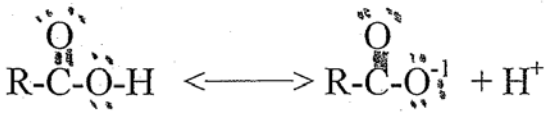
 can be written in condensed notation as

CH_3CH_2COOH or $CH_3CH_2CO_2H$. One has to be careful not to confuse this shorthand notation with a hydroperoxide group, which would have the shorthand notation: $CH_3CH_2C\mathbf{H_2}OOH$.Note the extra H_2 in the formula. Examples:

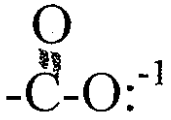
 has a carboxylic acid group, not a hydroperoxide group, because there are not 2 H atoms on the C of the COOH.

In  the CO_2H group is a carboxylic acid group, not a hydroperoxide group, which would be abbreviated CH_2OOH.

By definition, an acid is a substance which produces H^+. Carboxylic acids produce H^{+1} ions by ionizing the H on the carboxylic acid group.



The resulting negative ion is called a **carboxylate ion**. The dissociation of the carboxylic acid is reversible and so carboxylic acids are **weak acids.**

4)Carboxylate ion: 

The carboxylate ion structure is often condensed to COO^{-1} or CO_2^{-1}.

Example: $CH_3(CH_2)_4COO^{-1}$ or $(CH_2)_4CO_2^{-1}$.

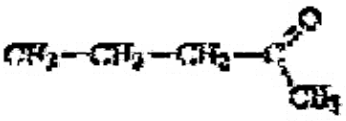
When a C=O is covalently bonded to an O-C linkage, it is called an **ester** functional group. Examples

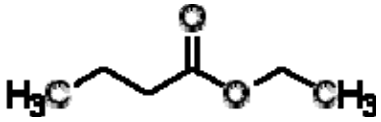
5)Ester:

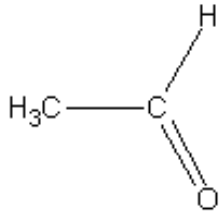
In shorthand notation esters may be abbreviated COOC, although this can easily be confused with a peroxide bond. Usually keeping track of the number of bonds and H atoms on each C will help you tell the difference.

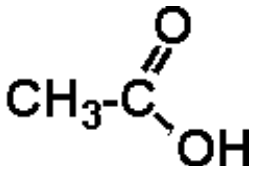
CH_3COOCH_3 is an ester. $CH_3C\mathbf{H_2}OOCH_3$ is a peroxide.

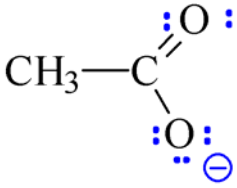
Identify the functional groups in the following molecules:

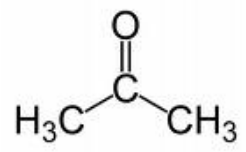




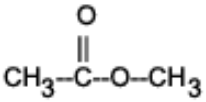


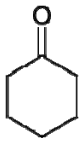


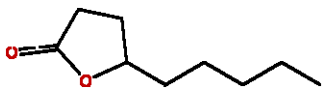


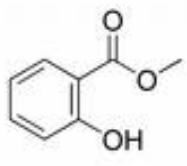


acetone

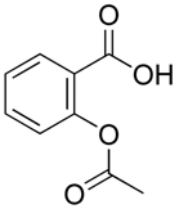




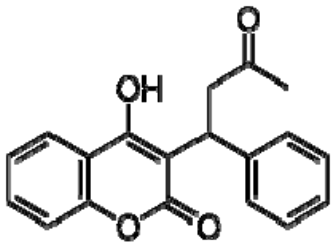


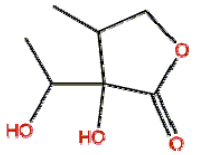


wintergreen

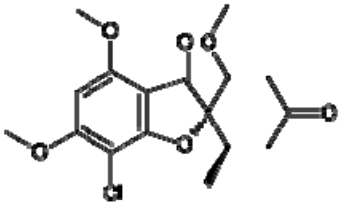


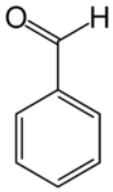
aspirin



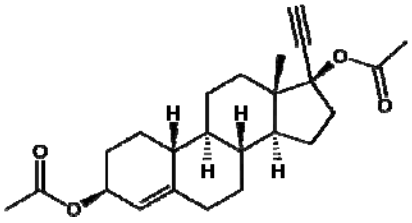


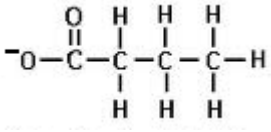
Warfarin(Coumadin), structure shown above on left, is a very commonly used anticoagulant



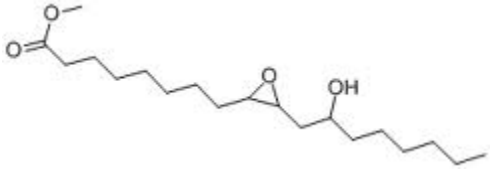


Griseofulvin



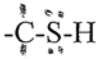


Ethynodiol diacetate(BC pills)



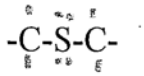
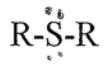
1.64 Compounds with S atoms:

a)Sulfhydryl

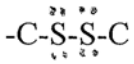
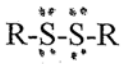


Sulfhydryl groups are also sometimes referred to as thiol or mercaptan groups.

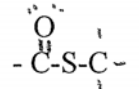
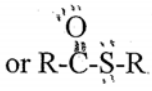
Sulfide(do not confuse with the inorganic sulfide ion S^{-2})

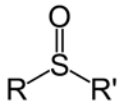
Disulfide:

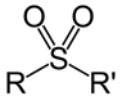
Thioester: (notice similarity to regular ester; important in metabolic biochemistry)

Sulfoxide:

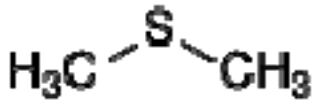
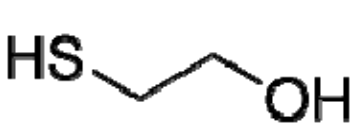
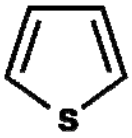


Sulfone:

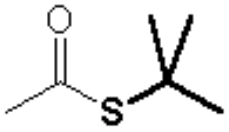
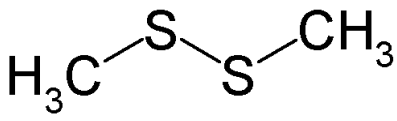
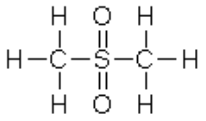


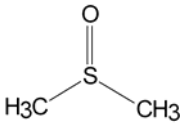
Note that in sulfoxides and sulfones, the S atom has more than 2 bonds.

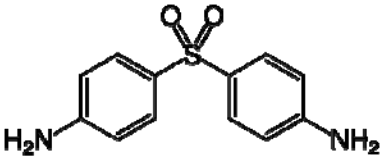
Identify the functional groups in the structures shown below:

(cooked cabbage smell)



DMSO

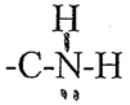

dapsone(antibiotic for leprosy and other conditions

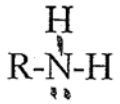
1.65 Functional groups containing N

1)Amines are molecules in which a N is single bonded to one or more C atoms. Their chemistry is similar to that of ammonia, NH_3, except that there are one or more C atoms bonded to the N atom.

a)A **primary amine** is a functional group that has a N atom with one C atom bonded to it by a single bond.

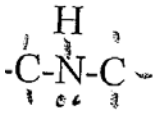
Primary amine

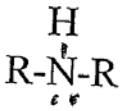


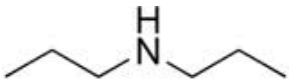


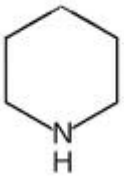
b)A **secondary amine** is a N atom that has two C atoms bonded to it by single bonds.

Secondary amine



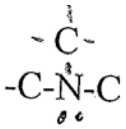


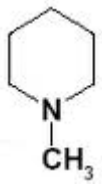




c)A **tertiary amine** is a N atom that has three C atoms bonded to it by single bonds.

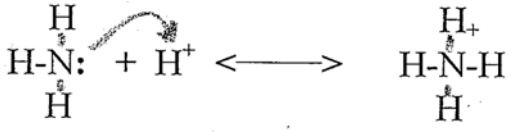
Tertiary amine





2) Ammonium ions

The non-bonding pair of electrons in **ammonia** (NH_3) can react with a H^+ (from an acid such as HCl) to form an **ammonium** ion, NH_4^+.



This reaction can occur because the H^+ needs a pair of electrons to have a full n=1 shell and the N atom has a pair of electrons which it is not sharing (a non-bonding pair of electrons). When the neutral NH_3 combines with the

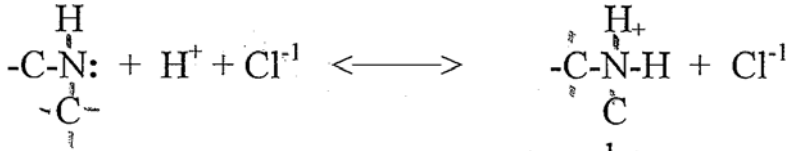
positively charged H^+, the resulting ammonium ion has a positive charge. (Another way of looking at it: when the N atom shares the fourth pair of electrons, it is sharing more electrons than normal and this is equivalent to giving one electron away, putting a positive charge on the N atom.)

A very similar reaction occurs if we add an acid (containing H^+) to an amine the non-bonding pair of electrons of the N can bond to the H^+ and we can form an alkyl **ammonium ion.**

a)If we add acid to a primary amine, we form a **primary ammonium ion.**

primary ammonium ion

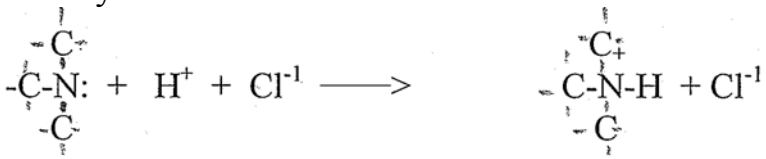
b)We can add acid to a secondary amine and form a **secondary ammonium** ion:



secondary ammonium ion

c) We can add acid to a tertiary amine and form a **tertiary ammonium** ion:

Tertiary Ammonium ion

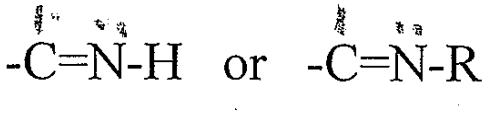


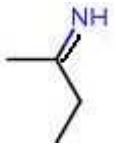
d) We can also have a N atom with 4 C atoms bonded to it, which is called a **quaternary ammonium ion**.

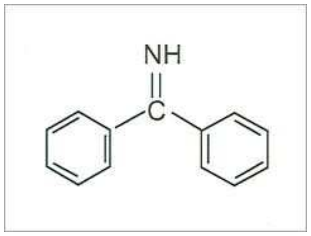
Cl^- (or other negative ion)

3)Imines

A N atom which has a **double bond** to a C atom is called an **imine**.



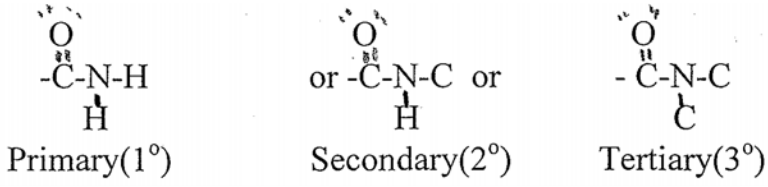


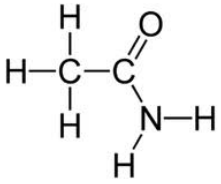


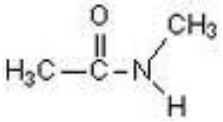
4)**Amides**

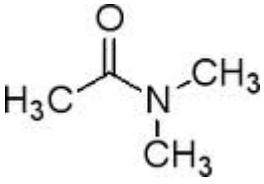
A N atom which is bonded to a C=O (carbonyl) group is called an **amide.** Amides are called primary amides if the N is bonded to one C atom, secondary amides if the N is bonded to two C atoms, or tertiary amides if the N atom is bonded to 3 C atoms.

Amide



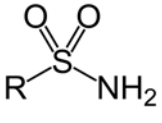


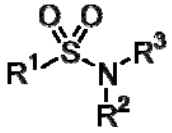




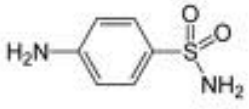
5**) Sulfonamides**

When a N atom is bonded to a O=S=O group, it is referred to as a sulfonamide. The sulfonamide drugs were one of the first effective antibiotic families and are frequently referred to as the "sulfa" drugs.

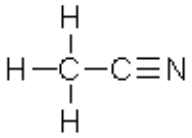
Sulfonamide 

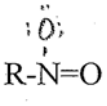
or 

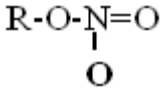
(Note S has more than two bonds in the sulfonamides.)



6)**Cyanide (nitrile)**



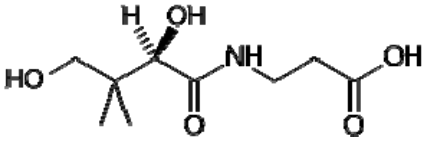


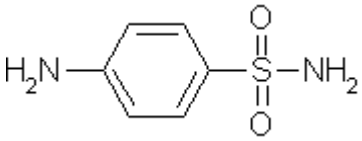


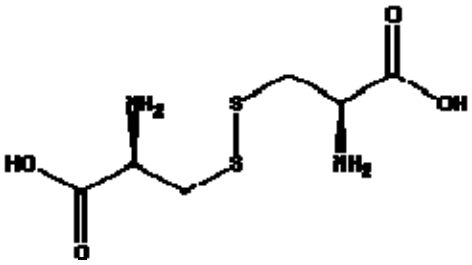
7)Nitro and **nitrate**

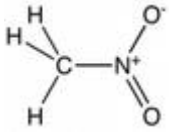
In the nitro group the N atom is directly bonded to the C, while in a nitrate group it is an O atom that connects the C and the N. Common names sometimes can be misleading in this regard however.

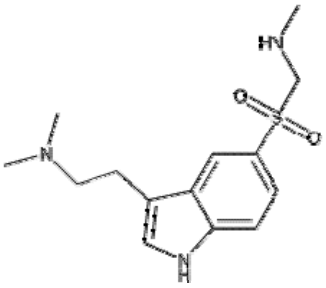
Identify the functional groups in the following biologically important molecules:





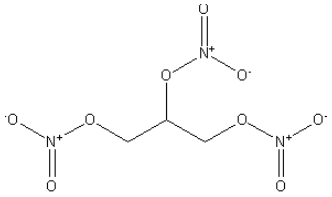


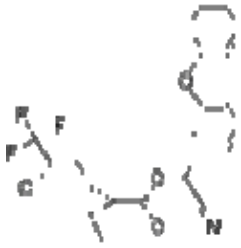


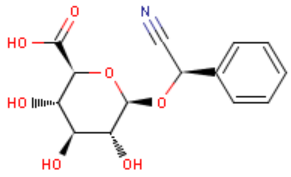


(Cystine)

Sumatriptan(Imitrex)

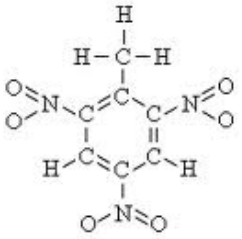




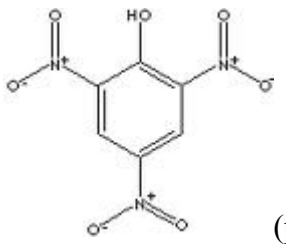


Nitroglycerin-what's wrong with this name?

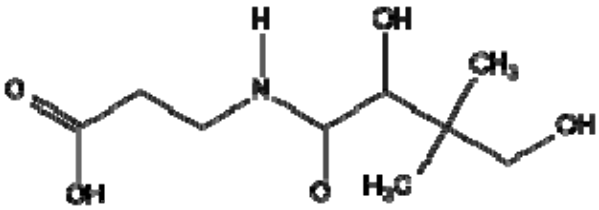
Amygdalin



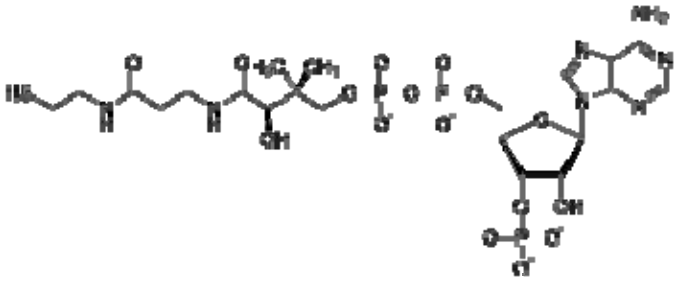
TNT(trinitrotoluene)



(picric acid)

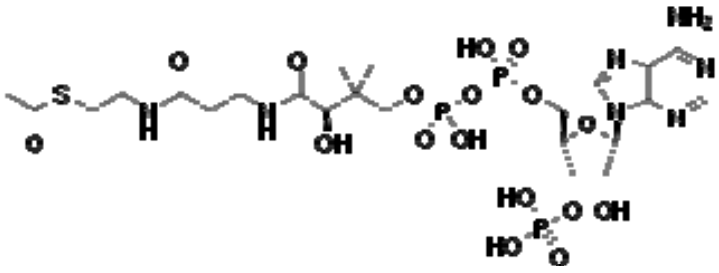


(pantothenic acid)



Coenzyme A

Can you find the pantothenic acid structure within the structure of coenzyme A?



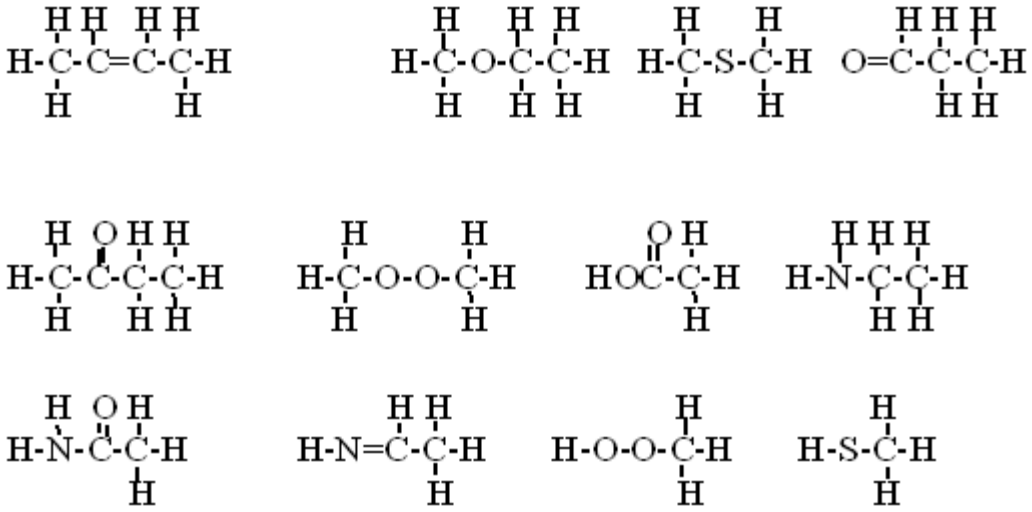
acetyl Coenzyme A

What new functional group is in acetyl CoA that is not in coenzyme A itself?

For practice flash cards see: http://www.flashcardmachine.com/1543843/i54f

1.66 Additional Practice recognizing functional groups

Using the examples given above, identify the functional groups in the following molecules:



Study Guide Questions

1. Define the terms covalent, polar covalent and ionic bonds in terms of a) concepts b) differences in electronegativity values between two atoms (Δ EN).
2.Be able to determine what sort of bond (covalent, polar, ionic) in the following bonds without referring to notes.

a)C-H b)C-O c)C-N d)N-H e)C-Cl f)O-H g) S-H

3. Be able to draw the Lewis dot for C, N, O, S, F, Cl, Br and I without referring to a periodic table.

4. Draw a picture showing how the p orbitals of two F atoms overlap in diatomic F_2. Is the molecular orbital formed σ or π?

5. Draw a picture showing how hydrogen bonds are formed between water molecules. Draw a picture showing how the p orbitals of two O atoms overlap to form a sigma bond and a pi bond. Which type of bond(sigma or pi) is more strongly attracted to the positively charged nuclei? Which pair is more reactive?

6. Give the names of the alkanes containing 1-10 C atoms.

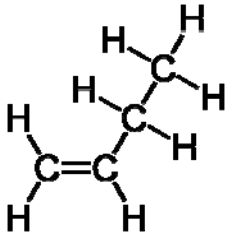
7. What is the molecular shape of the methane molecule, CH_4? Draw a picture using the "wedge and dash" notation. Do the same for the ethane

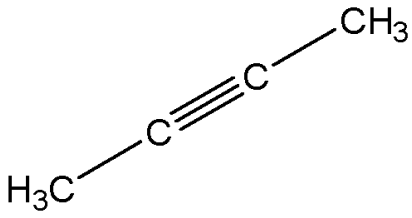
molecule. What is the bond angle in each of these molecules? What is the name of this geometry?

8. The ammonia molecule, NH_3, can accept a hydrogen ion from a water molecule to form the ammonium ion, NH_4^{+1}. The geometry of the ammonium ion is analogous to that of the methane molecule. What is that geometry? Draw a picture of the ammonium ion using "wedge and dash" notation.

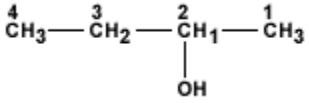
9. Name the geometry of ethane (C_2H_6), ethene (C_2H_4), and ethyne(acetylene). What are the bond angles in each case? In which molecule is there free rotation around the bond between the two C atoms?

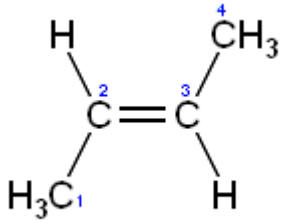
10. Describe the molecular shape and geometry around each C atom of the molecules shown below.

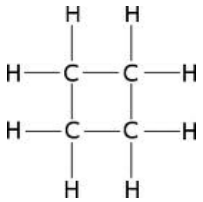


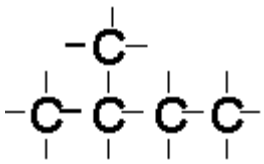


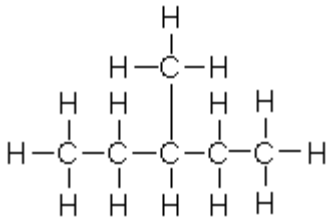
11.a)Write the line-bond notation for the following molecules:

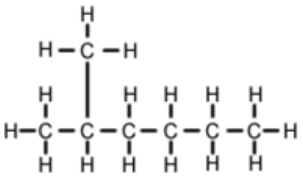


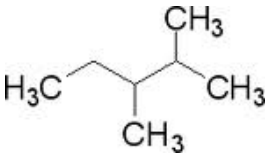


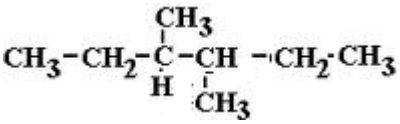


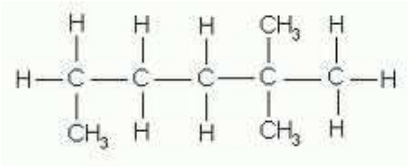












(Watch out, the longest unbranched chain is NOT 5 C atoms!)

b) Write the line-bond notation for the following molecules:

butane hexane octane decane

12.Write the expanded structural formulas for all isomers with following formulas. You should be able to draw the number of isomers given in parentheses.

a) $C_2H_3Br_3$(2) b) C_3H_7Cl(2) c)$C_3H_6Cl_2$ (4) d)$C_3H_5Cl_3$(5) e)C_3H_8O(3) f)C_4H_{10}(2) g)C_5H_{12}(3) h) $C_4H_{10}O$(6)

13. Draw all the possible isomers with the formula $C_2H_2F_2$. Indicate two that are geometric isomers of each other and two which are structural isomers of each other. Please note that the same structure can be a structural isomer of one molecule and a geometric isomer of another molecule.

14. What is the difference between a structural isomer and a geometric isomer? Draw 2 structural isomers with the formula C_3H_6 and 2 structural isomers with the formula $C_3H_4Cl_2$.

15. Explain the various uses for DES. Explain why the concept of cis and trans isomers relates to DES. Which geometric isomer is the active one?

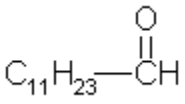
16. Draw all the different isomers that are possible when two F atoms are substituted on a three-membered cyclopropane ring.

17. Write structures for all the isomers with the following formulas. The number of isomers you should be able to find is given in parentheses.

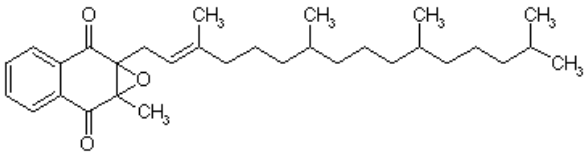
a) C_3H_9N (4) b)$C_4H_{11}N$(7) c) C_3H_5F(7;there are more) d) $C_3H_4Cl_2$(10)

You will need to have a double bond or a ring in c) and d).

18. Label the functional groups in the following molecules

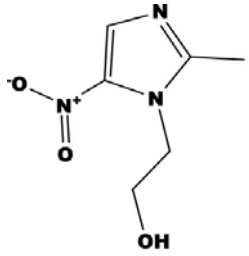


(One of the ingredients in Chanel#5 perfume)

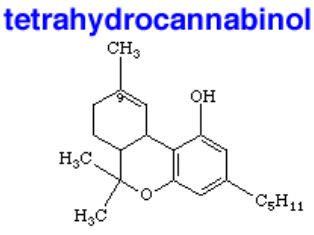


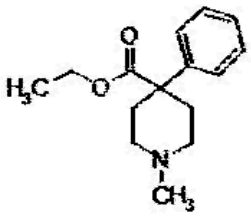
Vitamin K derivative

19. Label the functional groups in the following drug molecules

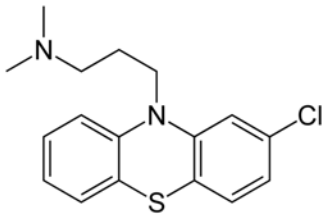


Metronidazole (Flagyl)

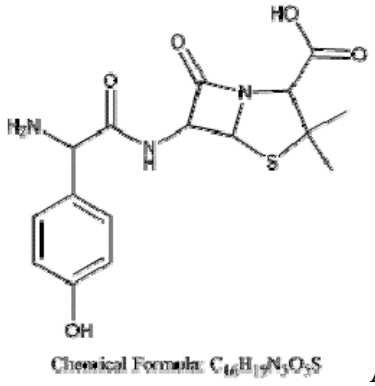




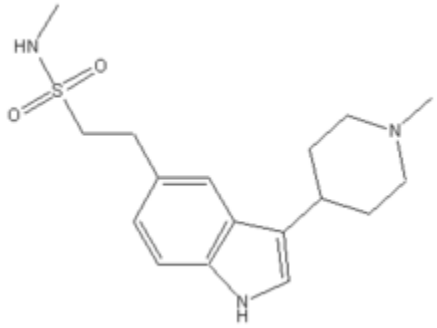
Meperidine
Demerol)



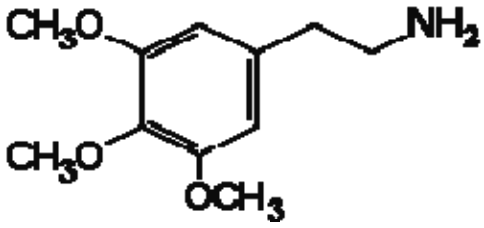
chloropromazine



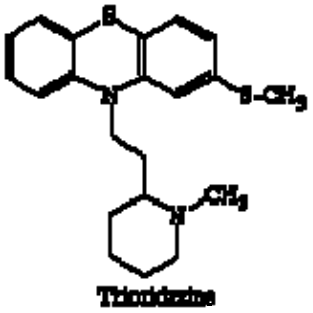
Amoxicillin

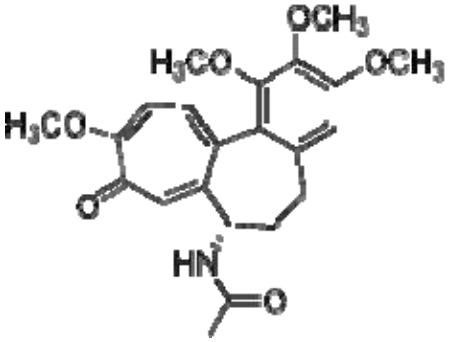


Naratriptan(Amerge)

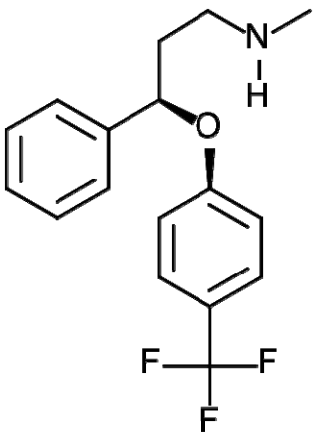


Mescaline

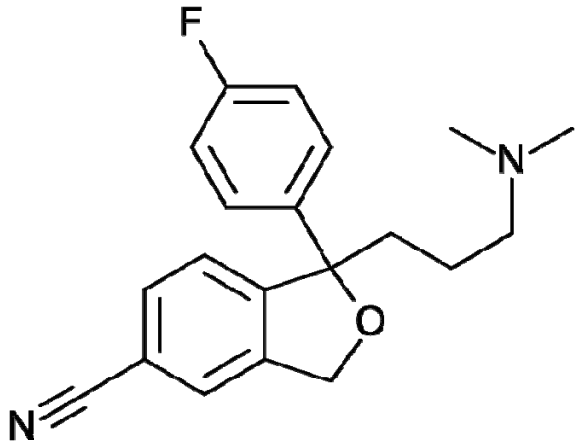




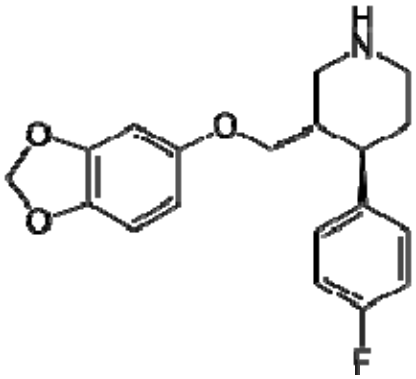
Colchicine



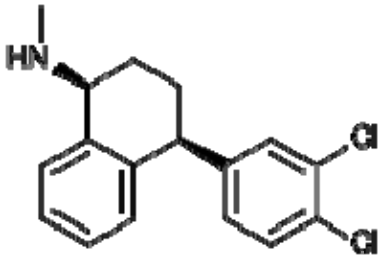
Fluoxetine(Prozac)



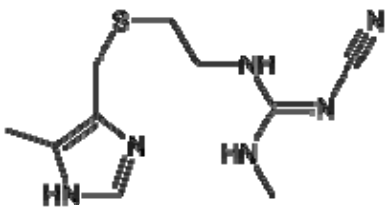
escitalopram(Lexapro)



Paroxetine(Paxil)

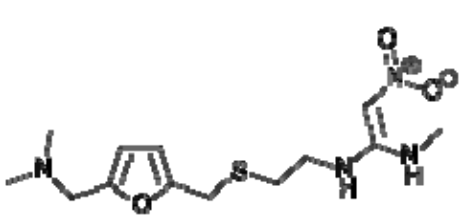


Sertraline(Zoloft)

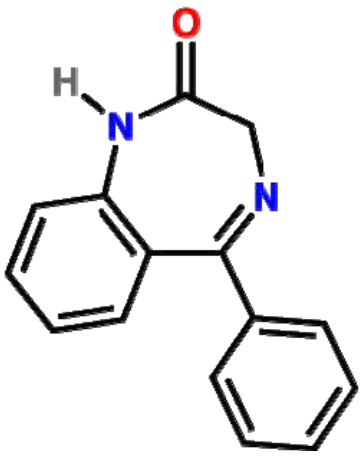


Cimetidine(Tagamet)

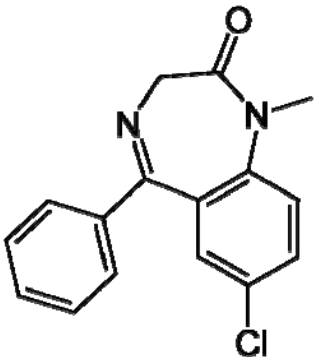
Grapefruit flavor

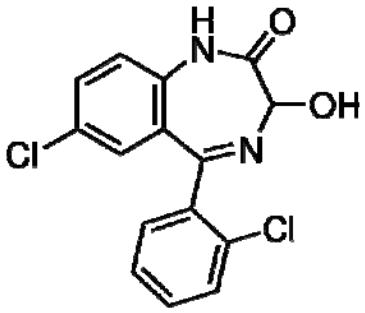


Ranitidine (Pepcid) nizatidine(trade name Axid)

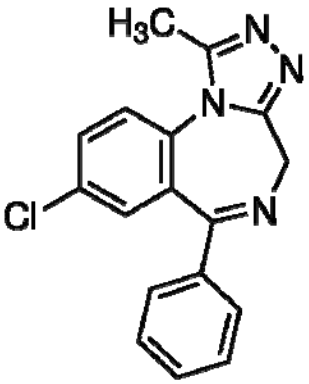


Benzodiazepine



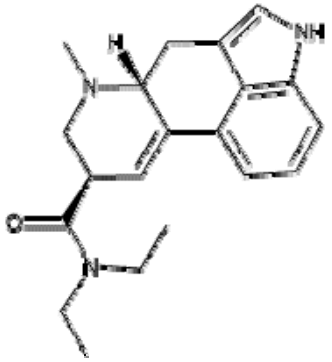


Diazepam(Valium) lorazepam(Ativan)



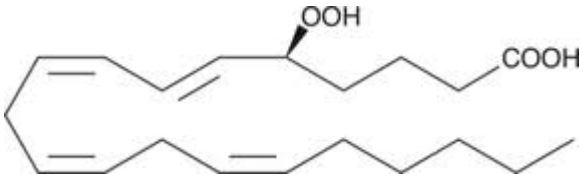
alprazolam(Xanax)

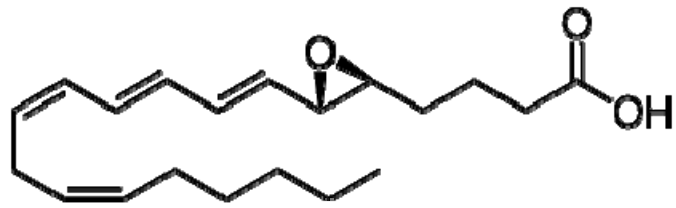
Can you see why the drugs Valium, Ativan and Xanax are all classified in the same family? (the benzodiazepine class of sedative drugs)?



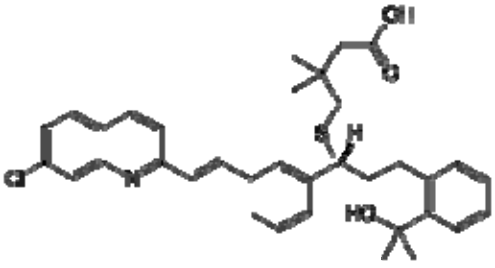
LSD

LSD is the abbreviation for lysergic acid diethylamide. Can you find the amide group in the structure above?

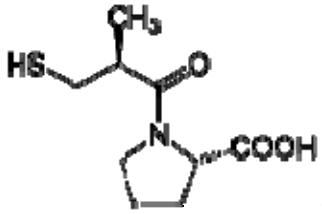




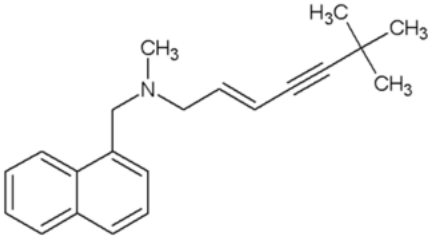
Leukotriene A4



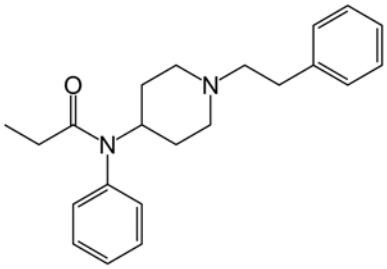
montelukast(Singulair)



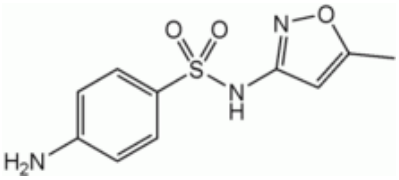
captopril(ACE inhibitor)



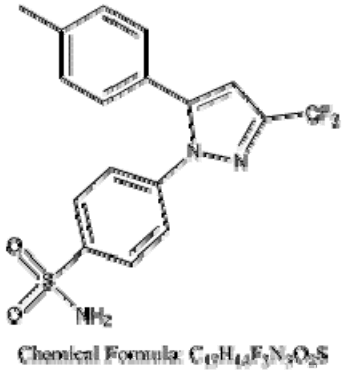
Terbinafine(Lamisil)



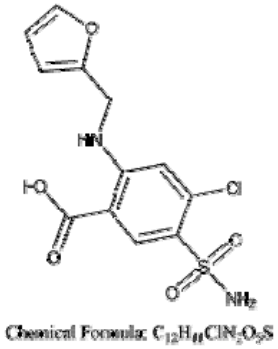
Fentanyl



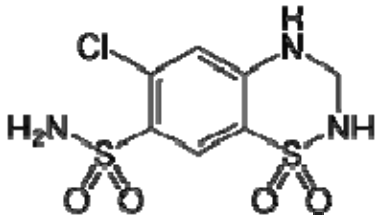
Sulfamethoxazole(SMX)



celecoxib(Celebrex)



furosemide(Lasix)



Hydrochlorothiazide(HCTZ)

Do an internet search and find out what 5 of the above drugs are commonly used for.

Identify the functional groups in prochlorperazine(structure below) and find out its main clinical uses.