EXPERIMENT 3

TESTING AND EXTENDING VSEPR WITH COMPUTATIONAL CHEMISTRY

INTRODUCTION

It has been more than 50 years since the first appearance of the VSEPR model.[1-3] In that time it has become a standard topic in first-year chemistry textbooks.[4] As with any model, it has strengths and weaknesses. Its strengths include an almost infallible ability to predict the correct point group of compounds containing main-group elements, ease of application, and frequently correct predictions of the effects that lone pairs on the central atom have on angles, bond lengths, and point group. Among its weaknesses are the occasional qualitatively wrong predictions for the effect of lone pairs and an inability to predict the correct point group for a few compounds containing metals (both main-group and transition).

The AXE system

North American chemistry textbooks[4] adopt the excellent AX_mE_n system, where A is the central atom, m the number of ligands X, and n the number of nonbonded lone-pairs of electrons, E, about the central atom. In this system, methane, CH_4, is AX_4; ammonia, NH_3, is AX_3E_1; water, H_2O, is AX_2E_2. Note that different AX_mE_n designations can give rise to the same overall geometry or shape. For example, AX_2E_1 and AX_2E_2 both give rise to bent or angular geometries and AX_2 and AX_2E_3 both give rise to linear geometries.

The AXE system gives rise to a pattern, from which the various atomic geometric shapes can be determined/assigned as shown in Figure 1. Note that parent categories are often described as AB_q, where q is the steric number and is a sum of m and n.

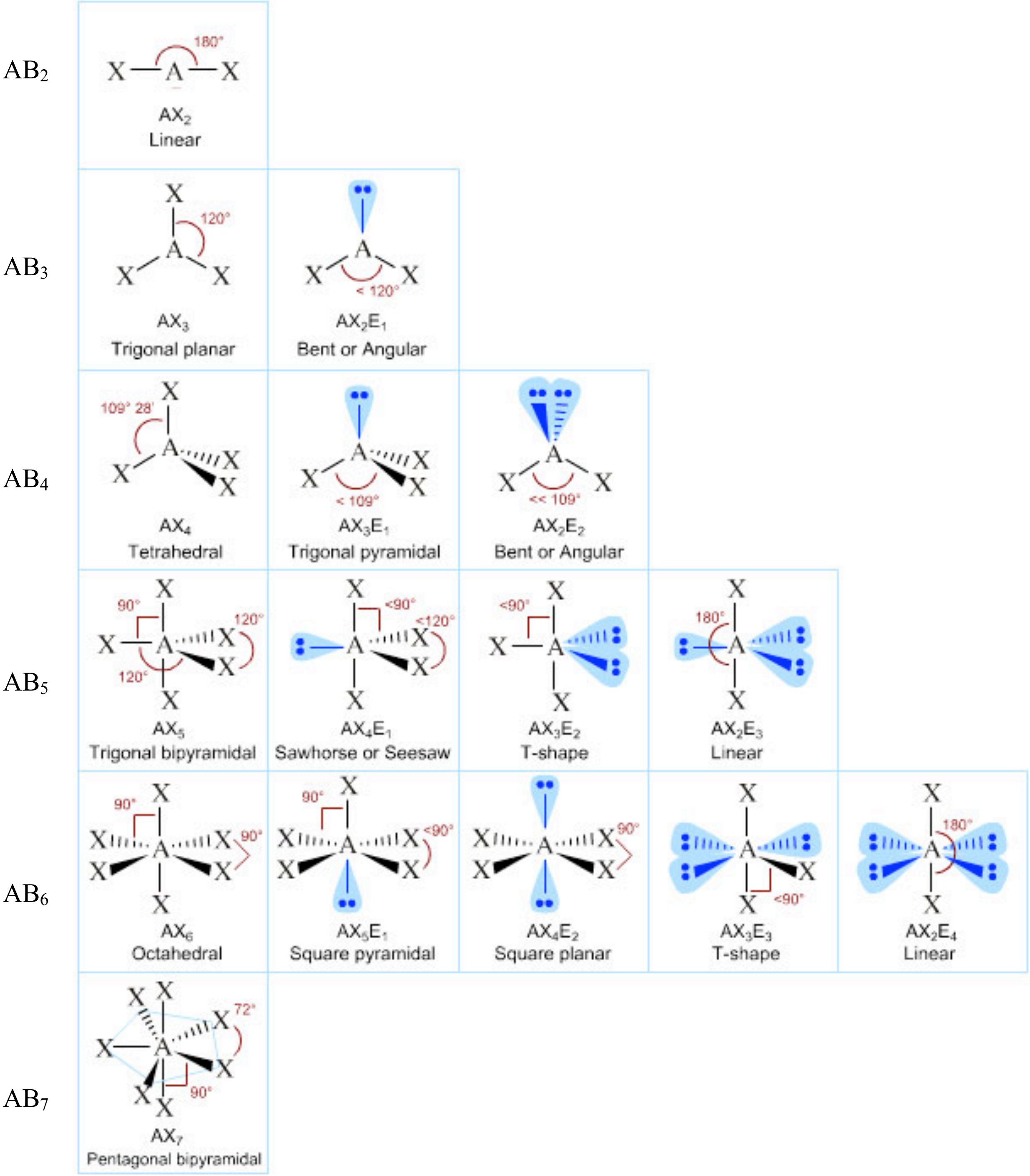

Figure 1: The VSEPR geometric shapes as predicted using the AXE system.

VSEPR can be used to make quantitative predictions of bond angles in molecules with no lone pairs on the central atom. It also makes qualitative predictions of (i) changes in bond angles for molecules with lone pairs on the central atom, (ii) changes in bond lengths as a consequence of differing electronegativities of substituents, and (iii) bond-length differences between axial and equatorial ligands.

The qualitative predictions of the VSEPR theory can be organized into nine areas for the purpose of a quantitative evaluation:

1. For molecules with lone pairs and single bonds on a central atom, the angles subtended by the single bonds are smaller than the ideal angle because lone-pair regions are larger than single bond regions.
2. Bond angles decrease as the electronegativity of the substituent increases because the electrons are farther away from the central atom and require less volume at the central atom. Similarly, bond angles increase as the electronegativity of the central atom increases because the electrons are closer to the central atom and require a greater volume.
3. Bond angles involving multiple bonds are larger than those involving only single bonds because multiple-bond regions are larger than single-bond regions.
4. The axial bonds are longer than the equatorial bonds for $AX_{5-n}E_n$ molecules ($n = 0$-2) because the axial positions have more close neighbors (three at 90°) than the equatorial positions (two at 90°), pushing the axial substituents farther from the central atom.
5. The equatorial bonds are longer than the axial bonds for AX_5Y molecules (where Y is a lone pair or multiply bonded atom) because Y pushes the equatorial bonding domains away from itself.

6. Introducing a more electronegative substituent at the less electronegative of two bonded atoms decreases the bond length to the more electronegative atom.
7. Lone pairs are always equatorial in $AX_{5-n}E_n$ molecules (n =1-3) because there is more space available in the equatorial positions.
8. Double bonds are equatorial in AX_4Y because there is more space available in the equatorial positions.
9. The less-electronegative substituents occupy the equatorial positions in $AX_{5-n}Y_n$ molecules (n = 0 – 2) and $AX_{5-(m+n)}Y_mE_n$ molecules (m = 2-4, n = 1, 2; m + n < 5) because the less electronegative substituents produce expansion of their bonding region close to the central atom, forcing them into the less crowded equatorial positions.

The purpose of this lab is to use computational chemistry to test, quantitatively, the qualitative VSEPR predictions listed above. Your informal write-up should include Tables of results from each of the exercises below (120 marks, distributed as described in each exercise) and in the discussion address each of the nine VSEPR theory predictions by referring to the relevant results given in the tables (54 marks).

PROCEDURE

Calculation

For this lab you will perform Geometry Optimizations using the B3LYP functional and the LANL2DZ basis set. Once you have built the molecule, symmetrize the molecule but do not use the "clean" functionality.

EXERCISES

1. Bond lengths and bond angles for common homoleptic systems (26 marks)

   Optimize the following set of molecules within the given VSEPR characterization and record bond lengths and bond angles.

- AB_2: CO_2 (AX_2)2
- AB_3: BF_3 (AX_3)2, $SnCl_2$ (AX_2E)2
- AB_4: SiH_4 (AX_4)2, PCl_3 (AX_3E)2, SCl_2 (AX_2E_2)2
- AB_5: PCl_5 (AX_5)4, $TeCl_4$ (AX_4E)4, ClF_3 (AX_3E_2)4, XeF_2 (AX_2E_3)4
- AB_6: SF_6 (AX_6)2, BrF_5 (AX_5E), XeF_4 (AX_4E_2).

2. Effect of electronegativity on bond angles and bond lengths (22 marks)

   Optimize the following set of molecules within the given VSEPR characterization and record the bond lengths and bond angles.

- AX_3E: SbF_3, AsF_3, PF_3, NF_3, AsI_3, $AsBr_3$, $AsCl_3$
- $AX_{4-n}Y_n$: CH_3F, CH_2F_2, CH_3F, CF_4

3. Effect of multiple bonds on bond angles (12 marks)

   Optimize the following set of molecules within the given VSEPR characterization and record the bond lengths and bond angles.

- AX_2Y: CCl_2O
- AX_3Y: PF_3O, SF_3N
- AX_2Y_2: SO_2F_2
- AX_4Y: SF_4O
- AX_5Y: IF_5O

4. Lone pairs and multiple bonds occupy equatorial positions (30 marks)

   Optimize the following set of molecules within the given VSEPR characterization and symmetry and record the energies, bond lengths and bond angles.

- SF_4 (AX_4E) with 0 (C_{3v}) or 1 (C_{2v}) equatorial lone pair
- ClF_3 (AX_3E_2) with 0 (D_{3h}), 1 (C_S) or 2 (C_{2v}) equatorial lone pairs
- XeF_2 (AX_2E_3) with 1 (C_{2v} 120°), 2 (C_{2v} 90°) or 3 ($D_{\infty h}$) equatorial lone pairs
- SF_4O (AX_4Y) with 0 (C_{3v}) or 1 (C_{2v}) equatorial multiple bond.

5. Energies of $PF_{5-n}Cl_n$ Isomers as a Function of Geometry (30 marks)

Optimize the following set of molecules within the given symmetry and record the energies, bond lengths and bond angles

- PF_4Cl with 0 (C_{3v}) or 1 (C_{2v}) equatorial Cl atom
- PF_3Cl_2 with 0 (D_{3h}), 1 (C_S) or 2 (C_{2v}) equatorial Cl atoms
- PF_2Cl_3 with 1 (C_{2v}), 2 (C_S) or 3 (D_{3h}) equatorial Cl atoms
- $PFCl_4$ with 2 (C_{2v}) or 3 (C_{3v}) equatorial Cl atoms.

REFERENCES

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(4) Zumdahl, S. S.; Zumdahl, S. A. *Zumdahl/Zumdahl's Chemistry*; Thomson Brooks/Cole, 2009.