

THE COMPLETE EXAMINATION BOOKLET MUST BE RETURNED

HAPPY HOLIDAYS AND GOOD LUCK!

Q1 12 points

Arrange the following in increasing (lowest to highest) order. Explain your answer, briefly.

a) Increasing order of boiling point

(i) Carbon tetrabromide (CBr_4)

(ii) Carbon tetraiodide (Cl_4)

(iii) Methane (CH_4)

$\text{CH}_4 < \text{CBr}_4 < \text{Cl}_4$ (iii) < (i) < (ii)

All are non-polar.

Cl_4 has the largest molar mass and hence the largest intermolecular forces, and hence the highest

b) Increasing order of intermolecular forces

(i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

(ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$

(iii) $\text{CH}_3\text{CH}_2\text{CH}_3$

$\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{CH}_2\text{CH}_2\text{F} < \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (iii < ii < i)

(i) has hydrogen bonding (and is polar)

(ii) is polar but no hydrogen bonding

(iii) non polar- only London dispersion forces

c) Increasing order of C-N bond length:

(i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

(ii) $\text{CH}_3\text{CH}_2\text{CN}$

(iii) $\text{CH}_3\text{CH}_2\text{CHNH}$

$\text{CH}_3\text{CH}_2\text{CN} < \text{CH}_3\text{CH}_2\text{CHNH} < \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (ii) < (iii) < (i)

Based on Lewis structures, the C-N bond in (i) is a single bond, in (iii) is a double bond, and in (ii) is a triple bond. Larger the bond order, shorter the bond length

d) Increasing order of *frequency* of a photon for the following transitions in a H atom (assume all given transitions are possible):

(i) 1s to 3d

(ii) 5p to 1s

(iii) 7p to 2s

(iii) < (i) < (ii)

H atom (Bohr's model applies). Largest energy gap in consecutive levels is between $n=1$ and $n=2$. So any transition to or from $n=1$ will be larger than a transition to/from another level. Energy and frequency are directly related.

The energy difference between 5 to 1 is greater than that between 3 to 1, so Energy and hence frequency of (ii) > (i)

Q2 10 points

a) The research group of Prof. Brad Siwick (McGill) works on understanding materials with unique optoelectronic properties. Their lab uses ultrafast laser pulse (wavelength = 400 nm) to study these materials. **(5 points)**

(i) Which one of the following metals (A, B, or C) will emit the slowest (lowest velocity) electron when excited with a photon of the ultrafast laser pulse (400 nm)? Explain your choice and show your work. **(4 points)**

A: Work function = $6.63 \times 10^{-19} \text{ J}$; B: Work function = $3.06 \times 10^{-19} \text{ J}$; C: Work function = $3.98 \times 10^{-19} \text{ J}$

$\lambda = 400 \text{ nm}$; $E_{\text{photon}} = 4.97 \times 10^{-19} \text{ J}$, $E_{\text{photon}} = \text{KE} + \text{Work function}$.

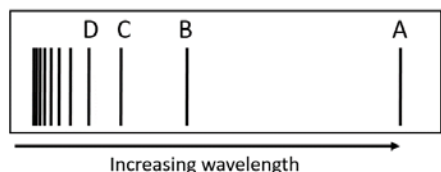
The energy of the photon is higher than the work function for metals B and C, so both of those will eject an electron. However, the slowest electron emitted will be for Metal C, as the work function for metal C is higher, and based on the photoelectric effect equation, for the same E_{photon} , lower the work function, higher the kinetic energy and hence velocity.

(ii) At a frequency above the threshold frequency for a metal, what will be the effect of *decreasing* the wavelength, on the kinetic energy of the ejected electron. Kinetic energy will _____ (fill in the blank)

Circle one of the following: Decrease **Increase** Remain unchanged

b) The figure given represents a part of a **calculated emission** spectrum of a one-electron ion in the gas phase (Assume Bohr's model can apply). Each line (line A, line B, line C, line D etc.) represents the wavelength of a photon resulting from the transition from an initial state to a final state of $n = 6$.

The four longest wavelengths (A, B, C, and D) are denoted in the figure. **(5 points)**



(i) What transition corresponds to line C? **(1 point)**

$n_{\text{initial}} = 9$; $n_{\text{final}} = 6$

(ii) If line B is at a wavelength of 300 nm, which ion does this calculated emission spectrum correspond to? Show your calculations, including equations used. **(4 points)**

Line B: $n_{\text{initial}} = 8$; $n_{\text{final}} = 6$

Can use Bohr's or Rydberg's equation

$$(1/\lambda) = R_H (Z^2/n_1^2 - Z^2/n_2^2)$$

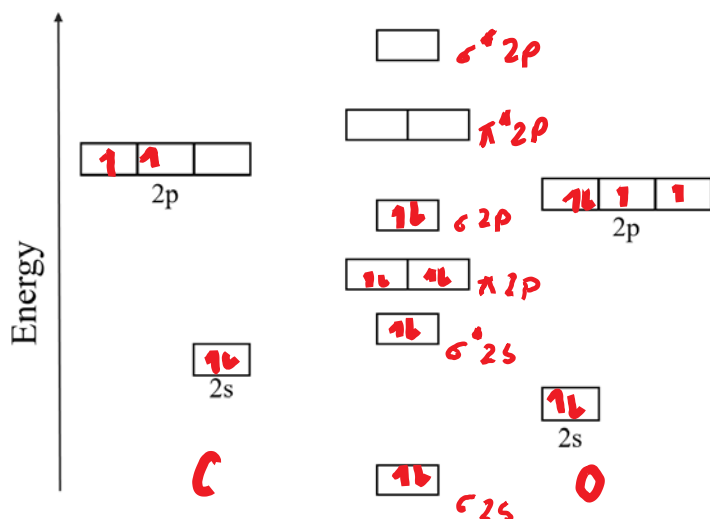
$$= 1/(300 \times 10^{-9}) = 1.097 \times 10^7 (Z^2/36 - Z^2/64)$$

$$= 0.313859 = (Z^2/36 - Z^2/64)$$

$$Z^2 = 25; Z = 5; \text{ So the ion is } B^{4+}$$

Q3 10 points

a) Given below is an incomplete MO diagram for the molecule CO (carbon monoxide). Complete the MO diagram. Make sure to include the label for each atom (atomic orbitals are labeled but the atoms are not), label the molecular orbitals, show the electrons in the atomic orbitals and molecular orbitals. **(4 points)**



b) Using MO theory, predict which of the following will have the shortest bond length. **(2 points)**

CO

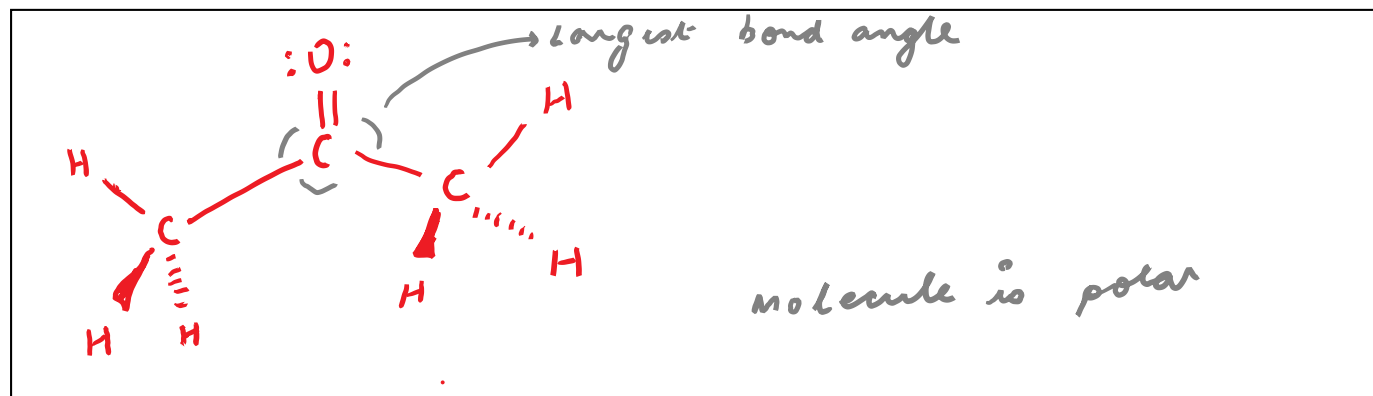
CO⁻

CO⁺

CO bond order = $(8-2)/2 = 3$; CO⁻ bond order = $(8-3)/2 = 2.5$; CO⁺ bond order = $(7-2)/2 = 2.5$
 So, the shortest bond length is CO since bond length and bond order are inversely proportional.

c) Molecule A has a molecular formula of C₃H₆O. The molecule does not contain any sp²-s sigma bonds.

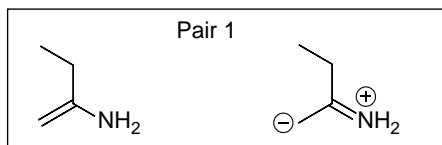
Draw the most stable Lewis structure showing appropriate shape and dashed/wedged bond where appropriate, based on VSEPR. Show lone pairs. Is the molecule *polar*? Denote the *largest* bond angle in the Lewis structure. (If there are multiple bond angles of the same value, denote any one). **(4 points)**



Monocyclic molecules (e.g. cyclopropanol) also acceptable answers.

Q4 10 points

- a) Circle True or False in the space provided for each statement for Pair 1 and 2, below. Briefly explain your reasoning. **(6 points)**



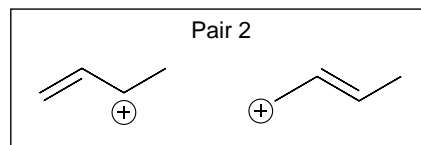
Statement:

Pair 1 is a pair of resonance structures.

Circle One: **True** or False

Explain your choice:

Only electrons move between the two structures, no atoms are moving.



Statement:

There are 4 delocalized electrons in the given resonance structures in pair 2.

Circle One: True or **False**

Explain your choice:

There are 2 electrons delocalized between the resonance structures

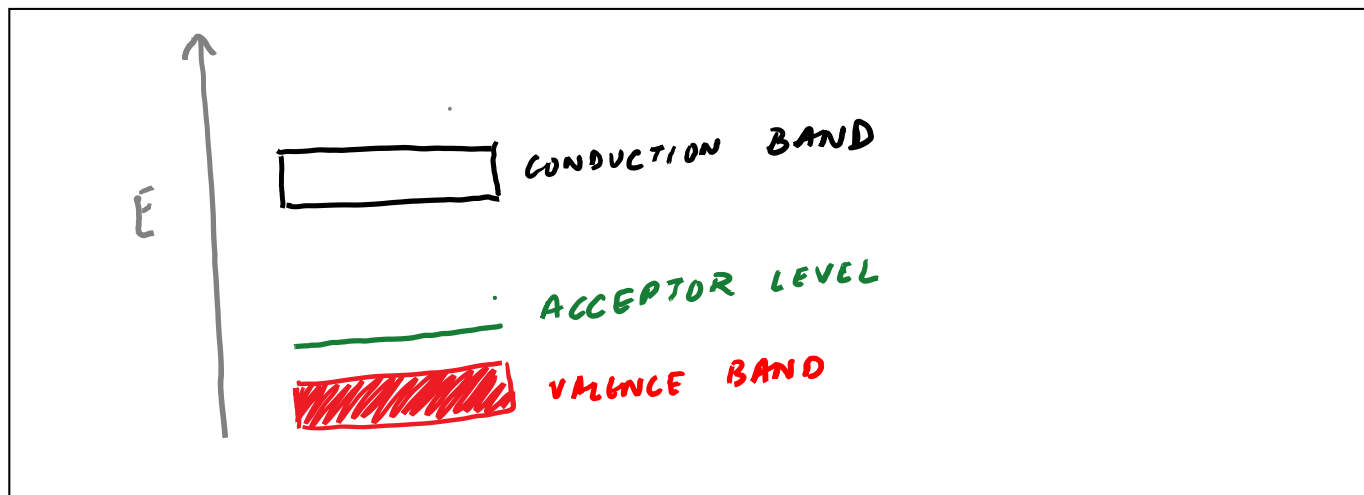
(There is only a single pi bond delocalized)

- b) In Pair 2 shown above, how many total pi molecular orbitals are in the resonance hybrid structure?

(1 point)

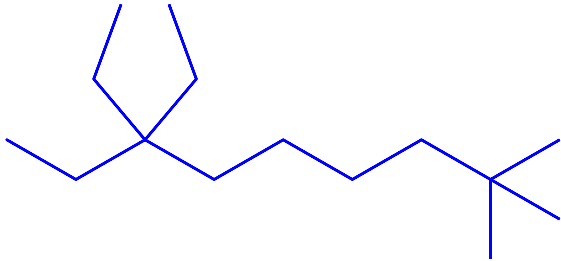
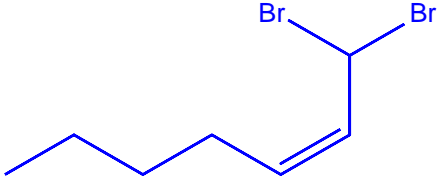
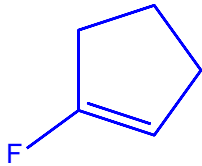
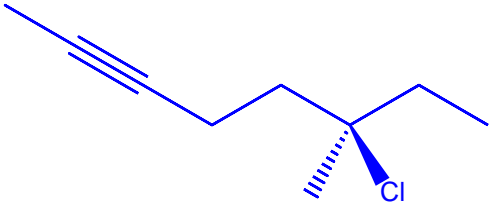
3 pi MOs

- c) Based on band theory, draw the energy level diagram (valence band, conduction band, acceptor/donor level) for a Silicon ($Z = 14$) semiconductor doped with Gallium ($Z = 31$). Show the energy axis. **(3 points)**



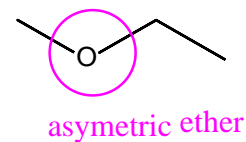
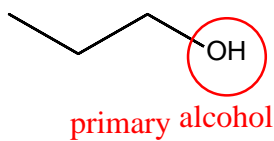
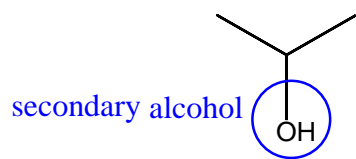
Question 5 (12 points)

- a) Draw the following molecules using skeletal structures. Be sure to use dash/wedged lines if necessary.
(8 points)

<p>7,7-diethyl-2,2-dimethylnonane</p> 	<p>(Z)-1,1-dibromohept-2-ene</p> 
<p>1-fluorocyclopentene</p> 	<p>(R)-6-chloro-6-methyloct-2-yne</p> 

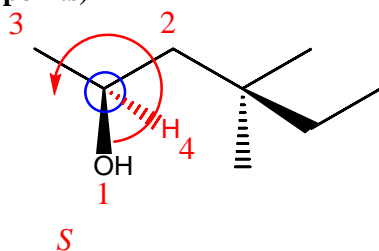
- b) Draw two molecules with the molecular formula C_3H_8O that are functional isomers of each other. Circle and specify the exact type of functional groups in these molecules. Use skeletal structures.
(4 points)

either one of the alcohols + the ether



Question 6 (9 points)

- a) For the molecule shown below, circle all chiral centers. Assign *R* vs *S* (show your work). (3 points)



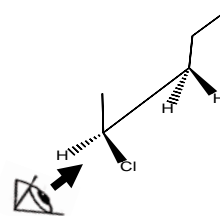
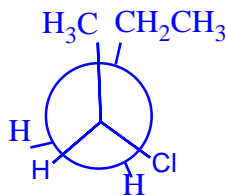
Note that the other one is not a chiral center. There is only one (in blue). For assigning *R* vs *S*, it's ok if they do not draw in the "H"; but they should show the group priority at least.

- b) For the molecule from part a above, draw an example of the indicated isomer (use skeletal structures). (3 points)

Functional isomer	Positional isomer	Enantiomer
<p>or putting an ether in the molecule somewhere</p>	<p>or basically putting the OH group coming off of any other carbon</p>	<p>students are likely to draw this as it is the mirror image</p> <p>but anything where the chiral center becomes <i>R</i> is good</p>

- c) For the molecule below, indicated in the sawhorse diagram (3 points):

- i. Draw the correct Newman projection from the perspective indicated.



- ii. Is the conformation shown above stable? Why or why not?

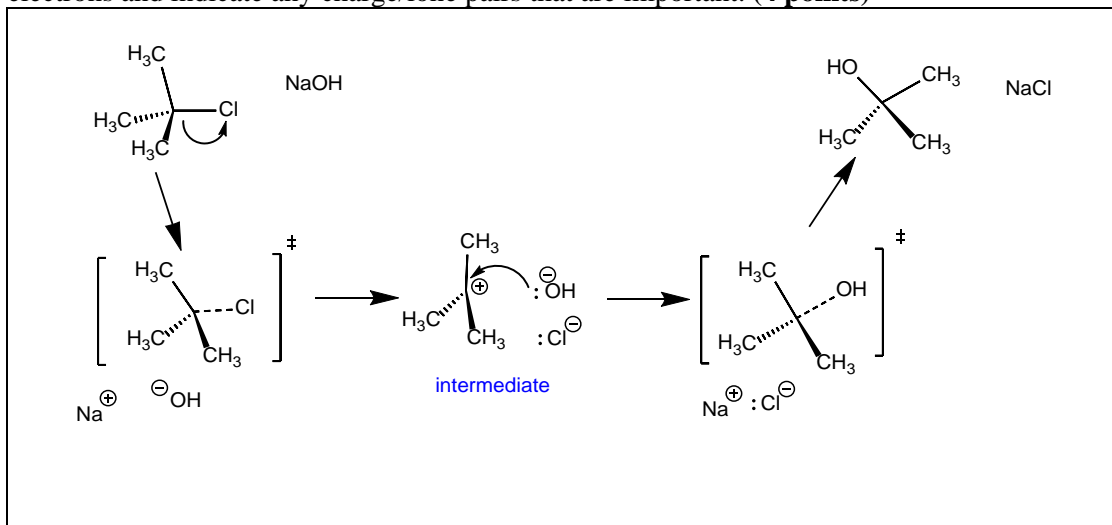
No, because it is "eclipsed" it must be staggered to be stable.

- iii. Provide the IUPAC name for the molecule, indicating *R* and *S* if appropriate.

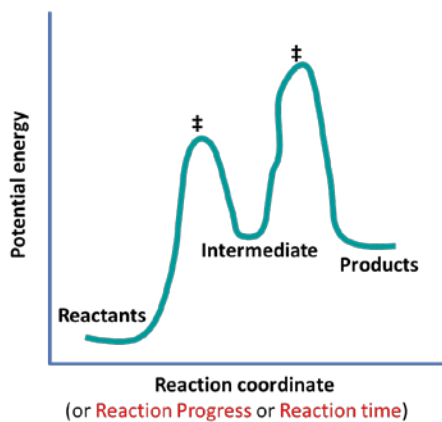
(*S*)-2-chloropentane

Question 7 (12 points)

- a) Provide the detailed mechanism of the S_N1 reaction of sodium hydroxide with 2-chloro-2-methylpropane. Include all transition states and intermediates. Use arrows to indicate the flow of electrons and indicate any charge/lone pairs that are important. **(4 points)**

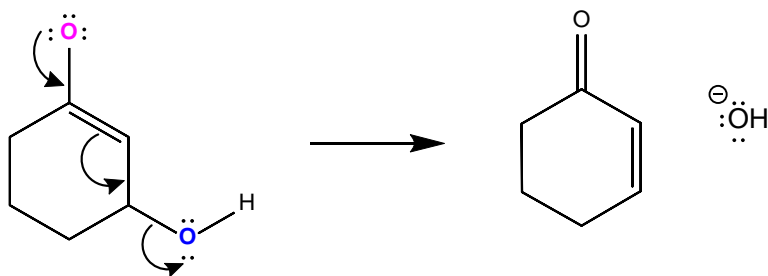


- b) In the reaction above, draw or name the following. **(2 points)**
- Nucleophile: :OH^- (hydroxide)
 - Electrophile: carbocation
- c) Assume that the S_N1 reaction above is endothermic, draw the associated reaction energy diagram for this reaction. Include all the necessary labels. **(3 points)**



- d) The following molecule is missing appropriate charges. Calculate and indicate the formal charge on the two oxygens. Finally, draw the product(s) of this arrow pushing using skeletal structures. **(3 points)**

FC is $6-7 = -1$, so this should be negative



FC is $6-6$ so this is 0 (neutral)

Question 8 (14 points)

a) Consider the complexes $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (9 points).

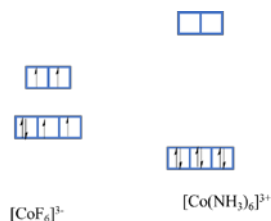
i. Fill in the table.

	$[\text{CoF}_6]^{3-}$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
Oxidation state	$[\text{CoF}_6]^{3-}$ $x + 6(-1) = -3$ $x = +3$ oxidation state	$[\text{Co}(\text{NH}_3)_6]^{3+}$ $x + 6(0) = +3$ $x = +3$ oxidation state
Coordination Number	6	6
IUPAC name	Hexafluorocobaltate(III) ion	Hexamminecobalt(III) chloride
Paramagnetic or diamagnetic?	paramagnetic	diamagnetic

ii. Draw d-orbital energy diagrams to compare the energy splitting of these complexes.

Co is $[\text{Ar}] 4s^2 3d^7$

$\text{Co}^{3+} = 3d^6$



iii. Which complex is more likely to absorb blue light? Why?

$[\text{Co}(\text{NH}_3)_6]^{3+}$, since it will absorb higher energy (therefore, lower wavelength light)

b) Draw an example of the isomer listed for each of the complexes indicated. (4 points)

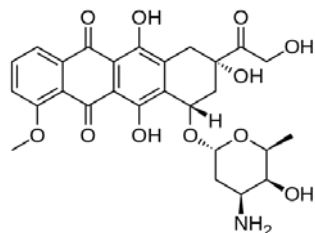
Isomer type	Complex	Isomer
Coordination isomer		
Linkage isomer		

c) What is lanthanide contraction? 1 point.

The lanthanide contraction is the greater than-expected decrease in ionic radii of the elements in the lanthanide series from atomic number 57 to 71. This is because of the drastic increased nuclear charge (14 extra protons)

d) Question 9 (11 points)

- a) To help improve the safe and effective delivery of the drug doxorubicin to cancer cells, Prof. Janine Mauzeroll developed liposomes to “carry” this drug. How many units of unsaturation are present in doxorubicin (shown below)? Explain your answer. **(2 points)**



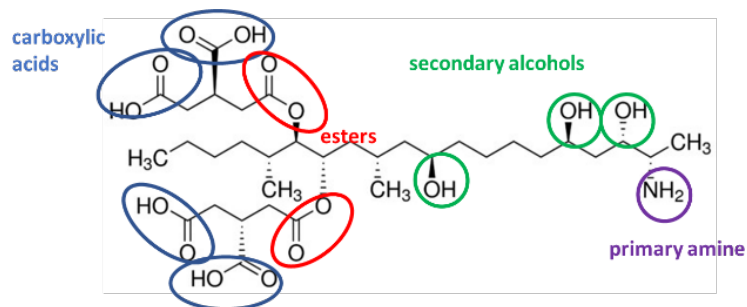
5 rings = 5 units

No triple bonds

9 double bonds = 9 units; so 14 in total

- b) At Carleton University, I (Prof. McKeague) developed a “biosensor” to screen food for the presence of fumonisin B1. Fumonisin B1 (shown below) is a toxin often occurring in corn. **(9 points)**

(i) Circle and identify all the functional groups in the molecule. Be sure to specify if they are primary, secondary, tertiary, asymmetric, symmetric, substituted, or unsubstituted if appropriate. Indicate directly on the diagram. **(4 points)**



(ii) Describe all bonds (include sigma and pi, where necessary) formed by the indicated oxygen atom (ii). What is the expected H-O-C bond angle? **(2.5 points)**

sp³-s sigma; sp³-sp² sigma

Bond angle : <109.5

(iii) Describe all bonds (include sigma and pi, where necessary) formed by the indicated carbon atom (iii). What is the molecular geometry at the carbon atom? **(2.5 points)**

sp²-sp² sigma, 2 sp²-sp³ sigma, p-p pi bond

Molecular Geometry: Trigonal Planar