Chapter 9
Molecular Geometries
and Bonding Theories
Molecular Shapes
•The shape of a molecule plays an important role in its reactivity.
•By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.
What Determines the Shape of a Molecule?
•Simply put, electron pairs, whether they be bonding or nonbonding, repel each other.
•By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.
Electron Domains
•We can refer to the electron pairs as electron domains.
•In a double or triple bond, all electrons shared between those two atoms are on the same side of the central atom; therefore, they count as one electron domain.
Valence Shell Electron Pair Repulsion Theory (VSEPR)

"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

Electron-Domain Geometries

These are the electron-domain geometries for two through six electron domains around a central atom.

Electron-Domain Geometries
•All one must do is count the number of electron domains in the Lewis structure.
•The geometry will be that which corresponds to that number of electron domains.
Molecular Geometries
•The electron-domain geometry is often *not* the shape of the molecule, however.
•The molecular geometry is that defined by the positions of *only* the atoms in the molecules, not the nonbonding pairs.
Molecular Geometries

Within each electron domain, then, there might be more than one molecular geometry.

Linear Electron Domain
•In this domain, there is only one molecular geometry: linear.

•NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

Trigonal Planar Electron Domain

•There are two molecular geometries:

➢Trigonal planar, if all the electron domains are bonding

➢Bent, if one of the domains is a nonbonding pair.

Nonbonding Pairs and Bond Angle

•Nonbonding pairs are physically larger than bonding pairs.

•Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.

Multiple Bonds and Bond Angles

•Double and triple bonds place greater electron density on one side of the central atom than do single bonds.

•Therefore, they also affect bond angles.

Tetrahedral Electron Domain

•There are three molecular geometries:

➢Tetrahedral, if all are bonding pairs

➢Trigonal pyramidal if one is a nonbonding pair

➢Bent if there are two nonbonding pairs

Trigonal Bipyramidal Electron Domain

•There are two distinct positions in this geometry:

➢Axial

➢Equatorial

Trigonal Bipyramidal Electron Domain

Lower-energy conformations result from having nonbonding electron pairs in equatorial, rather than axial, positions in this geometry.

Trigonal Bipyramidal Electron Domain

•There are four distinct molecular geometries in this domain:

➢Trigonal bipyramidal

➢Seesaw

➢T-shaped

➢Linear

Octahedral Electron Domain

•All positions are equivalent in the octahedral domain.

•There are three molecular geometries:

➢Octahedral

➢Square pyramidal

➢Square planar

Larger Molecules

In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.

Larger Molecules

This approach makes sense, especially because larger molecules tend to react at a particular site in the molecule.

Polarity

- In Chapter 8 we discussed bond dipoles.
- But just because a molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.

Polarity

By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.

Polarity

Overlap and Bonding

- We think of covalent bonds forming through the sharing of electrons by adjacent atoms.
- In such an approach this can only occur when orbitals on the two atoms overlap.

Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together while simultaneously decreasing electron-electron repulsion.
- However, if atoms get too close, the internuclear repulsion greatly raises the energy.

Hybrid Orbitals

But it's hard to imagine tetrahedral, trigonal bipyramidal, and other geometries arising from the atomic orbitals we recognize.

Hybrid Orbitals

- Consider beryllium:
  - In its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals.

Hybrid Orbitals

But if it absorbs the small amount of energy needed to promote an electron from the 2*s* to the 2*p* orbital, it can form two bonds.

Hybrid Orbitals

- Mixing the *s* and *p* orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
  - These *sp* hybrid orbitals have two lobes like a *p* orbital.
  - One of the lobes is larger and more rounded as is the *s* orbital.

Hybrid Orbitals

•These two degenerate orbitals would align themselves 180° from each other.

•This is consistent with the observed geometry of beryllium compounds: linear.

Hybrid Orbitals

•With hybrid orbitals the orbital diagram for beryllium would look like this.

•The *sp* orbitals are higher in energy than the 1*s* orbital but lower than the 2*p*.

Hybrid Orbitals

Using a similar model for boron leads to…

Hybrid Orbitals

…three degenerate sp^2 orbitals.

Hybrid Orbitals

With carbon we get…

Hybrid Orbitals

…four degenerate
sp^3 orbitals.

Hybrid Orbitals

For geometries involving expanded octets on the central atom, we must use *d* orbitals in our hybrids.

Hybrid Orbitals

This leads to five degenerate sp^3d orbitals…

…or six degenerate sp^3d^2 orbitals.

Hybrid Orbitals

Once you know the electron-domain geometry, you know the hybridization state of the atom.

Valence Bond Theory

•Hybridization is a major player in this approach to bonding.

•There are two ways orbitals can overlap to form bonds between atoms.

Sigma (σ) Bonds

•Sigma bonds are characterized by

➢Head-to-head overlap.

➢Cylindrical symmetry of electron density about the internuclear axis.

Pi (π) Bonds

•Pi bonds are characterized by

➢Side-to-side overlap.

➢Electron density above and below the internuclear axis.

Single Bonds

Single bonds are always σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.

Multiple Bonds

In a multiple bond one of the bonds is a σ bond and the rest are π bonds.

Multiple Bonds

•In a molecule like formaldehyde (shown at left) an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.

•The unhybridized *p* orbitals overlap in π fashion.

Multiple Bonds

In triple bonds, as in acetylene, two *sp* orbitals form a σ bond between the carbons, and two pairs of *p* orbitals overlap in π fashion to form the two π bonds.

Delocalized Electrons: Resonance

When writing Lewis structures for species like the nitrate ion, we draw resonance structures to more accurately reflect the structure of the molecule or ion.

Delocalized Electrons: Resonance

•In reality, each of the four atoms in the nitrate ion has a *p* orbital.

•The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen.

Delocalized Electrons: Resonance

This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.

Resonance

The organic molecule benzene has six σ bonds and a *p* orbital on each carbon atom.

Resonance

•In reality the π electrons in benzene are not localized, but delocalized.

•The even distribution of the π electrons in benzene makes the molecule unusually stable.

Molecular Orbital (MO) Theory

Though valence bond theory effectively conveys most observed properties of ions and molecules, there are some concepts better represented by molecular orbitals.

Molecular Orbital (MO) Theory

•In MO theory, we invoke the wave nature of electrons.

•If waves interact constructively, the resulting orbital is lower in energy: a bonding molecular orbital.

Molecular Orbital (MO) Theory

If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.

MO Theory

- In H_2 the two electrons go into the bonding molecular orbital.
- The bond order is one half the difference between the number of bonding and antibonding electrons.

MO Theory

For hydrogen, with two electrons in the bonding MO and none in the antibonding MO, the bond order is

MO Theory

- In the case of He_2, the bond order would be

MO Theory

- For atoms with both *s* and *p* orbitals, there are two types of interactions:
  - The *s* and the *p* orbitals that face each other overlap in σ fashion.
  - The other two sets of *p* orbitals overlap in π fashion.

MO Theory

- The resulting MO diagram looks like this.
- There are both □ and □ bonding molecular orbitals and □* and π* antibonding molecular orbitals.

MO Theory

- The smaller *p*-block elements in the second period have a sizeable interaction between the *s* and *p* orbitals.
- This flips the order of the s and p molecular orbitals in these elements.

Second-Row MO Diagrams