Chapter 2:

VSEPR and Other Representations of Molecular Structure

A judge reminisces about a young woman he tried many years ago for murder,
and what she said just before her sentencing. In her statement she said:

“‘What I have been listening to in court is not my life.
It is the shape and shadow of my life. With the accidents of truth taken out of it.’”
– *The Chalk Garden* and quoted again in real life
by Alger Hiss in his own defense against charges of
espionage and perjury-he was convicted of perjury in 1950.

2-1. Introduction:

Lewis structures are one of the many types of molecular representations used in chemistry. The VSEPR model transforms those 2-D Lewis structures (Ch 1) into more realistic 3-D molecular representations for both electronic geometries and their associated molecular shapes. This distinction between molecular shape and electronic geometry is at the heart of a fundamental issue with any type of molecular representation: Just what is it that we want to illustrate or show using a particular representation?

2-2. What will be presented:

1. More about the difference between an electronic geometry and possible molecular shapes.
2. How bond dipoles interact to create molecular dipoles that can combine to produce polar molecules.
3. The different types of representations used to describe molecular structure.
4. Suggestions for how to draw these different types of molecular representations.

“For Christmas, 1939, a girl friend gave me a book token which I used to
buy Linus Pauling’s recently published *Nature of the Chemical Bond*.
His book transformed the chemical flatland of my earlier textbooks into
a world of three-dimensional structures.”

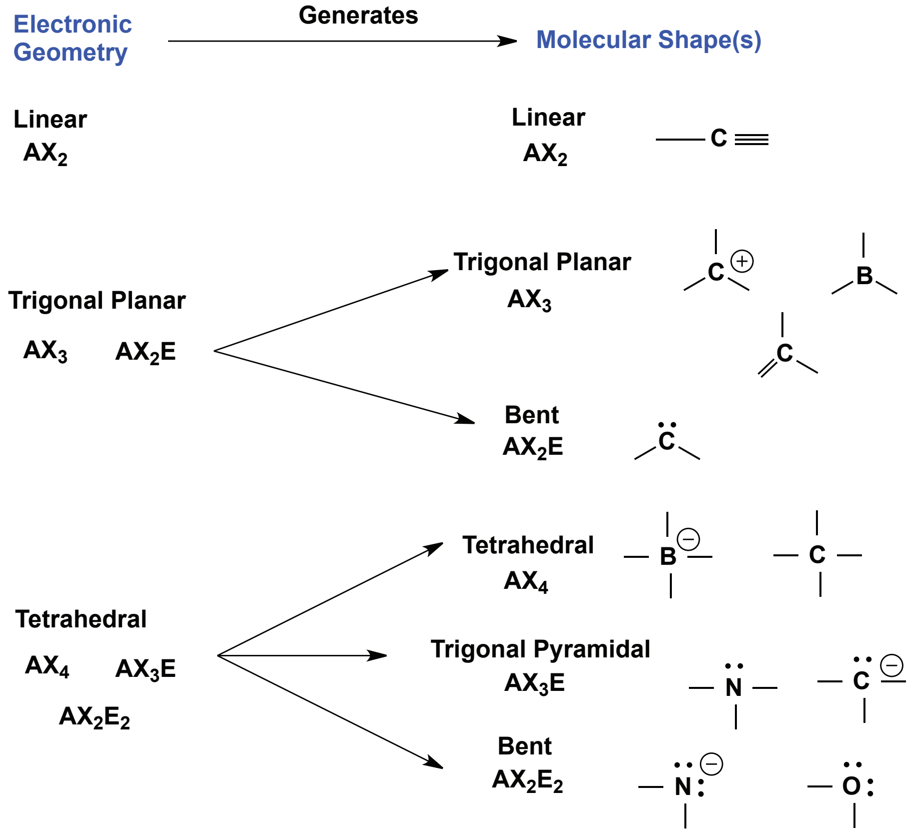
– Max Ferdinand Perutz from “What Holds Molecules Together”,
in the book: *I Wish I’d Made You Angry Earlier* (1998), p165.

2-3. Electronic Geometry and Molecular Shape:

In Chapter 1, an algorithm was used to produce Lewis structures and then those “best” Lewis structures were analyzed using the VSEPR (valence shell electron pair repulsion) theory to determine electronic geometries (Ch.1, Figure 1-16) and then their attendant molecular shapes (Ch. 1, Figure 1-17). Although electronic geometry is relatively easy to determine for a Lewis structure, assigning a molecular shape takes a bit more effort simply because there are more possible molecular shapes than there are electronic geometries.

Those particular electronic geometries and their attendant molecular shapes frequently encountered in Organic Chemistry are emphasized again in Fig. 2-1:

Figure 2-1. Electronic geometries and molecular shapes most important to Organic Chemistry:


Electronic Geometry
Generates
Molecular Shape(s)
Linear
AX_2
Linear
AX_2
C
Trigonal Planar
AX_3
AX_2E
Trigonal Planar
AX_3
C
B
C
Bent
AX_2E
C
Tetrahedral
AX_4
AX_3E
AX_2E_2
Tetrahedral
AX_4
B
C
Trigonal Pyramidal
AX_3E
N
C
Bent
AX_2E_2
N
O

Notice that both (AX_2E and AX_2E_2) have bent molecular shapes but they each belong to different electronic geometries.

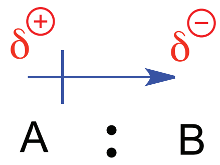
Take some time to familiarize yourself with this smaller selection in Fig. 2-1 because it will be assumed, going forward, that you understand this terminology and that you also know how use this AXE notation to describe molecular structures.

2-4. Electronic geometry, molecular shape and polar molecules:

As was mentioned in Ch 1, heteroatom covalent bonds are polarized because each atom at either end of such a bond possess different values of EN. The polarization created by these unequally shared bonding electron pair(s) adds some additional partial ionic character (i.e. δ^+ and δ^-) to an A-B bond. This partial ionic character not only stabilizes a covalent bond but this dislocation of an electron pair towards the more electronegative end of that A-B bond also creates a bond dipole (within both single and also multiple bonds). This dipole lies along the bond axis connecting these two A and B atoms:

Figure 2-2. Bond dipole for polar A-B bond:

Bond dipole for A-B:

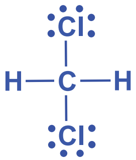
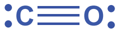
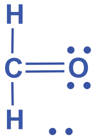
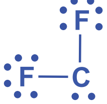
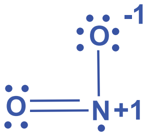
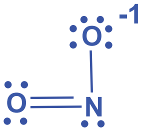


EN(B) > EN(A)

⇨ as the bonding e^-pair is pulled closer to B, it creates partial ionic charges at the ends of the A-B bonding axis. Thus dipole arrow points at the partially negatively charged B atom .

These A-B bond dipoles have a magnitude that depends on both ΔEN(A-B) and A-B bond length. Multiple bond dipoles also will have relative orientations within the geometry of a molecular structure. After evaluating the number of dipoles, their magnitudes and relative orientations, one can use vector summation to determine whether or not these bond dipoles combine to create a total or net molecular dipole. If there is a net molecular dipole (no matter the magnitude) then that molecule, in that geometry, is said to be a polar molecule. Not all polar molecules have molecular dipoles of the same magnitude, and as a result, polar molecules often possess molecular dipoles with differing magnitudes.

Q: For the following molecules, construct their Lewis structures. Then using the VSEPR model determine their 3-D structures (i.e. electronic geom and mol shape). Next use their VSEPR structures to both identify bond dipoles and then use this information to determine whether or not a molecule is polar or non-polar:

				(elec. geom, mol. shape)
a) CH_2Cl_2	$2(1)+1(4)+2(7)= 20e^-$; $10e^-$pairs		AX_4	(Td, Td)
b) CO	$1(4)+1(6)= 10e^-$; $5e^-$pairs		AXE	(Linear, Linear)
c) CH_2O	$2(1)+1(4)+1(6)= 12e^-$; $6e^-$pairs		AX_3	(Trig. Planar, Trig. Planar)
d) CF_2	$1(4)+2(7)= 18e^-$; $9e^-$pairs		AX_2E	(Trig. Planar, Bent)
e) NO_2	$1(5)+2(7)= 19e^-$; $9e^-$pairs + 1 e^-		$AX_2E^{1/2}$	(Trig. Planar, Bent)
f) $^{-1}NO_2$	$1(5)+2(7) +1e^- = 10e^-$; $10e^-$pairs		AX_2E	(Trig. Planar, Bent)

2-5. Just Connectivity information: (Condensed, Kekule, Lewis, and Skeletal Molecular Representations)

Notice that Lewis structures indicate a specific atom connectivity- which atoms are bonded to which atoms, and whether those bonds between atoms are (single, or multiple), and also which atoms in a Lewis structure, if any, possess non-bonding electrons. Interpreting a 2-D (2-demensional) Lewis structure within the VSEPR model provides a 3-D (3-demensional) representation for that Lewis structure. This VSEPR translation of a 2-D Lewis structure into a 3-D structure is a natural segue into a more general discussion of several graphical notations that chemists use to represent more complex molecular structures than those with only one central atom (i.e. AX_mE_n).

So how do chemists represent 3-D molecules using 2-D media? The choice of representation will depend on what information we wish to communicate about a given molecular structure. An important first question to ask is: Does one just need to emphasize connectivity information, electronic geometry for a molecule, or is it also necessary to communicate something additional about the 3-D shape of that molecule?

a. Condensed Notation: This is a flat 2-D representation, easy to do on a word processor. However, this notation becomes too cumbersome for large or complex molecules.

$$\mathrm{CH_3CH_2CH(CH_3)CH_2CH(CH_3)_2}$$

2-1

Since it is easy to type set this representation, it often is used on standardized tests to explicitly identify atom type and molecular connectivity for small molecules. For the molecule above we interpret or "read" a representation like 2-1 starting from the left and moving to right.

Parentheses indicate that those atoms inside a parenthesis are attached to that **atom immediately to the left of the parenthesis.**

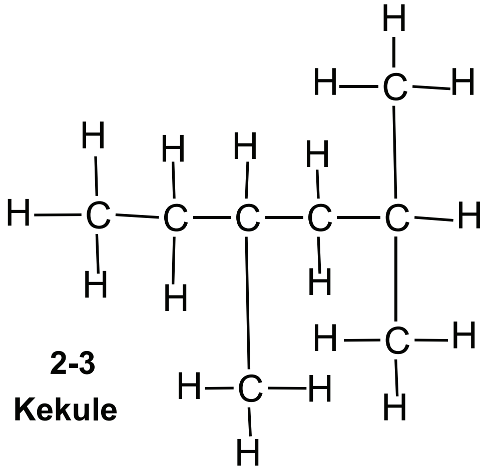
Warning*This notation can be particularly treacherous in high pressure situations. Thus one needs to interpret such representations with both concentration and caution.**

A good first step in interpreting this type of representation is to redraw a condensed notation, like 2-1, by placing a dash between groups of atoms along a designated chain of atoms **just as they are presented to the reader**. For example, this is how this process is applied to the condensed notation for structure 2-1 to form an extended condensed hybrid structure 2-2:

$$\mathrm{CH_3\text{-}CH_2\text{-}CH(\text{-}CH_3)\text{-}CH_2CH(\text{-}CH_3)_2}$$

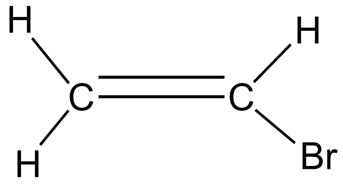
2-2

Then one can translate structure 2-2 into a Lewis structure, or into one of the other representations like a Kekule representation (2-3):

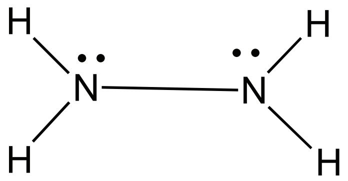


2-3
Kekule

b. Lewis vs Kekule representations: Both Lewis and Kekule representations are flat representations — that only represent connectivity. These particular representations are useful for simple molecules, but also like the condensed notation, they rapidly become too cumbersome for large molecules. These representations for large complex molecules require too much space to represent both the number and location of all their bonds. The required space for large molecule representations become so cluttered that significant structural features often are easily hidden in plain sight.



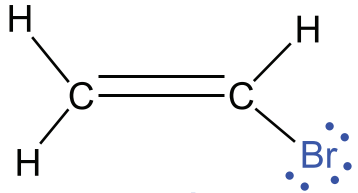
Kekule
2-4



Lewis
2-5

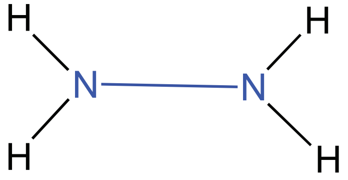
The technical difference between Kekule structures (e.g. structure 2-4) and Lewis representations (e.g. Structure 2-5) is that Kekule structures only illustrate the connectivity of covalent bonds where as **Lewis structures show BOTH bond connectivity and locations of non-bonding electrons**.

Q: Draw a Lewis representation for structure 2-4 and a Kekule representation for structure 2-5:



Lewis

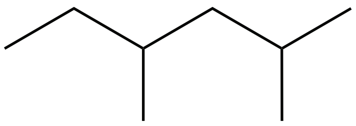
2-4



Kekule

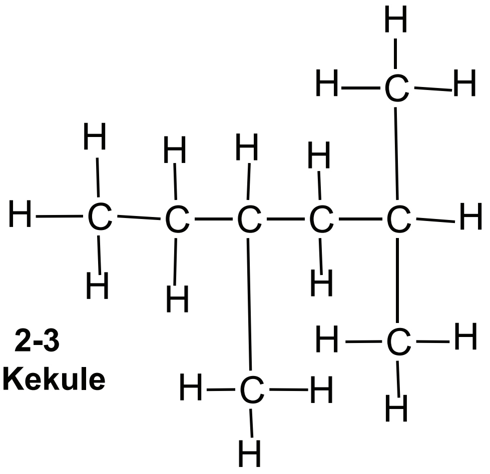
2-5

c Line-angle or skeletal representations:



2-6

Skeletal



2-3

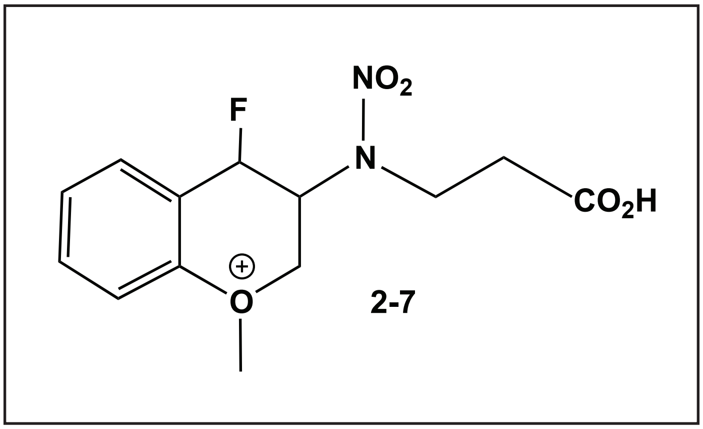
Kekule

Both structure 2-3 and structure 2-6 represent the same molecule, but for skeletal representations (e.g. 2-6), it much easier to see the forest (i.e. C-C connectivity) without getting lost in the trees (i.e. C-H connectivity). The interpretation of connectivity information presented by skeletal representations assumes:

1. Unless specified otherwise, any carbon atom in a molecule is assumed to have 4 covalent bonds and any un-bonded valences will be indicated by adding electrons (e.g. ↑) and/or charges (e.g. +, or –) onto such carbon atoms if they have less than 4 covalent bonds and if they also differ from a formal charge of zero.

2. Methyl groups (-CH_3) are located at the end of lines, methylene groups (-CH_2-) are represented by what might be called "vertices" or even "kinks" in a line. If needed, any of these terminal or kink positions can be replaced by a heteroatom or some other functional group.

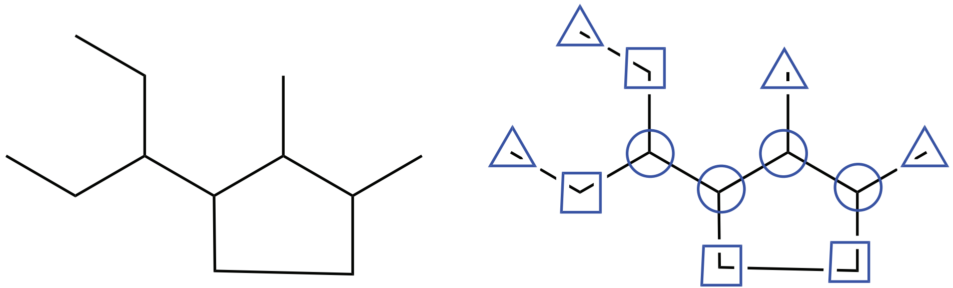
3. Other heteroatoms, typically include: O, N, S, P, Si or perhaps even a functional group like –CO_2H are drawn "as required" and attached to their appropriate carbon positions. An example of a more complex molecular structure that illustrates these rules for a line/angle or skeletal representation is shown for structure 2-7:



Skeletal or line/angle notation is both very efficient and compact. We'll also see a bit later just how this skeletal notation can be easily modified to also include important 3-D information.

Take a moment to compare the side-by-side representations for structures 2-3 and 2-6 shown above. Once you can interpret a skeletal representation, it very easy to see that for structure 2-6 this molecule consists of three types of carbon groups: 4(-CH_3), 2(-CH_2-) and 2(CH). This process would take a bit longer if one has to interpret the information from a corresponding Kekule representation like 2-3.

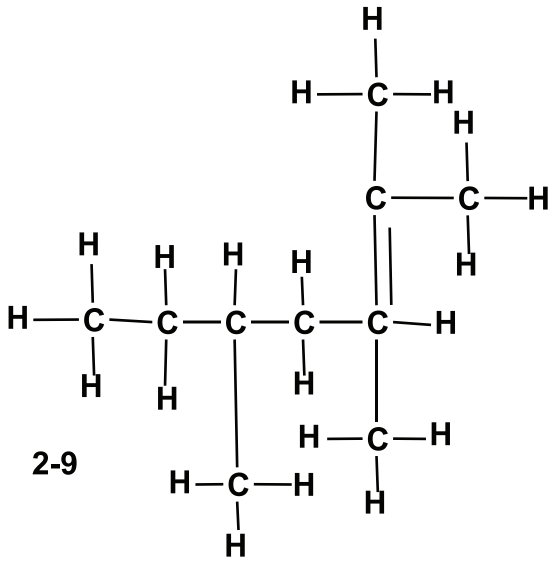
Q: Using triangles for –CH_3, squares for –CH_2–, and circles for CH or even three different colored pens, locate these three different types of carbon groups in the Kekule representation for structure 2-8:



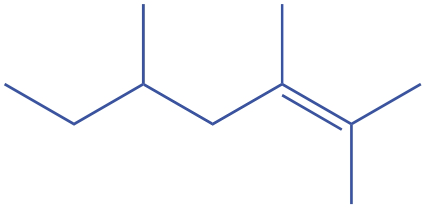
2-8

4 CH_3 4CH_2 4 CH

Q: Redraw the Kekule structure (2-9) using skeletal notation: (Hint: first find the longest carbon chain):



2-9



How quickly did you notice the C=C bond and its location within structure 2-9?

Q: What is the longest chain of carbon atoms possible for the compressed molecular representation 2-10:

$CH_3CH_2CH(CH_3)CH_2CH(CH_2CH_3)_2CH_3$

2-10

$$\underset{1}{CH_3}\text{-}\underset{2}{CH_2}\text{-}\underset{3}{CH}(CH_3)\text{-}\underset{4}{CH_2}\text{-}\underset{5}{CH}(\underset{6}{CH_2}\text{-}\underset{7}{CH_3})_2\text{-}\underset{6'}{CH_3}$$

Q: If the longest carbon chain above for 2-10 is renumbered (starting from the far right end), then at what numbered positions or locations are the pendant methyl groups (i.e. -CH_3) attached? (Hint: First analyze the compressed notation to determine the longest chain of carbons.)

reversing the numbering $\underset{7}{CH_3}\text{-}\underset{6}{CH_2}\text{-}\underset{5}{CH}(CH_3)\text{-}\underset{4}{CH_2}\text{-}\underset{3}{CH}(\underset{2}{CH_2}\text{-}\underset{1}{CH_3})_2\text{-}CH_3$

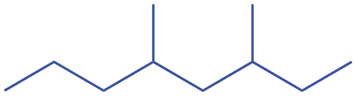
moving down the C7 chain, the methyl groups are at positions: C3 and C5

Q: What is a skeletal structure for the 2-11 condensed representation?

$CH_3CH_2CH_2CH(CH_3)CH_2CH(CH_2CH_3)_2CH_3$

2-11

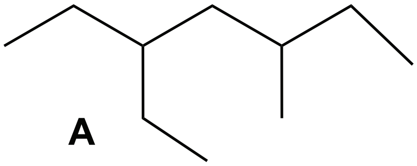
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_2CH_3)_2\text{-}CH_3 \Longrightarrow$



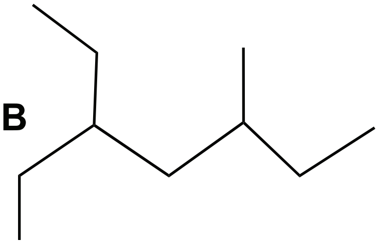
Q: Which of the skeletal representations below also could be used to represent the condensed structure 2-12?

$CH_3CH_2CH(CH_2CH_3)CH_2CH(CH_2CH_3)CH_3$

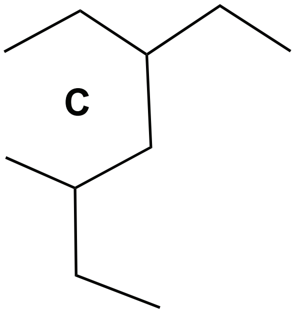
2-12



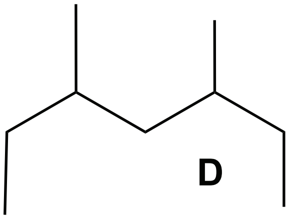
A



B



C



D

A , B, C

2-6. Representations that provide 3-D information:

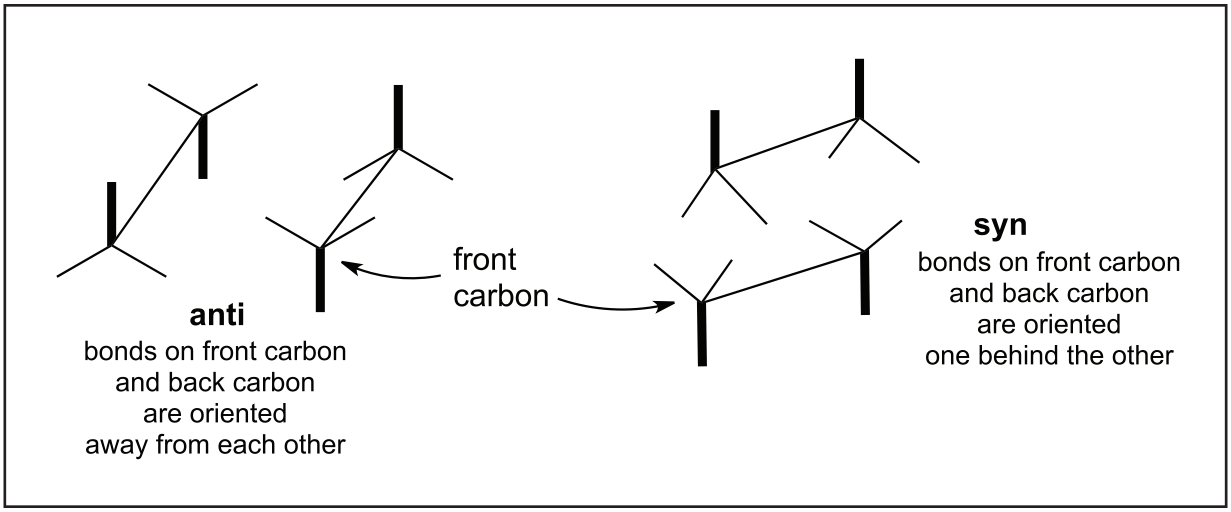
There are 5 basic types of representations that provide 3-D information about the orientation of atoms or groups within a molecule:

a. Sawhorse: This representation also is old school; only practice will help you master drawing, interpreting and manipulating this representational form. One needs to be careful in determining which carbon and groups are in front (typically drawn just below their back carbon atoms). Front carbon atoms are those carbons "orientated" towards the reader, where as the back carbons are "oriented" farther away from the reader. In the beginning, working from molecular models will be both useful and often essential.

Note, I am a big fan of Darling Models, because they are big in size, easily manipulated and also relatively inexpensive. However, many students have difficulty assembling the pieces in a kit. To solve this problem I have created several YouTube videos that assist with assembly and also illustrate the basics for how models are used in Organic Chemistry:

Darling Model Assembly: https://youtu.be/m2uuZumLojQ
Using models to determine whether structures are the Same or Different? https://youtu.be/Urrkjz5poUg
Using models to solve a problem: https://youtu.be/iIDR4CLyjgM

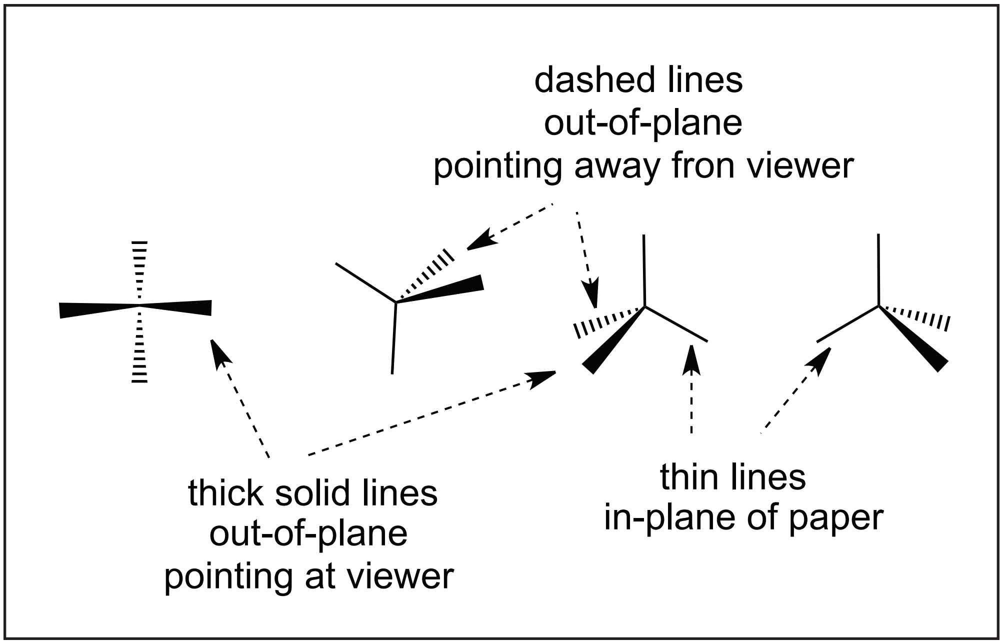
Figure 2-3. Sawhorse representations for both syn and anti-oriented structures:


front
carbon
anti
bonds on front carbon
and back carbon
are oriented
away from each other
syn
bonds on front carbon
and back carbon
are oriented
one behind the other

It is recommended that if one does not have access to molecular models, that rather than manipulating a sawhorse representation on paper, such representations should be translated into an equivalent wedge-dash representation (see below). This act should help provide a less visually confusing 3-D interpretation of just what is being portrayed by a given sawhorse representation.

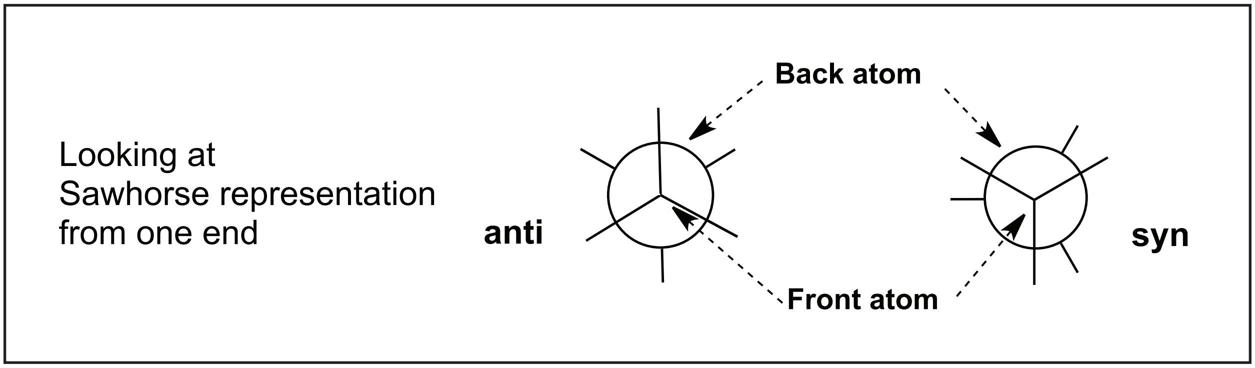
b. Wedge-Dash: Wedge-dash is easy to draw — very informative and easy to learn to manipulate. It can be applied to express the stereochemistry even for large complex molecules when this notation also is combined with skeletal notations.

Figure 2-4. Wedge-dash representation for tetrahedral centers:


dashed lines
out-of-plane
pointing away fron viewer
thick solid lines
out-of-plane
pointing at viewer
thin lines
in-plane of paper

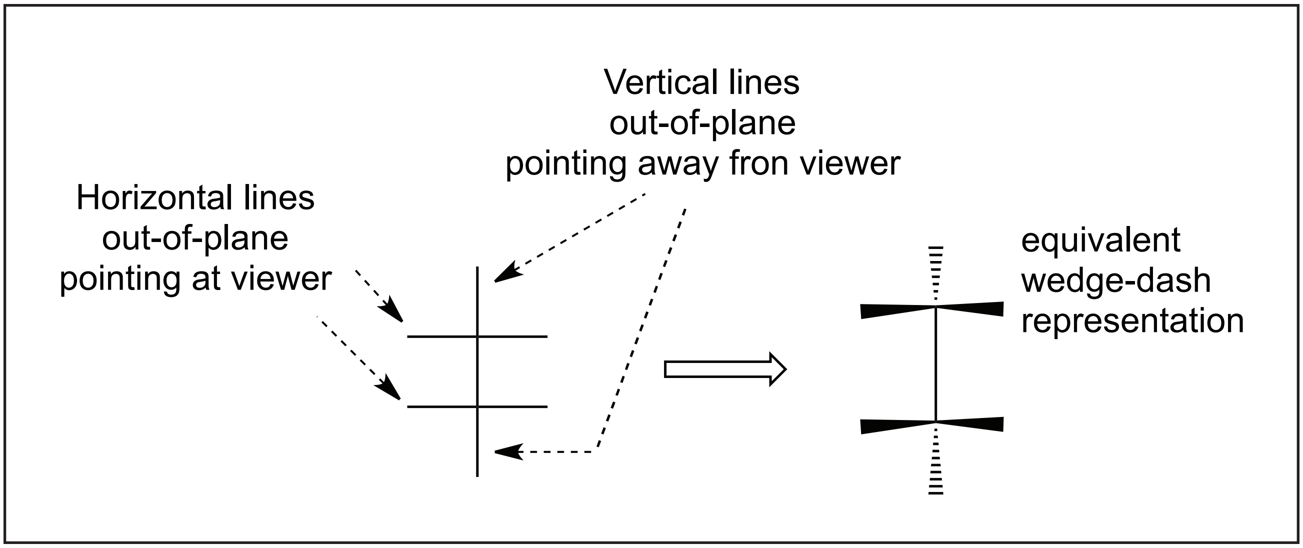
c. Newman: Newman projections are easy to draw, very informative in providing stereochemical information immediately around two bonded central atoms.

Figure 2-5. Newman Projection for two adjacent tetrahedral carbon centers:


Looking at
Sawhorse representation
from one end
Back atom
anti
Front atom
syn

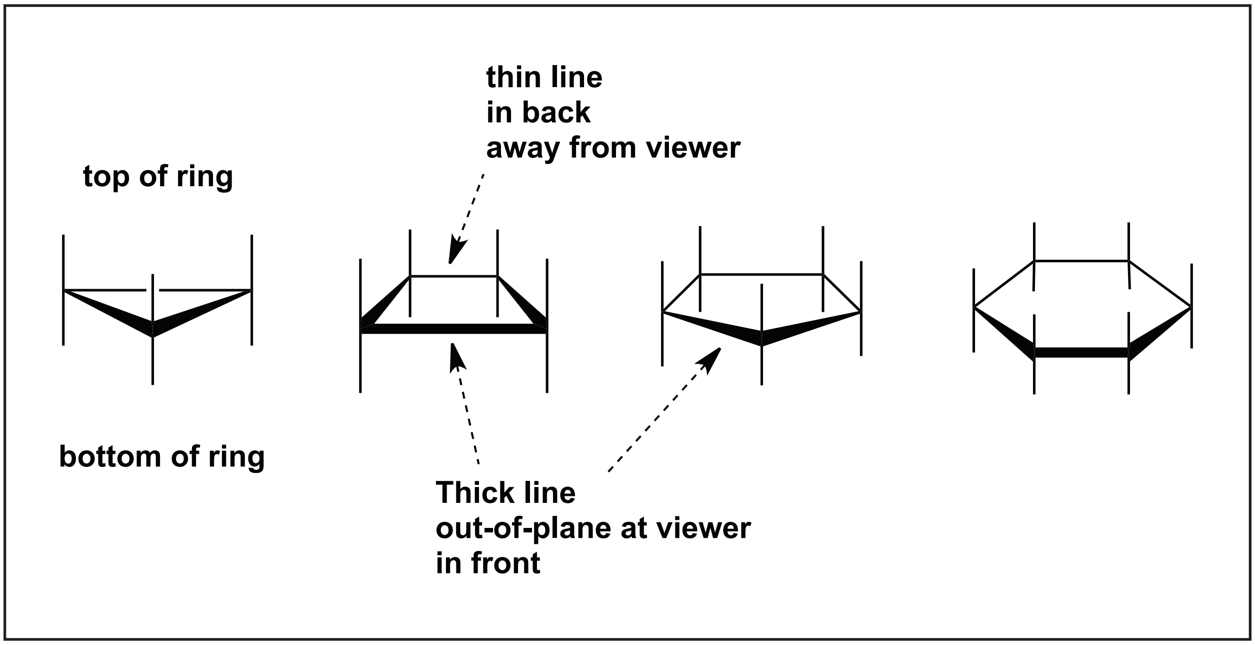
d. Fischer: Fischer is old school — it’s easy to learn and also interpret. However, only practice will make manipulation of this representation accurate. In the beginning, molecular models will be useful in interpreting what is represented in a Fischer representation. It's the manipulation of a Fischer representation, without the aid of models, which often leads the novice into problems.

Figure 2-6: Fischer Projection is a representation ONLY of a syn structure:


Vertical lines
out-of-plane
pointing away fron viewer
Horizontal lines
out-of-plane
pointing at viewer
equivalent
wedge-dash
representation

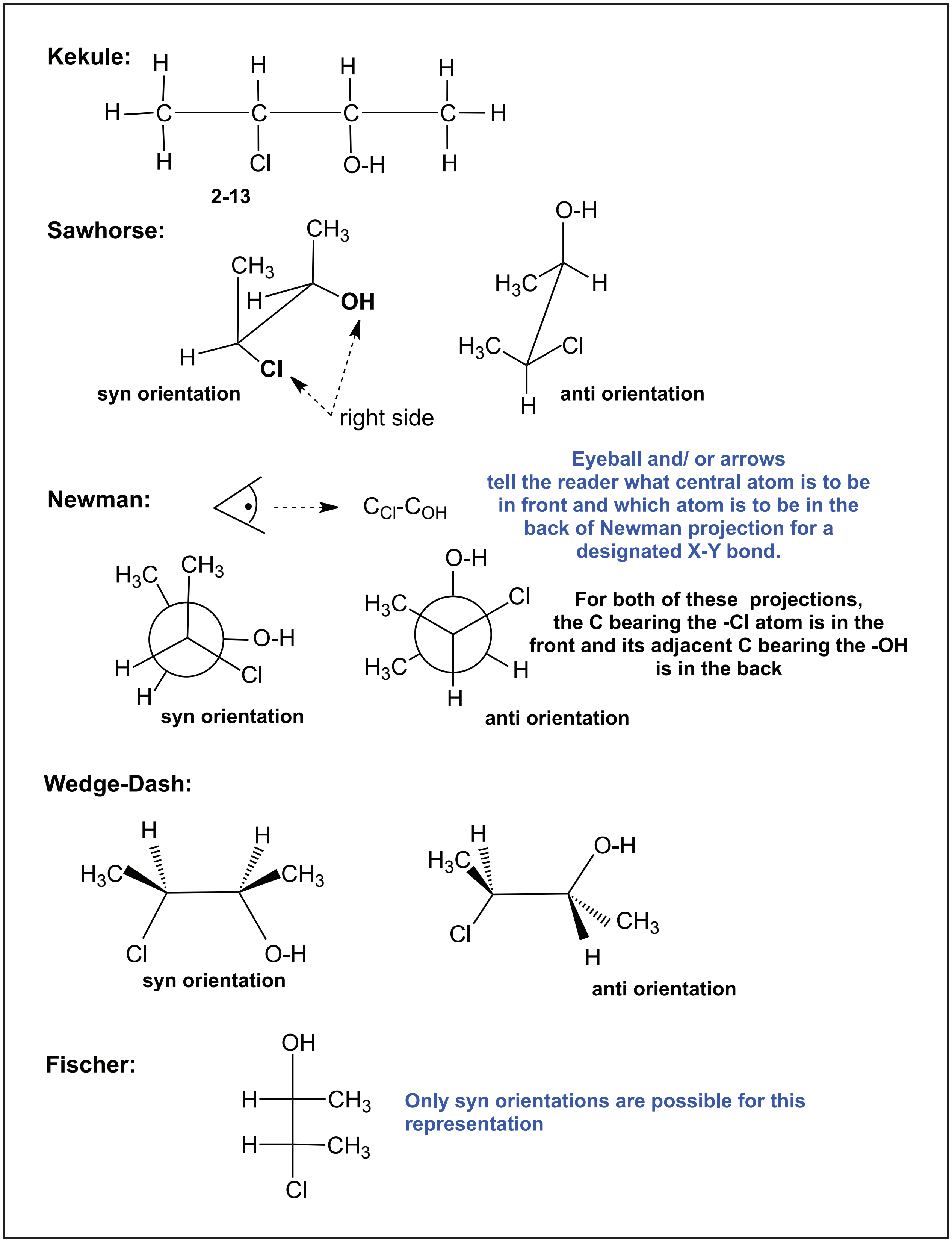
e. Haworth: Haworth also is another of the of the old school representations-It too is easy to learn and interpret. Care is required, especially when this representation is used to describe carbohydrates. There is additional information about using Haworth representations to represent carbohydrate structures in Appendix 21h. You'll probably need to wait until after Ch 5 has been completed before you can fully comprehend all the information presented in this appendix.

Figure 2-7. Haworth representations for 3, 4, 5, 6 membered rings:


thin line
in back
away from viewer
top of ring
bottom of ring
Thick line
out-of-plane at viewer
in front

Samples of these various molecular representations that go beyond a Kekule representation like 2-13 to also include stereochemical information are shown in Fig. 2-8:

Figure 2-8. Examples of these different stereochemical representations applied to a Kekule structure for molecule 2-13:


Kekule:
2-13
Sawhorse:
syn orientation
right side
anti orientation
Newman:
C_{Cl}-C_{OH}
syn orientation
anti orientation
Wedge-Dash:
syn orientation
anti orientation
Fischer:

Eyeball and/ or arrows tell the reader what central atom is to be in front and which atom is to be in the back of Newman projection for a designated X-Y bond.

For both of these projections, the C bearing the -Cl atom is in the front and its adjacent C bearing the -OH is in the back

Only syn orientations are possible for this representation

Correctly drawing AND then interpreting structural representations are vital to understanding the physical and chemical properties of molecules. In upcoming chapters we will discuss the stereochemistry of molecular structures in more detail so you'll need to learn how to draw, manipulate, and interpret these types of representations.

2-7. Drawing suggestions for some of these different representations:

In addition to the VSEPR problems, there also will be problems that involve drawing, converting, and also manipulating these different types of molecular representations. The Lewis structure questions are relatively straight forward because you already have used this type of representation in your general chemistry courses.

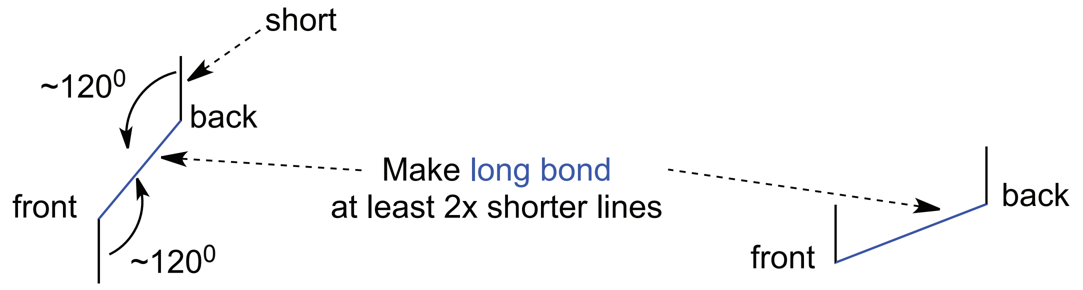
You'll need to learn how to draw organic structures and then you can learn how to manipulate their 2-D representations. Initially practice by learning to draw structures cleanly and with the necessary structural information all within a 3 x 3 square. Don't make your drawings too small. Keeping your drawings within a 3x3 square initially will take a bit of effort and practice, but stick with it because this skill will pay some big dividends in just a few chapters. As you get better, then you can get smaller say down to a 2 x 2 square. However, if you try to get too small too fast, your representations will become too confused and you'll lose track of the structural information that you are trying to represent.

Drawing clean structures generally requires first drawing the skeleton of a representation, and then filling in the remaining structural details (e.g. functional groups and substituents). Too often students get lost because they try to draw a representation at the same time they are trying to attach substituents or functional groups to that representation. Also, DO NOT draw over the top of an existing drawing — sloppy corrections often lead to confusion and erroneous interpretations of structural information.

a. Suggestions for drawing Sawhorse representations:

(Complete a sawhorse structure first, then attach its pendant groups)

Step 1: Get the vertical lines/bonds and long bond properly oriented.



Make long bond
at least 2x shorter lines

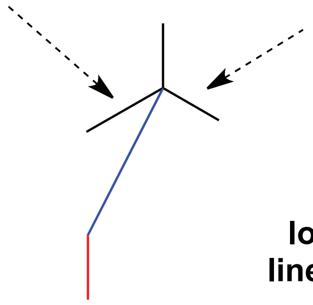
anti orientation

syn orientation

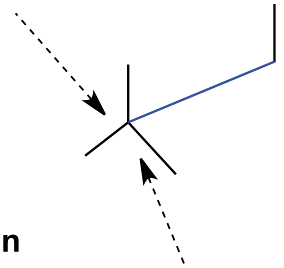
Step 2: Fill in all of the bonds to one center first before completing bonds to the second center.

Fill in either the front
or back bonds

keep additional bond
lines shorter than
long bond

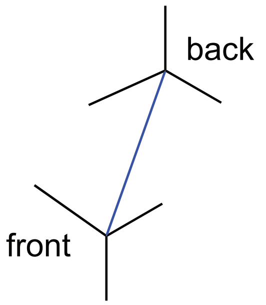


Be consistent:
Keep lines coming
at the front, either
longer or shorter than
lines on the back carbon

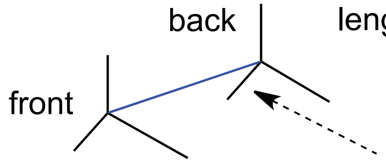


Hint: fill in this
front bonds first
to help get the
angles and
lengths right.

Step 3: Fill in the missing carbon bonds.



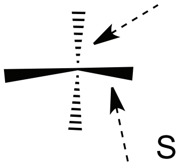
completed anti orientation



completed syn orientation

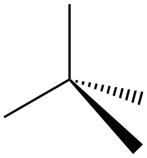
Make sure this
short bond
is clear of the
long bond

b. Suggestions for drawing Wedge-Dash representations:



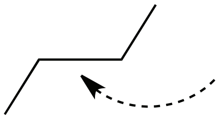
Dashed lines are bonds
going behind the plane of paper
away from the viewer

Solid Wedges are bonds
coming from the plane of paper
towards the viewer

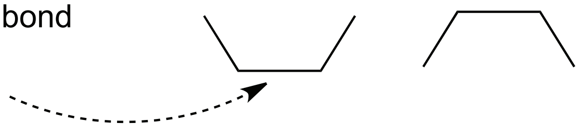


thin lines are bonds
in the plane of paper

Step 1: First draw those bonds that belong in the plane of the paper:



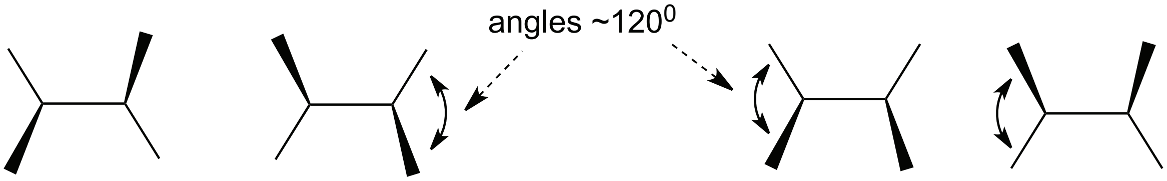
make sure that center bond
is a bit longer than
wedges and dashes



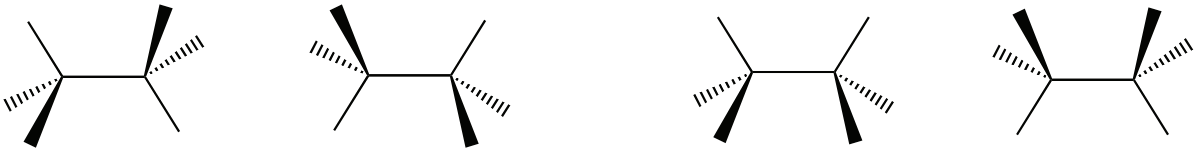
For anti-orientation use
twisted Z or lightning bolt

For syn-orientation use
a splayed U-pointed up
or pointed down

Step 2: Fill in Wedges:

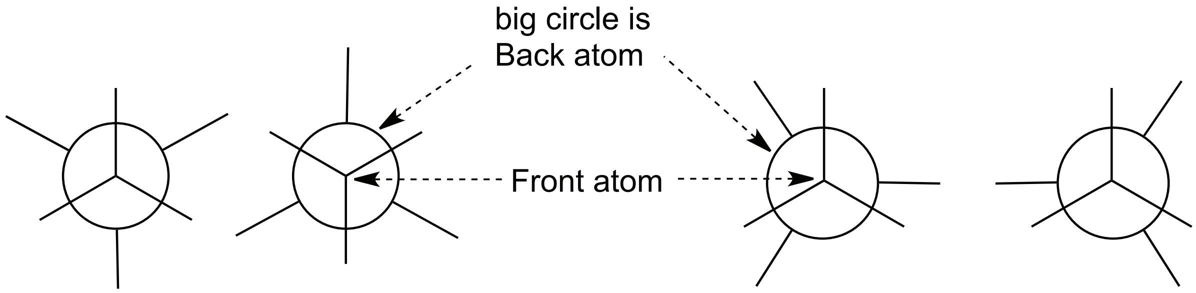


Step 3: Fill in missing dashes:



anti-orientation **syn-orientation**

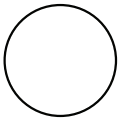
C. Suggestions for drawing Newman projections:



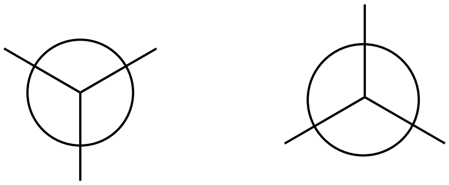
anti-orientation

syn-orientation

Step 1: First draw the circle:

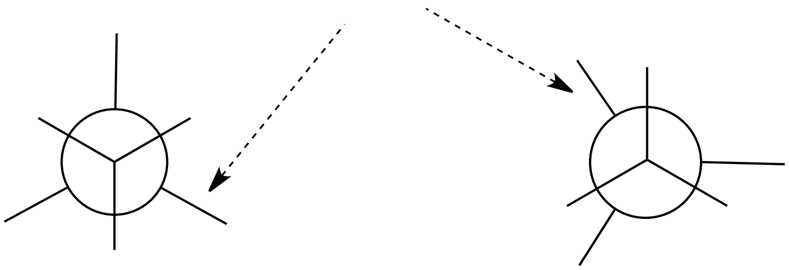


Step 2: Fill in front atom:



Step 3: Decide if projection will be syn or anti, then fill bonds around back atom:

Draw back bonds slightly noticably longer than front bonds



anti-orientation

syn-orientation

2-8. Conclusion:

In a larger sense how we represent the world around us is both liberating and constraining. It's liberating because models and representations permit simplification, and that simplification facilitates conceptualization. However, models also may become constraining if we become too infatuated and thus so captured by representations that they become **the** reality, rather than **a** reality. Never forget that representations and models are approximations of reality, they are not reality. For representations and models, it not so much about what they show as it is about how they can be used to first understand and then to make predictions.

In the case of molecular representations, there are a variety of models that can be used to both represent and visualize molecular structure. However, this visualization also comes with a subtle price that was articulated by one of the major contributors to the quantum mechanical description of covalent bonds and bonding:

> *"One is almost tempted to say... at last I can almost see a bond. But that will never be,*
> *for a bond does not really exist at all: it is a most convenient fiction which, as we have seen,*
> *is convenient both to experimental and theoretical chemists."*
>
> *– Charles A. Coulson, 'What is a Chemical Bond?', Coulson Papers, p25, Bodleian Library, Oxford.*
> *Also see Mary-Jo Nye,* From Chemical Philosophy to Theoretical Chemistry *(1993), p261.*

2-9. What you should know and be able to do:

1. Use the VSEPR rules to determine electronic geometry and molecular shape for Lewis structures.

2. Identify these different types of molecular representations.

3. Be able to select which is the best representation for a given molecular structure. To do this you'll need to evaluate and determine whether the emphasis should be on just connectivity information or is information about the 3-D structure or stereochemistry also required?

4. Make drawings of molecular structures using these different molecular representations.

5. Convert from one molecular representation into another, equivalent molecular representation.

6. Determine the longest chain of atoms from a representation.

7. Understand the difference between syn and anti representations.

8. Begin to interpret some of the information provided by a molecular representation. Does a set of representations describe the same molecule or are these representations for different molecules?

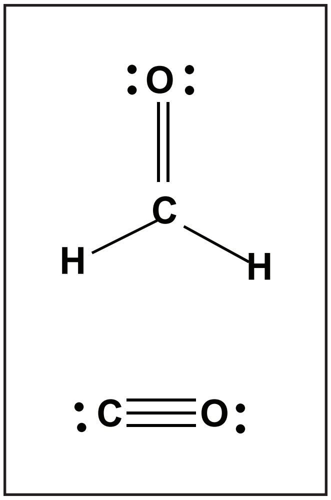
2-10. Problems:

1. Complete the table for the molecules shown below:

Molecule	Electronic Geometry	Molecular shape	Direction of bond dipole? Positive end-Negative end[1] (P_{left}-N_{right})	Polar Molecule? Yes/no
BeF_2				
NH_3				
NO_2				
O_3				

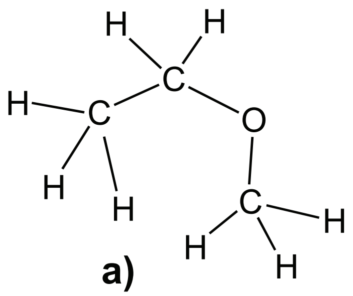
1) As an example, for HF your answer would be: H-F

2. Would you expect formaldehyde (H_2CO) or carbon monoxide (CO) to have the larger molecular dipole moment and why? (Hint: consider formal charges)

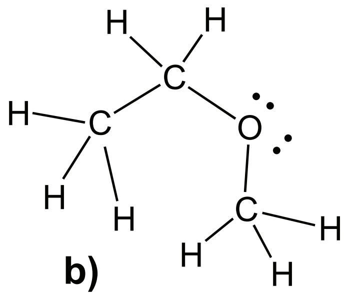


3. A molecule with a molecular formula AX_4 is found to be a polar molecule. Which of the following molecular shapes is it most likely to possess?
a. Tetrahedral
b. Seesaw
c. Square planar
d. Either tetrahedral or square planar
e. Either tetrahedral or seesaw

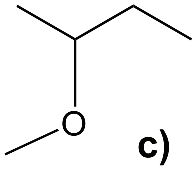
4. Name the following types of molecular representations:


H
H
H
C
C
O
H
H
C
H
H
H

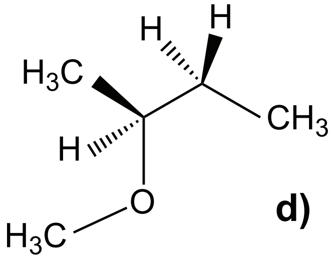
a)


H
H
H
C
C
O
H
H
C
H
H
H

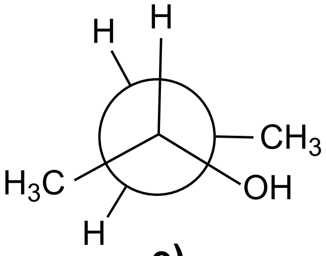
b)



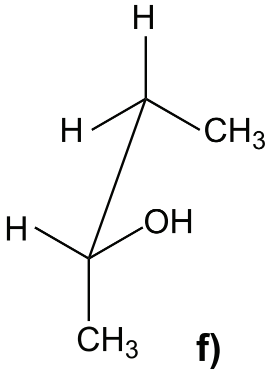
c)


H
H
H$_3$C
CH$_3$
H
O
H$_3$C

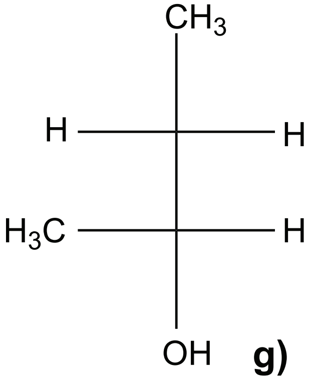
d)


H
H
CH$_3$
H$_3$C
OH
H

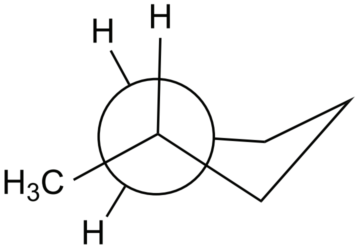
e)


H
H
CH$_3$
H
OH
CH$_3$

f)

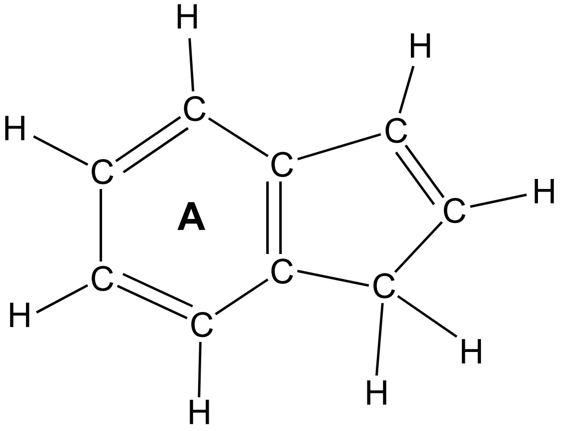

CH$_3$
H
H
H$_3$C
H
OH

g)

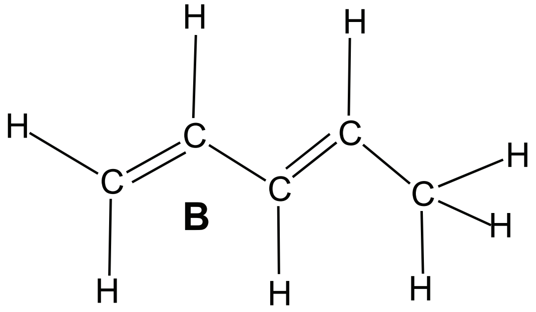


h)

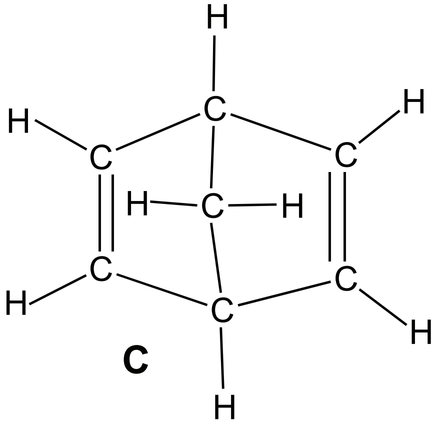
5. Convert the following Kekule structures into their skeletal representations:



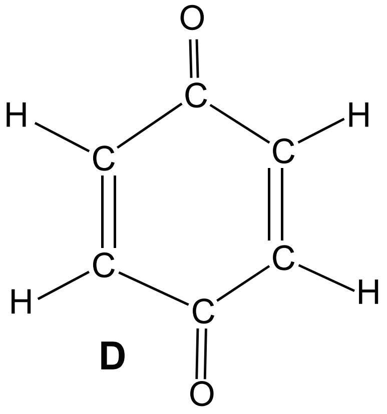
A



B

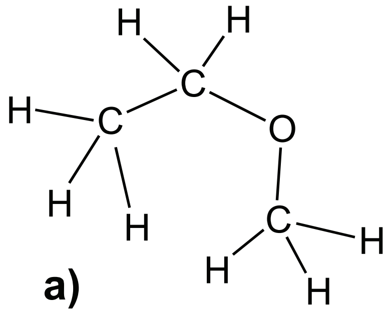


C

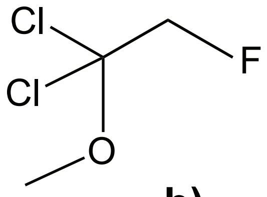


D

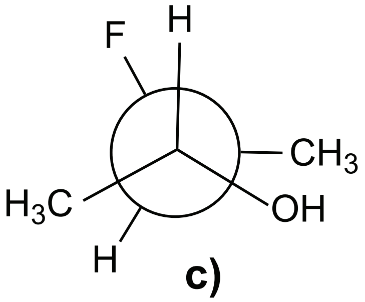
6. USE YOUR MOLECULAR MODEL KIT to help you to determine a wedge-dash representation for each of the following molecules **from the relative orientations as they are shown below**:


H
H
C
H
C
O
H
H
C
H
H
H

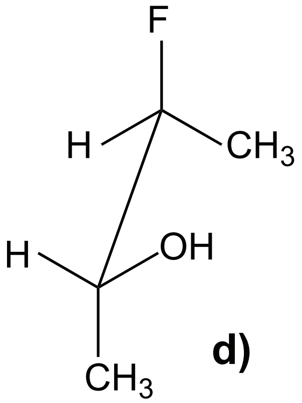
a)



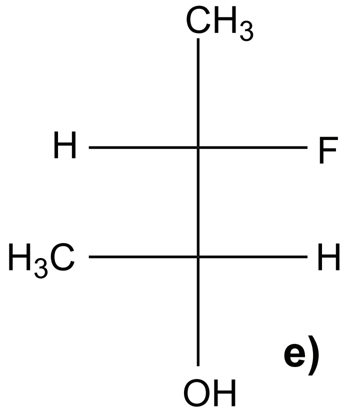
b)


F
H
CH3
H3C
OH
H

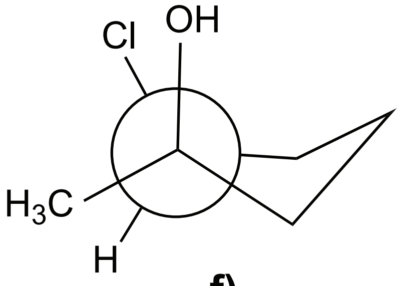
c)


F
H
CH3
H
OH
CH3

d)

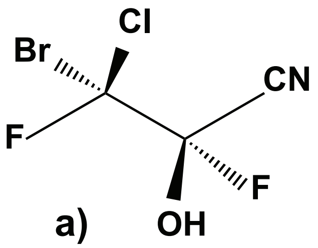

CH3
H
F
H3C
H
OH

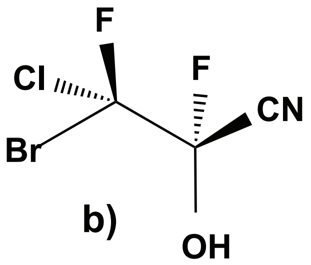
e)

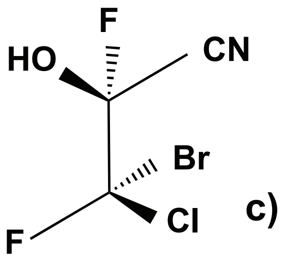


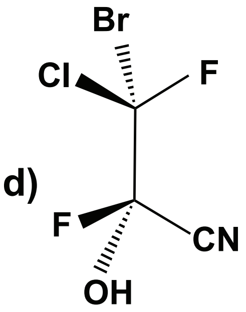
f)

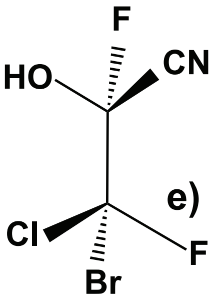
7. USE YOUR MOLECULAR MODEL KIT to help you convert the following wedge-dash representations into their Fischer representations. To do this you may need to rotate around the central C-C bonds in order to **place the two fluorine groups into a syn orientation** and then determine where the other groups will be located on a corresponding Fischer diagram for each of these molecules:

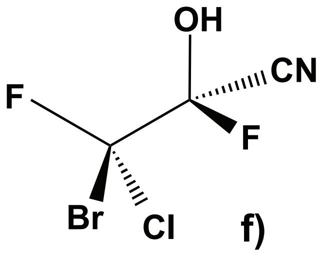

a)
Cl
Br
F
CN
F
OH


b)
F
Cl
Br
F
CN
OH


c)
F
HO
CN
Br
Cl
F


d)
Br
Cl
F
F
CN
OH

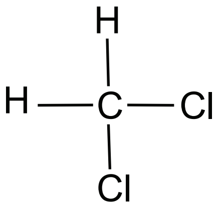

e)
F
HO
CN
Cl
F
Br


f)
OH
CN
F
F
Br
Cl

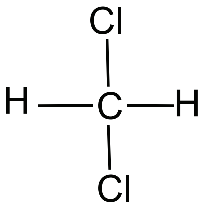
8. It is recommended that you use your molecular models to determine whether the following structural pairs reopresent the same or different molecules:

a) $\mathrm{ClCH_2CH_2CH(CH_3)_2}$ $\mathrm{ClCH_2CH(CH_3)CH_2CH_3}$

b)

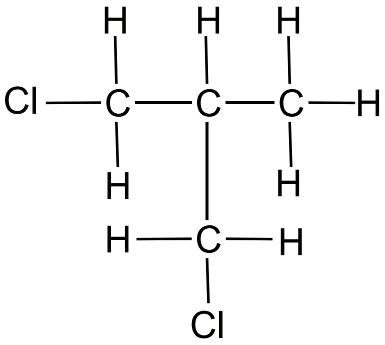


$\mathrm{H-\overset{H}{\underset{Cl}{C}}-Cl}$



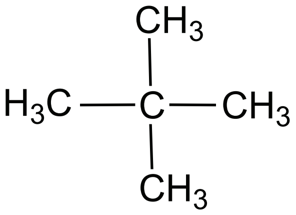
$\mathrm{H-\overset{Cl}{\underset{Cl}{C}}-H}$

c)



$\mathrm{ClCH_2CH(CH_3)CH_2Cl}$

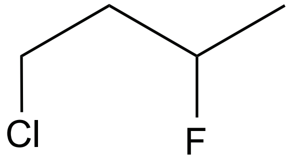
d)

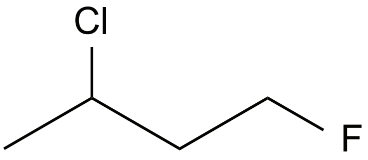


$\mathrm{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3}$

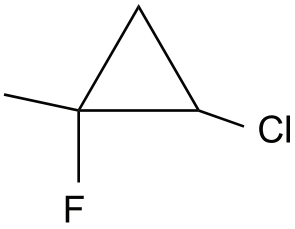
$\mathrm{(CH_3)_3CCH_3}$

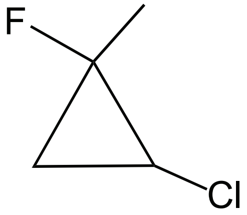
e)



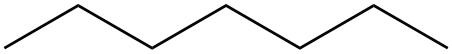


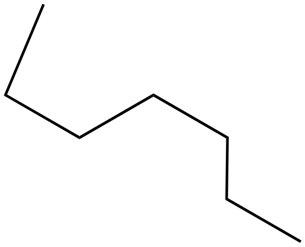
f)



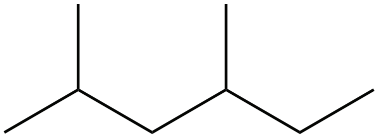


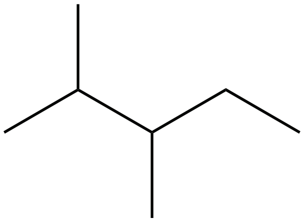
g)



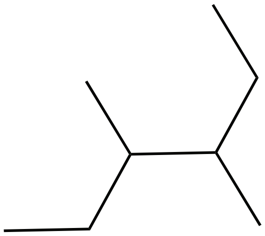


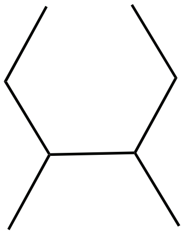
h)



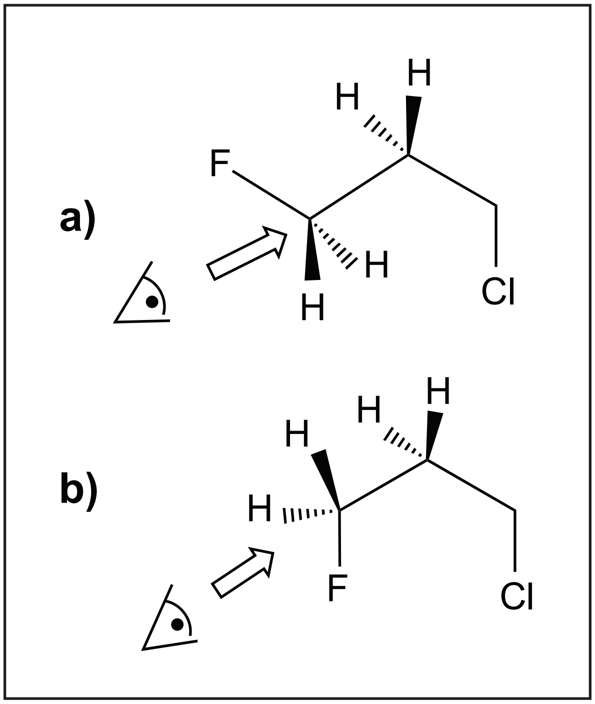


i)



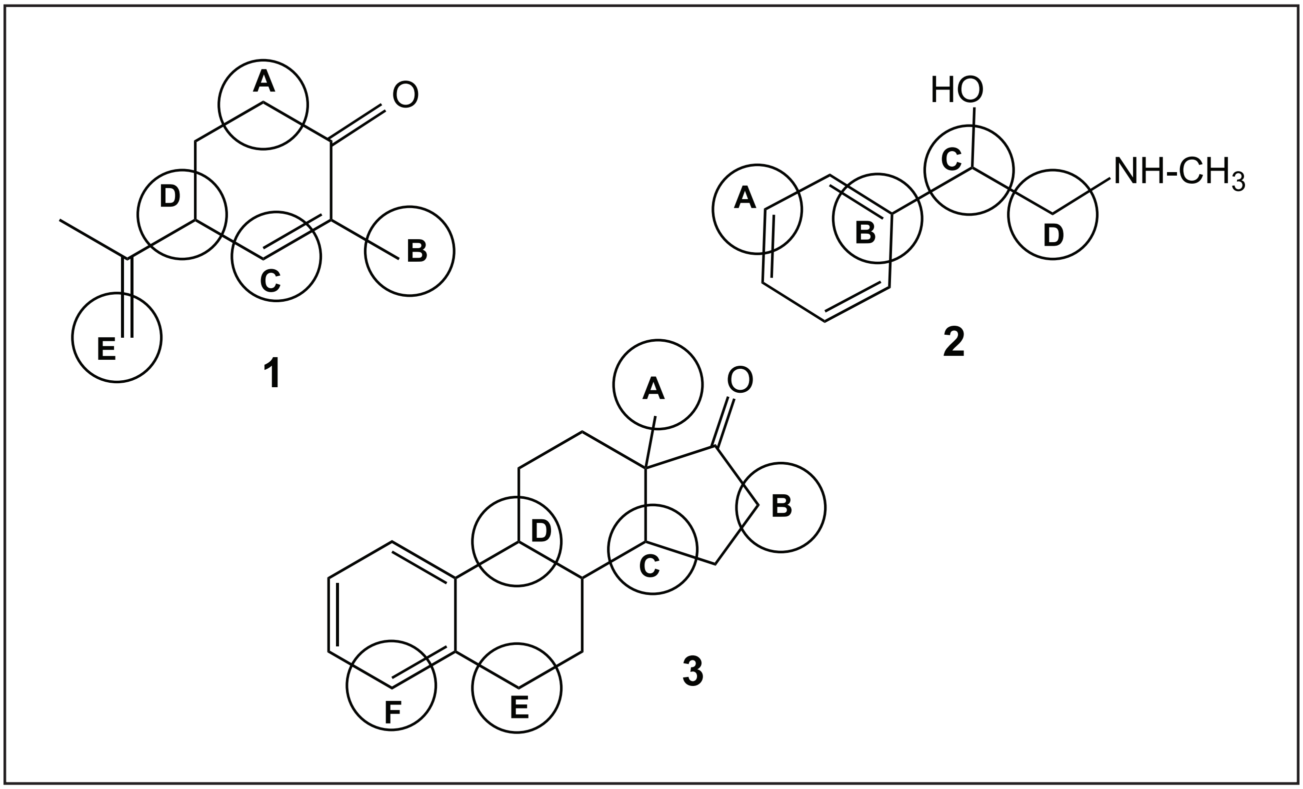


9. What is the Newman projection along the indicated bond for those structures **as they are shown below?**

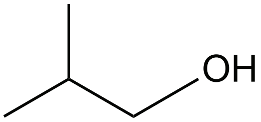

a)
H
H
F
H
H
Cl
b)
H
H
H
H
F
Cl

10. How many hydrogen atoms are at the circled positions on the structures below?

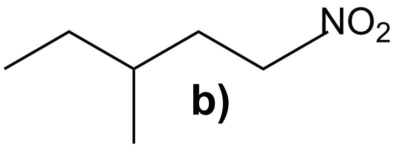
Show answers for each structure in the following order: (A,B,C,D,E,F)


A
O
D
C
B
E
1
HO
C
A
B
D
NH-CH$_3$
2
A
O
B
D
C
F
E
3

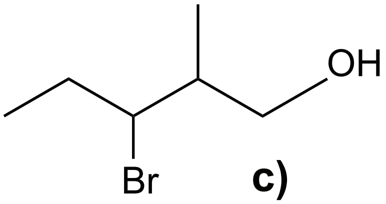
11. Write a condensed representation for each of the molecules below:



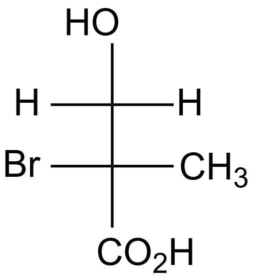
a)



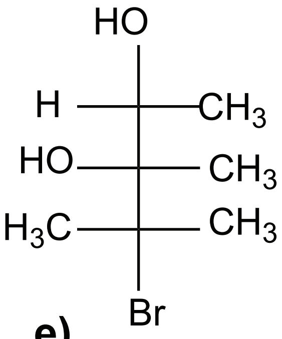
b)



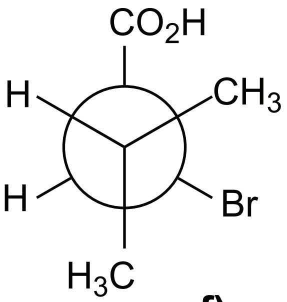
c)


HO
H
H
Br
CH3
CO2H

d)

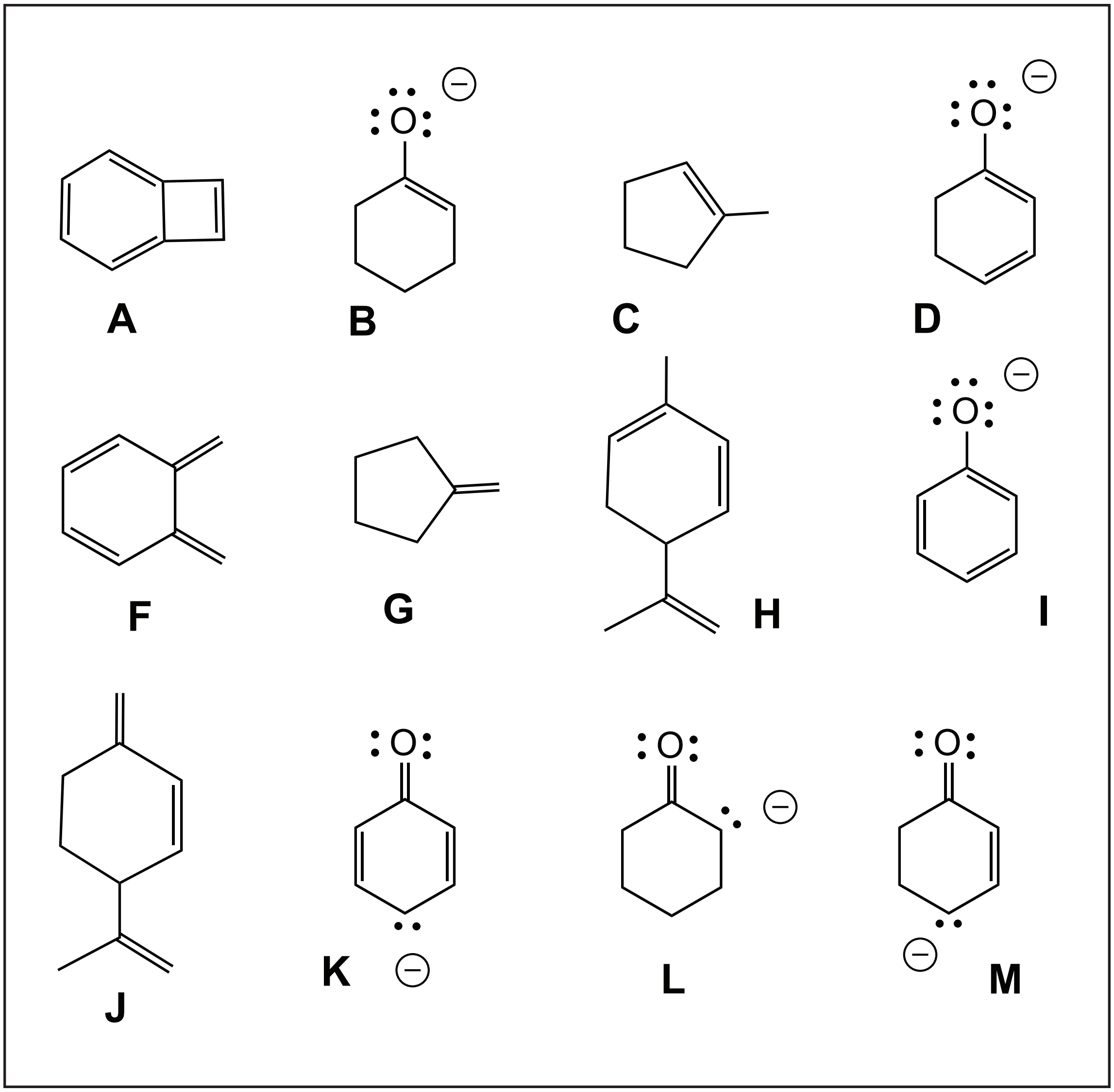

HO
H
CH3
HO
CH3
H3C
CH3
Br

e)

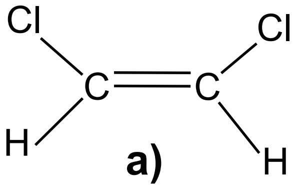

CO2H
H
CH3
H
Br
H3C

f)

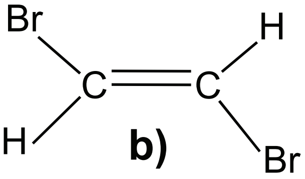
12. Identify the pairs of resonance structures from among the set of representations shown below:



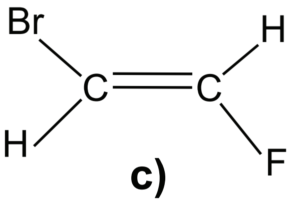
13. Which molecules can be expected to have molecular dipole moments (i.e. are polar molecules)? If a molecule is polar, then draw the direction for that molecular dipole moment.



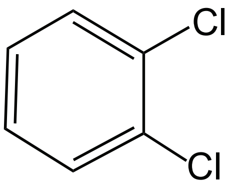
a)



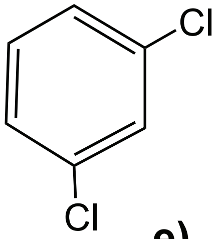
b)



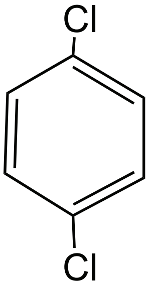
c)



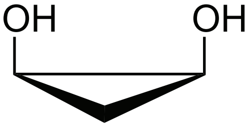
d)



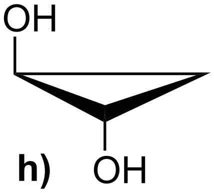
e)



f)



g)



h)