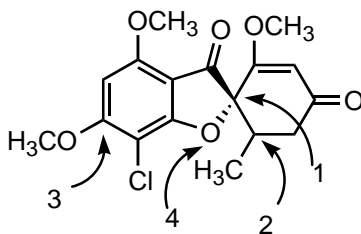


HOMEWORK PROBLEMS: STRUCTURE, BONDING & HYBRIDIZATION

1. The molecule shown below is Griseofulvin, an antifungal compound.



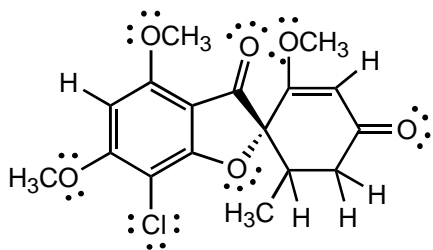
a. Give the hybridization of carbons 1, 2, 3 and oxygen 4.

C1: sp³ C2: sp³ C3: sp² O4: sp³

b. What is the geometry at each of these atoms? (Ignore distortions.)

C1: tetrahedral C2: tetrahedral C3: trigonal planar O4: tetrahedral

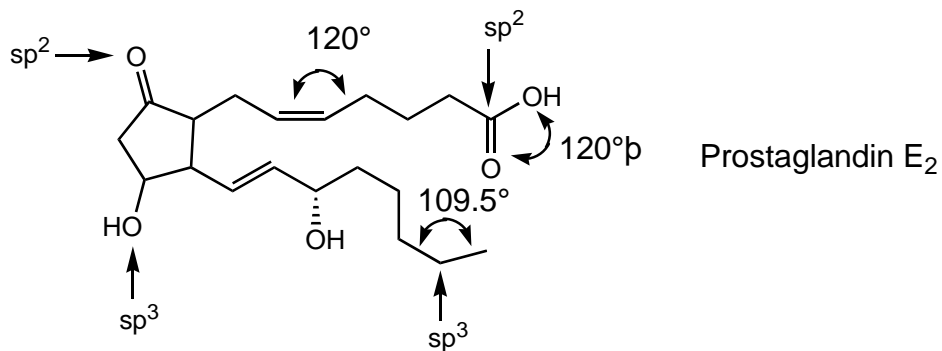
c. Fill in all nonbonding electrons and H's on the structure below. (Assume neutral charge.)



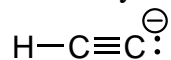
2. For the molecule shown give the information corresponding to each letter as indicated below.

a. give the hybridization of these atoms.

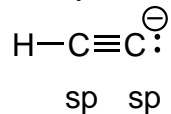
b. give these bond angles.



3. Consider acetylene anion, shown below.



a. Give the hybridization of all carbon atoms.

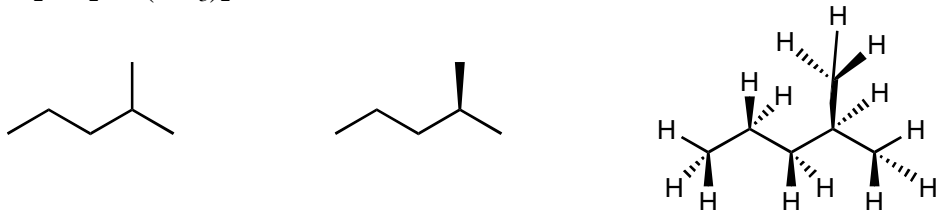


b. In what type of orbital does the nonbonding pair of electrons reside?
sp orbital

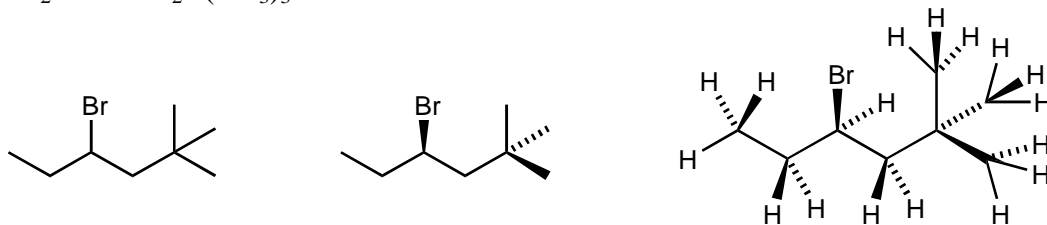
4. Draw reasonable skeletal (line/angle) formulas for the following condensed formulas/structures. Next, draw good 3D structures by adding wedges and dashes to your simple skeletal structures.

The answers include the 3D of the skeletal and an expanded idea of the 3D structure with the hydrogens added back in (essentially hybrids of the skeletal and Lewis).

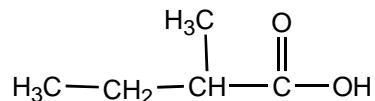
a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$

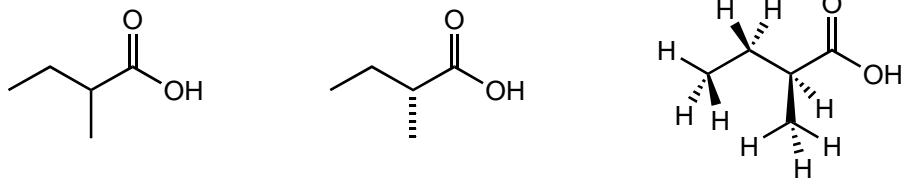


b. $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{C}(\text{CH}_3)_3$

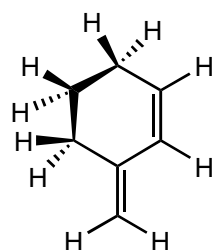
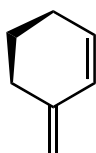
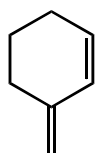
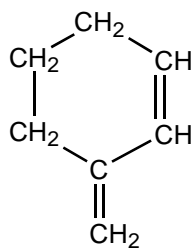


c.

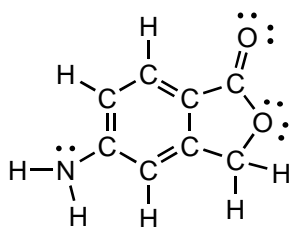
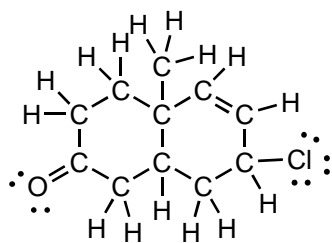




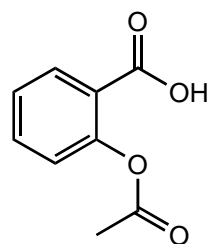
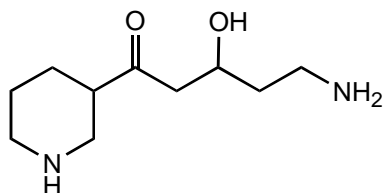
d.



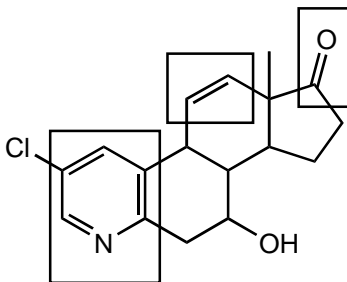
5. Convert the following skeletal structures to Lewis structures. Make sure to include all atoms and lone pairs.



6. Convert the following Lewis structures to skeletal structures.

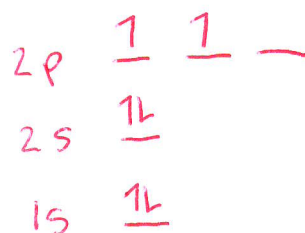


7. In the following molecule, identify all atoms that have a trigonal planar geometry. Can you make any correlations between obvious structural features and the geometries? Explain.



All the atoms here that are involved in double bonds have trigonal planar geometry and will be best described as sp^2 -hybridized. This trend is generally true (note allenes as special cases). The key feature overall is that large regions of the molecule are flat. Interconnected groups of trigonal planar atoms lead to planar regions of a molecule. Moreover, as we think about the orbital pictures, we recognize that these planar regions have electrons residing above and below them because the p-orbitals used to make the pi bonds lie perpendicular to the plane with the sigma bonds. Interesting chemistry will result from these electron clouds.

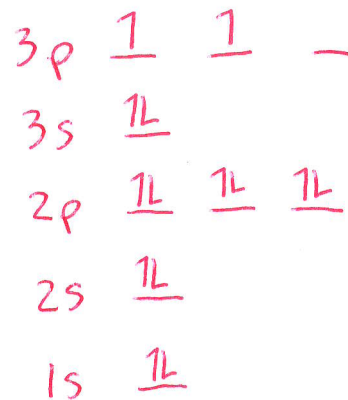
8. (a) Provide the ground state electron configuration and the number of valence electrons for carbon and silicon. Describe how these two atoms are similar. (b) Which bond do you think is stronger, a C-C bond or Si-Si? Explain.



Carbon

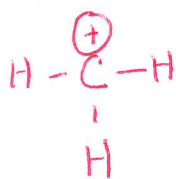
Both C and Si have same # of valence electrons (4).

However, a C-C bond is likely stronger than Si-Si as it uses orbitals from 2nd shell as opposed to 3rd shell (remember, better overlap with smaller/similar sized orbitals)



Silicon

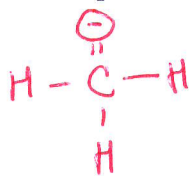
9. (a) What hybridization do you predict for the carbon atom in CH_3^+ , CH_3^- , and $:\text{CH}_2$? (b) What do you predict for the H-C-H bond angle for each of these species? (c) What do you predict for the molecular geometry?



hybrid: sp^2

H-C-H angle: 120°

molecular geometry: trigonal planar



hybrid: sp^3

H-C-H angle: 109.5°

molecular geometry: trigonal pyramidal

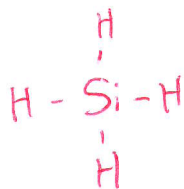


hybrid: sp^2

H-C-H angle: 120°

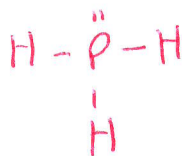
molecular geometry: bent

10. Draw the Lewis/Kekule structures for SiH_4 , PH_3 and H_2S . Provide the electronic geometry and the molecular geometry for each as predicted by VSEPR theory.



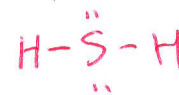
e^- geom: tetrahedral

molecular geom: tetrahedral



e^- geom: tetrahedral

molecular geom: trigonal pyramidal



e^- geom: tetrahedral

molecular geom: bent

11. Consider the Lewis/Kekule structure for PH_3 . (a) What value do you predict for the H-P-H bond angle? (b) Is P-H a stronger bond or weaker bond than an N-H bond in NH_3 ? Explain. (c) Is hybridization necessary to explain the trivalent nature of phosphorus? Explain. If it does undergo hybridization, what hybridization state would PH_3 have and why would it undergo hybridization?

(a) bond angle $\cong 109.5^\circ$ (ignore distortions)

(b) P-H is a weaker bond than N-H due to poor overlap of larger $\text{P}sp^3$ orbital (from 3rd shell) with H vs $\text{N}sp^3$ orbital (2nd shell)

(c) NO! Unhybridized P can form 3 bonds (draw e^- configuration)

(d) IF no hybridization, 90° bond angles + weaker bonds (poorer overlap w/ p-orbitals). sp^3 hybridization gives stronger bonds and 109.5° bond angles to satisfy VSEPR theory.

12. Draw an organic molecule which contains the following type of bonds:

(a) a $\text{C}sp^3 - \text{O}sp^3$ sigma bond



(c) $\text{N}sp^2 - \text{C}sp^2$ sigma and pi bond



(b) $\text{C}sp^3 - \text{C}sp^2$ sigma bond



(d) $\text{N}sp^2 - \text{C}sp^2$ sigma bond (with no pi bond) (at least not between N and C)

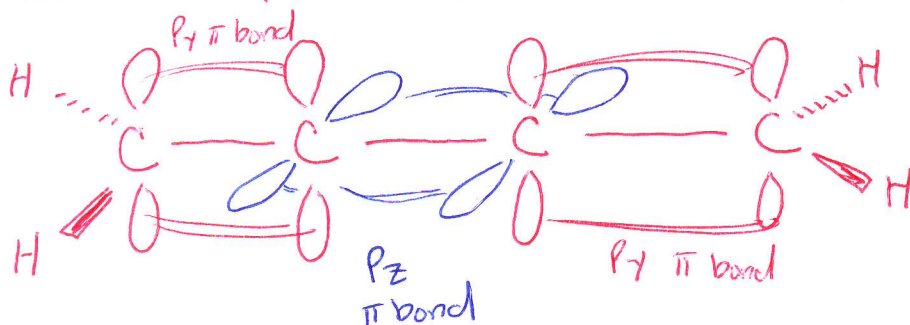


13. Why is an sp hybridized C-H bond stronger than an sp^2 C-H bond?

An sp orbital is more directional (spherical) since it is "50% s" compared to sp^2 that is only "33% s". A more directional orbital will overlap better with H's orbital to give a stronger bond.

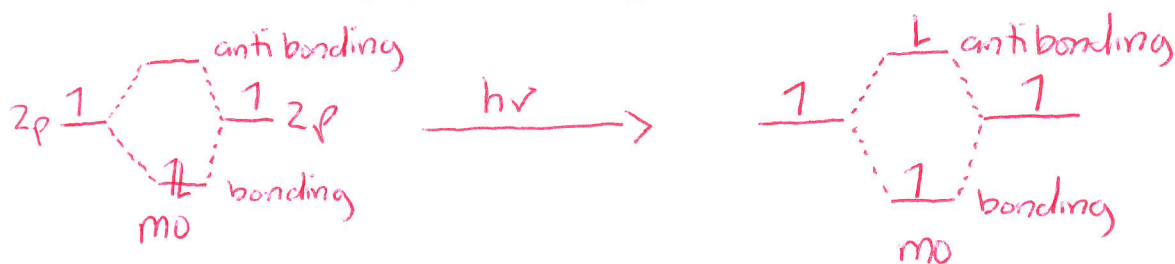
14. Are the hydrogen atoms in the molecule $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$ in the same plane or in planes perpendicular to each other? Explain using the hybridization of each carbon atom.

All in same plane! Must consider where π bonds are located



all H's are in plane perpendicular to paper

15. When energy is supplied to the π bond of ethylene, one electron is promoted from a molecular orbital of lower energy to one of higher energy. (a) Show what this excited state MO diagram would look like. (b) What happens to the π bond if this occurs (consider bond order before and after)? (c) Based on values of bond strengths, how much energy is needed for this excitation to occur?



π bond will break! Bond order changes from 1 to 0 (for π bond)

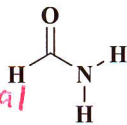
C=C bond strength = 611 kJ/mol

C-C bond strength = 350 kJ/mol

so π bond = 261 kJ/mol = energy needed to excite

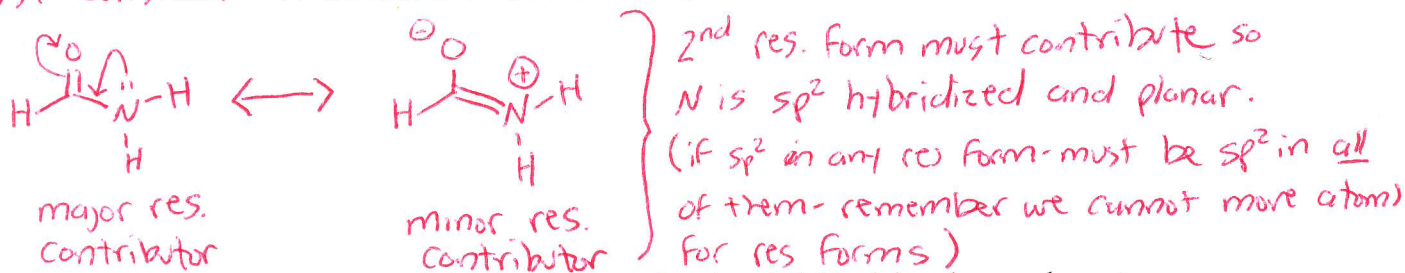
16. For the following molecule, all the atoms are in the same plane, i.e. the plane of the paper. Is this expected? Why or why not? If it is not expected, what does this tell you about this compound?

Not expected! If N is sp^3 hybridized, N is trigonal pyramidal



so N and two H's not in same plane as carbon atom!

Must consider Resonance Form (topic 2)

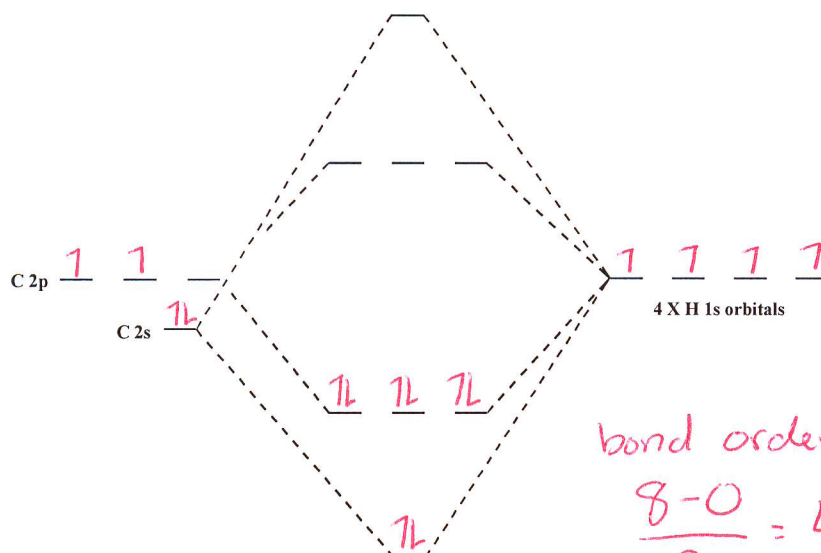


17. Can boron satisfy the octet rule by forming covalent bonds? Explain why or why not.

Not directly. Boron has only 3 valence electrons to share, giving 3 covalent bonds and 6 electrons not 8.

It can satisfy octet if it bonds to a 4th atom that supplies both electrons (a preview to a Lewis base in topic 2)

18. Given below is the molecular orbital diagram for CH₄. Mathematical combination of the carbon 2s and 2p orbitals with the four hydrogen 1s orbitals generates the eight molecular orbitals as shown (note, recall these orbitals and their energy levels must be determined through calculations and cannot be predicted). In this diagram, fill in the valence electrons in the atomic and molecular orbitals and label bonding and antibonding molecular orbitals. What does MO theory predict for the number of bonds (or bond order) for CH₄. Is this consistent with the way we draw the Lewis structure?



For your information:

The MO diagram for CH₄ illustrates that of the 8 bonding electrons in this molecule, two are lower in energy than the other six. This result cannot be predicted based on Lewis structures or valence bond theory, and the question becomes is this truly the case? In a technique called photoelectron spectroscopy, the ionization potential (the energy needed to remove an electron from a molecule) of CH₄ can be measured. If all electrons had the same energy value, photoelectron spectroscopy would give a single value for the ionization potential. This is not the case. Photoelectron spectroscopy provides two values for the ionization potential of CH₄ (depending on which electrons are ejected) as predicted from MO theory – since there are electrons at two different energy levels, they require a different amount of energy to be removed.

MO is a more accurate theory to describe bonding, but it is very mathematical and not as easy to understand as valence bond theory. For this course, valence bond theory and Lewis structures only run into trouble when no one single Lewis structure can be drawn and the concept of resonance is used. Consider ozone, the only difference in the two major resonance structures is in the location of the π bond (or π electrons) and nonbonding electrons. The atoms are in the same position, and the geometry is the same in each case. As a result, valence bond theory gives a good description of the σ bonds but a poor description of the π bonds, where the electrons are delocalized over the molecule. This delocalization is precisely what MO theory does best! During this course we will primarily utilize valence bond theory to describe the electrons in σ bonds (or bonds forming in a reaction) as localized between the two atoms, and in later chapters use MO theory to show how the π electrons of certain molecules (and reactions) are delocalized over the entire molecular structure.

