

Chemistry 210

Exam 1

University of Missouri-Columbia
Dr. Rainer Glaser
September 25, 1992

Name:
Answer Key

	Max.	Yours
Question 1 (Atoms)	12	
Question 2 (Lewis)	13	
Question 3 (Resonance)	27	
Question 4 (Names)	20	
Question 5 (DBE)	16	
Question 6 (Carbenes)	12	
Total	100	

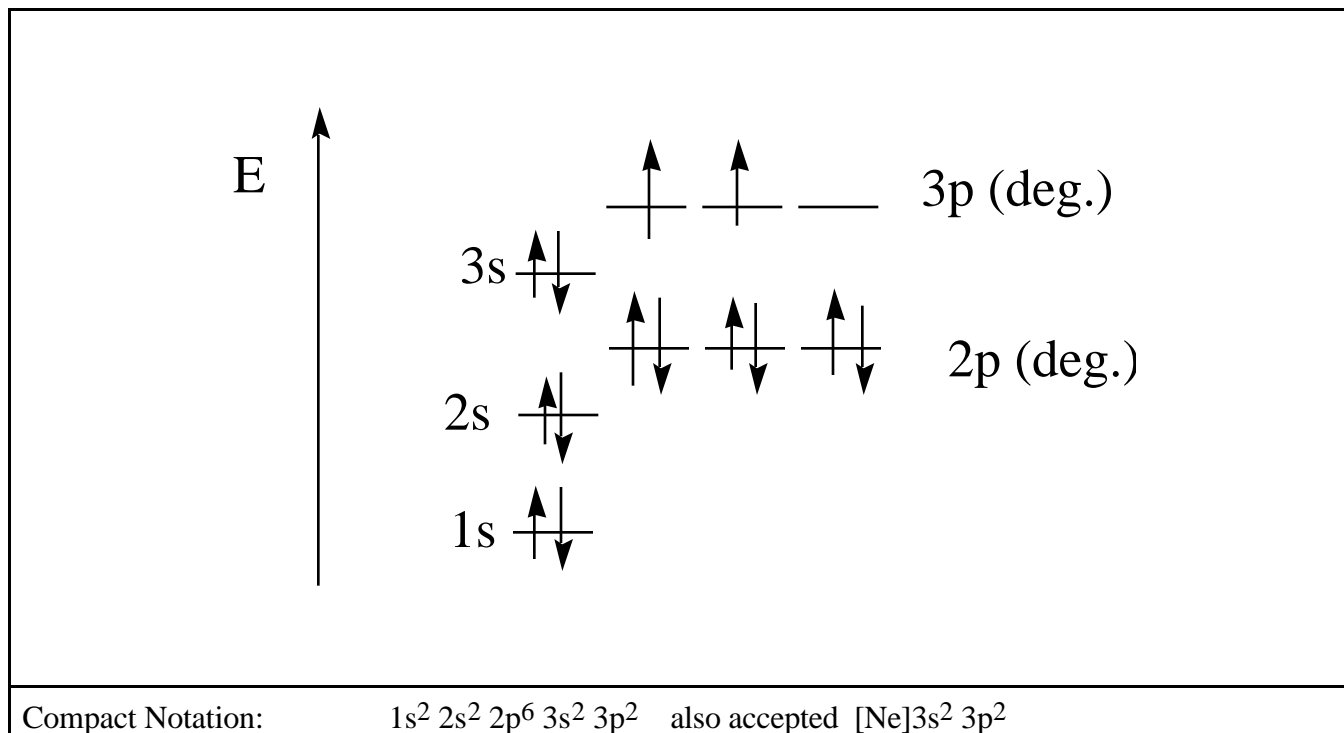
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Question 1. Electronic Structure of Carbon and Silicon. (12 points)

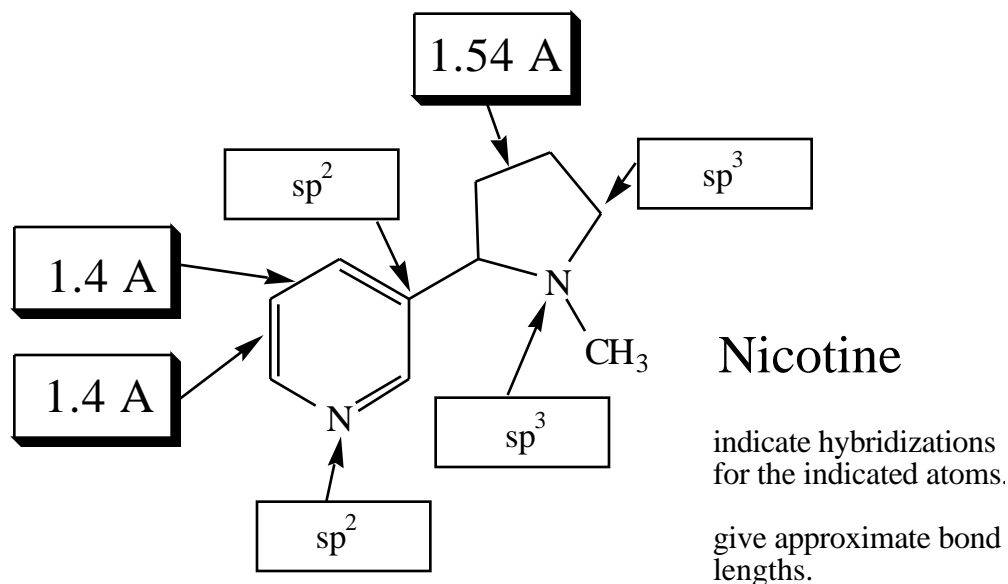
(a) Silicon is located just below carbon in the Periodic System of the Elements. Given that, answer the following questions. (6 points)

	Carbon	Silicon
Total number of electrons?	6	14
Number of valence electrons?	4	4
What shell <i>number</i> are the valence electrons in?	n = 2	n = 3
What is the <i>name</i> of that shell in Bohr's model?	L	M
Electronegativity? (For Si, indicate < or > EN of C)	2.5	1.8 (less)
Indicate the polarity of the respective bonds to hydrogen.	C(-) <--- (+)H	Si(+) ---> (-)H

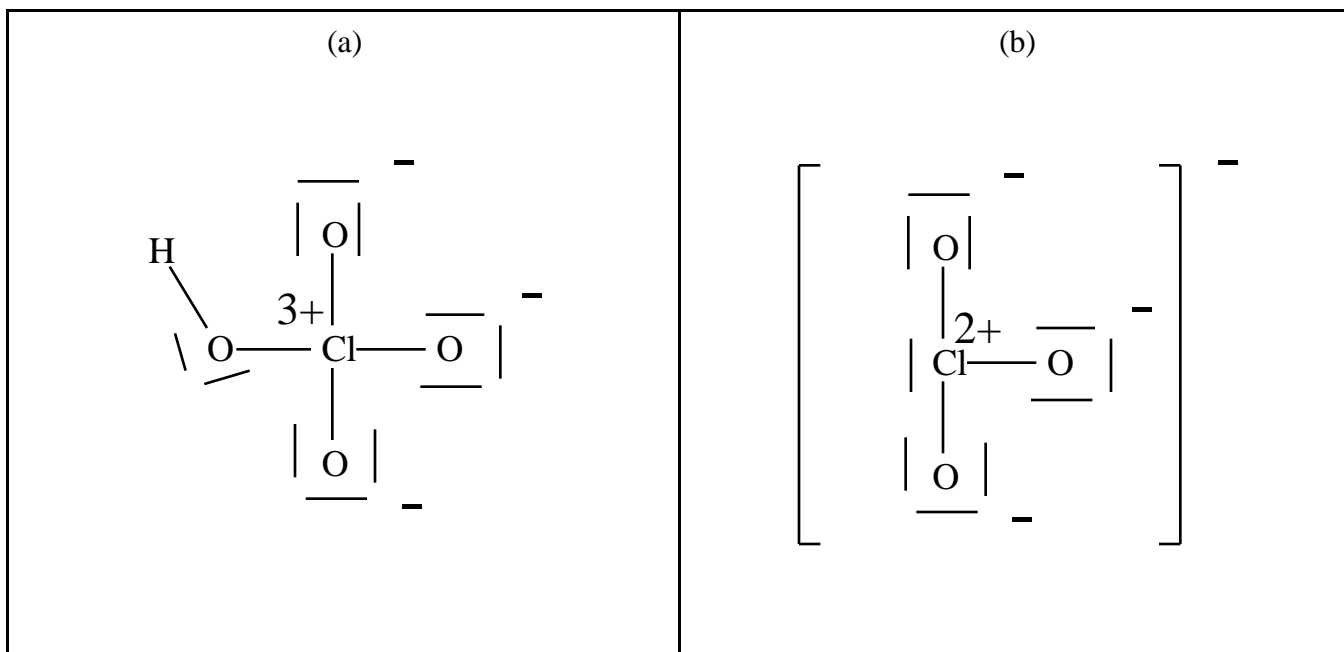
(b) Draw an energy level diagram of the atomic orbitals of Si and -- for the ground state -- indicate the occupation of these AOs with arrows. If their are degenerate AOs, clearly indicate that. Also give the electron configuration in the compact notation (e.g. for Li this would be $1s^2 2s^1$). (6 points)



Question 2. Kekule Structures, Hybridization and Geometry. (13 points)

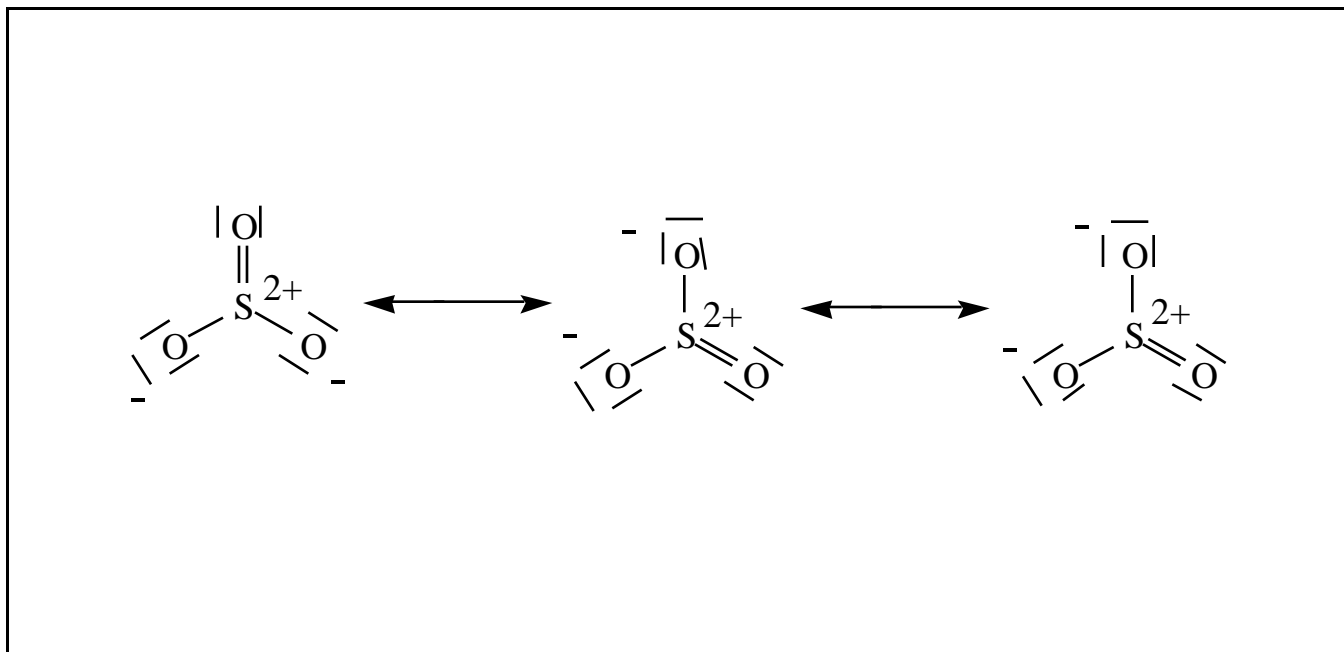


HClO₄ and HClO₃ both are strong acids and the former is stronger than the latter. Thus the pK_a value of the HClO₄ is lower (higher, lower) than that of HClO₃. On the other hand, it is also clear then that the conjugate base of HClO₄ is a weaker (stronger, weaker) base compared to the conjugate base of HClO₃. Give the Kekule structures (a) of the acid HClO₄ and (b) of the conjugate base of HClO₃. Draw all electrons, show all formal charges, show overall charge (if any).

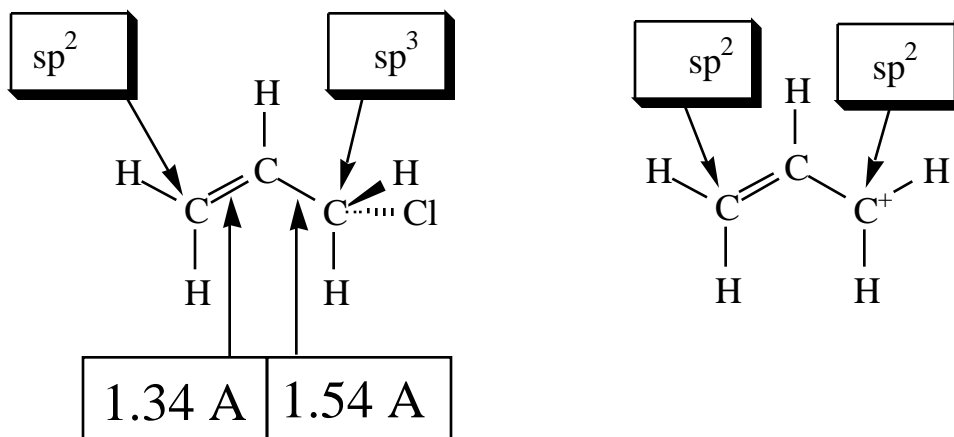


Question 3. Resonance Forms. (27 points)

(a) In the first quiz, you had to give the Kekule structure of sulfur trioxide, SO_3 . Experimentally it is well established that all of the SO bonds in SO_3 have the same length. Draw all necessary resonance forms. As always, draw all lone pairs and indicate formal charges (if any). (6 points)

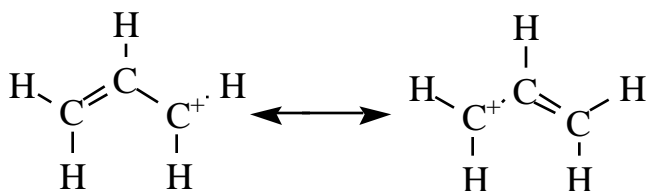


(b) Heterolytic bond dissociation of the C-Cl bond of the halide on the left results in the formation of the cation on the right. The cation formed is the allyl cation. Indicate the approximate lengths of the C=C and C-C bonds in the halide. Indicate hybridizations in the appropriate boxes (on top). (6 points)



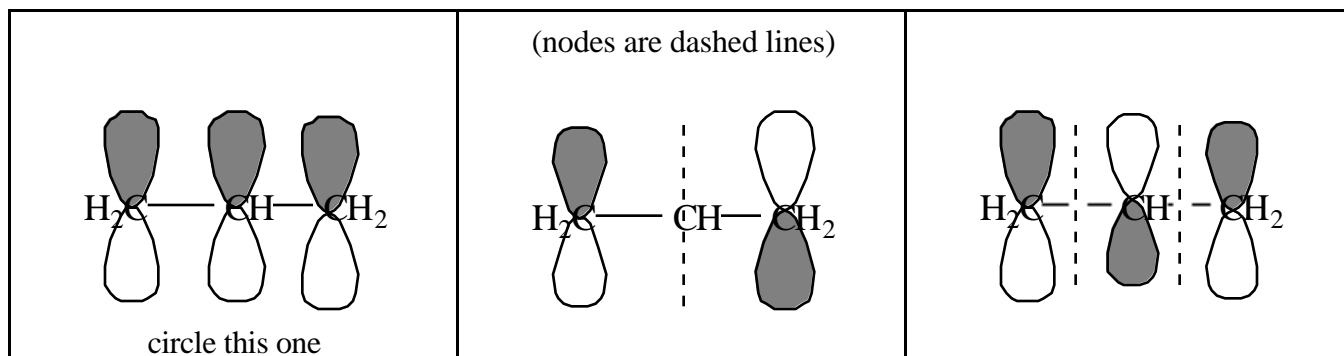
(c) In allyl cation, both CC bonds have *the same length*. In Valence Bond Theory, we explain this fact using resonance forms. Show how and briefly explain. (3 points)

Resonance forms:



Both contribute with equal weight.

(d) Now let's turn to LCAO theory. Complete the drawing of the first MO by drawing the nodes and by shading of the lobes depending on their signs. Draw MOs 2 and 3 in analogy. Circle that -MO (or those -MOs) that is (are) occupied in allyl cation. (9 points)

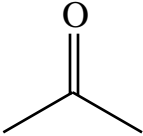
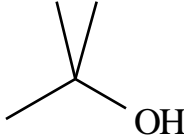
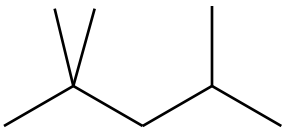
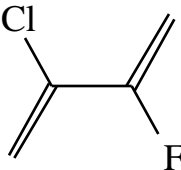
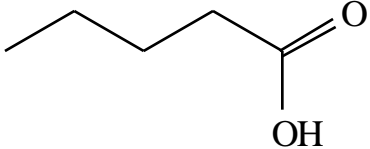
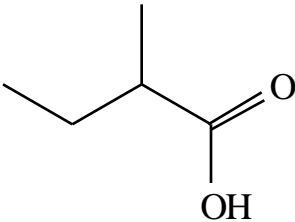
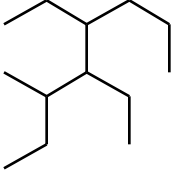


(d) In LCAO theory, the equivalence of the two CC bonds is a direct reflection of the properties of the molecular orbitals. Briefly explain. (3 points)

In the occupied MO, the overlap between C1-C2 and C2-C3 is identical.

Question 4. Nomenclature. (20 points)

When names are given, then draw the structural formula with all electrons. When structures are given, then give the correct and complete name. (2 points each)

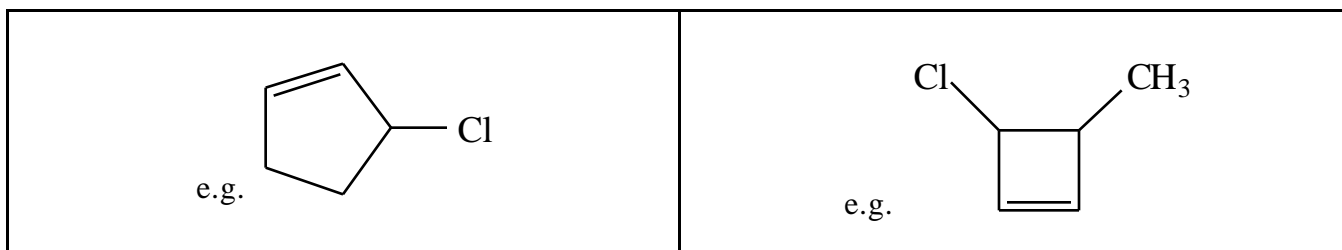
<p>n-propanal</p> <p>acetone </p>	<p>tert butanol </p>
<p>2,2,4-trimethylpentane </p>	<p>2-chloro-3-fluoro-butadiene </p>
<p>pentanoic acid </p>	<p>2-methylbutanoic acid </p>
<p>$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ <u>acetic acid</u> or ethanoic acid</p>	<p>$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ <u>acetaldehyde</u> or ethanal</p>
<p>$\text{H}_3\text{C}-\overset{\text{CH}_3}{\text{CH}}-\text{C}\equiv\text{N}$ iso propyl nitrile</p>	<p> 3,4-diethyl-5-methyloctane</p>

Question 5. Double Bond Equivalent and Structure Isomers. (16 points)

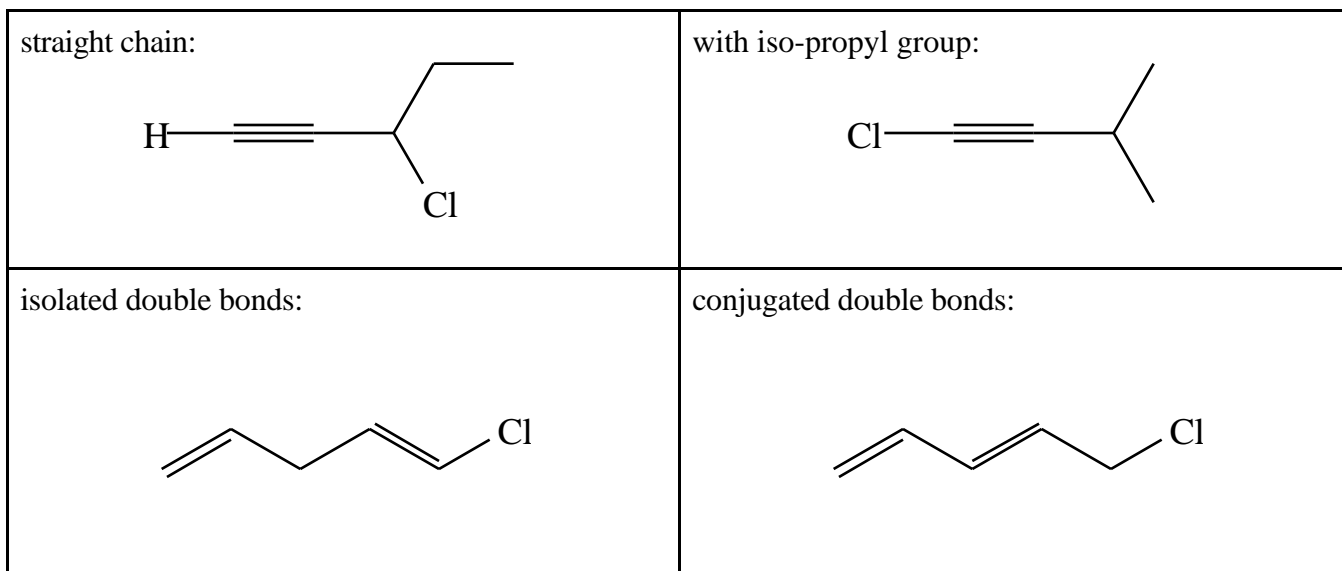
Let's look at structural isomers of C_5H_7Cl . In all cases, draw structural formulas. You may use condensed structural formulas so long as it is clearly indicated where all the hydrogens are.

(a) The double bond equivalent (DBE for short) of C_5H_8 is 2. The DBE is calculated as the number of H_2 molecules that needs to be added to obtain the corresponding *acyclic alkane* with the general formula C_nH_{2n+2} (give the formula). The Cl just replaces one H and thus C_5H_8 and C_5H_7Cl have the same DBE. (4 points, 2 for each blank)

(b) One mole of C_5H_7Cl was treated with H_2 / Ni and the addition of one mole of H_2 was observed. Draw two possible structures.



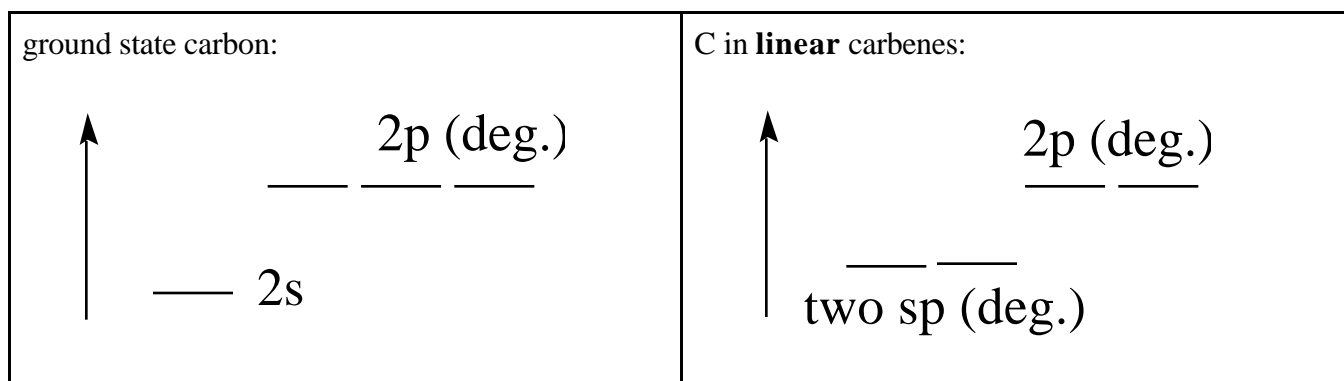
(c) Draw two isomers that contain at least one triple bond. The first one should have a *straight chain*. The second one should contain an *iso-propyl group attached to one of the sp -hybridized carbons*. Further below, draw two structures that contain at least two double bonds and in which these double bonds are *isolated* or *conjugated*. (2 points for each)



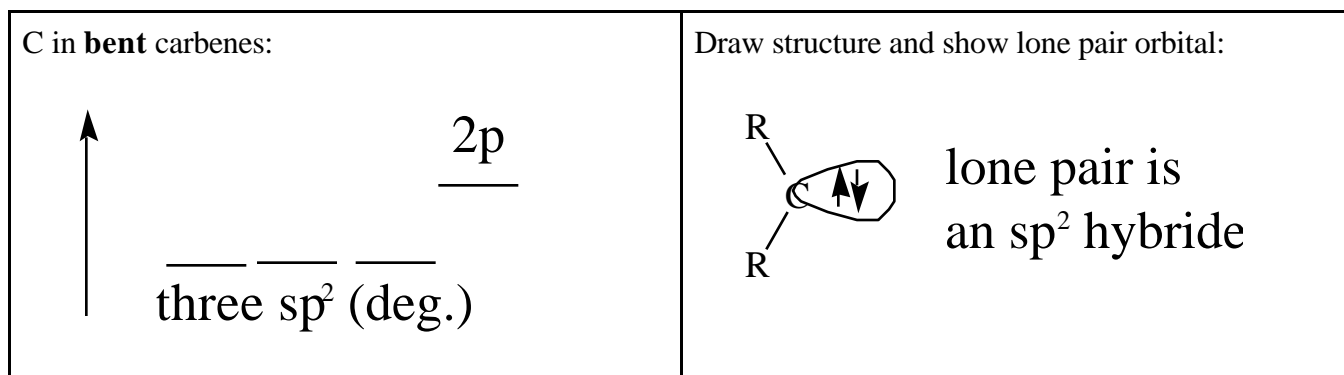
Question 6. Carbenes, CR_2 . (12 points)

Carbenes can have different structures -- either linear or bent -- depending on the nature of the substituents R that are attached. Let's look at the orbitals in the two cases.

(a) For **linear** carbenes, the C hybridization is sp . Draw an energy level diagram for the ground state of carbon and for the carbon hybridization in these linear carbenes. Indicate degeneracies clearly. Label the atomic orbitals. (6 points)



(b) In **bent** carbenes, the H-C-H angle is about 120° and thus carbon is sp^2 hybridized. Draw an energy level diagram for the C-hybridization in bent carbenes. Indicate degeneracies and label AOs. Clearly indicate the occupancy of the AOs. Draw the structure and show the shape of the lone pair orbital (e.g. is it an s-, a p-, or some hybrid orbital, in the plane or out of plane). (6 points)



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