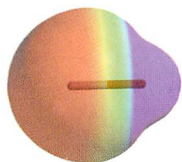


1

Are All Chemical Bonds the Same?



Electron density surface for hydrogen fluoride depicts overall molecular size and shape.



Electrostatic potential map for lithium hydride shows negatively-charged regions (in red) and positively-charged regions (in blue).

Electronegativities

H 2.2	Li 1.0	Be 1.6	B 2.0
C 2.6	N 3.0	O 3.4	F 4.0

Chemists refer to the bond in a molecule like sodium chloride as “ionic”, meaning that its electron pair resides entirely on chlorine. At the other extreme is the “covalent” bond in the hydrogen molecule, where the electron pair is shared equally between the two hydrogens. Intermediate cases, such as the bond in hydrogen fluoride which is clearly “polarized” toward fluorine, are generally referred to as “polar covalent” bonds (rather than “partially ionic” bonds). Are these situations really all different or do they instead represent different degrees of the same thing?

Examine electron density surfaces for *hydrogen, lithium hydride, beryllium hydride, borane, methane, ammonia, water* and *hydrogen fluoride*. First, focus on the shape of the surface (corresponding to the shape of the underlying electron density). For which molecule is the “size” of hydrogen the smallest? For which is it the largest? Is there a correlation between size of the density around hydrogen and the difference in electronegativities between hydrogen and the element to which it is bonded? (See table at left.) Explain.

Next, examine electrostatic potential maps for the same set of compounds. Focus your attention on the value of the potential around hydrogen. For which molecule is it most positive? For which is it most negative? Is there a correlation between the value of the potential and the difference in electronegativities? Plot charge on hydrogen (vertical axis) vs. difference in electronegativities (horizontal axis). Is there a correlation?

What electronegativity difference, large or small, creates a more polar bond? A more covalent bond?

Bond Lengths in Hydrocarbons

2

Carbon-carbon bond lengths in hydrocarbons depend both on the formal bond order (single, double, triple) and on the detailed environment.

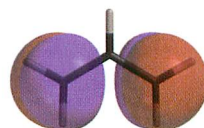
Measure and record the carbon-carbon bond lengths in *ethane*, *ethene* and *ethyne*. These will serve as “standards” for single, double and triple bonds, respectively.

Is the single bond incorporated into *1,3-butadiene* shorter, longer or about the same length as that in ethane? Is the double bond significantly different (more than $\pm 0.05 \text{ \AA}$) from that in ethene? Rationalize your results based on what you know about the different hybrid orbitals used in the construction of ethane, ethene and 1,3-butadiene. What changes from standard bond lengths would you expect for the single and triple bonds incorporated into *1,3-butadiyne*? Compare its structure to those of ethane and ethyne to see if you are correct.

Is the double bond incorporated into *allene* significantly shorter, significantly longer or about the same length as the bond in ethene? Draw a Lewis structure for allene to justify your conclusion.

Measure the carbon-carbon bond length in *benzene*. Would you describe it as a single bond, a double bond, or somewhere in between? Draw whatever resonance contributors are needed to justify your conclusion.

Are the carbon-carbon bond distances in *allyl cation*, *allyl radical* and *allyl anion* all similar, or are they significantly different? The three molecules differ mainly in the number of electrons they assign to one particular molecular orbital. (This is the lowest-unoccupied molecular orbital (LUMO) in allyl cation, and the highest-occupied molecular orbital (HOMO) in allyl radical and allyl anion.) Examine the shape of this orbital. Are the changes in electron occupancy consistent with the changes in CC bond length? Explain.



Allyl cation, allyl radical and allyl anion differ in the number of electrons contained in a nonbonding π -type orbital, the LUMO in the cation and the HOMO in the radical and anion.

3

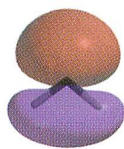
Dipole Moments and Molecular Polarity

$$\mu \text{ (debyes)} = 4.8 \left| q_A r_{AB} \right| \quad (1)$$

q_A is the charge on atom A

r_{AB} is the distance between atoms A and B (in Å)

Electronegativities			
H	2.2	C	2.6
F	4.0	Cl	3.2
Br	3.0	I	2.7



HOMO of methylene shows location of highest-energy electrons.

The dipole moment provides a measure of charge separation in a molecule. Measure the bond distance and the charge on hydrogen in *hydrogen fluoride*, *hydrogen chloride*, *hydrogen bromide* and *hydrogen iodide*. Using equation (1) at left, estimate the dipole moment in each molecule. Next, measure the “exact” dipole moments. How well do these agree with dipole moments estimated from equation (1)?

Large dipole moments are generally associated with large differences in electronegativity. Do the dipole moments in hydrogen halides parallel electronegativity differences between hydrogen and the halogens?

The exact expression for the dipole moment does not consider atoms as point charges, but rather as nuclei (each with a positive charge equal to the atomic number) and electrons (each with unit negative charge). Atoms with lone pairs may contribute to the dipole moment, even if the atom is neutral, as long as the lone pair electrons are not symmetrically placed around the nucleus.

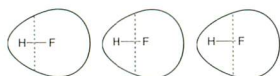
Draw a Lewis structure for singlet methylene, CH_2 (all of the electrons in singlet methylene are spin-paired). How many electrons remain after all bonds have been formed? Where are the “extra” electrons located, in the plane of the molecule or perpendicular to the plane? Examine the highest-occupied molecular orbital (HOMO) of *methylene* to tell.

Hydrocarbons normally have very small dipole moments. Why? (Hint: Consider the relationship between electronegativity differences and dipole moments established above for hydrogen halides.) Does singlet methylene possess a small dipole moment? Explain. What direction do you expect singlet methylene’s dipole to point? Explain. In what direction does it point?

5

Formal Charge vs. Atomic Charges

There is actually no unique way to calculate (or measure) atomic charges, simply because there is no way to uniquely partition a molecule's electrons among the atoms. For example, it is impossible to say what fraction of the electrons contained in the electron density surface for hydrogen fluoride belongs to fluorine. None of the partitions shown below is "more reasonable" than any of the others.



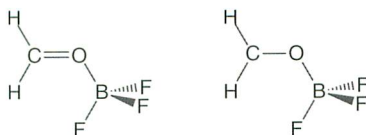
Organic chemists have devised a very simple set of rules allowing assignment of a formal charge for each atom of a particular Lewis structure.

- 1) Start with the number of valence electrons in the neutral atom, e.g., H=1, C=4, O=6.
- 2) Subtract all nonbonding electrons (2 for each lone pair).
- 3) Subtract half the number of bonding electrons, e.g., 1 for each single bond, 2 for each double bond, etc.

Formal charges are merely a bookkeeping device, and do not reflect the actual charge on an atom. Molecular modeling may provide a more realistic description.

Draw Lewis structures for methanol, protonated methanol and methoxide, and assign formal charges. Which atom bears the formal positive charge in protonated methanol? Which atom bears the formal negative charge in methoxide? Are your results consistent with the ordering of atomic electronegativities: O>C>H? Obtain atomic charges for *methanol*, *protonated methanol* and *methoxide anion*. Which atom bears the greatest positive charge in protonated methanol? Which atom bears the greatest negative charge in methoxide? Are these data in "better accord" with the ordering of electronegativities?

Lewis acids such as BF₃ coordinate to carbonyl groups. Two "reasonable" bonding patterns for a formaldehyde/BF₃ complex are provided below.



Add lone pair electrons and assign formal atomic charges in each (do not change bond types). Compare to calculated charges for *formaldehyde BF₃ complex*. Which structure, if either, is more reasonable?

Resonance Structures.

The Sum of the Parts

6

While the majority of molecules may be adequately represented by a single resonance contributor, there are numerous situations where two or more contributors are needed. The simplest case is where all the contributing resonance structures are equivalent. Here, the proper description is in terms of an unweighted average.

Draw appropriate resonance contributors for benzene. Are all contributors equivalent? Measure the six carbon-carbon bond lengths in *benzene*. Are they all the same? Are they intermediate in length between “normal” single bonds (in *ethane*) and “normal” double bonds (in *ethene*)? Is benzene properly described in terms of an equal weighting among its resonance contributors? Repeat your analysis with *formate anion*, and address the same issues as above. Refer to *methanol* and *formaldehyde* as examples of molecules incorporating carbon-oxygen single and double bonds, respectively.

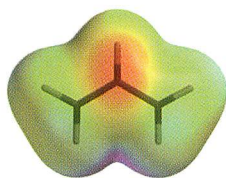
The situation is more complicated when the set of “reasonable” contributing structures are not all equivalent. Examine the geometry and atomic charges for *phenoxide anion*. Do these data fit any one of the possible resonance structures (draw all reasonable possibilities), or is a combination of two or more resonance contributors necessary?

Repeat your analysis for *pyridazine*. Do any of the resonance contributors provide an adequate description of its geometry? Does pyridazine incorporate a nitrogen-nitrogen double bond? (Refer to *hydrazine* and to *diimide* as examples of molecules incorporating NN single and double bonds, respectively.)

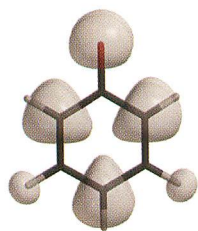
7

Resonance Energy

CC bond distances in localized allylic systems have been held at 1.5 Å and 1.3 Å (typical of CC single and double bond lengths, respectively), and at 1.4 Å for delocalized systems.



Electrostatic potential map for delocalized allyl cation shows most positively-charged regions (in blue) and less positively-charged regions (in red).



Spin density for phenoxy radical shows location of unpaired electron.

Resonance theory tells us that molecules which cannot be adequately represented in terms of a single Lewis structure are likely to be unusually stable. What the simple theory does not tell us is the magnitude of the effect, the so-called resonance energy. This can be assessed via molecular modeling.

Draw Lewis structures for allyl cation. Where is the positive charge? Examine atomic charges as well as the electrostatic potential map for *localized* and *delocalized* forms of *allyl cation*. Which carbon (s) carries the charge in each?

Repeat your analysis for *localized* and *delocalized allyl radical* and *allyl anion*. Focus on location of the spin density in the former and on the negative charge in the latter.

Calculate the difference in energy between localized and delocalized forms for allyl cation, radical and anion. Does it increase, decrease or remain approximately the same with increasing number of π electrons? Rationalize your result.

Compare atomic charges as well as electrostatic potential maps for *formate anion* and *formate anion at formic acid geometry*, and for *phenoxide anions* and *phenoxide anion at phenol geometry*. Is there a large shift in negative charge in going from the geometries of neutral precursors to “relaxed” geometries? Does charge delocalization require reorganization of geometry? Calculate the energy gained by allowing the two ions to “relax” from these initial geometries to their final geometries.

Repeat your analysis for *phenoxy radical*. Instead of charge, focus on the spin density. Calculate the delocalization energy using *phenoxy radical at phenol geometry*. Is it of the same order of magnitude as that for phenoxy anion? Explain.