NAME: _____   **Lab Day/Time: _____**

Molecular Modeling

Purpose

The purposes of this experiment are:

To learn how to use molecular modeling software, a commonly used tool in the chemical and pharmaceutical industry.

To examine the structures of a number of simple molecules to search for common factors affecting molecular structure.

Procedure

There are a variety of software programs available to perform molecular modeling experiments, with names such as Spartan, Mopac, and Gaussian. The one we use is CAChe, and we have a "site license" for it. This means that, although a single copy costs upwards of $1,000, each of you can install a copy on your own computer and use it at will.

In this experiment you will learn how to:

- "build" molecules in the program
- analyze bond lengths
- analyze bond angles
- analyze torsion angles
- use these skills to perform an analysis of the structures of a series of small molecules.

Prelab Assignment

**Before coming to lab, fill in the
Lewis structures in Tables 1, 2A, 2B, and 4.
Determine the formal charges and oxidation
numbers requested in Table 4.**

How to Use CAChe/Scigress

1. Building Molecules

Run Workspace from either the CAChe or Scigress folders in All Programs. If a query comes up the first time, just say yes.

Choose **New** if a workspace window does not come up.
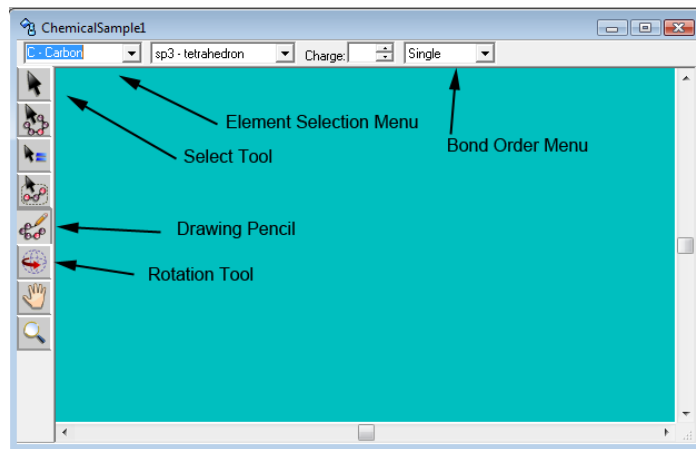
Use the **Drawing Pencil** to sketch out your molecule.
- To add the first atom, select the element and click in the middle of the workspace.
- To add addition atoms, select the element and then click-and-drag from the element you want it bonded to.
- To make a double or triple bond, either drag again between the two atoms, or use the Select tool to select the bond and change the drop-down menu to change it.
- Once complete, finalize the molecule using **Beautify**/**Comprehensive**, or Ctrl-B.

2. Performing Advanced Calculations (Experiments)

Save the molecule using a name of your choice.

Choose the **Experiment**/**New**.
Select the **Property** to be determined. Popular selections are "HOMO-5 to LUMO+4" and "electrostatic potential on electron density."

Click Start and wait for the calculation to run its course. For small molecules this is usually less than 10 seconds.

Close the **Experiment** windows.

3. Making Measurements

Bond Length: select the two bonded atoms using the **Select** tool. Click on one atom, hold down shift, and click on the second atom. Then choose **Adjust**/**Atom Distance**, or press F2. The units used are Angstroms. 1 A = 10^{-10} m, or 10^{-8} cm.

Bond Angle: select three atoms- in order with the central atom second. Then choose **Adjust**/**Bond Angle**.

Torsion Angle: select four atoms- in order following the bonding linkages. Then choose **Adjust**/**Torsion Angle**.

Partial Charge: Build the molecule and save it. Run **Experiment**/**New**/**Property** = **current energy**. When the calculation is done, choose **View**/**Atom Attributes**/**Label**/**Partial Charge**. The numbers will be seen with the atoms. You'll probably need to rotate the molecule to see them.

Experiment #1. What controls bond length?

For each molecule, draw the Lewis structure, build the molecule, beautify it, and measure the bond lengths indicated.

Formula	Lewis Structure	Bond lengths to measure:
CH_4		C-H
CH_3F		C-F
CH_3Cl		C-Cl
CH_3Br		C-Br
CH_3OH		C-H O-H
CH_3NH_2		C-H N-H
CH_3CH_3		C-C
CH_2CH_2		C-C
CHCH		C-C

Part 1. Questions:

1a. What are the two factors that control bond length?

1b. Which of these has the largest effect on bond length?

1c. Given your ideas, design a molecule on paper that contains specific bonds you have not yet measured. For example, you could make a molecule that contained a S-F bond, or a P-Cl bond. Predict the bond length and then test your prediction using CAChe.

Formula	Lewis Structure	Predicted Bond Length	Measured Bond Length
		Which bond: Length:	

Experiment #2. What controls bond angle?

We have learned that the angle between two bonds depends mainly on electron-pair geometry of the central atom, which in turn depends on the number of structurally important electron pairs on the central atom. Confirm this by again drawing the Lewis structures for the following molecules and then analyzing the indicated bond angles in CAChe. Build the molecule and choose **Beautify/Comprehensive**.

When viewing the molecules in CAChe, also view the positions of the lone pair electrons by selecting **View/Show Electrons**.

Part 2a. Control via number of Structural Electron Pairs

Formula	Lewis Structure	Number of Structure Pairs	Bond Angle
CH_3CN		On central C:	C-C-N:
BF_3		B:	F-B-F:
CH_2O		C:	H-C-H:
CH_4		C:	H-C-H:
PF_5		F:	F-P-F:
SF_6		S:	F-S-F:

The following three measurements need a more exact calculation of molecular shape. CAChe uses the most simple hybrid orbital/VSEPR rules to create structures when "beautifying." In order to obtain a more accurate shape for the molecule, you must **Save** the built and beautified molecule and then optimize the geometry using **Experiment/New/Property** = **optimized geometry**.

Formula	Lewis Structure	Number of Structure Pairs	Number of Lone Pairs on Central Atom	Bond Angle
CH_4		C:		H-C-H:
NH_3		N:		H-N-H:
H_2O		O:		H-O-H:

Part 2. Questions

2a. Does the number of structural pairs on the central atom control bond angles around that atom?

      yes   or   no

2b. Compare BF_3 and CH_2O. Each has a central atom with 3 structural pairs, but the C in CH_2O has a total of 4 bonds whereas B in BF_3 has only three bonds. Which matters more about the central atom:
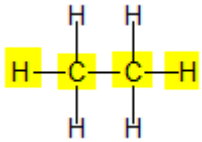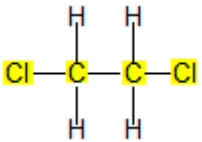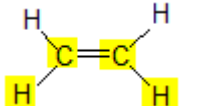
      the number of structural pairs   or   the number of total bonds

2c. Now consider the bond angles in Part 2b. In effect, the trend going from CH_4 to NH_3 to H_2O is to replace a bonded H atom with a lone pair. What effect does that have on the bond angles?

2d. Give a reason why the trend you state in Question 2c occurs.

Experiment #3. Torsion (Dihedral) angles.

When a series of atoms are connected together, their relative positions are referred to as a conformation. Conformations describe twisting of one part of the molecules with respect to another. The easiest way to observe this is to examine atoms bonded to adjacent central atoms and see if they line up (they are eclipsed) or seem to avoid each other (they are staggered). **Build** and **Beautify** the molecules below and describe the manner in which the outermost atoms line up, or don't.

Lewis Structure and torsion to measure.	Describe the relative positions of the outermost atoms.
H–C–C–H (with H atoms above and below each C)	
Cl–C–C–Cl (with H atoms above and below each C)	
C=C (with H atoms on each C)	

Part 3. Questions

There are two factors that might control how one fragment of a molecule will twist with respect to another fragment.

Steric Hinderance: This comes about when atoms just get in each other's way and take up space. The result is atoms being arranged in order to avoid other atoms to which they are not bonded. In the modeling program, this is more easily visualized by examining the structure in "Space Filling" mode.

Bonding: This comes about when certain types of bonds require a particular orientation of the atoms involved. The most common and important of these are pi bonds.

3a. In the structure for CH_3CH_3, are the H atoms on adjacent C atoms aligned or staggered?

3b. Which factor controls this:

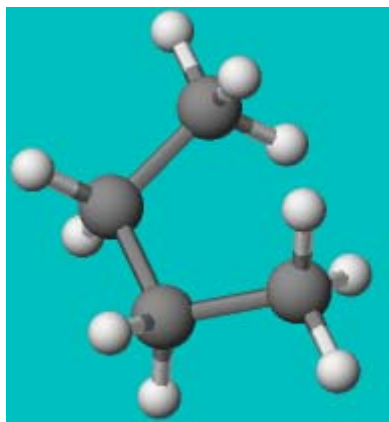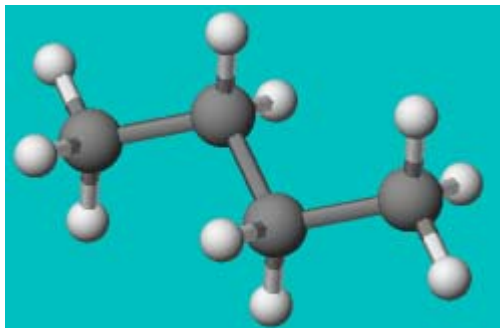   steric hinderance   or   bonding

3c. Describe the relative positions of the two Cl atoms in the second structure. Is this due to steric hinderance or to bonding?

3d. Are the H atoms in the last structure aligned or staggered?

3e. Explain why.

3f. Predict which of the following shapes will be the more stable for butane, $CH_3CH_2CH_2CH_3$. Circle it.

Experiment #4. Partial Charges on Atoms

Draw the Lewis structures for the compounds in the table below. Calculate the oxidation number and formal charge for the C and O atoms in CO_2. Using CAChe, measure the partial charges for the atoms listed in the last column.

Compound	Lewis Structure	Oxidation Number	Formal Charge	CAChe Measured Charge
CO_2		C: O:	C: O:	C: O:
CH_3OH		--------	---------	H:
CF_3OH		--------	--------	H:

Part 4. Questions

4a. Formal charge and oxidation numbers are the two main crude methods chemists use for counting electrons on atoms inside molecules. Partial charges are the reality. Consider the data you collected for CO_2. Which method more correctly represents the true distribution of electrons in molecules?

4b. Explain why the partial charge on H differs for CH_3OH and CF_3OH.

4c. Which would you expect to have stronger intermolecular hydrogen bonds,

        CH_3OH or CF_3OH

4d. Which would you expect to have stronger intermolecular hydrogen bonds,

        acetic acid: CH_3CO_2H or   trifluoracetic acid: CF_3CO_2H