Chemistry 111 Laboratory
Experiment 3: An Exploration of Molecular Shapes: MacSpartan Pro and Molecular Models

(This activity will be conducted in Olin-Rice 341)

Introduction

The three-dimensionality of a molecule is critically linked to its chemical and physical properties. For example, the bent geometry of water causes its polarity. The polarity of a molecule (or lack thereof) strongly influences its boiling point, freezing point, reactivity, and countless other properties. The key biochemical interactions between an enzyme and a substrate rely on specific structural characteristics of each molecule. A sound understanding of molecular shapes is necessary to fundamentally understand chemical and biological phenomena. Chemists routinely predict the structural characteristics of proposed molecules when designing substances for specific applications. The *structure* of a molecule is inherently linked to its *function*.

Valence Shell Electron Pair Repulsion Theory (VSEPR) is a systematic methodology for linking a two-dimensional Lewis structure to a molecule's three-dimensional shape. The application of VSEPR permits the reliable prediction of molecular structure and bond angles. This information can be used to subsequently determine other molecular properties (*e.g.*, dipole moments).

This experiment will provide an opportunity for you to use computational chemistry software to calculate and observe shapes of molecules. Concurrent with your construction of molecules in MacSpartan Pro, we will ask you to build representations of molecules with a molecular model kit. A successful study of chemistry requires that one be able to visualize molecules in three-dimensional space using both hand-held models and via a computer screen. We hope that you enjoy using the MacSpartan Pro software to gain a new perspective on VSEPR. MacSpartan Pro is a "common thread" through our chemistry curriculum, as it is used in General Chemistry II, Organic, Physical, and Advanced Inorganic Chemistry courses at Macalester College. MacSpartan Pro is also a critical aspect of next week's Chemistry 112 experiment, as we continue to explore chemical bonding.

Ground Rules

We encourage you to work in groups of two for this experiment. However, please take turns at the mouse so that everyone gains a solid proficiency with MacSpartan Pro. In addition, it is important that all students learn how to use the Molecular Visions® model kit. **All information documented in your laboratory notebook should be turned in as your report for this experiment.** Make sure that each table/answer is clearly labeled to help us follow your work.

Drawing Molecules and Calculating Bond Angles with MacSpartan Pro:
A Good Starting Point: Identical Coordination and Steric Numbers

The best way to start an investigation of VSEPR is to consider some fundamental molecular shapes that are free of distortions. Let's explore the molecule BF_3 as our first example!

- Design a laboratory notebook table to clearly present information with the following headings: "Lewis Structure," "Coordination Number," "Steric Number," "Shape Name," and "Calculated Bond Angles."

- Draw the Lewis structure of BF_3.

The following molecular geometries apply when the steric number equals the coordination number:

Steric Number	Shape
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

- Record the "Shape Name" for BF_3 in your laboratory notebook.

To start MacSpartan Pro, click on the desktop icon labeled "Macintosh HD". Select "Chemistry Applications" from the left field of the window. Choose the icon labeled "MacSpartan Pro Alias" from the applications that appear. MacSpartan Pro may take a few moments to load.

Will MacSpartan Pro predict the same structure for boron trifluoride? Let's find out!

- Select **New** from the **File** menu. The Model Kit window will appear. This is your palette for drawing chemical species (atoms, molecules, ions, or even groups of molecules/ions).

- Select the **Expert** tab.

A common practice in computational chemistry, the study of molecular properties with computer software, is to begin with a structure that the chemist believes approximates the naturally occurring structure. This makes for more efficient calculations as it saves computer time. We'll take this strategy (using VSEPR as our guide) with the molecules in this experiment.

- Select the arrangement of electron pairs (with X as the central atom) that best matches your prediction for boron trifluoride.

- Change the central atom to boron by clicking on **Element** and choosing Boron from the periodic table.

- Click in the center of the green drawing workspace to place a three-coordinate boron atom. Rotate the molecular fragment so that you can see all three "half-bonds" by clicking and dragging on the green workspace background.

- If you make a mistake and need to start over, choose **Clear** from the **Edit** menu.

Our next objective is to add the three fluorine atoms.

- Select the **Entry** tab. Select the **fluorine atom** icon.

- Click on each "half-bond" of the boron atom to complete the three boron-fluorine bonds.

Now we are ready to begin our computer calculation.

- Select **Save As** under the **File** menu. Save your structure with a generic name, like your name, because if you follow these directions correctly this should be the only time you save! Don't use a specific name like "Boron Trifluoride."

- Select **Calculations** from the **Setup** menu.

- Setup the calculation to determine the "**Equilibrium Geometry**" with "**Molecular Mechanics**" and "**MMFF**" (Molecular Mechanics Force Field). Start from the "**Initial**" geometry. <u>Deselect</u> "**symmetry**". Click "**OK**".

- Select **Submit** from the **Setup** menu to begin the calculation. Select **OK** to acknowledge the beginning and the end of the calculation.

The trigonal planar boron trifluoride molecule should be in the workspace. In this case, the calculation should have verified that the entered geometry is the optimum structure for BF_3. We encourage you to rotate the molecule by clicking and dragging on the workspace. Verify that the molecule is planar by viewing it from different perspectives. Before we examine the bond angles of boron trifluoride, let's play with our optimized molecule to learn more about MacSpartan Pro.

- <u>Enlarge/Reduce the Molecule</u>: Depress the option and apple keys simultaneously while dragging the mouse in the appropriate direction to achieve the desired effect.

- <u>Molecule Representation</u>: The way in which a molecule is displayed can be changed by switching between the "wire", "ball and wire", "tube", "ball and spoke", and "space filling" options under the Model menu. Try out these different options for fun.

- <u>Move the Molecule</u>: Depress the mouse and option key simultaneously while moving the mouse.

- <u>Rotate the Molecule in the X/Y Plane</u>: Click on the background and drag the mouse in the desired direction.

- <u>Rotate the Molecule in the Z Plane</u>: Depress the mouse and apple key simultaneously while dragging the mouse in the desired direction.

Now let's examine the molecule in terms of its bond angles! The shape of a molecule is defined by its bond angles.

- From the **Geometry** menu, select **Measure Angle**.

- Determine the three bond angles by sequentially clicking on each set of three atoms that define each molecular angle. It is important to select boron as the second atom during the determination of each angle. Each angle will be displayed in the lower right corner of the workspace. Click on the workspace background to "deselect" each angle before finding the next one.

- Record the calculated angles for boron trifluoride, a classic trigonal planar molecule, in your laboratory notebook. If they are all identical, you don't need to list them all separately, just say "All bond angles = " and specify what the angle was.

Our next goal is to determine bond angles for other chemicals with identical coordination and steric numbers. In this regard, we need to conduct calculations on linear, tetrahedral, trigonal bipyramidal, and octahedral molecules.

- Delete your BF_3 molecule by selecting **Clear** from the **Edit** menu.

- Conduct the same steps in your notebook (write the "Lewis Structure," "Coordination Number," "Steric Number," "Shape Name," and "Calculated Bond Angles") for the following molecules: CO_2, CH_4, PF_5, SF_6. (Note: Students who enroll in Physical Chemistry I (CHEM 311) have the opportunity to study SF_6 in the laboratory.)

<u>Useful Information (Ask for assistance with any of the molecules/calculations if necessary)</u>

1. Use the Expert window for the complete construction of CO_2. Select carbon as the element. Choose the icon from the first two rows that represents the geometry about the carbon. Click the central atom into the workspace. Next, select the bond type (from the third row of icons) that matches the carbon-oxygen bonds of your Lewis structure. Double click on each bond to change the bond type. Finally, add the terminal oxygens from the Entry Model Kit.

2. For CH_4, PF_5 and SF_6, use the Expert Model Kit window for the central atom and the Entry Model Kit window to add the outer atoms.

3. The tetrahedral icon is the first one in the second row of the Expert Model Kit window. The trigonal bipyramidal icon is second from the left in the second row. The octahedral icon is the last one in the second row. The funny little circle on the trigonal bipyramidal structure is just supposed to indicate that the bond it is on is coplanar with the top and bottom bonds. It will not show up when you click your P for PF_5 into the green drawing space.

4. You will need to rotate some of the structures to add outer atoms.

5. Use the same calculation parameters (Molecular Mechanics, MMFF, <u>deselect</u> symmetry) for all of these molecules.

6. Record the two unique bond angles for the trigonal bipyramidal molecule.

7. Rotate each molecule to obtain a good perspective of these molecular geometries.

8. We strongly recommend AGAINST using **Open** and **Close** on the **File** menu. If you do decide to go that route, be sure to re-set the calculation parameters for each molecule!

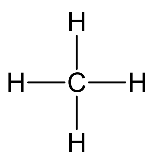
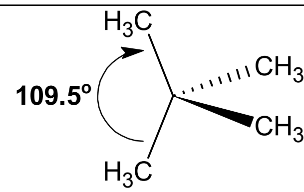
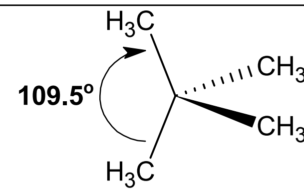
- Make sure that your notebook entry is complete before going on to the next part of the experiment. You should specify which columns in your table were calculated using Spartan Pro, and what calculation parameters were used. It is important that someone reading your lab book be able to ascertain what calculation parameters were used in calculating each of your results, but since these parameters are generally held constant throughout a given table, you can usually just specify what they were for an entire given table.

VSEPR and Molecular Distortions: Molecules with Different Coordination and Steric Numbers

Molecules with bonding and nonbonding electrons on their central atoms are susceptible to distortions (*i.e.*, non-ideal bond angles). Let's investigate some of the features that lead to distortions. **Our goal is not only to rationalize why molecules possess distortions, but ultimately to estimate distorted bond angles from Lewis structures.**

Let's look at the impact of nonbonding pairs on molecules whose central atoms have a steric number of 4. A classic series includes CH_4, NH_3, and H_2O. We've already examined methane, so let's look at ammonia next!

- Start a new table, whose headings and first row look like this:

Lewis Structure	CN	SN	Undistorted Geometry	Calculated Geometry
	4	4	 All angles 109.5°	 All angles 109.5°

- Write the "Lewis Structure," "Coordination Number," "Steric Number," and "Shape Name" for NH_3 on the next row of this table. Based on your Lewis structure, draw in the undistorted geometry for ammonia (NH_3).

- Since the arrangement of the electron pairs around nitrogen is tetrahedral,, let's draw NH_3 in **Expert** mode by selecting a tetrahedral nitrogen and placing it in the workspace. Add the three hydrogen atoms in either **Expert** or **Entry** mode.

- The remaining "half-bond" is the tetrahedral environment associated with the nonbonding pair in your Lewis structure. Although we can't see the lone pair, these electrons impact the shape of this molecule. Delete the "half-bond" by clicking on the minus sign button on the left-hand palette, and then clicking on the "half-bond". If a rogue atom appears after deletion of the "half-bond," delete that too.

- Before you **submit** the calculation, **measure the bond angles** and record them ("undistorted geometry") in your laboratory notebook. Since you employed tetrahedral nitrogen during the construction, your angle should be identical to that of methane.

- Setup and **submit** the calculation using the familiar parameters (Molecular Mechanics, MMFF, Initial geometry, deselect symmetry).

- **Measure the bond angles** and record the calculated values. In this case, the calculation determined that 109.5° isn't the optimum angle for NH_3. The angles determined by MacSpartan Pro reasonably approximate the actual angles of ammonia.

It's very important to realize the importance of **submitting** your molecule. Until you do so, Spartan makes assumptions that aren't any more sophisticated than the ones you make when you use Lewis dot structures and VSEPR. Spartan is an expensive and useful program precisely because of what it does when you hit **submit**: it carries out detailed quantum mechanical calculations on your molecule, which do a decent job of predicting the *real* shape of the molecule, including the impact of distortions. Throughout the remainder of this lab, if you neglect to **submit** you molecule, or don't use the specified calculation parameters, you'll be unhappy. I know some of you aren't into submissive behavior, but this is a good time and place to get into it, at least for a little while. =>

Ammonia, with CN = 3 and SN = 4, has a trigonal pyramidal geometry. Enlarge/rotate your molecule as necessary to view the trigonal pyramidal shape.

- **Measure the bond distances** using the same menu. Record these data (in Angstroms) on the "calculated geometry" structure you've sketched in your notebook.

To investigate the impact of nonbonding pairs further, let's examine H_2O.

- Follow steps analogous to those for NH_3. Measure and record the undistorted bond angles before you **submit**. Then calculate and record the **actual geometry's bond angle** and **bond distances**.

Water, with CN = 2 and SN = 4, has a bent geometry. Hydrogen atoms occupy two of the tetrahedral sites, while the other two sites are associated with the nonbonding pairs. The atomic positions define the molecular shape.

- <u>Discuss the bond angles of CH_4, NH_3, and H_2O in your notebook</u>. Describe the relative impact of bonding vs. bonding electron pairs on the distortion of SN = 4 molecules. Hypothesize about the origin of these distortions (i.e., Why does a nonbonding pair exert a different influence relative to a pair of bonding electrons?).

<u>Other Factors that Influence Molecular Shapes</u>

Okay, so we've got a pretty good grip on how unbonded electrons can distort molecules…what else might impact distortions? Let's consider two more molecules and see. Adding to your table above, and using an analogous approach, investigate these two molecules:

1) Formaldehyde, $H_2C{=}O$ (CH_2O, with the oxygen double-bonded to the carbon)
2) Hydrogen sulfide, H_2S

Comparing the distorted and undistorted bond angles in formaldehyde will give you some idea of the impact that a double bond can have on the geometry of a molecule. Comparing H_2S with H_2O will give you some indication of the importance of atomic radius on distortions. Based on these results**, comment in your lab book on the effect of double bonds and atomic radius on bond angle distortions.**

Hand-Held Models, Bond Angle Predictions, and MacSpartan Pro:

Although the inspection of molecular shapes on the computer screen is instructive, it is also useful to hold a representation of a molecule in your hand. Molecular model kits are valuable tools to essentially all chemists. The Molecular Visions® model kit is used extensively by Macalester students in Organic Chemistry (CHEM 211-212).

The labels on the components of this model kit feature hybridization terminology (sp-3, sp-2, etc.) that will be discussed in class very soon. For now, use this information to guide your selection of appropriate pieces:

Description of Model Kit Piece	Element	Geometry
Black, SP-3	Carbon	Tetrahedral
Red, SP-3	Oxygen	Tetrahedral
Blue, SP-3	Nitrogen	Tetrahedral
Light Green, SP-3	Fluorine	Tetrahedral
Pink, SP-3	Chlorine	Tetrahedral
Grey, SP-2	Carbon, Nitrogen or oxygen	Trigonal Planar
Grey, rectangle	Carbon-Carbon Double Bond	
Grey, U-shaped	Two of these can be assembled to create a carbon-carbon double bond.	
Red, U-shaped	Two of these can be assembled to create an oxygen-oxygen double bond. Note that red and grey half-length U-shaped pieces are assembled to best indicate a carbon (or nitrogen) to oxygen double bond.	
Pink, T-shaped	Two of these can be assembled to create an octahedral electron-group geometry.	
Grey, Triangle and Grey, Straight	These two pieces can be assembled to create a trigonal bipyramidal electron-group geometry.	
Any Color Ball	Hydrogen atom	

- Draw the Lewis dot structure of acetone, C_3H_6O, in your lab book. **The oxygen atom in acetone is connected to a single carbon atom, with no hydrogen atoms connected to this same carbon atom.** Acetone is the primary component of fingernail polish remover.

- Construct a molecular model of acetone, C_3H_6O, using the Molecular Visions model kit. You will need to obtain two black carbon clusters, one grey carbon center and one grey double bond, and one red oxygen atom from the drawers of the rolling cart. You can use balls of any color to represent your hydrogen atoms – you'll need six. Lone pairs will "appear" in your model as bonds with nothing at the end of them. Feel free to ask your lab instructor or assistant for help.

- Ask your lab assistant or instructor to inspect your hand-held model before disassembly. Your lab assistant/instructor will initial your Lewis Structure if all aspects of your model and structure are correct.

- Select **Molecular Mechanics**, **MMFF, Initial geometry,** and **<u>deselect</u> symmetry** for your MacSpartan Pro acetone calculation. Determine the calculated <OCH and <CCC angles and record these appropriately on a Lewis structure in your laboratory notebook.

- Rationalize the distortions of the two bond angles you studied for acetone. What's causing them to distort the way they do?

- Repeat the same procedure [construct hand-held model, show your lab instructor/assistant, calculate angles using MacSpartan Pro (Molecular Mechanics, MMFF, deselect symmetry), and rationalize deviations] for the following molecules:

Ethylene, C_2H_4

Diethylamine, $NH(CH_2CH_3)_2$ — Set "Start from:" to **MMFF Conformer** for diethylamine. **Analyze only the <CNC bond angle.**

Nitrate anion, NO_3^- — Nitrate ion has a steric number of 3. Include reasonable resonance forms with formal charges in your Lewis Structure representation. Enter one of these resonance forms into Spartan Pro using **Expert** mode. Indicate "Anion" (-1) as the Total Charge in the Setup:Calculations menu, and set "Start from:" back to Initial Geometry.

Return each of your MolecularVisions® model kit components to the drawer it came from.

Trigonal Bipyramidal Preferences

The "placement" of the nonbonding pairs was straightforward in the previous examples, since each site about the central atom was equivalent. This is not the case with trigonal bipyramidal molecules. The sites that are 120^o apart are called "equatorial," while the sites that are 90^o relative to the equatorial sites are called "axial". These two types of sites are geometrically distinct – they are qualitatively different environments. **Do nonbonding pairs prefer equatorial or axial sites in molecules with trigonal bipyramidal electron-group geometries?**

The molecule iodine trifluoride, IF_3, which has CN = 3 and SN =5, serves as a good example. There are three unique relative placements of the nonbonding pairs between the equatorial and axial sites of this molecule. They can be both axial, both equatorial, or one axial and one equatorial.

- Draw each of these possible three-dimensional shapes in your notebook. Sketch the molecules to indicate the positions of nonbonding pairs on the trigonal bipyramid as best you can. Come up with a unique name for each structure, based on the locations of the two nonbonding pairs.

- Generate a table in your notebook to clearly communicate the following structural features for each possibility. Consider an ideal structure trigonal bipyramidal structure (*i.e.*, no distortions) for these determinations.

    1. **Number of 90^o angles between nonbonding pairs.** (Note: This angle cannot be experimentally measured since electron positions cannot be located with high precision. However, this "angle" is useful in rationalizing trigonal bipyramidal preferences.)
    2. **Number of 90^o angles between nonbonding pairs and bonding pairs.** (Note: This angle is also impossible to measure experimentally.)
    3. **Number of 90° angles between bonding pairs.** (These angles *can* be measured experimentally, and provide some insight into the immeasurable ones above.)

Hint: Each structure has a total of **six** 90^o interactions. All that differs is what type these six are. Feel free to ask for help to verify your approach to counting these angles.

Based on what you have learned already during this experiment, can you speculate on which structure might be the "best" (*i.e.*, the lowest energy of IF_3)? **Rank the structures from "best" to "worst" and briefly provide your rationale.** It is important for chemists to try to anticipate the outcome of computer calculations, and not accept the computed results blindly. Computer calculations don't rely on "chemical intuition," so hypotheses held by the experimentalist can help rule out unreasonable outcomes. Don't worry. Points won't be deducted for your selection of "best" and "worst," but only for the clarity of your discussion/rationale.

Let's find out which structure MacSpartan thinks is the lowest energy geometry for IF_3. Nature defaults to the lowest energy state available, so **the geometry with the lowest energy best represents the naturally occurring structure.**

MacSpartan Pro can calculate the approximate energies of molecules. Indeed, the calculation of these energies is one of the primary applications of computational chemistry software. **In this study, the <u>relative</u> energies of the three possible structures are of more interest than their absolute energies.**

- Draw one of the structures by starting with a trigonal bipyramidal iodine fragment in the **Expert** mode. Add the fluorine atoms into the appropriate equatorial or axial locations via either **Entry** or **Expert** mode. **Delete** the remaining "half-bonds" (and resulting extraneous atoms) to indicate the locations of the nonbonding electrons.

In this case, a calculation of "Equilibrium Geometry" isn't appropriate. Our objective is to determine the energy of each structural possibility for comparison purposes. A calculation of "Equilibrium Geometry" starting with any of these three possibilities should (if the proper level of theory (calculation method) is applied) provide the naturally occurring structure, along with any distortions in the actual molecule. The appropriate calculation here is called "Single Point Energy." A Single Point Energy calculation simply provides the energy associated with the submitted structure. The shape of the molecule won't change during the calculation, in contrast to previous calculations. In this way, a "Single Point Energy" calculation doesn't provide information about distorted angles. However, it will permit a ranking of our three possibilities in terms of energy.

- Conduct a calculation (**Single Point Energy**, **Semi-Empirical**, **AM1**, <u>deselect</u> **symmetry**) on your structure.

- Record its energy (provided in kcal/mol at the bottom of the workspace) next to the corresponding structure in your notebook.

- Repeat these steps for the remaining two structures.

- Which structure best represents naturally occurring IF_3? Was your prediction correct? **Based on your ranking of possible structures, discuss the "rules" that govern trigonal bipyramidal preferences**. If you already (correctly) outlined these rules in making your hypotheses up above, it's enough to simply state that here. (What feature is most "destabilizing" for a CN = 3, SN = 5 molecule? What distinguishes the best structure from the second best possibility? Be specific.).

Starting with the best structure of IF_3 (redraw in a new window), calculate the distorted bond angles in this molecule. For this calculation, use "Equilibrium Geometry", "Semi-Empirical", "AM1" and <u>deselect</u> "symmetry". This geometry is called "T-shaped".

Name________________________________

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Advance Study Assignment

Read through the experiment carefully and then provide a 1-2 sentence synopsis of the objectives of the experiment in the box below.

Please provide the answers to the following questions on this page. Bring it with you, completed, when you come to lab.

1. Knowledge of periodic trends is important to understand the subtler aspects of VSEPR theory. Explain fundamentally why a sulfur atom is larger than an oxygen atom.

2. Rank the following isoelectronic species in order of increasing (a) size, (b) ionization energy, and (c) electron affinity.

   Cl^-, K^+, Ca^{2+}