Exam III

CH 301H Fall '10

Vanden Bout

Name: DVB

Carefully read all the problems

Show all your work on numerical problems

Clearly mark your answers

If you think a problem cannot be worked out with the information provided write "this problem can not be worked with the information provided"

Problems may contain extraneous information

Work problems you know first.
Go back to work harder problems.
Don't spend too much time on any given problem.

Please sign at the bottom to certify that you have worked on your own.

I certify that I have worked the following exam without the help of others, and that the work I am turning in is my own.

Signed: --

Signature Date

Potentially Useful Information

e 1.602×10^{-19} C

m_e 9.109×10^{-31} kg

m_p 1.67×10^{-27} kg

m_n 1.67×10^{-27} kg

ε_0 8.854×10^{-12} C^2 J^{-1} m^{-1}

c 2.998×10^{8} m s^{-1}

1Å 10^{-10} m

$h = 6.626 \times 10^{-34}$ J s

$E = h\nu$

$\lambda\nu = c$

1 Rhydberg 2.18×10^{-18} J

1 eV = 1.602×10^{-19} J

N_A 6.02×10^{23}

$$\lambda = \frac{h}{p}$$

Particle in a box

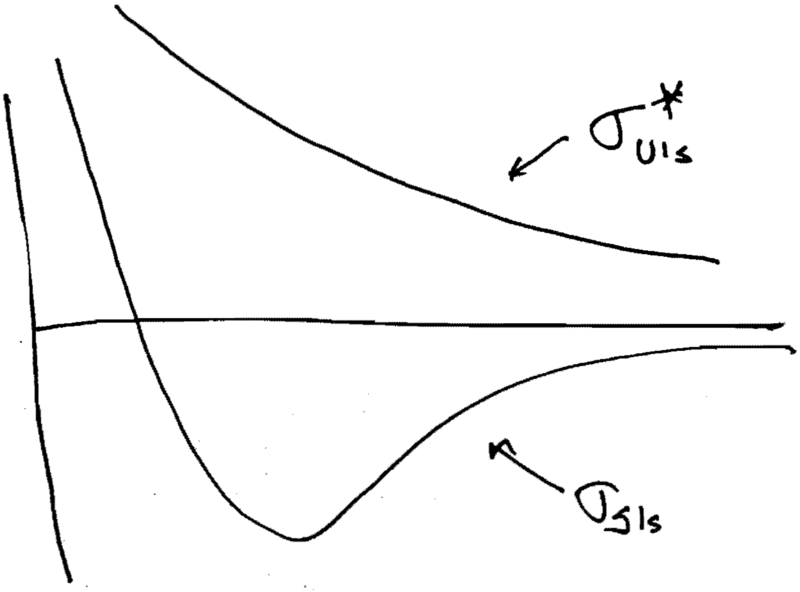
$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$$

$$E_n = \frac{h^2 n^2}{8mL^2}$$

$$\psi_n(x,y,z) = \sqrt{\frac{2}{L_x}}\sin(\frac{n_x\pi x}{L_x})\sqrt{\frac{2}{L_y}}\sin(\frac{n_y\pi y}{L_y})\sqrt{\frac{2}{L_z}}\sin(\frac{n_z\pi z}{L_z})$$

$$E_n = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

1. Make a sketch of the energy associated with the two lowest energy wavefunctions in H_2^+ as a function of internuclear separation. (10 points)



2. I found the following gem of an explanation of the Born-Oppenheimer approximation on the web.

"In principle, what you do, is to decouple the electronic states from the position of the nuclei."

Briefly explain the key problem with this statement? (10 points)

The electronic energy is highly dependant (coupled) to the position of the nuclei.

The B-O approx. is that essentially the nuclei have fixed position.

The position matter

the KE of nuclei does not.

3. Based on the MO for 2nd row diatomics answer the following. (21 points)

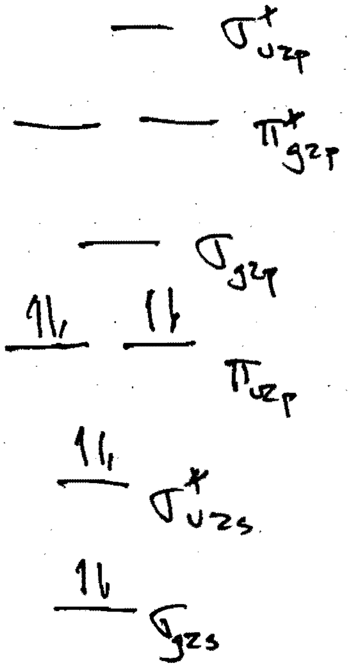
Which 2nd row diatomics do you predict will have a bond order of zero?

Be_2 Ne_2

What is the electronic configuration of C_2?

$$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^4$$

Which would you predict to have a longer bond C_2 or C_2^+?



C_2

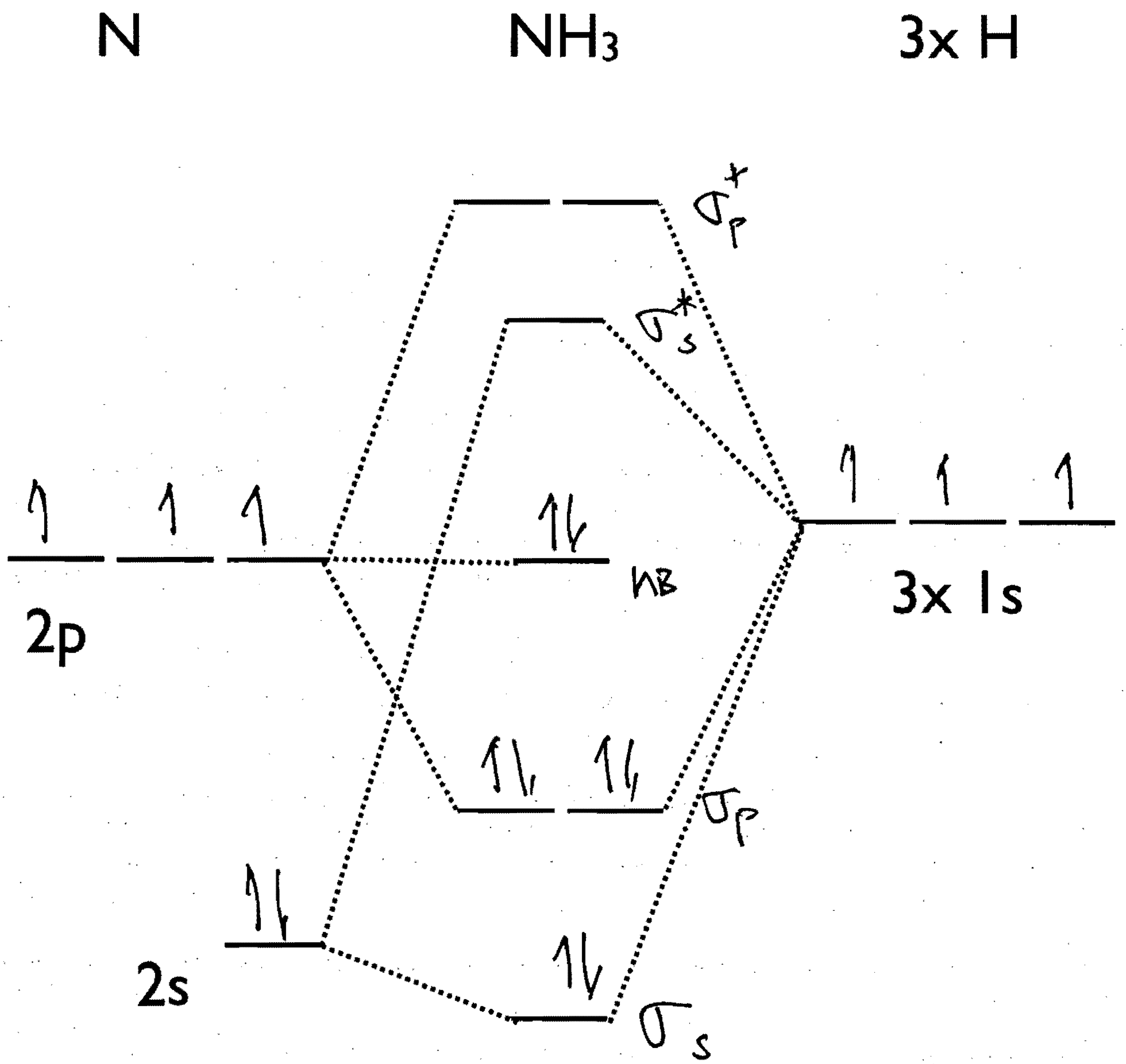
B.O → $C_2 = 2$

$C_2^+ = 1.5$

C_2^+ will have a longer bond.

4.

Below is an approximate MO diagram for ammonia. (15 points)



Fill the electrons in both the AO and MO.

Label each MO as bonding or anti-bonding, and sigma or pi.

What is the total Bond Order in NH_3?

B.O = $\frac{1}{2}(6-0) = 3$ 3x σ bonds.

5. (15 points)

Below is a diagram showing the AO in BeH_2 that combine to form the two bonding and the two anti-bonding MO's.

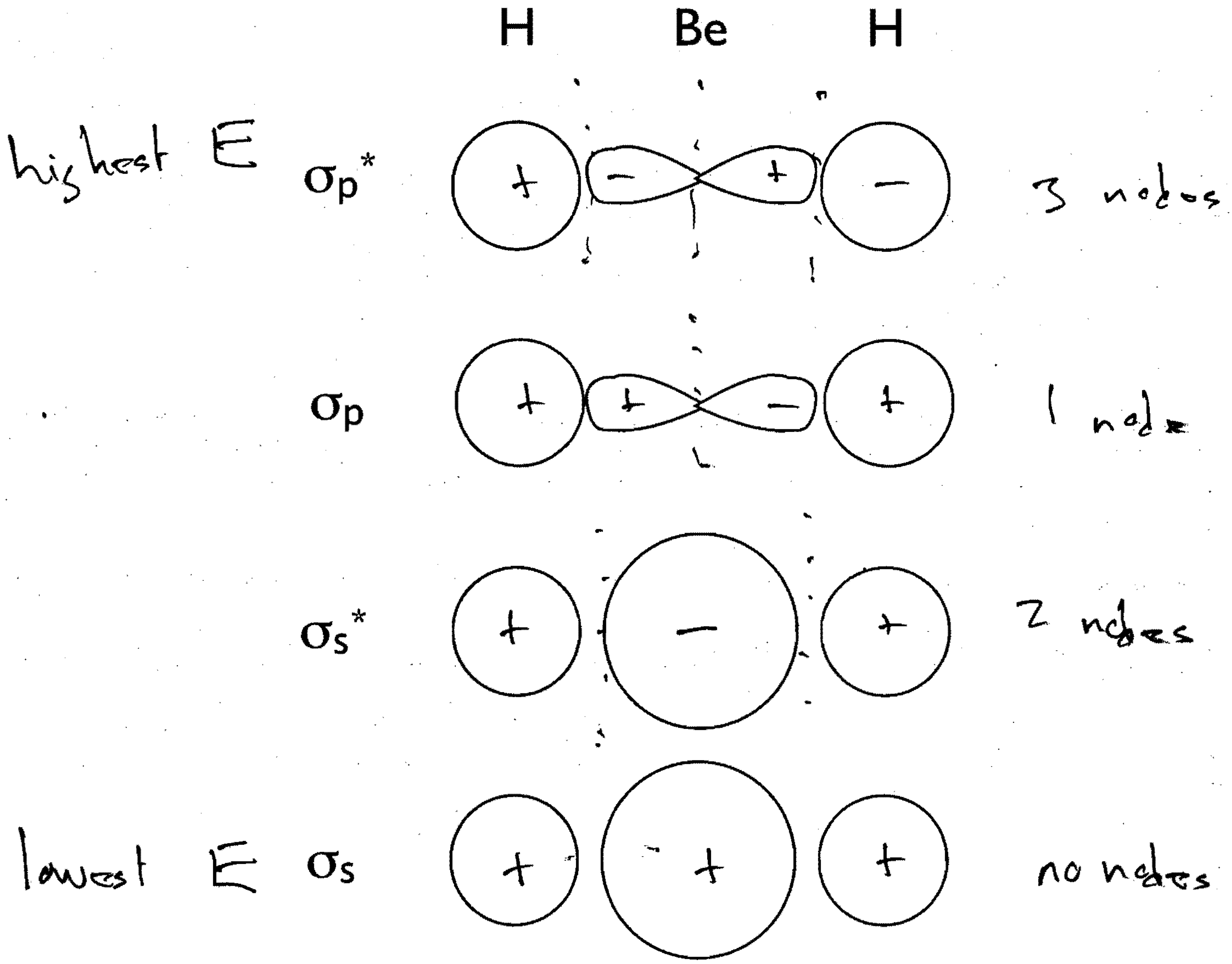
Put in the phase (sign) of the AO wavefunctions that you think would lead to these MOs. [Draw little +/- signs in the picture]

For each MO mark where you think there will be a node.(if any)

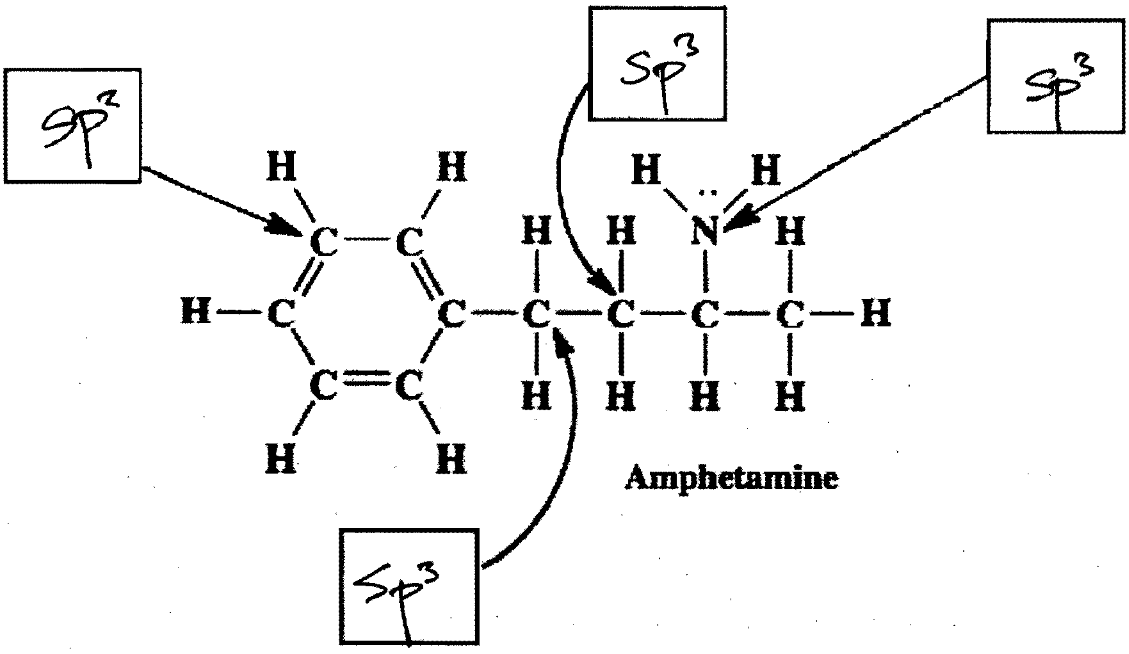
Which orbital do you think would have the lowest energy and which would have the highest? Why?

σ_s has no nodes → lowest E

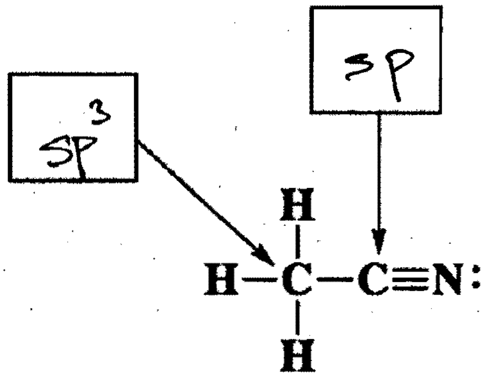
σ_p^* has most nodes → highest E



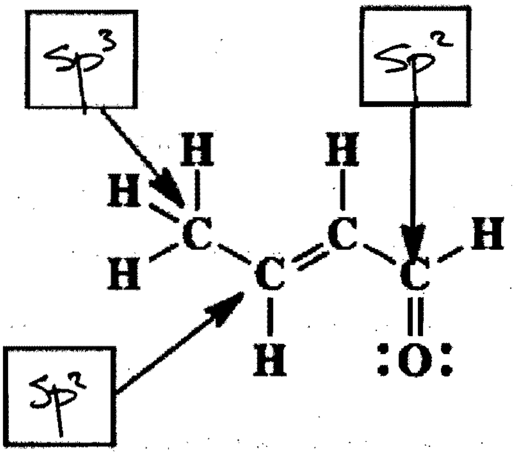
6. Write the valence bond description hybridization for the atoms indicated by the arrows in each of the following molecules. (18 points)



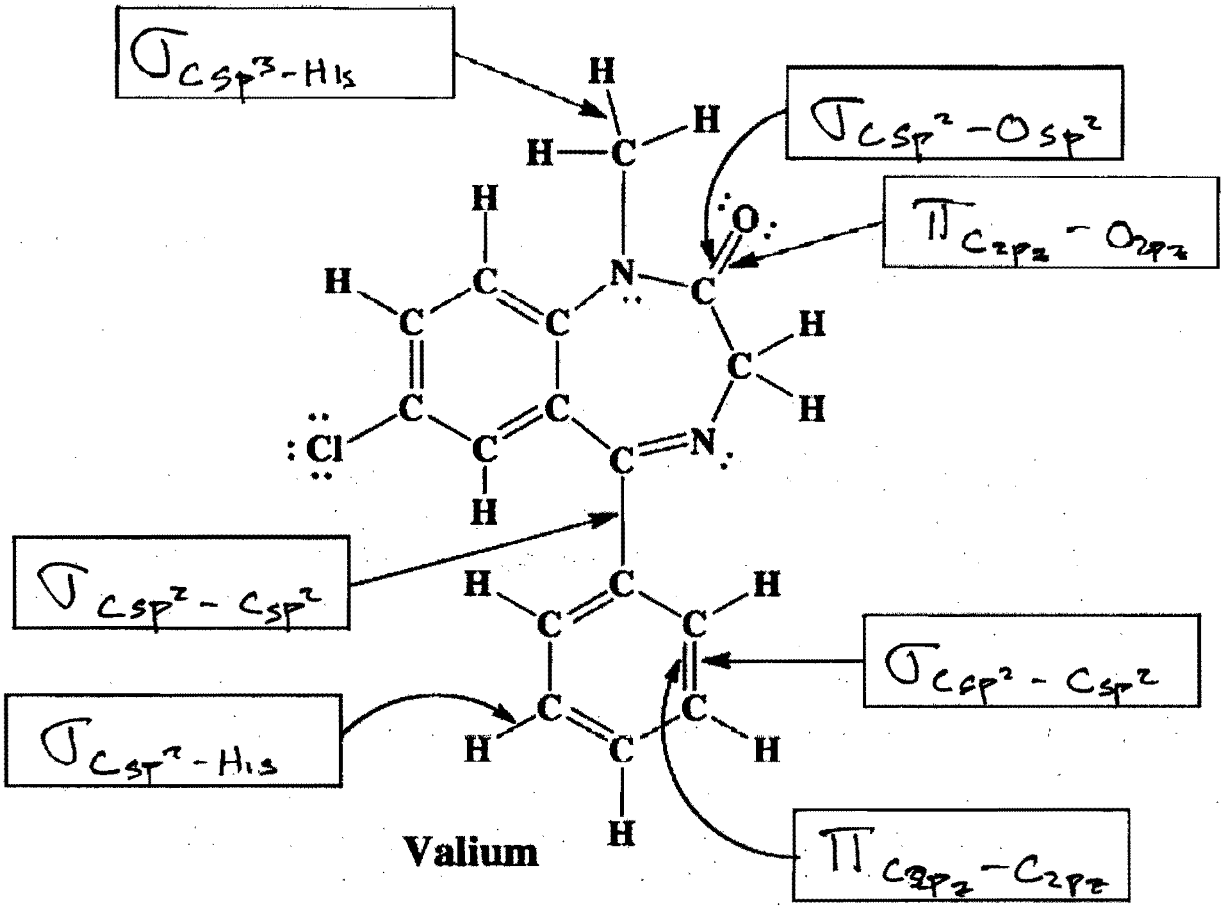
Amphetamine



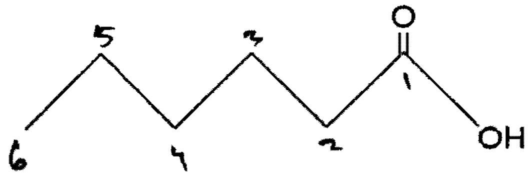
Acetonitrile (a solvent)



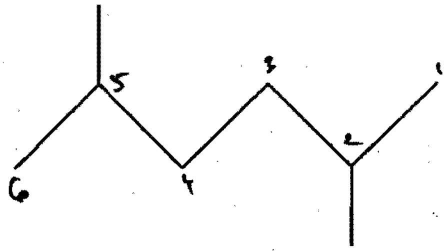
7. For the following give the valence bond description of the bond that result from the overlap of the hybridized orbital. For example the answer might be $\sigma_{Csp3\text{-}H1s}$ (for the double bonds give the description of both bonds. It doesn't matter which answer goes in which of the two blanks that are pointing at the double bond) (21 points)



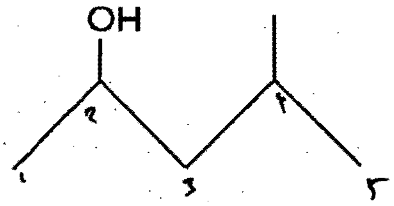
8. Name the following 3 compounds (18 points)



hexanoic acid



2,5 dimethyl hexane

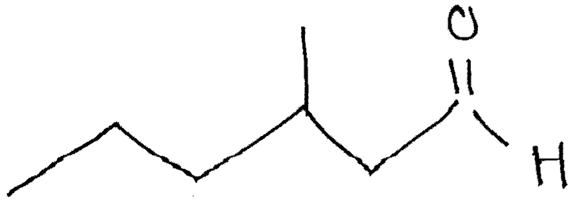


4 methyl 2 pentanol

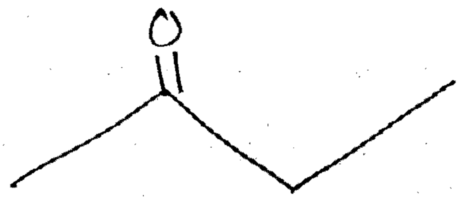
4 methyl pentan-2-ol

9. Draw the following (18 points)

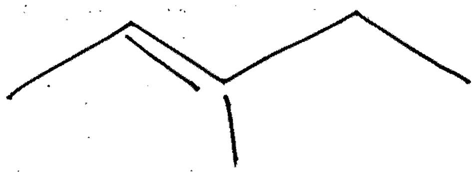
3 methyl hexanal



2 butanone (butan-2-one)

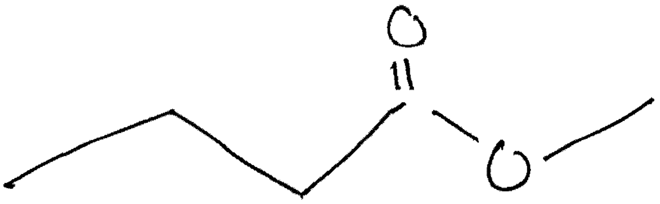


3 methyl 2 pentene (3 methyl pent-2-ene)



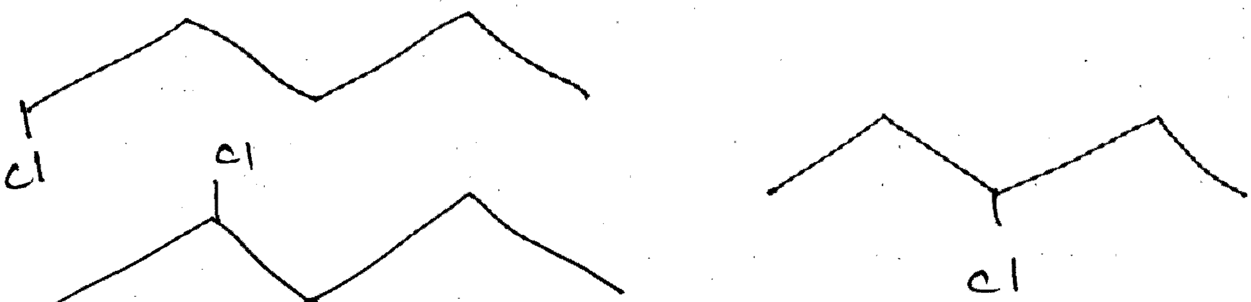
10.What products would you predict form from a condensation reaction of butanoic acid and methanol?
Draw and name the organic molecule. (10 points)

methyl butanoate → ester + H_2O



+ H_2O

11. How many geometric isomers are there for chloro pentane? Name them all.
(assume an unbranched pentane chain and ignore any stereo isomers). (10 points)



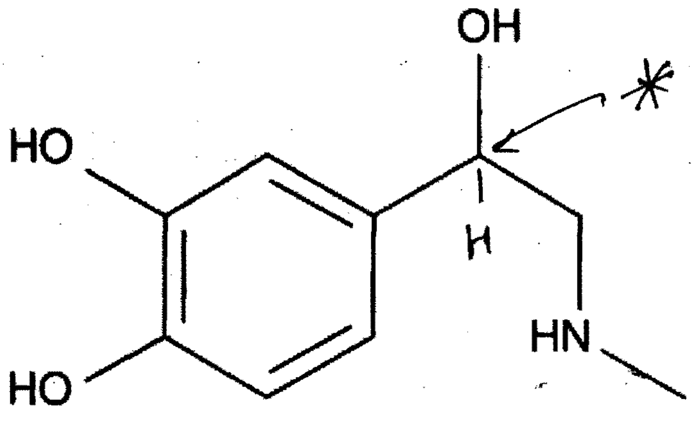
3x

1 chloro pentane

2 chloro pentane

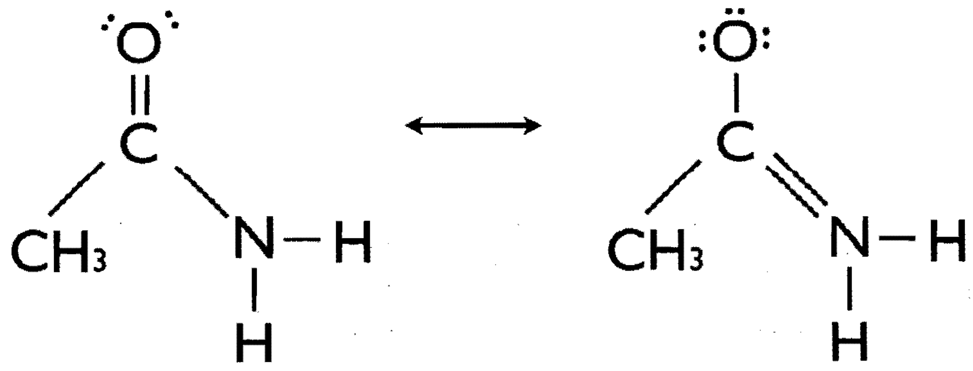
3 chloro pentane

12. Does this molecule (epinephrine/adrenaline) have any chiral centers? If so, clearly mark the chiral center(s) with an arrow at the central atom. (10 points)



one chiral center.

13. While the dominant Lewis dot structure for an amide (in this case ethanamide) is given on the left, another contributing resonance structure is the one on the right which has the double bond between the carbon and the nitrogen. Given that there are resonance structures, a good way to think about the bonding in an amide is a mix of valence bond theory for the sigma bonds and MO theory for the pi bonds. (24 points)



In this description, what hybridization would the C, O, and N have?

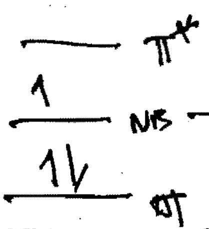
all sp^2

How many MO's would there be? How many bonding, non-bonding, and antibonding?

3 2p from C, O, N → 3 MO

1 bonding, 1 non bond, 1 anti bonding

What is the BO order for the entire pi system?



→ B.O = 1

Finally, given this description do you think the NH_2 group on the amide would be found in the same plane as the C=O, or could this group freely rotate? Why or why not?

Can't rotate. This would break the delocalized π bond.

Extra Credit (5 points each. No partial credit)

The electrons delocalized in a pi molecular orbital system can often be thought of as behaving like a particle in a box that is the length of the molecule. (you can estimate the length of the molecule from the average C-C bond length of 1.4Å)

Given this, can you predict the lowest energy absorption of the following molecule?

$h\nu = \Delta E$

$\nu = \frac{\Delta E}{h} = 1.3 \cdot 10^{15} s^{-1}$

$\lambda = \frac{c}{\nu} = \boxed{231 \text{ nm}}$

(Note: you'll need to think about how many electrons are in the pi MOs)

6 π e^- in MO formed by 6 2p AO.

total box length is 5 x 1.4 Å = 7 Å = 0.7 nm

n=4

↑↓ n=3

↑↓ n=2

↑↓ n=1

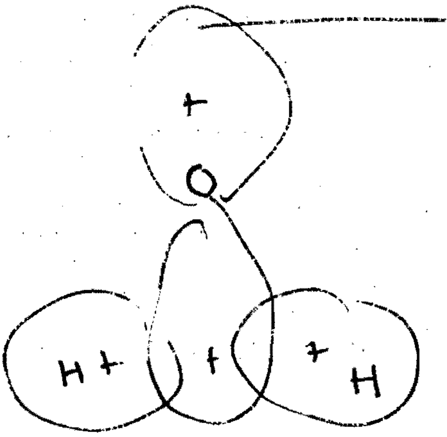
$$E = \frac{h^2 n^2}{8 m L^2} = \frac{(6.626 \cdot 10^{-34})^2 (n^2)}{8 (9.109 \cdot 10^{-31})(7 \cdot 10^{-10} m)^2} = 1.23 \cdot 10^{-19} J \, n^2$$

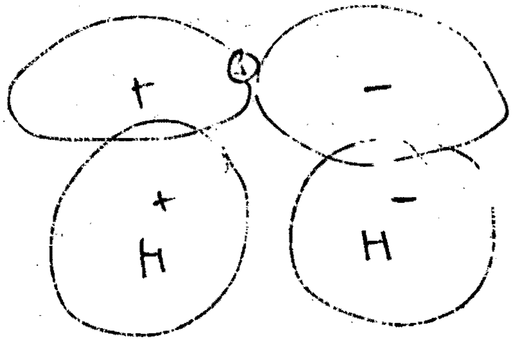
$\Delta E \Rightarrow n=3 \rightarrow n=4$

$$\Delta E = (16-9) \times 1.23 \cdot 10^{-19} J = 8.61 \cdot 10^{-19} J$$

In water, the MO's with significant contributions to the bonding are generated from combinations of oxygen 2p orbitals and the hydrogen 1s. Can you sketch a picture of how you think these MO's are formed from the AOs? (kind of like problem 5)

Not LINER





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BONUS	____________
TOTAL	____________/200

Periodic Table of the Elements

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.41	31 **Ga** 69.72	32 **Ge** 72.64	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)							

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

McCord (2006)