Experiment 6
Seeing is Believing: Models of Molecular Structure

Not until the early part of this century was the experimental determination of the arrangements of atoms in molecules (molecular structure) possible. Between 1912 and 1915, William Bragg and his son Lawrence developed the technique of X-ray diffraction and determined the structure of crystalline NaCl and KCl. (For this achievement, they were awarded the 1915 Nobel Prize in Physics - the only father/son team so honored.) Since that time, X-ray diffraction has been applied to study molecules of ever-increasing size and complexity. In 1960, John Kendrew and Max Perutz finally solved the crystal and molecular structures of two proteins, myoglobin and hemoglobin. (A 1963 Nobel Prize was their reward.) Such investigations were extremely laborious, with many months, perhaps years, of work involved. Perutz, for example, worked on the structure of hemoglobin for 23 years. Recent advances in computer technology and automated equipment have greatly reduced the effort involved and now many thousands of molecular and dozens of protein structures have been elucidated by X-ray techniques. Many of the structures drawn in your text, together with the bond angles and bond distances discussed therein, are based on X-ray crystal structures. However, if a suitable single crystal cannot be made, X-ray diffraction is much less useful. Other techniques for experimentally determining structures of molecules have been developed and are briefly summarized below.

Technique	Useful Molecular Size Range and Limitations
X-Ray diffraction	Small to very large molecules but suitable crystals only
Electron diffraction	Small to medium molecules
Microwave spectroscopy	Small molecules only; gas phase
Neutron diffraction	Small to large molecules; crystals required
X-ray absorption	Small to large molecules; but only one atom of the absorbing species present per molecule, can only be done at a few laboratories.
NMR spectroscopy	Small to large molecules, including proteins; molecules are in solution. 2002 Nobel prize in chemistry awarded, in part, for development of NMR as a method for protein structure determination.

As structural data accumulated, useful generalizations about bond lengths, bond angles, and sizes of atoms in molecules became possible (e.g. C-C bond lengths are l.54Å (1 Å = 10^{-10} m), C-H bond lengths l.l0 Å, bond angles around carbon bonded to four other atoms are l09°). Molecular models are one important result of the systematic investigation of molecular structure because it is possible to build macroscopic structures that resemble the three-dimensional arrangement of atoms in molecules. Even simple models can provide much insight into molecular structure. James Watson and Francis Crick used model building (inspired by an X-ray

crystal structure of DNA experimentally measured by Rosalind Franklin) to determine the structure of DNA in 1953 (they won a Nobel Prize in 1962). Models continue to have an important role in research. For example, a chemist may build a model of a molecule whose structure has not been experimentally established, as an aid to designing a synthesis of the molecule or to making an informed guess about its structural properties (such as interatomic distances).

A practicing chemist often employs several different kinds of molecular models. Each may be most useful for examining one particular aspect of molecular structure. For example, the models you use today are helpful for studying the geometry of molecules. They do not convey much information about the size of the atoms that constitute a molecule. So-called "space-filling" models (ask your instructor what they look like) do that--but they mask the geometry of the molecule of interest.

A chemist also carries around several different mental models for molecular structure. Today we examine one such model − the so-called VSEPR approach (Valence Shell Electron Pair Repulsion). It is discussed carefully in your text, but use of the molecular models should illustrate that 'Seeing is Believing.'

Pre-lab Preparation

Reading

Zumdahl, 6th edition, Section 13.13.

Laboratory Notebook

1. Write a one-paragraph summary that outlines the goals and methods for this experiment.
2. What are the main ingredients of VSEPR theory? Consider the following points (plus any others you think warrant mention):
   a) What defines SN, the 'steric number' of the atom of interest?
   b) In terms of steric number, how do we count double and triple bonds?
   c) What preferred geometry does VSEPR assign to each SN, for steric numbers 2-6? (We shall only consider molecules with steric numbers in this range.)
   d) What principle underlies the linking of each SN to its particular geometry?
   e) Are all electron pair repulsions between steric groups (bonding groups and lone pairs) equivalent? If not, state their relative order of importance (if you are on the right track, there are three and only three kinds of interactions to consider).
3. Bring your textbook with you to the lab.

Procedure

Do the exercises listed below, answering the questions as you go.

Spend 10-15 minutes familiarizing yourself with the molecular models set provided. Compare the models to the descriptions on pp. 2-3 of the direction booklet. Assemble the models for water and ethane (see pp. 6-7) of the direction booklet. When you are reasonably confident you know how to manipulate the models, go on to part I. In each part:

a) Draw a proper Lewis structure for the molecule specified,

b) Make a model of the molecule and determine its expected geometry,

c) Draw a sketch of the 3-D structure, indicating bond angles, and

d) Answer any questions asked.

If you get confused, ask for HELP!

In predicting the expected geometry, remember that experimentally one only observes the relative positions of atomic nuclei. Lone pairs of electrons are invisible.

I. SF_6. Are all the S-F bonds identical? If not, how many different kinds are there? Indicate on a sketch those that are equivalent.

II. IF_5. Remember, lone pairs are invisible! Are all the I-F bonds equivalent? If not, indicate on a diagram the equivalent sets.

III. PF_5. Five fluorine atoms surround P in PF_5 and I in IF_5. Explain why the geometries of the two molecules are, or are not, the same. If all the P-F bonds in PF_5 are not equivalent indicate the sets of equivalent bonds on a diagram.

IV. A former Chem 11 student groups PF_5, SF_4, BrF_3 and XeF_2 (Xe = xenon, once termed an "inert" gas but clearly not totally inert) together. Draw a Lewis structure for each. What do the four molecules have in common besides some fluorine atoms? Your aim now is to deduce the geometries for the last three molecules of the group and designate equivalent sets of bonds for each. This is not so easy so look back at your answers to part I before starting. Begin with two (or more) reasonable alternative structures for each, draw these possible structures in your notebook and make their models, enumerate the relevant interactions present and show why, on balance, the structure you ultimately select is preferable over the other possibilities. Note that lone pair-lone pair repulsions are sensitive to the angle between the lone pairs (and so forth).

V. XeF_4. Is its geometry like that of SF_4? Why/why not? Designate the equivalent sets of Xe-F bonds.

VI. CH_4, NH_3 and H_2O are termed "isoelectronic" molecules. Show they deserve the name. These three molecules have been studied by physical chemists for many, many years. Predict the expected geometry for each. The H-X-H bond angles in the substances are 104.5°, 107.3°, and 109.5°. Which angle goes with which compound? Explain your assignments.

VII. Thus far VSEPR plus Lewis structures have fared very well. Make a Lewis diagram and model for benzene, C_6H_6 that is compatible with the fact that all the carbon-carbon bonds of benzene are equivalent (see p. 10 of the instruction book). Typical carbon-

carbon bonds lengths are: single bond, 1.54 Å; double bond, 1.33 Å; in benzene, 1.39 Å. Can you build a model of this compound? Give it a try. A similar dilemma is presented by the nitrate anion, NO_3^- and many other ions. What is the 'problem' common to such species in terms of their description by the Lewis/VSEPR approach?

When you are done, please replace all the model parts in the boxes.

Laboratory Report

Record your observations from each part in your laboratory notebook and answer all of the questions posed in the procedure. In a paragraph, summarize the lessons you learned and conclusions you have drawn from this experiment. Submit the yellow duplicate pages to your T.A. at the end of the laboratory period.