

Contents

Week 4

Wednesday, October 21	2
Monday, October 19.	4

Week 3

Friday, October 16	7
Wednesday, October 14	9
Notes on Drawing Curved Arrows.	10
Monday, October 12.	12

Week 2

Friday, October 9.	14
Wednesday, October 7	16
Monday, October 5	18

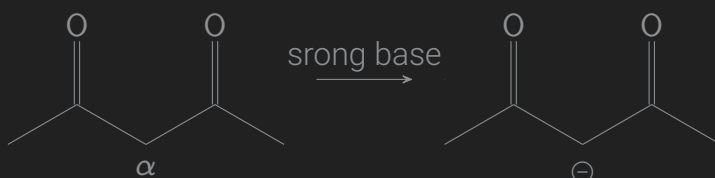
Week 1

Friday, October 2.	20
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Week 4

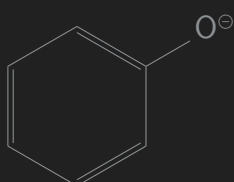
Wednesday, October 21

1. A common reaction for carbonyls occurs by removing an alpha hydrogen to generate a carbanion, as shown for 2,4-pentanedione. Most C–H bonds are not acidic enough to react with any base, no matter how strong the base. Why do you think that this happens in 2,4-pentanedione?

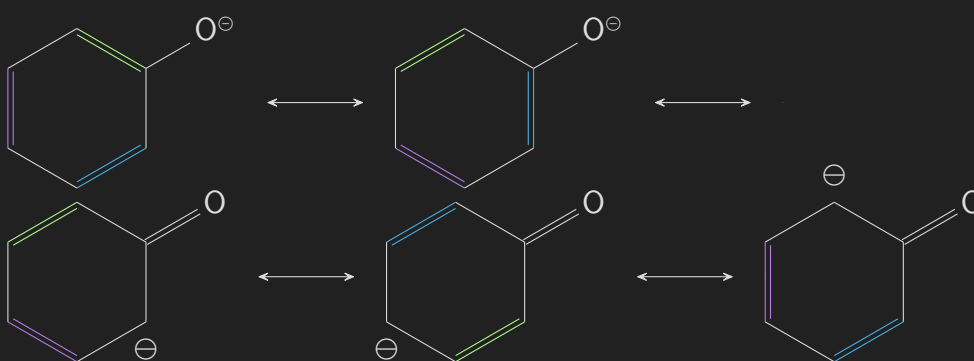


▷ **the negative charge is resonance stabilized over two C=O bonds**

- The negative charge on the carbanion can be pushed to the double bond between the carbon and the oxygen, which then pushes those electrons into lone pairs around the oxygen.
 - **Negative charges** prefer to be on the **most electronegative** element, in this case oxygen.
 - Both C=O bonds can share the charge, as sharing between each one forms separate resonance structures that form together form the resonance hybrid.
2. Most alcohols, ROH, are not very acidic, an exception is phenol, ArOH, which is "mildly" acidic. Including the starting structure, how many resonance forms can be drawn for the benzylic anion (shown below)?



▷ **5**

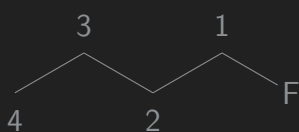


3. For the molecule in the previous question, how will the C–O bond length compare to C–O single bonds and C=O double bonds?

▷ **shorter than a single bond and longer than a double bond**

- Electron delocalization around the ring makes the C–O in the stronger than a normal single bond, but weaker than a double bond.
- The stronger the bond, the shorter the length.
- So after delocalization its now **shorter/stronger** than C–O, but **longer/weaker** than C=O.

4. For the molecule 1-fluorobutane, on which carbon will the inductive effect of the F be most prominent?

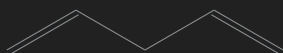


▷ **1**

- Inductive effects only influence atoms they are bonded to due to unequal sharing of electrons.

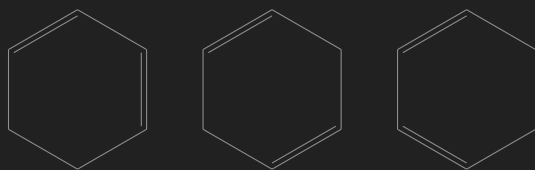
Monday, October 19

1. When electrons are delocalized over several carbon centers, this results in
 - ▷ **greater stability of the molecule**
 - Resonance allows for delocalization of electrons, which spreads the charge between multiple atoms and lowers overall energy of molecule; termed **resonance stabilization**.
2. When showing electron movement with curved arrows,
 - ▷ **the arrow head points towards the lewis acid**
 - the tail "pushes" **electrons** from a **electronegative (lewis base:donor)** towards the **less electronegative (lewis acid:acceptor)**.
3. For electron delocalization, which of the following is allowed?
 - ▷ electrons can move from a lone pair to an sp^2 hybridized carbon.
 - ▷ electrons can move as a pair from an anion to an sp^2 hybridized carbon.
 - ▷ electrons can move from pi bonding orbitals to an sp^2 hybridized carbon.
 - ▷ **all of the above**
 - No good explanation. I don't think of it in terms of hybridized carbons.
4. What is wrong with the electron movement shown in the following
 - ▷ **electrons cannot move towards an sp^3 hybridized carbon**
 - electrons from π bonding orbitals can move, just not towards a carbon with a full octet (sp^3).
5. Is electron delocalization possible in the following molecule?



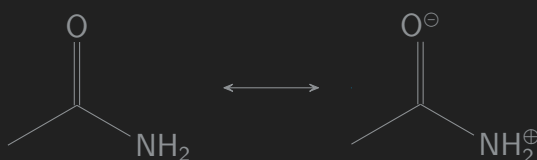
- ▷ **no**
 - Currently the CH_2 in the middle has a full octet. You can't move the electrons from the π bonds
 - There would have to be a carbocation in order to move the electrons.

6. Which of the following molecules will be resonance stabilized by electron delocalization?



▷ **A and C**

- A and C can push the electrons twice, since they are conjugated bonds (π bonds separated by a σ bond).
 - B would be too, if there was a carbocation on either of the carbons with two σ bonds.
7. Acetamide exists in a delocalized form that results from the two resonance forms shown below. Will the "real" structure be more like the one on the left, the one on the right, or an equal average of the two?



▷ **structure on the left**

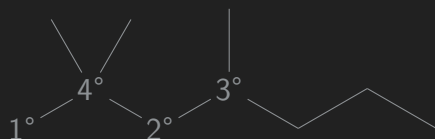
- Rules for contributing significance, descending:
 - The greatest number of filled octets.
 - The greatest number of covalent bonds.
 - **Minimize formally charged atoms.**
 - Separation of unlike and like charges, minimized and maximized respectively.
 - Negative charges placed on the most electronegativity atoms, positive charges placed on the less electronegative atoms.
 - Do not deviate substantially from idealized bond lengths and angles.
 - Maintain aromatic substructures locally while avoiding anti-aromatic ones.
8. Which statement(s) is(are) true?
- ▷ the more resonance structures, the greater the stability of the molecule.
 - ▷ the more atoms over which the electrons can be delocalized, the greater the stability.

- ▷ when charges develop due delocalization, the structure with the negative charge on the most electronegative element is the most stable.
- ▷ a resonance structure in which all the atoms are neutral is more stable than one in which some of the atoms bear charges
- ▷ **all of the above**
 - see rules above on contributing significance; more of the major contributors result in more stability of the molecule, generally.

Week 3

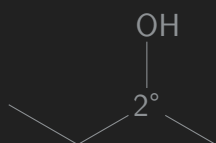
Friday, October 16

1. What is the classification for the carbon centers, from left to right, in the following molecule?



▷ 1°, 4°, 2°, 3°

2. What is the classification of the following alcohol?



▷ 2°

- Two carbons are attached to the carbon with the alcohol.

3. How is the following amine classified?



▷ 2°

- $\text{CH}_3\text{CH}_2\text{NHCH}_3$, looks like a dimethylamine with an extra CH_2 . I don't know nomenclature yet, but the functional group (NH) remains the same. Has two carbons connected to it.

4. Which of the following is NOT an intermolecular force (IMF)?

▷ **covalent bonding**

- Any kind of bonding is not an intermolecular force. Hydrogen bonding isn't actually bonding, but instead just the strongest IMF mainly due to close proximity of charges compared to other IMFs.

5. Which of the following is the strongest IMF?

▷ **hydrogen bonding**

- See above answer.

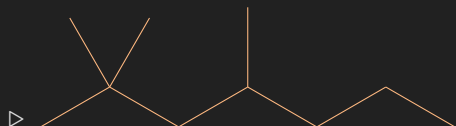
6. For a molecule to be polar, what conditions must exist?

▷ **all of the above**

- A molecule must have a molecular dipole moment in order to be polar, which means two or more bonds must not cancel each other out.

- Polar bonds must exist in order to create the net dipole moment.
- Has to have F O N Cl; I don't know why it must, but the other are true so this has to be true.

7. Of the following molecules, which will have the largest LDFs?



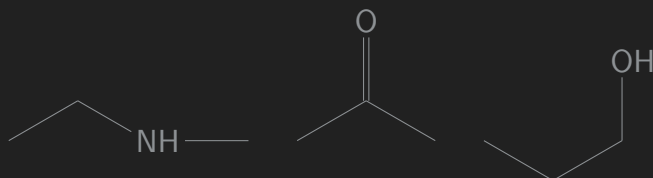
- London dispersion forces (LDF) related to molar mass, so generally the larger and heavier the compound, then the more atoms there are to randomly create dipole moments.

8. Which two molecules will be the least miscible?

▷ **O₂ and H₂O**

- Least miscible means least likely to form a homogeneous mixture.
- "Like dissolves like" regarding to polar molecules, meaning polarity must match in order to become homogenous.
- All other choices are either both polar or both nonpolar.

9. Which molecule will have the highest boiling point?



▷ **C**

- When comparing boiling points of compounds, look for following factors:
 - Any dipole-dipole interactions? (increases boiling point)
 - Formation of hydrogen bonds? (increase boiling point)
 - Number of electrons. (more electrons, higher boiling point)
 - Number of carbon atoms. (more surface area, higher boiling point)
 - Degree of branching of compound. (more branching, more surface area)
- A and C both have more hydrogen bonding than B, but only really differ in the element (O vs N). Neither have dipole-dipole moments (no polar bonds). Oxygen is more electronegative, so it has more electrons.

Wednesday, October 14

1. The reason that there is free rotation about any single sigma bond is because

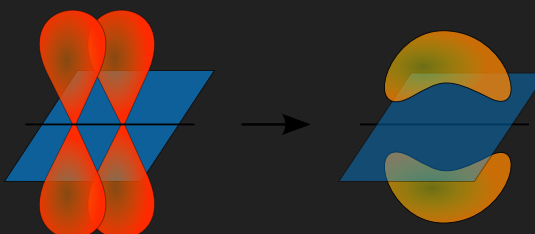
▷ **orbital overlap doesn't change with rotation**

- Electron density lies along the axis that connects the two nuclei forming the σ bond; no issue during rotation as one atom can freely rotate and stay connected.

2. The reason there is restricted rotation about a C=C double bond is because

▷ **rotation would eliminate the parallel overlap of the p orbitals**

- π bonds lie above and below the axis and must break the overlap between the p orbitals during rotation, *unless they rotated in unison?*



3. What is a nucleophile?

▷ **all of the above**

- a nucleophile is an electron rich atom that is capable of donating a pair of electrons, which is the same definition as a Lewis base.
- Electron rich means Lewis bases are negative and thus attracted to a positive charged center (nuclei are generally positively charged) and capable of forming a bond due to excess of electrons.

4. What is an electrophile?

- a. a species that is attracted to a negative charge
- b. a species that contains extra electrons
- c. a Lewis acid
- d. **a and c**

- An electrophile is an electron-deficient atom that is capable of accepting a pair of electrons, which is the same as a Lewis acid.

5. When drawing curved arrows, the arrow head always points towards the Lewis acid.

▷ **True**

Notes on Drawing Curved Arrows

- **Tails** must be placed on either a bond or a lone pair.
 - Shows the **source**, i.e., the electron donor (base).
 - Electrons can only be found in lone pairs or bonds, so **never place the tail** of a curved arrow on a **positive charge**.
- **Heads** must be placed so that it shows either the formation of a bond or the formation of a lone pair.
 - Shows the **destination**, i.e., the electron acceptor (acid).
 - Avoid drawing an arrow that violates the octet rule, so never draw an arrow that gives more than four orbitals to a second-row element.

6. What factors contribute to making something a good EWG?

▷ **all of the above**

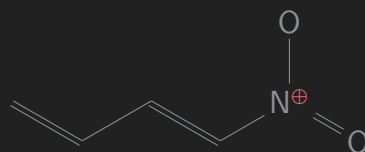
- Both inductive and resonance effects can have an impact on electronegativity, which governs substituent effects, such as the electron withdrawing group.

7. Given either the presence of a highly electronegative element that results in good inductive effects, or a group that, through resonance can delocalize positive charge, which has the greater effect as an EWG?

▷ **a group that is capable of delocalizing positive charge through resonance**

- The spreading of π bonds is called **delocalization**, which is a major **stabilizing factor** since the electrons are shared between multiple atoms.
- Inductive effect is due to electrons being shifted towards the more electronegative atom, but staying in the same place, providing less stability compared to resonance electron sharing.

8. On your own, you can show how electron distribution in the structure below results in the delocalization of positive charge, which increases the electronegativity at the terminal carbon atom.

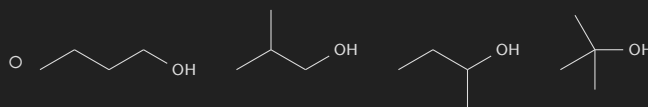


- ▷ I briefly read some sections on resonance, not expecting it to be on this quiz much since he talked about it very little. I'm not super confident in my explanation but I'll give it shot.
- ▷ There are some patterns for identifying lone pairs of oxygen and nitrogen, excerpt from today's notes:
 - **Associated Patterns for Oxygen**
 - A **negative** (\ominus) charge corresponds with **one bond** and **three lone pairs**.
 - The absence of charge corresponds with **two bonds** and **two lone pairs**.
 - A **positive** (\oplus) charge corresponds with **three bonds** and **one lone pair**.
 - **Associated Patterns for Nitrogen**
 - A **negative** charge corresponds with **two bond** and **two lone pairs**.
 - The absence of charge corresponds with **three bonds** and **one lone pair**.
 - A **positive** charge corresponds with **four bonds** and **no lone pairs**.
- ▷ Thus, the nitrogen should have a **positive formal** charge, due to the four bonds (including the π bond) and no lone pairs.
- ▷ I don't know how to draw resonance arrows yet in the bond-line diagrams... but that charge is **delocalized** down the carbon chain, in reality it's being shared with **the four carbons and thus the electronegativity at the terminal carbon.**? (? Less confident about the validity of this statement, but seems reasonable)

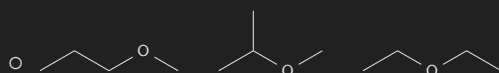
Monday, October 12

1. How many isomers exist for a molecule with the molecular formula $C_4H_{10}O$?

▷ **7**



- These are the alcohols, or *all the possible combinations where the oxygen is on the end?* (? I'm sure when we get into nomenclature this will make more senses and lead to better explanation)



- These are the ethers, or *all the possible combinations where the oxygen is within the chain?* (? same disclaimer as above)
- Seems like drawing is only way to get good at this. Eventually we will probably get some intuition or memorize certain compounds with continual practice, similar to practicing math problems.

2. How many degrees of unsaturation are there in $C_4H_{10}O$?

▷ **0**

- Determining saturation using molecular formula: C_nH_{2n+2}
 n = carbon atoms.
 - **Halogens:** takes the place of a hydrogen atom; *add one H* for each halogen.
 - **Oxygen:** no affect on saturation; *ignore*.
 - **Nitrogen:** needs an extra hydrogen; *subtract one H* for each nitrogen.
- Or use HDI formula: $HDI = \frac{1}{2}(2C + 2 + N - H - X)$ X : halogen atoms.
 - HDI: hydrogen deficiency index, which is the measure of degrees of freedom.
 - For $C_4H_{10}O$: $\frac{1}{2}(8 + 2 + 0 - 10 - 0) = \frac{1}{2}(0) = 0$

3. Based upon the previous question, which structure(s) can be eliminated as possible for $C_4H_{10}O$?

▷ **all of the above**

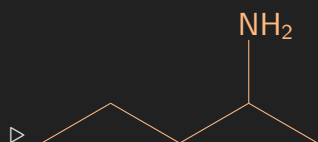
- Zero degrees of freedom means no double/triple bonds or rings are possible.
- Degrees of freedom help represent possible structures, indicating possible double bonds, triple bonds, rings, or various combinations of each.

4. How many degrees of unsaturation are there in C_5H_{13} ?

▷ **0**

- Again, general formula: $HDI = \frac{1}{2}(2C + 2 + N - H - X)$ X: halogen atoms.
- For $C_5H_{13}N$: $\frac{1}{2}(2(5) + 2 + 1 - 13 - 0) = \frac{1}{2}(0) = 0$

5. Based upon the previous question, what is a possible structure for $C_5H_{13}N$?



- Same as question three, zero degrees of freedom means no double/triple bonds or rings are possible.

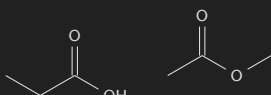

6. How many degrees of unsaturation exist for a molecule with the formula $C_3H_6O_2$?

▷ **1**

- $\frac{1}{2}(2(3) + 2 + 0 - 6 - 0) = \frac{1}{2}(2) = 1$

7. What structures are possible for the $C_3H_6O_2$ molecule?

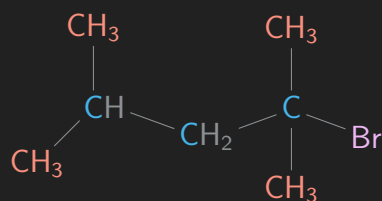
▷ **both the first and second structures are possible**

- For reference: 
- Has one degree of freedom so it has to have at least a double/triple bond or ring structure.
 - Makes  invalid due to lack of any double/triple/rings.

Week 2

Friday, October 9

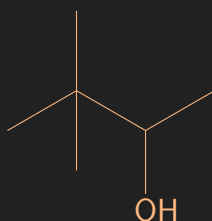
1. What is the condensed formula for the following molecule?



▷ **$(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{Br}$**

- Breaking down answer: $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{Br}$

2. What is the structural formula for $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_3$?



- ▷ Each line with an end is a CH_3 (need 4)
 - ▷ Three points touching is a CH . (need 1)
 - ▷ (OH) is on the CH
3. For any two molecules to be constitutional isomers of each other, at the very least, they:
- ▷ **must have the same chemical formula**
 - isomers: same chemical formula.
 - constitution: ways it connects; connect must be **different** to be a constitutional isomer.
4. How many constitutional isomers can be formed with the molecular formula $\text{C}_4\text{H}_{10}\text{O}$?
- ▷ **7**
 - See Monday, October 12 quiz. Same question asked and a better explanation given there.

5. The SO₂ molecule has two resonance forms, each of which is a constitutional isomer of the other. Which of the two structures shown below is the most stable? (The S→O bond is a dative bond in which both bonding electrons come from only one atom.)

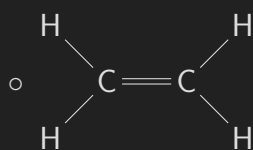
▷ **the structure on the right**

- *Delocalized electrons being shared in multiple bonds are more stable than a the dative bond.*[?] (? Not sufficient enough information yet to be confident of this explanation, though I'd be willing to bet that its along the right lines)

Wednesday, October 7

1. What is the hybridization of the orbitals on C in ethylene?

▷ **sp^2**



- Each C has 3 groups (number of bonds, π bonds count as 1, or lone pairs)
- For atoms with groups between 1 and 4; sp^x ; $x = \text{groups} - 1 = (2)$

2. What is the hybridization of the orbitals on C in acetylene?

▷ **sp**

- $\text{H} - \text{C} \equiv \text{C} - \text{H}$
- 2 groups, thus $x = 1$.

3. What type of bonds combine to make a C=C double bond?

▷ **one sigma and one pi bond.**

- First bond is a σ bond.
- Additional bonds are π bonds that go above and below the axis that connects the nuclei.

4. What is the H-C-H bond angle in ethylene?

▷ **120°**

- sp^2 with no lone pairs, thus trigonal planar (according to VSEPR).
- $\frac{360}{3} = 120$; 3 angles maximized on a single plane.

5. Why is the geometry around the CH_2 fragment in ethylene, trigonal planar?

▷ **there are three regions of electron density**

- *regions electron density = ? groups* (? I'm combining a past youtube video with his lecture...)

6. There is completely free rotation around a sigma bond such as a C-C single bond. Propose a reason for why there is no free rotation around a C=C.

▷ **the rotation would require the C-C pi bond to break**

- σ bonds can rotate on the axis between the nuclei, but the π bonds are above and below and would break during rotation since *there are*

other orbitals that would block[?] their rotation. (? not completely sure on the mechanism that doesn't allow for rotation)

7. As the percent s character increases in a bond, what happens to the bond angle?

▷ **it increases**

- The more **s character**, the **shorter** and **stronger** the bond, and the **larger** the bond angle.

8. As the percent p character in a bond increases, what happens to the bond angle?

▷ **it decreases**

- the more p character, the less s character; inverse of s character.

9. Why is a pi bond weaker than a sigma bond?

▷ **all of the above**

10. Which statement(s) is(are) correct?

- ▷ the shorter the bond, the stronger the bond
- ▷ the more s character in the hybridization, the stronger the bond
- ▷ the more s character in the hybridization, the greater the bond angle
- ▷ sigma bonds are stronger than pi bonds
- ▷ the geometry around the C in the ethylene is trigonal planar
- ▷ a C=C bond is composed of one sigma and one pi bond
- ▷ the hybridization around C in the methyl anion, isoelectronic with CH₄, is sp³
- ▷ when 2s and 2p orbitals mix to form hybrid orbitals, the hybrid orbitals are higher in energy than the 2s orbitals, but lower in energy than the 2p orbitals
- ▷ the shapes of the hybrid orbitals match the electron domain geometry shapes predicted by VSEPR
- ▷ the potential energy of a covalent bond is lower than that of the potential energies of the free atoms from which it was formed

▷ **ALL OR THE ABOVE**

- This seems to be a review of important concepts.

Monday, October 5

1. The concept of orbital shapes comes directly from the wave model of the atom. What is the shape of an s orbital?

- ▷ **Spherical**

- S orbital is the most simple orbital, with only two electrons.
- Alternative shapes come from *nodes*; i.e. when *destructive interferences* cancels out the wave function.
- Not circular, orbitals are three-dimensional.

2. What is the shape of a p orbital?

- ▷ **Dumbbell shaped**

- P orbital can hold 6 electrons (3 pairs).
- Each pair has one angular node, squeezing shape into dumbbell in each direction (x, y, z).

3. When atomic orbitals overlap to form a covalent bond, the resultant bonding orbital is:

- ▷ **Lower in energy than the atomic orbitals from which it was formed**

- Electrons in a covalent bond are in a more stable (lower energy) state due to multiple nuclei holding them in place.
- Only when nodes are present do the electrons create a destabilized molecular orbit, increasing the energy.

4. Why can't pure p orbitals be used in forming four equivalent bonds as in methane?

- ▷ the three 2p orbitals can only hold 6 electrons.

- True, we need to make four bonds for methane.

- ▷ the bonds would have to be 90° apart.

- If p had enough space then it would result in planar geometry with 90°, but the true arrangement is tetrahedral with angles of 109.5°

- ▷ electron-electron repulsion would not be minimized.

- Planar minimization would be 90°, but we have 3d space to work with, so it's not minimized.

- ▷ **all of the above**

5. When s and p orbitals combine to form hybrid orbitals, the resultant hybridized orbitals are:

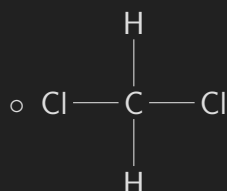
- ▷ lower in energy than the p orbitals
- ▷ higher in energy than the s orbitals
- ▷ **both of the above**
 - It takes energy to move the electron up from the s orbital and hybridize the p orbitals.
 - The new hybridized sp orbital also has more energy than the s orbital.

6. What is the difference between a sigma bond and a pi bond?

- ▷ **in a π bond, electron density lies above and below the axis that connects the two nuclei; in a σ bond, the electron density lies along the axis that connects the two nuclei**
 - σ bond has circular symmetry with respect to the bond axis (axis that connects the two nuclei). i.e. it's along the axis.

7. What is the hybridization of the C in CH₂Cl₂?

▷ **sp³**



- Look at central atom — C
- Determine groups (number of bonds, π bonds count as 1, and lone pairs attached) — 4
- for groups 1-4; sp^x; x = groups - 1 (3)

8. What is the hybridization of each C in benzene (shown below)?

▷ **sp²**

- Each carbon has 2H and π bond between, so groups = 3.
- Groups - 1 = 2, so sp²
- Though, each π bond is delocalized, or free to spread across all the carbons. Still counts as 1 group.

Week 1

Friday, October 2

▷ Determining formal charge:

◦ Formula: $FC = V - N - \frac{B}{2}$

◦ V = valence electrons of element

◦ N = lone pair electrons; B = bonded electrons

1. What is the formal charge on P in the following structure? Each F and O has three lone pair of electrons.

◦ $P = 5 - 0 - 8(0.5)$; P = +1

2. What is the formal charge on O in the structure above?

◦ $O = 6 - 6 - 2(0.5)$; O = -1

3. What is the formal charge on P in the following structure? Each F still has three lone pairs of electrons, and O had the two pairs indicated.

◦ $P = 5 - 0 - 10(0.5)$; P = 0

4. Of the two structures shown for POF_3 , which is the most stable, and will, therefore, be the most abundant form?

◦ **Structure II**

◦ O has formal charge of 0 and is the most electronegative element with difference in charge between the resonance structures.

◦ F has greater electronegativity, but remains the same between both structures, so it's not relevant.

◦ Key difference: the double bond in structure II gives oxygen the lower magnitude formal charge between the two.

5. The fundamental concept upon which VSEPR, and hence molecular shapes, is based is that:

◦ Electron pairs repel each other;

– negative charge repels other negative charges.

◦ Electron repulsion is minimized by maximum angular separation;

– in other words, angular separation maximizes distance between electrons.

- Bonding pair electrons and lone pair electrons both occupy regions around the central atom;
 - if they didn't occupy the same space than they wouldn't interact and thus wouldn't affect shape.
- The electron domain geometry and the molecular geometry is identical if there all of the electrons are bonding electrons;
 - the lone pairs are have a greater influence than bonded pairs, resulting in less space for bonded pairs.

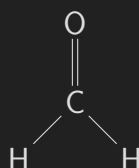
- **All of the above**

▷ General method of determining structure:

1. Count steric number—the total number of electron pairs in a molecule. Can be bonds or lone pairs.
 2. Determine predicted geometrical structure predicted (EDG) by VSEPR using steric number.
 - Octahedral:6, Bipyramid:5, Tetrahedral:4, Trigonal:3, Linear:2
 3. Determin impact (the MG) of lone pairs; more lone pairs results in less space between bonded pairs. Shape depends on EDG.
6. A resonance form of SOF_2 , completely consistent with the octet rule, is shown below. What is the electron domain geometry (EDG), and molecular geometry (MG) of this molecule?

- **Tetrahedral EDG and trigonal pyramidal MG**

7. Draw a Lewis dot structure of formaldehyde (CH_2O): what is the molecular shape of this molecule?



- Steric number = 3
 - Double bonds count as 1 for steric number.
- No lone pairs on central atom, C, so it's shape planar.

- **Trigonal planar**

8. The EDG for CH_3^- (a carbanion) is tetrahedral, and the MG is trigonal pyramidal. Why are the $\text{H}-\text{C}-\text{H}$ bond angles less than 109.5° as in a perfect tetrahedron?

- **The lone pair electrons take up more space than bonding pair electrons.**