4.1 ORBITALS AND HYBRIDIZATION STATES 77

chapter **4** GEOMETRY

In this chapter, we will see how to predict the 3D shape of molecules. This is important because it limits much of the reactivity that you will see in the second half of this course. For molecules to react with each other, the parts of the molecules that can react with each other must be able to get close in space. If the geometry of the molecules prevents them from getting close, then there cannot be a reaction. This concept is called *sterics*.

Let's use an analogy to help us see the importance of geometry. Imagine that you are stuffing a turkey for Thanksgiving dinner and your hand gets stuck inside the turkey. Just at that moment, someone wants to shake your hand. You can't shake the person's hand because your hand is unavailable at the moment. It's kind of the same way with molecules. When two molecules react with each other, there are specific sites on the molecules that are reacting with each other. If those sites cannot get close to each other, the reaction won't happen.

There will be many times in the second half of this course when you will be trying to determine which way a reaction will proceed from two possible outcomes. Many times, you will choose one outcome, because the other outcome has steric problems to overcome (the geometry of the molecules does not permit the reactive sites to get close together). In fact, you will learn to make decisions like this as soon as you learn your first reactions: $S_N 2$ versus $S_N 1$ reactions. Now that we know why geometry is so important, we need to brush up on some basic concepts.

To determine the geometry of an entire molecule, we need to be able to determine the geometry of each atom based on how it is connected to the atoms around it. After all, that is what determines the geometry—how the atoms are connected in 3D space. Since atoms are connected to each other with bonds, it makes sense that we need to take a close look at bonds. In particular, we need to know the exact locations and angles of every bond to every atom. This might sound difficult, but it is actually straightforward, and with a little bit of practice, you can get to the point where you know the geometry of a molecule as soon as you look at it (without even needing to think about it). That is the point that we need to get to, and that is what this chapter is all about.

4.1 ORBITALS AND HYBRIDIZATION STATES

To determine the geometry of a molecule, we need to know how atoms bond with each other three dimensionally, so it makes sense for our discussion to start with orbitals. After all, bonds come from overlapping orbitals. A bond is formed when an electron of one atom overlaps with an electron of another atom. The two electrons are shared between both atoms, and we call that a bond. Since electrons exist in regions of space called orbitals, then what we really need to know is; what are the locations and angles of the orbitals around every atom? It is not so complicated, because the number of possible arrangements of orbitals is very small. You need to learn the possibilities, and how to identify them when you see them. So, we need to talk about orbitals.

There are two simple orbitals: s and p orbitals (we don't really deal with d and f orbitals in organic chemistry). s orbitals are spherical and p orbitals have two lobes (one front lobe and one back lobe):



Atoms in the second row (such as C, N, O, and F) have one s orbital and three p orbitals in the valence shell. These orbitals are usually mixed together to give us hybridized orbitals (sp³, sp², and sp). We get these orbitals by mixing the *properties* of s and p orbitals. What do we mean by mixing?

Imagine one swimming pool shaped like a triangle and another shaped like a pentagon; now we put them next to each other. We wave a magic wand and they magically turn into two rectangular pools. That would be a neat trick. That's what sp orbitals are: we take one s orbital and one p orbital, then wave a magic wand, and poof—we now have two equivalent orbitals that look the same. The two new orbital have a different shape from the original two orbitals. This new shape is somewhat of an average of the two original shapes.

If we mix two p orbitals and one s orbital, then we get three equivalent sp² orbitals. Let's go back to the pool analogy. Imagine two pools shaped like octagons and one shaped like a triangle. We wave our magic wand and get three pools shaped like hexagons. We started with three pools and we ended with three pools. But the three pools in the end are all the same and their shape is an average of the shapes of the original three pools. The same thing is true here with orbitals. We start with three orbitals (two p orbitals and one s orbital). Then we mix them together and end up with three orbitals that all look the same. All three new orbitals have the "average" properties of the original three orbitals. The three new orbitals (since they came from one s orbital and two p orbitals) are called sp² orbitals. Similarly, when you combine three p orbitals and one s orbital, you get four equivalent sp³ orbitals.

To truly understand the geometry of bonds, we need to understand the geometry of these three different hybridization states. The hybridization state of an atom describes the type of hybridized atomic orbitals $(sp^3, sp^2, or sp)$ that contain the valence electrons. Each hybridized orbital can be used either to form a bond with another atom or to hold a lone pair.

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It is not difficult to determine hybridization states. If you can add, then you should have no trouble determining the hybridization state of an atom. Just count how many other atoms are bonded to your atom, and count how many lone pairs your atom has. Add these numbers. Now you have the total number of hybridized orbitals that contain the valence electrons. This number is all you need to determine the hybridization state of the atom. That probably sounded complicated, so let's look at an example to clear it up.

Consider the molecule below:

Let's try to determine the hybridization state of the carbon in the center. We begin by counting the number of atoms connected to this carbon atom. There are 3 atoms (O, H, and H). *The oxygen atom only counts as one.*

Next we count the number of lone pairs on the carbon atom. There are no lone pairs on the carbon atom. (If you are not sure how to tell that there are no lone pairs there, go back to Chapter 1 and review the section on counting lone pairs.) Now we take the sum of the attached atoms and the number of lone pairs—in this case, 3 + 0 = 3. Therefore, three hybridized orbitals are being used here. That means that we have mixed two p orbitals and one s orbital (a total of three orbitals) to get three equivalent sp² orbitals. Thus, the hybridization is sp². Let's take a closer look at how this works.

Recall that the second row elements have three p orbitals and one s orbital that can be hybridized in one of three ways: sp^3 , sp^2 , or sp. If we are using three hybridized orbitals, then we must have mixed two p orbitals with one s orbital:



So here's the rule: Just add the number of bonded atoms to the number of lone pairs. The number you get tells you how many hybridized orbitals you need according to the following:

If the sum is 4, then you have 4 sp³ orbitals

If the sum is 3, then you have 3 sp² orbitals and one p orbital (as in our example)

If the sum is 2, then you have 2 sp orbitals and two p orbitals

There is one exception, which you will see in the chapter on aromaticity in your textbook. For now, let's not worry about it.

Once you get used to looking at drawings of molecules, you should not have to count anymore. There are certain arrangements that are always sp^3 hybridized, and the same is true for sp^2 and sp. Here are some common examples:



If you can determine the hybridization state of any atom, you will be able to easily determine the geometry of that atom. Let's do another example.

EXERCISE 4.1 Identify the hybridization state for the nitrogen atom in ammonia (NH₃).

Answer First we need to ask how many atoms are connected to this nitrogen atom. There are three hydrogen atoms. Next we need to ask how many lone pairs the nitrogen atom has. It has 1 lone pair. Now, we take the sum. 3 + 1 = 4. If we need to have four hybridized orbitals, then the hybridization state must be sp³.

PROBLEMS For each compound below, identify the hybridization state for the central carbon atom.



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4.8 For each carbon atom in the following molecule, identify the hybridization state. Do not forget to count the hydrogen atoms (they are not shown). Use the following simple method: A carbon with 4 single bonds is sp^3 hybridized. A carbon with a double bond is sp^2 hybridized, and a carbon with a triple bond is sp hybridized.



Once you get used to it, you do not need to count anymore—just look at the number of bonds. If carbon has only single bonds, then it is sp^3 hybridized. If the carbon atom has a double bond, then it is sp^2 hybridized. If the carbon atom has a triple bond, then it is sp hybridized. Consult the chart of common examples on the previous page.

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Now that we know how to determine hybridization states, we need to know the geometry of each of the three hybridization states. One simple theory explains it all. This theory is called the *valence shell electron pair repulsion theory* (VSEPR). Stated simply, all orbitals containing electrons in the outermost shell (the valence shell) want to get as far apart from each other as possible. This one simple idea is all you need to predict the geometry around an atom. First, let's apply the theory to the three types of hybridized orbitals.

1. Four equivalent sp³-hybridized orbitals achieve maximum distance from one another when they arrange in a tetrahedral structure:



Think of this as a tripod with an additional leg sticking straight up in the air. In this arrangement, each of the four orbitals is exactly 109.5° from each of the other three orbitals.

2. Three equivalent sp²-hybridized orbitals achieve maximum distance from one another when they arrange in a trigonal planar structure:

All three orbitals are in the same plane, and each one is 120° from each of the other orbitals. The remaining p orbital is orthogonal to (perpendicular to the plane of) the three hybridized orbitals.

3. Two equivalent sp-hybridized orbitals achieve maximum distance from one another when they arrange in a linear structure:



Both orbitals are 180° from each other. The remaining two p orbitals are 90° from each other and from each of the hybridized orbitals.

So far its very simple:

- 1. $sp^3 = tetrahedral$
- 2. $sp^2 = trigonal planar$
- 3. sp = linear

But here's where students usually get confused. What happens when a hybridized orbital holds a lone pair? What does that do to the geometry? The answer is that the geometry of the orbitals does not change, but the geometry of the molecule is affected. Why?

Let's look at an example. In ammonia (NH₃), the nitrogen atom is sp^3 hybridized, so all four orbitals arrange in a tetrahedral structure, just as we would expect. But only three of the orbitals in this arrangement are responsible for bonds. So, if we look just at the atoms that are connected, we do not see a tetrahedron. Rather, we see a trigonal pyramidal arrangement:



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Trigonal, because there are three bonds pointing away from the central nitrogen atom, and pyramidal because it's shaped like a pyramid.

Similarly, in H_2O , the oxygen is sp³ hybridized. So all four orbitals are in a tetrahedral arrangement, just as we would expect for an sp³ hybridized atom. But only two of the orbitals are being used for bonds. So if we look just at the atoms that are connected, we do not see a tetrahedron. Rather, we see a bent arrangement:



Let's now put all of this information together:

sp ³	with	0 lone pairs = tetrahedral
sp ³	with	1 lone pair = trigonal pyramida
sp ³	with	2 lone pairs = bent
sp ²	with	0 lone pairs = trigonal planar
sp ²	with	1 lone pair $=$ bent
sp	with	0 lone pairs = linear

That's it. There are only six different types of geometry that we need to know. First we determine the hybridization state. Then, using the number of lone pairs, we can figure out which of the six different types of geometry we are dealing with. Let's try it out on a problem.

EXERCISE 4.9 Identify the geometry of the carbon atom below:



Answer First, we need to determine the hybridization state. We did this for this molecule earlier in this chapter and found that the hybridization state is sp^2 (there are 3 atoms connected and no lone pairs, so we need three hybridized orbitals; therefore, it is sp^2).

Next we remind ourselves how many lone pairs there are; in this case, there are none. So the geometry must be trigonal planar.

Once you can determine the geometry around an atom, you should have no problem determining the geometry, or shape, of a molecule. Simply repeat your analysis for each and every atom in the molecule. This may seem like a large task at first, but once you get the hang of it, you will be able to tell the geometry of an atom immediately upon seeing it.

For the next set of problems, you should get to the point where you can do these problems very quickly. The first few will take you longer than the last ones. If the last problem is still taking you a long time, then you have not mastered the process and you will need more practice. If this is the case, open to any page in the second half of your textbook. You will probably see drawings of structures. Point to any atom in a structure and try to determine what the geometry is. Use the list above to help you. Go from one drawing to the next until you can do it without the list. That is the important part—doing it without needing the list.

PROBLEMS For each compound below, identify the hybridization state and geometry for every atom in the compound.













