Lewis Dot Structure

Non Equivalent Valence Structures

It is important to know there is not a "correct" Lewis Dot structure. This a very simple model to help guide our understanding. We can how choose between what we think are better structures and worse as the better ones will correctly predict "real" properties like bond lengths.

We discussed a particular example of diazomethane CH2NN. This molecule had two reasonable structures that both satified the octet rule. In one the C,N is a double bond and the N,N is double bond. This structure has a formal charge of +1 on one N and a -1 on the other. In a second structure the C,N bond is a single bond and the N,N bond is a triple. In this structure the formal charge on the carbon is -1 and the on one N it is +1. The first structure is "better" as it has the negative formal charge on the more electronegative N. The "real" structure is likely somewhere in between these two.

We then discussed 2 other odd structures for this molecule that have zero formal charges but neither satisfies the octet rule. In one the C,N bond is a double and the N,N bond is triple. This is very strange as N should never make more than 4 bonds (expanded octet should be limited to 3rd row and beyond). The other has a N,N single bond. We compared all four structures to the measured bond length. The C,N bond appears to be like a double bond and the N,N like a triple. This is close to what we would predict from our resonance structures. This rules out the very odd non-octet structure with a single bond. This is exactly the structure with 5 bonds on the N. This 5 bonds on the end structure can be found in various places when people are discussing diazomethane, but it is strictly empirical based on the measured bond lengths!

Shape

Shape is really important for molecules. It determines their polarity which is a huge part of they interactions with other molecules. We can determine shape using Lewis Dot structures and VSEPR.

VSEPR

        Electron repel each other. Therefore regions of high electron density (bonds, lone pairs) in a molecule will obtain a geometry to minimize their repulsions.

        See the nice handout from Paul McCord that is on the webpage

Rules.

Use steric number to figure out the geometry of the electron pairs. Then find the correct molecular geometry that only looks at the positions of the atoms. For example. Water is steric number 4 around a central atom of O (2x H, and 2x LP). This is a tetrahedral arrangement of electron pairs, but the molecular geometry is bent.

Tweaking the geometries

If all the atoms bonded to a central atom are not identical then the geometry will not be perfectly symmetric. How to figure it out?

1. LP have large repulsions. Therefore LP-LP> >LP-BP> BP-BP   example H-O-H angle in water is less than H-N-H angle in ammonia is less than H-C-H angle in methane

2. partial charges matter. H-C-Cl angle is less than 109.5 in CH_3Cl. Why? Partial positive on H's make for larger repulsion, interaction of partial negative on Cl and partial positive on H makes for a smaller repulsion.

3. Size matters. Repulsion can be larger for larger atoms.

Dipole Moment

To have a dipole moment a molecule must have polar bonds (bonds between atoms with different EN) and a geometry such that these don't cancel and yield a net zero dipole.

The bigger the EN difference, the more polar the bonds, the larger the dipole.

What has a dipole?

H_2O, NH_3, HCl, CH_3Cl ….

What does not?

CH_4, CO_2, CCl_4, ….

Note in each case the molecules are perfectly symmetric. Add a different atom or a lone pair and you have a polar molecule.