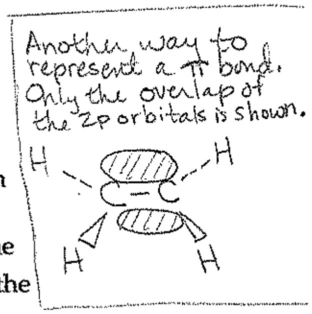
Experiment 8: Molecular Models Problem Set

A. Basic Problems

Proceed through the list **in the order given and do all the problems** (even for molecules whose structure you already know). The problem set is designed to introduce concepts in a logical order – skipping around or skipping problems entirely will mean you'll miss important details. Use one side of a report sheet for two ions or molecules (so that you can make large 3D sketches.). **Stop periodically to check your answers vs. those on the answer key.** Molecules in which the central atom does not obey the octet rule are marked with *.

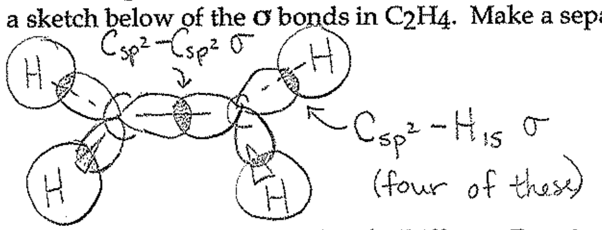
1. H_2O
2. H_3O^+
3. CH_4
4. C_2H_4 (save model for Part B)
5. H_2O_2 (save for Part C)
6. C_2H_2
7. * SF_6
8. * PF_5
9. N_2
10. * SF_4
11. CH_4O (save for Part C)
12. NH_2^-
13. $C_2H_4Cl_2$
14. SCN^- (save for Part E)
15. * XeF_2

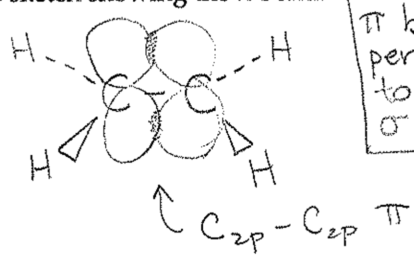


B. Two Ways of Representing Pi Bonds

1. Build a second model for C_2H_4. This one should use three-prong (trigonal planar) atom centers for C and rigid straw connectors for all sigma bonds.
2. Compare this new model with the one you constructed for C_2H_4 in Part A. What are the differences in the ways the two models represent σ and π bonds? Do the models yield the same molecular geometry?
3. Make a sketch below of the σ bonds in C_2H_4. Make a separate sketch showing the π bond.

all 5 σ bonds are in the same plane

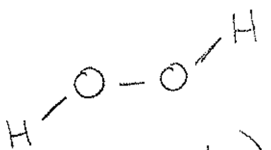




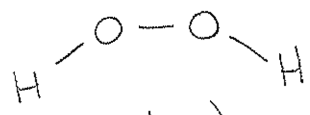
π bond is perpendicular to the σ bond plane

C. Conformational Isomerism (Same Molecule, Different Rotation)

1. Refer to your model of H_2O_2 from part A. The O-O σ bond can be rotated so that all the atoms lie in the same plane. Make a sketch of this. Rotate again to find another **conformational isomer (conformer)** that also has all the atoms in a single plane; sketch.



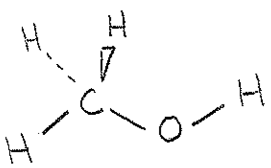
(non-polar)



(polar)

2. Can you find a conformation that allows all atoms in the CH_4O molecule to lie in a single plane? Draw a 3-D structure to illustrate your answer.

No.



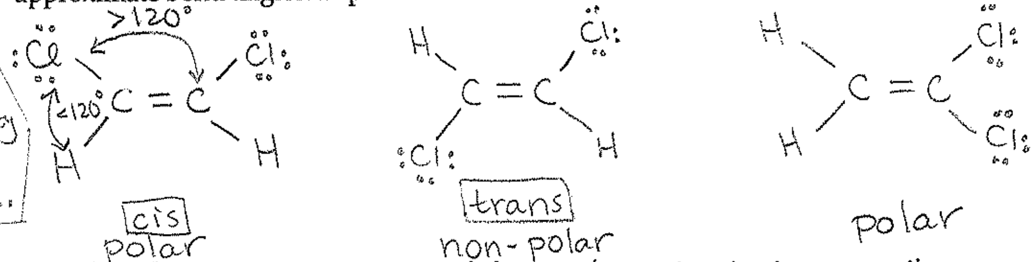
2 of the 4 H's at C are always out of the plane.

The tetrahedral e^- pair geometry at C makes it impossible for all atoms to lie in the same plane.

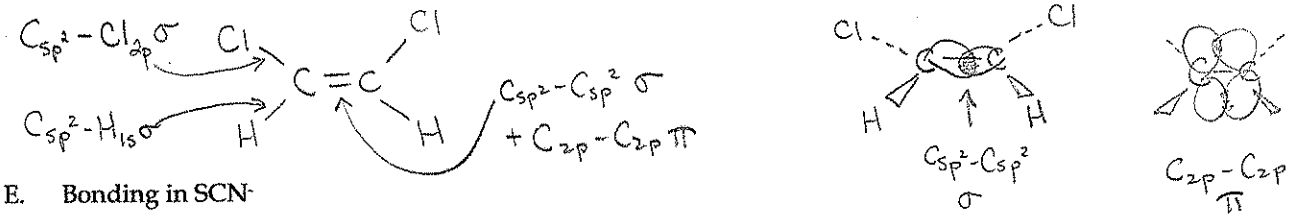
D. Structural and Geometric Isomerism

1. There are three possible structures for substances with the formula $C_2H_2Cl_2$, two of which are polar overall and one of which is not. Draw the three structures and indicate approximate bond angles. Explain how the molecules differ.

All bond ∠'s are ~120°. Greater e⁻ density of the double bond causes some distortion.

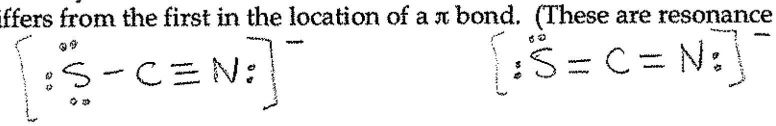


2. Two of the three structures are geometric isomers (same atom-to-atom connections, different spatial arrangements). Identify these. cis + trans
3. Which of the three structures is nonpolar and which two are polar?
4. For any one of these molecules, describe the orbitals used in bonding. Sketch the orbitals involved in the C to C bond and explain why the bond does not freely rotate. Rotation of the bond would require breaking the π bond.



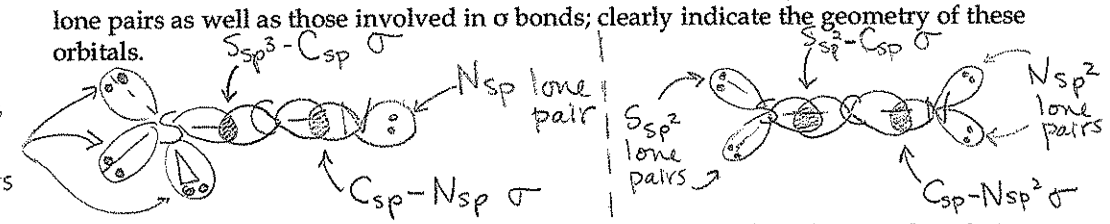
E. Bonding in SCN^-

1. Refer to your Lewis structure for SCN^- in Part A. Write an additional Lewis structure that differs from the first in the location of a π bond. (These are resonance structures.)



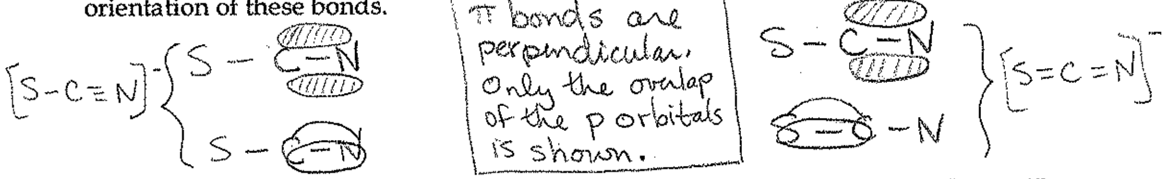
2. Sketch the σ orbital framework for each structure. Include the hybrid orbitals occupied by lone pairs as well as those involved in σ bonds; clearly indicate the geometry of these orbitals.

Three S_{sp^3} orbitals are out of the plane.

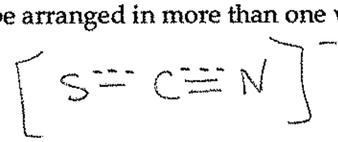


All the orbitals are in the same plane.

3. Sketch the π bonds for each of the two Lewis structures, clearly indicating the relative orientation of these bonds.

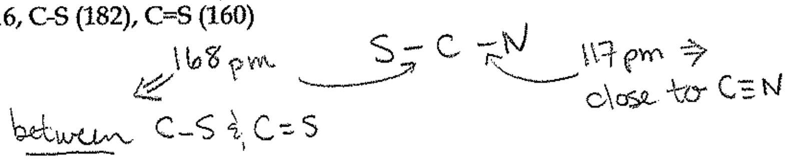


4. Draw a *composite* Lewis structure for SCN^- using a dashed line to represent "partial" π bonds (π bonds that can be arranged in more than one way). Omit the lone electron pairs.



one π bond is localized between C & N; the other is spread out between S, C, N

5. The bond lengths in this ion are SC = 168 pm, CN =117 pm. Use this information to decide whether the *composite* Lewis structure or one of the individual Lewis structures best describes the bonding in SCN^-. **Typical bond lengths in pm:** C-N (147), C=N (129), C≡N 116, C-S (182), C=S (160)

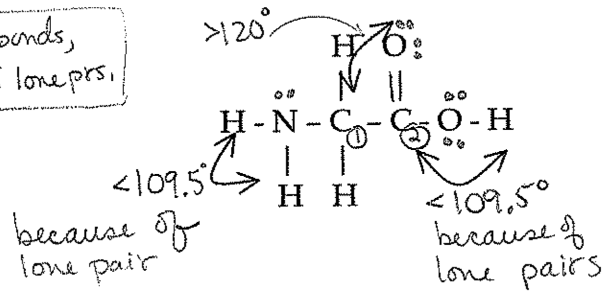


None of the structures explain all the bond lengths, but the composite comes closest.

F. Orbitals and Bond Angles

1. Consider the *skeleton* structure for glycine, an amino acid. Complete the structure to show glycine's Lewis structure. Estimate the approximate values of the marked bond angles as precisely as you can. $5(1) + 2(4) + 2(6) + 1(5) = 30e^-$

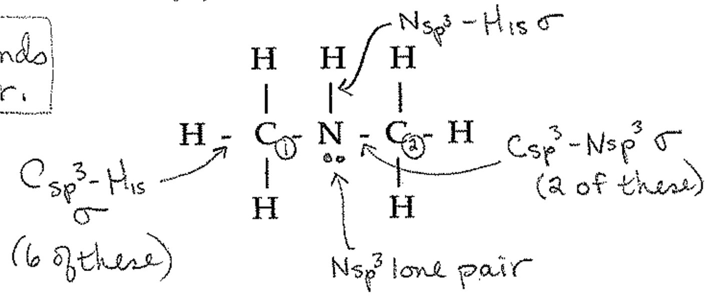
There are 9 σ bonds, 1 π bond, and 5 lone prs.



e⁻ pair geom
at N tetrahedral
at C① tetrahedral
at C② trigonal planar

2. Describe a bonding scheme (indicate the orbitals involved in each bond), based on simple and/or hybridized atomic orbitals to account for the structure of dimethylamine (*skeleton* stucture shown below). The easiest way to answer this question is to simply label each bond with the name of the orbitals involved. Also, indicate the molecular geometry at the C, N, and C atoms. $7(1) + 2(4) + 1(5) = 20e^-$

There are 9 σ bonds and 1 lone pair.

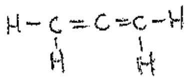


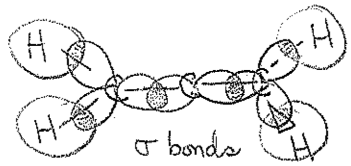
e⁻ pair geom
tetrahedral at C①, N, C②

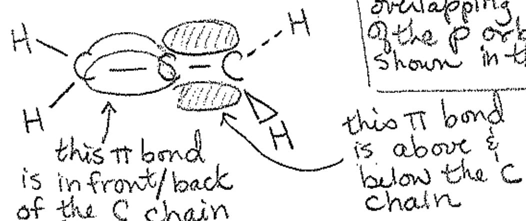
molecular geom
at C① = C② tetrahedral
at N trigonal pyramid

3. Allene has the formula H_2CCCH_2. Sketch the bonds in allene, keeping the sketch of the π bonds separate from the sketch of the σ framework. Do the H atoms all lie in the same plane? (It will be particularly helpful to make a model of this molecule before attempting to answer.) $4(1) + 3(4) = 16e^-$

Lewis



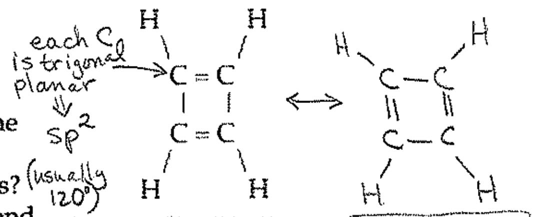




Note: Only the overlapping parts of the p orbitals are shown in the π bonds

The H's do not all lie in one plane.

4. The molecule C_4H_4 has the unusual structure shown at right.

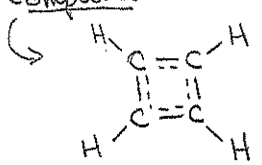


a. Is this molecule essential planar or non-planar?

b. The C-C-C bond angles are not those expected considering the preferred geometry of the hybrid orbitals the C atoms use in bonding. What are the hybrid orbitals that C uses in its bonds? What is the discrepancy in the actual and preferred C-C-C bond angles? Preferred = 120° (see right) but the square ring means that the angles must be 90°. This molecule has a lot of "ring strain."

c. In the valence bond approach, we would say that resonance exists in this molecule. In the molecular orbital view, we would say that the π bonds in this molecule are delocalized. Explain both views.

Composite Lewis structure represents the average of the two resonance structures (energy equivalent) shown above.



In MO theory, the two π bonding e⁻ pairs are viewed as being spread out (delocalized) over the entire 4-C ring.