Chapter 6 – The Structure and Reactivity of Molecules

The Structure of Molecules

This is the golden age of instrumentation. Many of the techniques you used in organic lab were used a hundred years ago as the sole method of structure determination. Remember the nucleus has been known for just over 100 years! Beginning in the 1920's and 30's through today, we have seen the invention and development of many analytical techniques used in structure determination. Infrared, NMR, UV-visible (electronic), and ESR spectroscopies, electrochemistry, X-ray crystallography are the major ones. Seventy years ago, an X-ray crystal structure could be an entire Ph.D. dissertation. Today, an undergraduate can frequently solve the same structure in a single afternoon. We will talk about some of these methods later in the chapter.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

While determining molecular structure is increasingly simple, a simple method of predicting structure is still invaluable. The method of choice is VSEPR theory. You saw this in CHM 211 so we'll only briefly review it. This method is a little different from the book's and can be found in my general chemistry notes. Movable images of the different shapes can be found at 3DChem.com. (You may search by shape. e.g. octahedral or example SF_6.)

1) Draw the Lewis structure of the molecule.
2) Determine the "base" shape (electron pair geometry, formally) of the molecule by adding the number of atoms bound to the central atom to the number of lone pairs on the central atom.

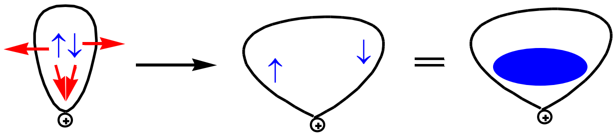
   Number of vertices = number of bound atoms + number of lone pairs

   If number of vertices = 2: linear
   = 3: trigonal planar
   = 4: tetrahedral
   = 5: trigonal bipyramid
   = 6: octahedral
3) If the molecule has no lone pairs (lp), its molecular shape is the same as its base shape. If it has lone pairs, place them in the least congested possible locations, then use the atoms for assigning a shape.

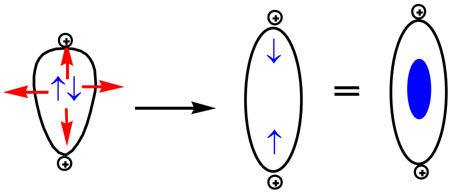
Base Shape	lp	Actual Shape	Example
trigonal planar	1	bent	
tetrahedral	1	trigonal pyramidal	NH_3
	2	bent	H_2O
trigonal bipyramidal	1	butterfly (seesaw)	SF_4
	2	T-shaped	BrF_3
	3	linear	BrF_2^-
octahedral	1	square pyramidal	TeF_5^-
	2	square planar	ICl_4^-
	3	T-shaped	
	4	linear	

This method has been extremely successful in predicting molecular structures. We will now look at the theory in a little more detail because some of what you learned or at least inferred then isn't quite right. For example, the Pauli Principle explains the repulsive force that moves the electron pairs as far away from each other as possible (not charge repulsion as you most likely assumed). (Same spins cannot occupy the same region of space.)

In rule three above, we placed lone pairs in the **least** congested positions available instead of the bonding pairs with their attached atoms. Why? Consider an atom with a lone pair. The nucleus attracts both electrons, while the electrons repel one another. This results in the electron density occupying a lot of space (volume) near the nucleus.



What happens if a proton is then added at the other end of the orbital? Some of the electron density located near atom 1 is pulled towards atom 2 and that reduces the electron-electron repulsion. Thus,



a bonding pair (bp) of electrons need not spread out as far (at its base) as a lone pair (lp). The result is that electron pair repulsions increase in the order bp-bp < bp-lp < lp-lp. Also, multiple bonds are larger than single bonds because of the presence of the off-axis π-clouds. As a result, when placing atoms around a molecule, atoms bound to the central atom by a multiple bond are placed in the least crowded positions.

This size difference also has some subtle effects. For example, the bond angles in CH_4 are all 109.5° as predicted. In contrast, the angles in ammonia are 107° and in water they drop to 104.5°. The angles aren't equal because lone pairs are larger than bonding pairs and push them together. The result is the bond angles within molecules with lone pairs are smaller than predicted for an idealized structure. The example of the phosphorus halides (p. 211) provides a particularly nice example (and discussion) of this effect.

Molecular Orbitals and Molecular Structure

VSEPR is basically a VB construct. This section briefly introduces the MO counterpart to VSEPR. The major thing we need to discuss in this section is how to read and interpret the Walsh diagram on p. 219. If you pursue an advanced degree in chemistry, there is a reasonable chance you will come across one of these in the literature or a textbook. In a Walsh diagram, two or more different atomic orbital overlap (or mixing in MO theory) combinations are presented. In Fig. 6.16 there are two such combinations, linear and bent. The diagram is generated by starting with one geometry, e.g. linear, and calculating the product MOs and their energies. The interaction is then changed slightly (e.g. putting in a 1° bend) and recalculating. This is done repeatedly until a new set of energy minima occur. To determine which geometry is right for the compound in question, one simply begins filling the MOs applying the *aufbau* principle is the geometry. Theory predicts the molecule will adopt the geometry with the lowest total energy.

Structure and Hybridization

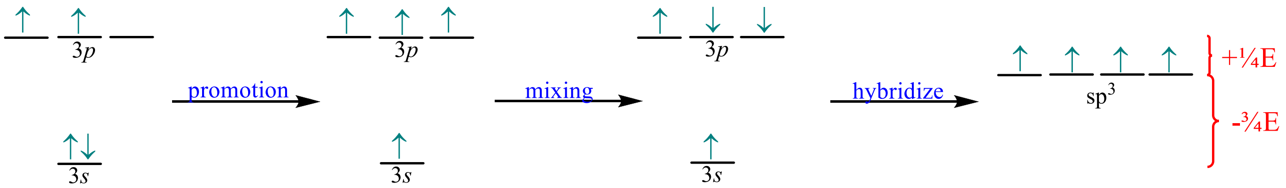
Mostly read this on your own: pp. 220-225. You are not responsible for knowing the formulae on p. 222 since this concept is better applied qualitatively in most cases. This section concerns itself primarily with the concept of partial hybridization. You have used hybridization since general chemistry and, by now, are comfortable with hybrid orbitals that result from the mixing of atomic orbitals. As you have seen it, hybridization has involved the mixing of orbitals in equal proportions in each hybrid. That is to say, the *sp* hybrid is equal parts (50/50) *s* and *p* orbitals, while an sp^3 hybrid is made of a 1/3 ratio of *s* to *p* orbitals, with each hybrid having the exact same ratio of *s* to *p* orbitals.

Although this has become quite familiar to you, there is no inherent reason that the hybrid orbitals must be identical. That is, there is no reason why we can't have two different "*sp*" hybrids with *s*/*p* ratios of 47/53 and 53/47, respectively. This probably looks strange because it is different from your past understanding, not because it is unreasonable. Deviations from ideal bond angles provide evidence for partial hybridization. As you have seen earlier in this chapter, the bond angles in CH_4, NH_3, and H_2O are 109.5º, 107º, and 104.5º. A reasonable question would be "if the orbitals in these molecules are identical, how can their angles be different?"

Partial hybridization is an attempt to generate a more realistic picture of the bonding in a molecule. The results will be closer to the MO description of the bonding than traditional hybridization. The big difference is that while in MO theory fractional mixing of atomic orbitals is a natural outcome of the math, partial hybridization represents a correction to the VB theory prediction. As you can see from eq. 6.1 – 6.4, one uses experimental bond angles to derive the orbital character rather than the other way around.

Bent's Rule and the Energetics of Hybridization

Earlier, when we discussed hybridization and VB theory, it was mentioned that PR_3 does not usually hybridize, but SiR_4 always does. We now discuss why. First recall how an atom is hybridized (using silicon as an example).



Just as in the case of carbon, silicon must hybridize to form 4 bonds. For phosphorus the picture is different. Both nitrogen and phosphorus already have three unpaired electrons in their *p* orbitals available for binding. Since hybridized orbitals are higher in energy than *s* orbitals, energy has to be put into the system to raise 1 net electron to that level (The three *p* electrons are stabilized by roughly the same amount as the *s* electron is destabilized. Thus, the energy needed to promote one of the *s* electrons to the hybrid orbitals roughly offsets.) Creating hybrid orbitals does 2 things: (i) generates orbitals with better overlap and (ii) provides a less crowded environment (109.5° *vs*. 90° bond angles). For the small nitrogen atom, crowding and efficient overlap make this a favorable trade-off. For the larger P atom crowding is not usually a factor and the large orbitals do not gain much from hybridization in the stereochemically inactive (does not affect geometry) *s* orbital. A result is that the X-P-X angles are much closer to 90° than the corresponding angles in the nitrogen trihalide compounds. The effect is even greater for the arsenic series of compounds.

X	NX_3 (angle,°)	PX_3 (angle, °)	AsX_3 (angle, °)
F	102.2	97.8	93.9
Cl	106.8	100.3	97.7
Br	108.1*	101	97.7
I	110.9*	102	99.7

Except where noted from: Galy, J.; Enjalbert, R. *J. Solid State Chem*. **1982**, *44*, 1.

*Calculated. Atanosov, M.; Reinen, D. *J. Phys. Chem. A* **2001**, *105*, 5450.

In compounds containing mixed substitutes and hybridized orbitals a trend has been observed that is called Bent's rule. It states that more electronegative substituents tend to bind to hybrid orbitals with less *s* character. Why? *s*-Orbitals are more penetrating and electron density is less available for bonding. Thus, more electronegative atoms would be able to withdraw more electron density from *p* orbitals than from *s* orbitals.

Non-bonded Repulsions and Structure

These are steric repulsions and their effect in pure inorganic chemistry is limited (the effects in organometallic chemistry are larger for the same reasons they are important in organic chemistry). One of the largest inorganic atomic ions is iodide, which is about the same size as methyl. Steric effects are usually important only in molecules with large number of substituents relative to central atom size and for small central atoms. Thus, electronic effects are generally much more important in inorganic chemistry.

Bent Bonds

In a normal σ-bond, the lobes point directly at one another along the internuclear axis. In contrast, π-bonding results from the side-to-side bonding of *p* or *d* orbitals. Since this type of bonding results in less overlap, π-bonds are always weaker than σ-bonds between the same two atoms.

Strained rings systems represent a situation wherein the bonding orbitals in a σ-bond do not lie along the internuclear axis. Consider cyclopropane, C_3H_6. In principle, each carbon is sp^3 hybridized, which suggests bond angles near 110º, yet the angles must be 60º. Since no combination of *s* and *p* orbitals can yield an angle below 90º, the bond must arise from orbital overlap outside of the internuclear axis. Just as in the case of π-bonding, this causes the lower bond energy (poorer overlap) and greater reactivity (poorer overlap coupled to more exposed electron density) observed for this and other strained ring systems. Thus, "bent" bonds are those that have the appearance of being curved if one looks at the overlapping orbitals.

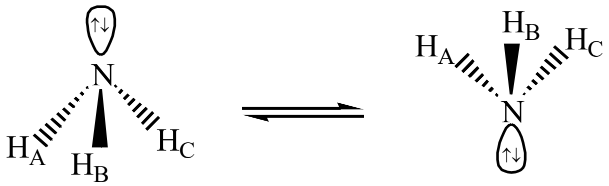
Bond Lengths – Skip

Experimental Determination of Molecular Structure

We will go over a handout (from online) separately in class. Read this section as a supplement to the handout.

Some Simple Reactions of Covalently Bonded Molecules

Inversions – This is different from the symmetry operation, since atoms cannot be pulled through other atoms. If all atoms around a central point are the same, chemical inversion yields an indistinguishable molecule.



Please note that H_B is projecting out of the paper in both pictures. (In a symmetry inversion, it would fade behind the paper.) This topic is not trivial for tertiary amines with three different substituents. Amines are common in biological systems (e.g. proteins) and so is chirality. Barriers are larger in trialkyl/aryl amines than ammonia (*ca*. 40 kJ/mol *vs.* 25 kJ/mol) but inversion is usually still rapid. In contrast, chiral phosphines generally have large inversion barriers (*ca*. 120 kJ/mol). This is probably because in phosphines the ligands are bound to hybrid orbitals containing a great deal of *p* character and have no pathway for inversion, whereas in amines only a change in hybridization is required ($sp^3 \rightarrow sp^2 \rightarrow sp^3$), which is energetically easier to accomplish.

Berry Pseudorotation

Consider the trigonal bipyramidal PF_5 molecule. You would expect that the ^{19}F NMR would consist of two multiplets in a 2:3 ratio. Instead only one is observed. Why? Because the F atoms exchange positions more rapidly than NMR can measure the spectrum. The ability of molecules to rearrange, by an intramolecular process, the sites of attachment of constituent atoms is called fluxionality. In the case of a trigonal bipyramid the simplest way of rearranging the atoms first requires you to imagine 2 planes passing through the molecule: 1 plane includes all 3 equatorial atoms, the other both axial atoms and one equatorial atom. This equatorial atom will remain in place throughout the motional process. Simultaneously, in scissor fashion, the axial atoms move toward each other (in their plane, and away from the equatorial atom in the plane) and the equatorial atoms move away from each other (a diagram of this is shown as Figure 6.29 on p. 241 and an animation is available online that breaks this down into steps). At some point the four moving atoms occupy equivalent positions and the molecule becomes a square pyramid. This motion continues until the formerly equatorial atoms are 180° apart (now axial) and the formerly axial atoms are 120° apart (now equatorial). As you can see the new arrangement is identical to the first except it appears to be rotated by 90°; hence the name, Berry pseudorotation.

Nucleophilic Displacement

Read this on your own. This is just like the organic S_N2 mechanism, but is called an associative mechanism in inorganic chemistry.

Free Radical Mechanism

Read this on your own. Again, this is just like similar organic mechanisms.

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