

Experiment 3: Modeling Molecular Structure, Part I

Reading: Read Chapter Section 9.2 and section on dipole moments in 9.5 in Olmstead and Williams, *General Chemistry*, before coming to lab.

Bring your textbook to lab and a pencil.

INTRODUCTION:

Chemists often use models to represent and understand the behavior of molecules. One example is the "ball and stick" type wooden or plastic models used to represent molecular structure. Such representations give us some sense of the way atoms are bonded and of the molecule's three-dimensional structure. However, a model must be more than an artistic representation to be really useful. Good models must serve as a tool for predicting properties and reactivity and must help us go beyond a simple appreciation of a static object to give us some sense of the object's potential.

In this experiment, we use traditional "ball and stick" molecular models as a source of information on molecular behavior and as a facilitator for predicting such behavior. In addition, we will relate the molecular structure obtained from the models to two powerful tools, the Lewis Structure representation for molecules and the VSEPR theory for predicting molecular shape and polarity. This model building exercise is designed to give you a more concrete and three-dimensional view of these representations to help you to get the most information possible out of simple molecular models. The exercises described in this experiment are designed to be somewhat open-ended. Redo things that are initially confusing or build new molecules and try to predict their shapes, polarity, etc. Such "play" is an ideal way to build your scientific understanding and intuition.

PROCEDURE:¹

Using models it is relatively easy to see both geometry and polarity, as well as to deduce Lewis structures. In this exercise you will assemble models for a sizable number of common chemical species and will use them to determine geometry, polarity, and possible isomerism of the molecules. You may work in pairs.

The models you will use consist of wooden balls (atoms), pegs (single bonds), and springs (used for multiple bonds). The balls represent the atomic nuclei and inner core electrons. The pegs and springs represent valence shell bonding or nonbonding (lone pair) electron pairs. Most of the heavy atoms in this exercise (C, N, O, F, S, Cl, Sb, Xe, and I) obey the octet rule. In their bonded structures, such atoms have four electron pairs around a central core and are represented in the model set as black balls with four holes. When these atoms participate in a multiple bond, more than one of their electron pairs (holes) are connected to the same atom. Springs are required for these bonds because of the rigid angles between the holes in these wooden atoms. A few of the structures will require "expanded octet" atoms. Atoms with an expanded octet can accommodate more than eight electrons. Atoms in the third and higher periods of the periodic table in the transition metal or representative groups (IIIA-VIIA) can have expanded octets. Initially we will assume that all heavy atoms obey the octet rule, and in our procedure we will *discover* the atoms that require "expanded octets".

A. Construction of Lewis Structures and Ball and Stick Molecular Models

In assembling molecular models of the kind we are considering, it is usually desirable to use a systematic approach. The method suggested below parallels the method for writing Lewis structures that we have discussed in class. We will illustrate this method by developing a model for formaldehyde, CH₂O.

1. *Determine the total number of valence electrons and select the appropriate number of pegs.* Recall that for the "main group elements," (of the Periodic Table) which we will be using (H, C, N, O, F, S, Cl, Sb, Xe, and I), the number of valence electrons on an atom is equal to the group number. If the structure to be constructed has one or more **electric charges** (+ or -), add one electron to the total for each negative charge and subtract one electron for each positive charge. Each peg in our models represents two electrons, so once you have determined the total number of electrons, count the number of pegs to be used in your structure.

¹ Developed from "The Geometrical Structure of Molecules: An Experiment using Molecular Models" from *Chemistry 103 Laboratory Manual*, S. F. Sontum ed, Department of Chemistry and Biochemistry, Middlebury College, Middlebury, Vermont, 1988, pp 75 - 91.

For formaldehyde each **H** contributes one valence electron, the **C** contributes four valence electrons and the **O** contributes six valence electrons to the overall structure, giving a total of $2(1) + 4 + 6$ or 12 valence electrons. Therefore, our structure requires six pegs.

2. *Select the appropriate wooden balls and deduce a skeletal structure for the molecule.* Each hydrogen atom in our models is represented by a yellow ball with one hole (accommodating one electron pair) and, initially, each "heavy atom" will be represented by a black ball having four holes (accommodating four electron pairs, an "octet"). Thus select one ball of the appropriate type for each atom in your molecular formula.

The **skeletal structure** is the sequence of attachments (or the connection of atoms to one another) within the molecule. Frequently the skeletal structure can be discerned from the order in which the atoms are written in the molecular formula. Often the first atom in the formula is the central atom (especially if it is the least electronegative element) with those following all being attached to it. For more complex structures (e.g., ethyl alcohol considered below) the skeletal structure will sometimes be suggested by subdivisions in the molecular formula ($\text{CH}_3\text{CH}_2\text{OH}$ for ethyl alcohol). Sometimes there will be several possible and/or reasonable skeletal structures for a given molecular formula. Such molecular formulas are said to have several possible structural isomers (discussed below). If your skeletal structure requires more than four atoms to be attached to a central atom, that central atom will require an "expanded octet". In such cases, replace the black ball (4 holes) with an appropriate expanded octet ball (5 holes, light blue or 6 holes, white) and proceed to Step 3.

Formaldehyde requires two yellow balls (two H atoms) and two black balls (one C and one O atom). Build the skeletal structure with **C** (black ball with four holes) as the central atom with the **H** atoms (yellow balls with one hole) and the **O** atom (black ball with four holes) attached to it.

3. *Assemble a single-bonded structure for the molecule.* Simply connect the adjacent atoms in your skeletal structure by inserting each end of a wooden peg into holes in adjacent atoms. If there are no empty holes in any of the atoms and no unused pegs after doing this, the structure is complete;² proceed to Part B. If there are empty holes or extra pegs, proceed to step 4.

For formaldehyde, three pegs are required and our single-bonded structure has three of the holes in the **C** filled with pegs attached to the **O** and two **H** atoms. In this case, there is one empty hole in the **C**, there are three empty holes in the **O** and there are three unused pegs. Thus, we proceed to Step 4.

4. *Add lone pairs.* If you have additional pegs, place them in the empty holes. If all of the holes are filled and all of the pegs are used at this point, the structure is complete;² proceed to Part B. If there are empty holes or extra pegs, proceed to Step 5.

For formaldehyde, we fill three of the four empty holes with lone pairs. Thus, we are left with one empty hole on either the **C** or the **O** atom so we proceed to Step 5.

5. *Add multiple bonds and/or expand octets.*

- a. *If you have empty holes*, your molecule is called **unsaturated** since there are insufficient electrons to fill the octets of all atoms. To reach octets, some atoms will need to share more than one electron pair with one or more of their neighbors. A double bond can be created by using a lone pair of electrons on one atom to help fill an empty hole on an adjacent atom (using two lone pairs from a single atom to fill two empty holes on a single adjacent atom produces a triple bond). To locate the most appropriate sites for multiple bonds, arrange the lone pairs in your single bonded structure so that each atom with an empty hole is adjacent to at least one atom with at least one lone pair. To complete the multiple bonds, we require more flexibility than the wooden pegs can provide, so we will use springs to form the double and triple bonds. At each site where there is an empty hole and an adjacent lone pair, replace both the lone pair peg and the peg representing the bond between the adjacent atoms with springs. Using springs provides the structural flexibility to allow you to create the multiple bond by inserting the free end of the lone pair spring into the empty hole on the adjacent atom. Complete octets of all atoms (fill all empty holes) by creating multiple bonds. Sometimes there is more than one arrangement of multiple bonds that fill all of the holes. At this point in our exercise, any one of the possible multiply bonded structures is sufficient. Your structure should now be complete; go to Part B.

²Such completely single bonded molecules are said to be **saturated molecules** since they have all of the electrons they can accommodate without expanding the octet of one of their atoms.

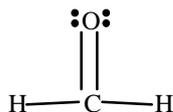
For formaldehyde we use a structure with an empty hole on C and three lone pairs on O or one with an empty hole on O and one lone pair on C. In either case we replace the C—O bond peg and one lone pair with springs and then form a double bond between C and O by connecting them with the two springs. This arrangement completes the structure for formaldehyde since all holes are filled and all pegs and springs are used.

- b. **If you have additional pegs.** Your molecule has more electrons than can be accommodated by octets on all heavy atoms so that the octet of one or more of the atoms in the structure will need to be "expanded". Atoms from the third row of the Periodic Table or below can accommodate more than eight valence electrons; thus they can have "expanded octets." Select the central atom in your structure that can have expanded octets, and replace it in the structure with either a light blue (5 holes — 10 electrons) or a white (6 holes — 12 electrons) ball depending on the number of extra lone pairs of electrons they need to hold in your final structure. Fill the extra holes with your unused pegs. Your structure should be complete; proceed to Part B.

B. Interpretation of Molecular Models

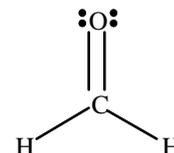
1. *Draw the Lewis Dot Formula for your Model.* Simply write down the atoms, bonds, and lone pairs from your model built in Part A. This exercise should help you gain a sense of the three dimensional structure represented by Lewis dot formulas. Ultimately, it will be very useful for you to use the two dimensional Lewis formulas to visualize three-dimensional structures without the aid of "ball and stick" models. Lewis structures are much quicker and easier to produce and when you can "see them in three dimensions" they will be very powerful reasoning tools for you to use in predicting the shape and properties of molecules.

For formaldehyde the Lewis dot formula is:

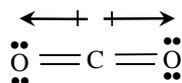


2. *Examine the Molecule's Molecular Geometry and describe the general overall shape of the molecule.* Do the outer most atoms form a recognizable solid form (e.g. a cube, a pyramid, a tetrahedron, a bipyramid, an octahedron, etc.)? Is the molecule flat (planar) or are the atoms all in a line (linear)? If the molecule is planar, does it have an easily recognizable regular shape (e.g., a triangle, a square, a pentagon, etc.)?

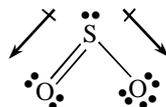
Formaldehyde is flat (all atoms lie in one plane) with its peripheral atoms forming the vertices of a triangle. Such a structure is called trigonal planar:



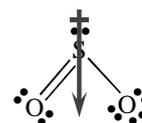
3. *Predict the Molecule's Polarity.* Polar bonds are formed between two atoms with different electronegativities. The more electronegative atom attracts more than its fair share of electrons to give a partial negative charge. The less electronegative atom has some electron density pulled away, so the less electronegative atom is partially positively charged. This polar bond creates a dipole (two poles) for that part of the molecule. The total dipole moment of the molecule is the vector sum of all the bond dipoles. For example, both CO₂ and SO₂ have polar bonds. However, the bond dipoles in carbon dioxide oppose each other and cancel out since CO₂ is a linear molecule (the dipoles are vectors, in this case, of exactly the same magnitude in opposite directions). In SO₂ the bond dipoles don't cancel, therefore, the whole molecule is polar. In drawings, an arrow is used to show the dipole, with the arrowhead pointing in the direction of the partial negative charge and the partial positive charge is depicted with a "plus" on the other end of the arrow, as shown below.



bond dipoles cancel
nonpolar

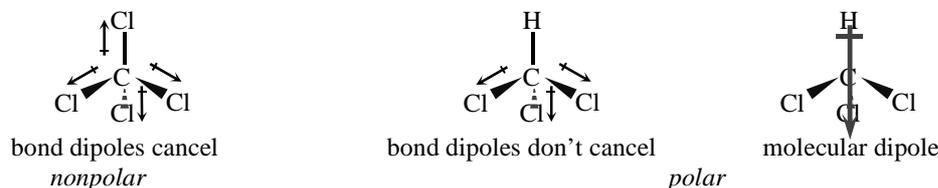


bond dipoles don't cancel
polar



molecular dipole

Symmetrically substituted linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral molecules are non-polar. For a tetrahedral example, CCl_4 is non-polar while CHCl_3 is polar.



A small electronegativity difference, such as that between C (2.6) and H (2.1) is not sufficient to create a noticeable bond dipole. However, the electronegativity difference between C (2.6) and O (3.5) is large and the C–O bond is markedly polar.

Does your molecule contain polar bonds? If so, which end of each polar bond is more positive and which is more negative? From the shape noted in 2 above, predict whether the molecule as a whole is polar. If so, indicate the direction of the molecule's dipole moment on the Lewis structure you drew in 1, above.

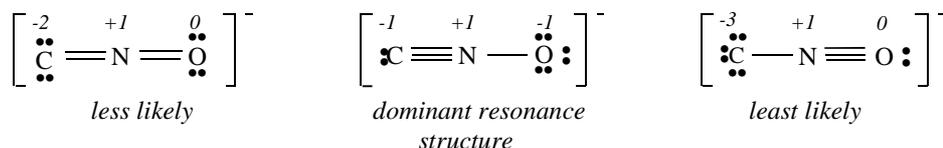
In formaldehyde the C–O bond is polar, with the C atom partially positively charged and the O partially negatively charged. The C–H bonds are essentially nonpolar. Thus, formaldehyde is a polar molecule with a net dipole mirroring the C–O bond polarity. In the polarity column of Part C enter yes and draw the arrow depicting the net molecular dipole on Lewis structure.

4. *Examine the Molecule's Potential for Resonance.* If your molecule has multiple bonds, resonance is possible. If the multiple bonds may be arranged in more than one way, while maintaining the same skeletal structure, then each of the possible structures is a resonance structure. SO_2 has two equivalent low energy resonance structures. The relative importance of inequivalent resonance structures is compared by calculating the formal charges on the atoms.

The formal charge on an atom is given by:

$$fc = \text{valence electrons} - \frac{1}{2}(\text{bonding electrons}) - \text{non-bonding electrons}$$

For example in SO_2 , the formal charge on the S-atom is $fc = 6 - \frac{1}{2}(6) - 2 = +1$, the formal charge on the doubly-bonded O-atom is $fc = 6 - \frac{1}{2}(4) - 4 = 0$, and the formal charge on the singly-bonded O-atom is $fc = 6 - \frac{1}{2}(2) - 6 = -1$. The sum of the formal charges is equal to the charge on the ion or molecule. The actual structure of the molecule is best represented by an average of all of the resonance structures weighted such that low energy resonance structures (those with minimal formal charges on atoms) contribute more to the average structure than do high energy resonance structures (those containing atoms with large formal charges). Consider the cyanate ion, CNO^- . The three inequivalent resonance structures of the cyanate ion are shown below with the formal charges:

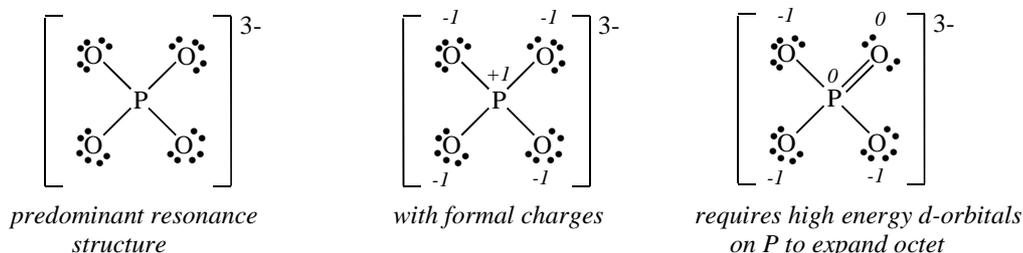


The $\text{C}\equiv\text{N}-\text{O}^-$ resonance form is the dominant contributor to the structure of the molecule, since this resonance structure has the smallest formal charges. In addition, negative formal charges are most stable on the most electronegative atoms. Now back to the formaldehyde example:

For formaldehyde, there is only one place for the double bond. Thus, formaldehyde has no resonance structures, so we enter “no” in the resonance column for the table in Part C (if there are resonance structures, indicate how many in the table and draw one additional structure in the table).

For species with expanded octets, additional caution is required when comparing resonance structures. Expanded octets require the incorporation of d-atomic orbitals on the central atom into the bonding framework of the molecule. For non-metals, these d-orbitals are higher in energy than the valence s- and p-orbitals. Comparing formal charges between resonance structures, one with and one without an expanded octet, is

invalid, since the expanded octet uses a different set of atomic orbitals than is used without an expanded octet. For example, there is no evidence for significant contribution of d-orbitals in PO_4^{3-} , even though the formal charges can be minimized by expanding the octet. At our current level of approximation, the P–O bonds in PO_4^{3-} are best described as single bonds. Expanding an octet requires a significant energy cost.



5. *Examine the Molecule's Potential for Structural Isomerism.* If it is possible to arrange the atoms of your molecule in another skeletal structure that is different from the one chosen in Part A.2., then its molecular formula does not describe a unique molecule. Two or more structures that have the **same molecular formula** but **different skeletal structures** (sequences of attachment of atoms) are called **structural isomers**. Note, if there is only one possible structure, there are no isomers (enter “no” in the table constructed in Part C). If your molecule has structural isomers, build a model of at least one of them, draw it in your table in Part C, and compare it with your original model.

It is possible to arrange the atoms of formaldehyde with the **O** as the central atom and the **C** and two **H** atoms to the **O** atom. Build a model for this structure. This second isomer is not a stable molecule, because the central **O** has a formal charge of +2 and the **C** has a formal charge of -2. Molecules with such large formal charges, especially those with a positive formal charge on the more electronegative atom and a negative formal charge on the less electronegative atom are not usually stable. The isomer with O as the central atom should not be listed as a stable isomer in the tables for this experiment.

C. Build Models and Interpret Molecular Properties with those Models

Build a model (using the provided kit) for each of the following molecules or ions and then analyze your model according to the procedures above. You will be provided with a worksheet upon which to record information on the compound or ion. Record the name, chemical formula, Lewis structure with the superimposed molecular dipole if present, geometry, polarity, resonance, and stable isomers. Complete the worksheet (in pencil) for the 20 chemical species that follow. Remember to add or remove the appropriate number of electrons for the charges of ions when calculating the total number of electrons for these species.

1. **Formaldehyde** (Follow along with the example described above to fill in your table).

2. **Methane**

3. **Dichloromethane**

Convert your methane molecule to dichloromethane (CH_2Cl_2) by replacing two H atoms with Cl atoms. Do the additional structural analyses described in *Part B* above. Draw the Lewis dot structures for *all* of the structural isomers of CH_2Cl_2 that you think may exist. Build structures of all of your isomers and compare them see if they are identical (i.e., not isomers, are superimposable) or isomers, not superimposable upon each other with rotation. How many structural isomers are there with the molecular formula CH_2Cl_2 ?

4. **Ethyl alcohol** (also called ethanol, $\text{CH}_3\text{CH}_2\text{OH}$) and

5. **Dimethyl ether** (CH_3OCH_3)

Construct models for ethyl alcohol (ethanol) and dimethyl ether. These two compounds are structural isomers, because of that they have very different properties. Ethanol is very soluble in water, while

dimethyl ether is not. The boiling point of ethanol is much higher (78.5°C) than dimethyl ether (-24°C). These differences are caused by the presence of the O-H bond, which allows hydrogen bonding to be an important contribution to the forces between molecules in ethanol.

Additional Molecules or Ions

6. H₂O
7. NH₃
8. H₂O₂
9. C₂H₄
10. C₂H₂Cl₂
11. NH₄⁺
12. XeO₂
13. SF₄
14. ClO₂⁻
15. SO₄²⁻
16. AsF₅
17. I₃⁻
18. NO₂
19. CO₃²⁻
20. NO

When this set of worksheets is completed, turn in the worksheet and you are then done for the day. Be sure to include the names of the people in your group (if any). There is no discussion to write. Once your graded worksheets are returned, pull apart the sheets and tape each one individually into your lab notebook under the heading for the experiment.