

**Open Book Problem 1 – Spectroscopy of Trigonal Planar Molecules**

a) The relation between vibrational frequency and force constant is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \longrightarrow k = 4\pi^2 \mu \nu^2$$

(2 pts for equation, 3 pts for rearrangement)

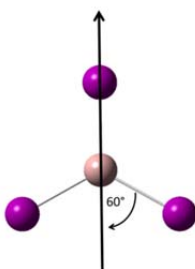
Plugging in the numbers for each molecule gives us

$$k_{\text{BH}_3} = 4\pi^2 \left( \frac{(13 \text{ amu})(1 \text{ amu})}{14 \text{ amu}} \right) \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) \left[ (2730 \text{ cm}^{-1}) (2.99792458 \times 10^{10} \text{ cm s}^{-1}) \right]^2 = 407.7 \text{ N m}^{-1}$$

$$k_{\text{GaI}_3} = 4\pi^2 \left( \frac{(324 \text{ amu})(127 \text{ amu})}{451 \text{ amu}} \right) \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) \left[ (280 \text{ cm}^{-1}) (2.99792458 \times 10^{10} \text{ cm s}^{-1}) \right]^2 = 421 \text{ N m}^{-1}$$

(5 pts per force constant. Award credit for answers obtained from an incorrect equation if the numbers and unit conversions were OK. No credit for incorrect units or sigfigs)

b) Consider the geometry of the planar triatomic:



Calculate the moment of inertia for this geometry:

$$I = \sum mR^2 = m_1 (R_{e,1} \sin[60^\circ])^2 + m_2 (R_{e,2} \sin[60^\circ])^2 \quad (5 \text{ pts}^*)$$

For our molecules,  $m_1=m_2$  and  $R_{e1}=R_{e2}$ . Substitute  $\sin[60^\circ] = \frac{\sqrt{3}}{2}$  to obtain

$$I = mR_e^2 \left( \frac{\sqrt{3}}{2} \right)^2 + mR_e^2 \left( \frac{\sqrt{3}}{2} \right)^2 = 2mR_e^2 \left( \frac{3}{4} \right) = \frac{3}{2} mR_e^2, \quad (5 \text{ pts}^*)$$

where  $m$  is the mass of H/I, and  $R_e$  is the theoretical bond length provided in the problem.

*\*Due to a typo, the problem statement in the exam was missing the factor of 3/2. Both answers are provided below: with and without the factor of 3/2. Either is acceptable for your response*

Using this equation, we obtain the following moments of inertia:

Without the factor of 3/2:

$$I_{\text{BH}_3} = \left[ (1 \text{ amu}) \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) \right] [1.19453 \times 10^{-10} \text{ m}]^2 = 2.36943 \times 10^{-47} \text{ kg m}^2$$

$$I_{\text{GaI}_3} = \left[ (127 \text{ amu}) \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) \right] [2.56357 \times 10^{-10} \text{ m}]^2 = 1.38594 \times 10^{-44} \text{ kg m}^2$$

With the factor of 3/2, we would obtain  $3.5541 \times 10^{-47} \text{ kg m}^2$  and  $2.07891 \times 10^{-44} \text{ kg m}^2$ .

(5 pts per moment of inertia. No credit for incorrect units or sigfigs. OK if factor of 3/2 is present or missing)

The rotational constants are calculated from  $\tilde{B} = \frac{h}{8\pi^2 Ic}$ .

Without the factor of 3/2:

$$\tilde{B}_{\text{BH}_3} = \frac{6.62608 \times 10^{-34} \text{ J s}}{8\pi^2 (2.36943 \times 10^{-47} \text{ kg m}^2) (2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 11.8141 \text{ cm}^{-1}$$

$$\tilde{B}_{\text{GaI}_3} = \frac{6.62608 \times 10^{-34} \text{ J s}}{8\pi^2 (1.38594 \times 10^{-44} \text{ kg m}^2) (2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 0.0201977 \text{ cm}^{-1}$$

With the factor of 3/2, we would obtain  $7.87610 \text{ cm}^{-1}$  and  $0.0134651 \text{ cm}^{-1}$ .

(5 pts per rotational constant consistent with the calculated moments of inertia. No credit for incorrect units or sigfigs.)

**There are no observed rotational lines, so you will not observe any spacing.** Neither  $\text{BH}_3$  nor  $\text{GaI}_3$  have a permanent dipole moment, which is the requirement to observe a rotational spectrum. (5 pts for stating that there is no observed spacing)

**If you simply gave the value of 2B, remember that chemistry and physics are not “plug and chug” subjects. Always pay attention to the science concepts that govern the mathematics.**

c) Molecular mass is the reason for the large difference in rotational constants. From part b), the rotational constant scales as  $I^{-1}$ , or  $m^{-1}$  and  $R^{-2}$ . The bond lengths are only different by a factor of 2 (changes B by a factor of 1/4), but the mass differs by a factor of 127 (changes B by a factor of 1/127). (5 pts for any reasonable explanation that correctly compares  $m^{-1}$  and  $R^{-2}$ )

d) Use the Boltzmann distribution to determine the relative populations:

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} \exp \left[ \frac{-(E_1 - E_0)}{kT} \right] \quad (5 \text{ pts})$$

For an individual vibration,  $g_i=1$ . Solving this equation for each molecule gives us

$$\left(\frac{n_1}{n_0}\right)_{\text{BH}_3} = \exp\left[\frac{-1146 \text{ cm}^{-1}}{(0.69503476 \text{ cm}^{-1} \text{ K}^{-1})(300 \text{ K})}\right] = \exp[-5.50] = 4.1 \times 10^{-3}$$

$$\left(\frac{n_1}{n_0}\right)_{\text{GaI}_3} = \exp\left[\frac{-88 \text{ cm}^{-1}}{(0.69503476 \text{ cm}^{-1} \text{ K}^{-1})(300 \text{ K})}\right] = \exp[-0.42] = 0.66$$

(5 pts per value. No credit for incorrect sigfigs, since we told you how many to use! If you're confused about why this is correct, re-read the rules for exponents: the final answer of an antilogarithm has sigfigs equal to the number of digits after the decimal place of the exponent.)

e) For  $\text{BH}_3$ , only 1% of the molecules will be vibrationally excited (because of the large vibrational frequencies, we do not need to consider populations in any mode with  $v > 1$ ).  $\text{BH}_3$  will have only a small vibrational motion due to zero point energy. (5 pts for anything reasonable)

Conversely, there are 3 times as many  $\text{GaI}_3$  molecules with one quantum of vibrational energy than in the ground state. We expect the typical  $\text{GaI}_3$  molecule to be undergoing significant vibration and bending. (5 pts for anything reasonable)

**Open Book Problem 2 – Jumpin’ Jack Flash, It’s a Gas!**

a) Parameter  $a$  corrects the faulty assumption that gas phase molecules do not interact with each other. Parameter  $b$  corrects the faulty assumption that gas molecules do not take up any volume. (5 pts per parameter)

b) Solve the van der Waals equation for pressure, and then carry out the integral for constant  $T$ .

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad (5 \text{ pts for solving for } p)$$

$$w = \int_{V_1}^{V_2} -pdV = - \int_{V_1}^{V_2} \left( \frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV = - \left[ nRT \ln(V - nb) + \frac{an^2}{V} \right]_{V_1}^{V_2}$$

$$w = -nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) - an^2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \quad (5 \text{ pts for integration})$$

c) We know that the parameters  $a$  and  $b$  are both positive. Examine each term separately, substituting in  $V_2 = \frac{1}{2}V_1$ :

$-nRT \ln \left( \frac{\frac{1}{2}V_1 - nb}{V_1 - nb} \right)$ : For any positive  $nb$  that is less than  $V$  (i.e. molecules take up less space

than the overall volume), the ratio  $\frac{\frac{1}{2}V_1 - nb}{V_1 - nb}$  will be less than  $\frac{1}{2}$ ,  $\ln \left( \frac{\frac{1}{2}V_1 - nb}{V_1 - nb} \right)$  will become

more negative, and  $w$  will increase. This indicates that it is harder to compress a gas when the molecules take up space, and thus cannot be compressed into the excluded space. (7 pt math analysis, 3 pts for physical interpretation)

$-an^2 \left( \frac{1}{V_1} \right)$ : This term scales as  $-a$ , so for positive  $a$ ,  $w$  decreases. Since  $a$  represents the

attractive forces between molecules, this means that it is easier to compress a gas (put molecules closer) when the molecules are more willing to be in close proximity. (7 pt math analysis, 3 pts for physical interpretation)

d) The major difference between the van der Waals (vdW) and Redlich-Kwong (RK) equations of state is the change in the form of parameter  $a$  (vdW) to  $\frac{a}{\sqrt{T}}$  (RK). The RK equation

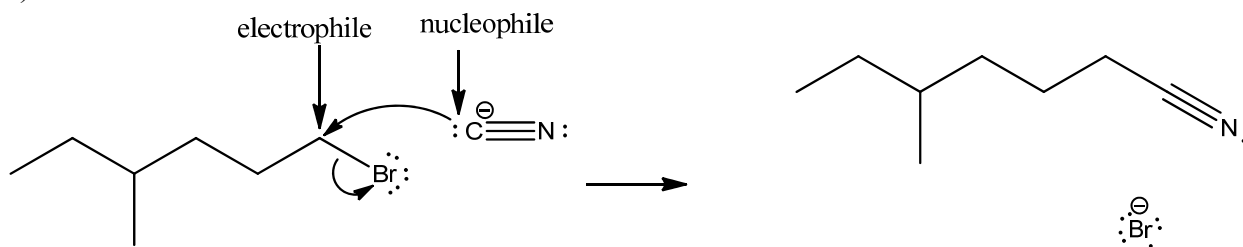
accounts for the fact that at high temperatures, the molecules will have sufficient energy to break their attractions. (5 pts for change in  $a$ , 5 pts for reasonable interpretation. May also award the full 10 pts for simply stating that the second term accounts for temperature)

**Open Book Problem 3 – Curved Arrow Mechanisms**

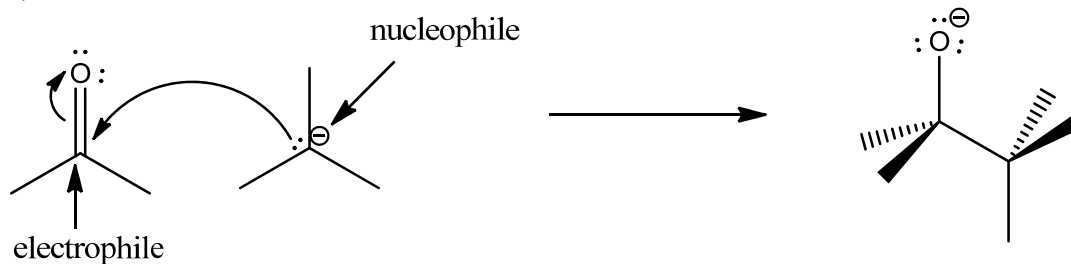
a–c) 4 pts for listing all correct reactants, 4 pts for listing all correct products, 3 pts for curved arrows, 2 pts for naming nucleophile, 2 pts for naming electrophile. No credit for any structure/arrows missing lone pairs or formal charges (still can earn points for naming nucleo/electrophile). No need for 3D structure.

Award full credit for stating Br (a) and O (b) are electrophiles, since they do accept electrons in the mechanisms.

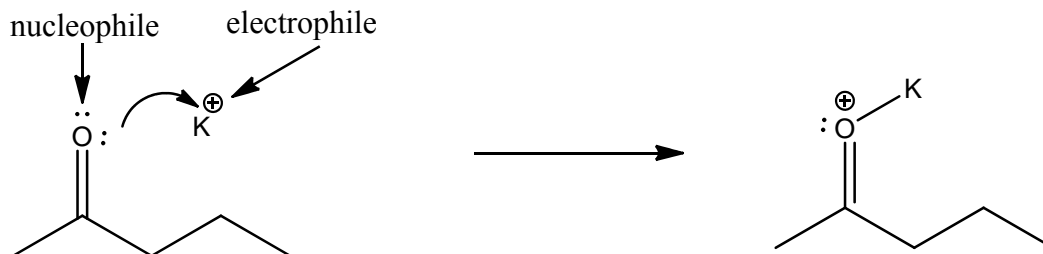
a)



b)



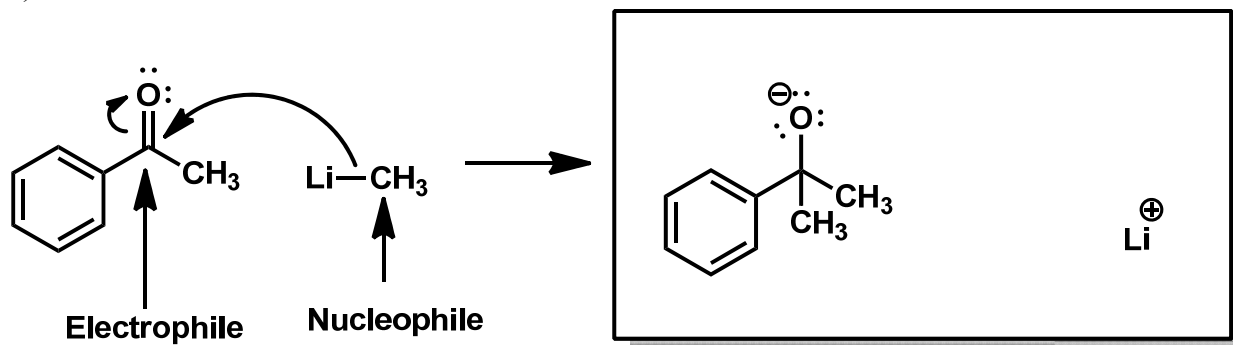
c)



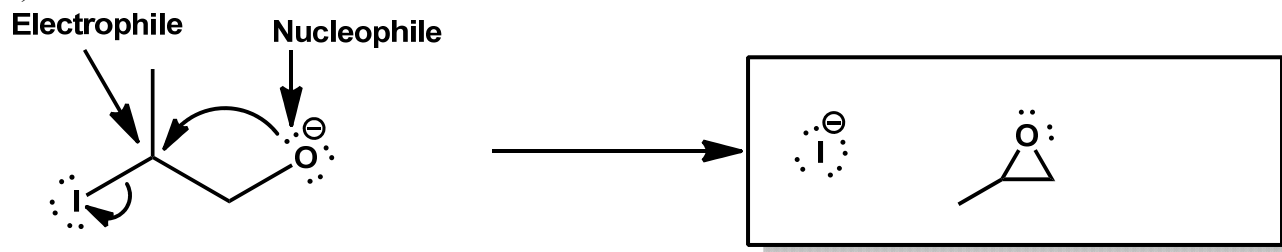
d-f) 3 pts for correct nucleophile, 3 pts for correct electrophile, 4 pts for all correct products. No credit for any structure missing lone pairs or formal charges (still can earn points for naming nucleo/electrophile).

Award full credit for stating O (d), I (e), and Cl (f) are electrophiles, since they do accept electrons in the mechanisms.

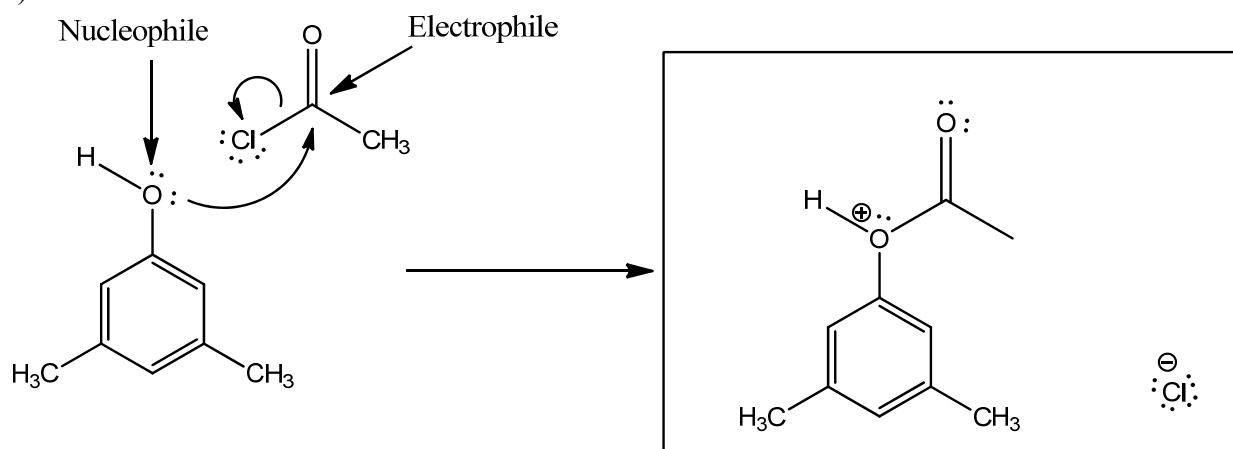
d)



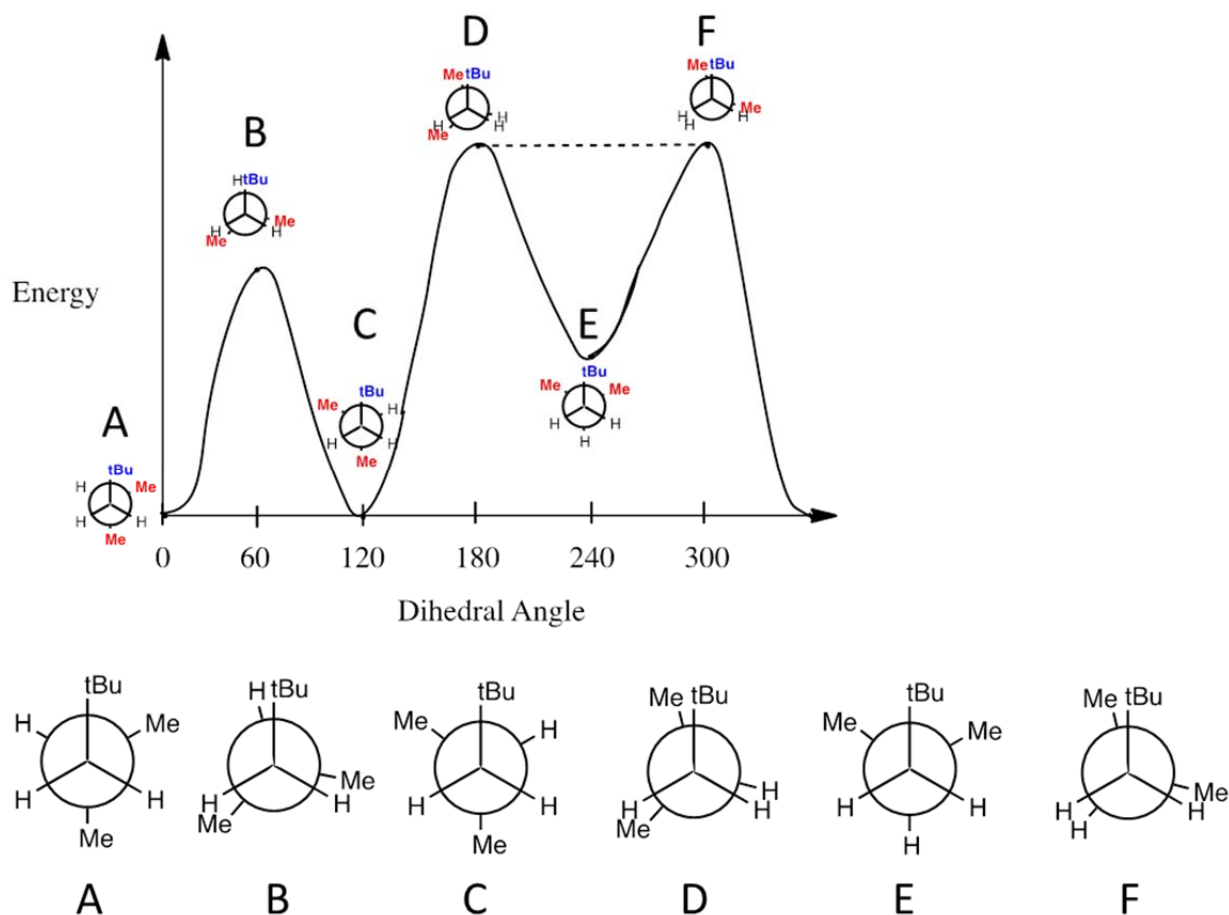
e)



f)



## Open Book Problem 4 – Conformational Energies



(For ease of reading, tBu and Me were color coded)

Key points:

- Gave all Newman projections, labeled with A–F and corresponds to 0°, 60°, etc. (15 pts, –3 per missing/unlabeled projection, max deduction –15)
- All eclipsing conformations are local maxima. (5 pts)
- All staggered conformations are local minima. (5 pts)
- tBu gauche to H has the same energy for two different angles (0 and 120 above). (5 pts)
- tBu eclipsing Me has the same energy for two different angles (180 and 300 above). (5 pts)
- tBu gauche to H (0/120) is lower energy than tBu anti to H (240). (5 pts)
- tBu eclipsing Me (180/300) is higher in energy than tBu eclipsing H (60). (5 pts)

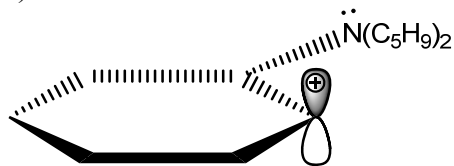
NOT NECESSARY: (do not take off points)

- The starting point (and direction of rotation) was not specified for the dihedral angle in the problem.
- The energy of tBu eclipse H (60) relative to tBu anti to H (240) could go either way a priori.
- Naming conformers is unnecessary.
- Does not have to draw conformer on the diagram (labels of A–F are acceptable)

**Note that the order of conformers may be different than shown above!**

**Open Book Problem 5 – Yay! No Heptagons!**

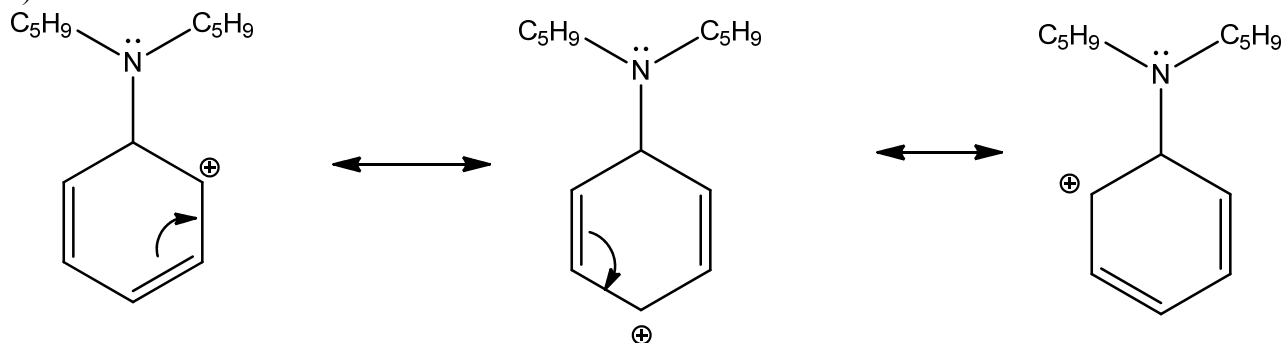
a)



The nucleophile must react with an empty orbital (LUMO). In this system, the unoccupied orbital is a p orbital on the hexadiene ring. A positive charge is a much stronger electrophile than the double bonds in the ring.

(14 pts for sketch of the correct orbital, not necessary to label as LUMO. No credit for an orbital with missing phases. -10 if p-orbital orientation is not clear. No deduction for leaving off the formal charge or lone pair on N. No deduction for leaving off double bonds on the ring. Any ring geometry OK)

b)



(4 pts per correct curved arrows on 1<sup>st</sup> and 2<sup>nd</sup> structures, 4 pts per correct 2<sup>nd</sup> and 3<sup>rd</sup> structure. -2 per extra incorrect structure. No credit for structures missing lone pairs or formal charges. Max overall deductions -16 pts)

c) The nucleophile will most likely attack the carbon across from (*para*) to the  $N(C_5H_9)_2$  group. The bulky  $N(C_5H_9)_2$  group sterically hinders the nucleophile from attacking the positions adjacent to the  $N(C_5H_9)_2$  group (*ortho*).

(10 pts for correct carbon, 10 pts for steric hindrance. No need to use the terms *para* or *ortho*)

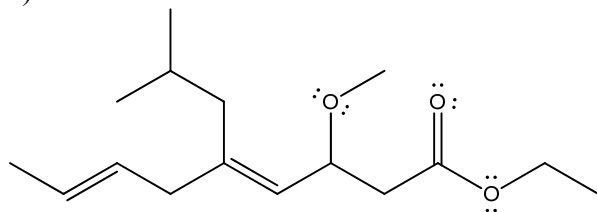


**Closed Book Problem 1 – IUPAC Naming**

- a) i) 6-methylhepta-4,6-dien-2-ynoic acid  
OR (Z)-6-methylhepta-4,6-dien-2-ynoic acid  
OR 6-methylhepta-4,6-dien-2-ynecarboxylic acid  
OR (Z)-6-methylhepta-4,6-dien-2-ynecarboxylic acid
- ii) 7-hydroxy-3-isopropylnon-7-en-5-yne-2,4-dione  
OR 7-hydroxy-3-methylethyl-non-7-en-5-yne-2,4-dione  
OR (E)-7-hydroxy-3-isopropylnon-7-en-5-yne-2,4-dione  
OR (E)-7-hydroxy-3-methylethyl-non-7-en-5-yne-2,4-dione

10 points per name. Half credit for an incorrect name that would lead to the correct structure. Half credit for incorrect use of E/Z. Half credit for a name with only one mistake (one missing functional group, one incorrectly named group, etc.). No credit otherwise. No penalties for extraneous “e” or hyphens. No deduction for correctly using or omitting E/Z. (Remember, we told you NOT to use E/Z. If you decided to disregard our directions, then you better have used the right designation!)

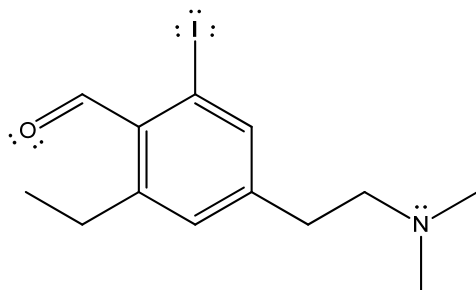
b)



(4E,7E)-ethyl 5-isobutyl-3-methoxynona-4,7-dienoate

OR

ethyl 5-(2-methylpropyl)-3-methoxynona-4,7-dienoate

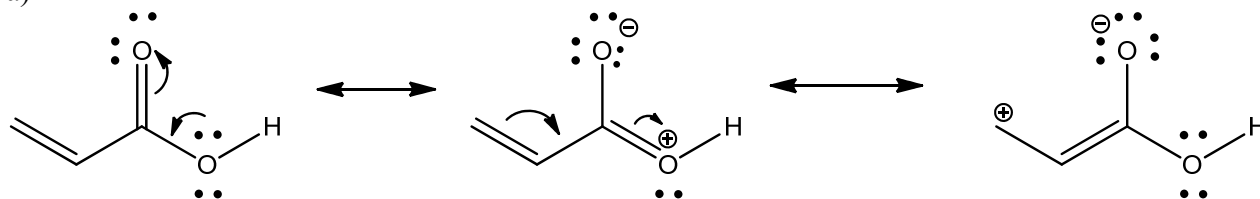


4-(2-(dimethylamino)ethyl)-2-ethyl-6-iodobenzaldehyde

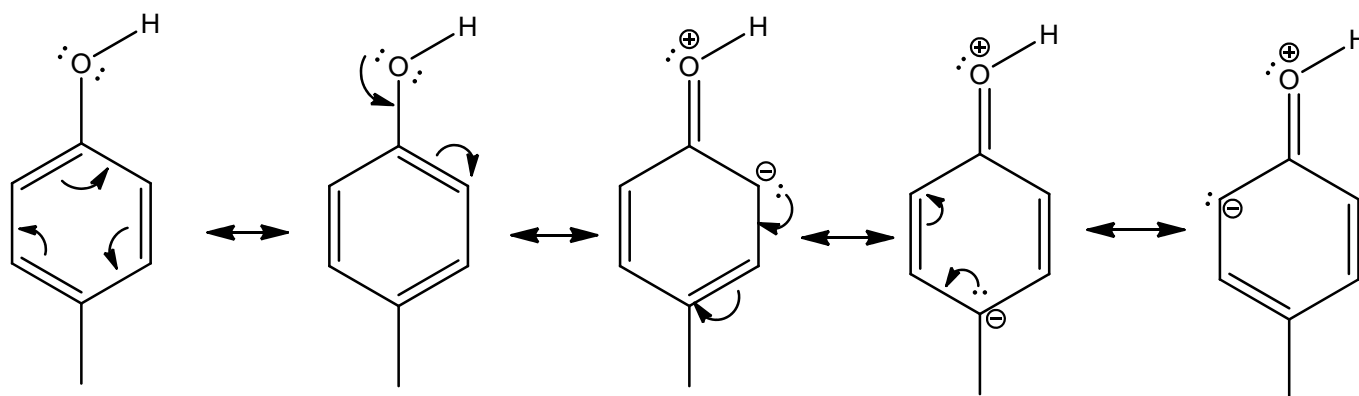
10 pts per structure. –5 for one mistake (connectivity of a listed group, wrong atom, missing double bonds), –8 for two mistakes, no credit otherwise. No deductions for missing lone pairs. OK to draw either E or Z across the double bonds.

**Closed Book Problem 2 – This Problem Will “Resonate” In Your Heart**

a)



4 pts per correct curved arrows on 1<sup>st</sup> and 2<sup>nd</sup> structures, 4 pts per correct 2<sup>nd</sup> and 3<sup>rd</sup> structures. No credit for structures without lone pairs or formal charges. OK if in a different order than presented above. -2 per additional incorrect structures (max overall deductions -16 pts)



4 pts per correct curved arrows on 1<sup>st</sup>–4<sup>th</sup> structures, 4 pts per correct 2<sup>nd</sup>–5<sup>th</sup> structures. No credit for structures without lone pairs or formal charges. OK if in a different order than presented above, particularly that you can get to all of the structures without needing to shift all of the double bonds. -2 per additional incorrect structures (max overall deductions -32 pts)

b) You cannot separate the three “molecules”. A real molecule is a “hybrid” of the resonance structures, not each one individually at different times. Resonance structures do not represent states of a molecule; they simply give us an approximation of the distribution of charges and bonds.

(4 pts cannot separate, 8 pts for any reasonable definition/description of resonance)

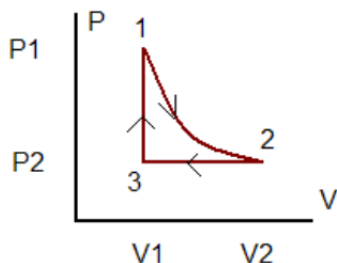
c) These are not valid resonance structures, because a hydrogen atom would have to move from the second carbon to the third.

(5 pts for not valid, 5 pts for anything related to different connectivity)

**Closed Book Problem 3 – A Three Step Engine**

a)

The pV diagram would look like:



(5 pts for correct diagram)

Consider each path separately. The equations that we need are

$$\Delta U = nc_v \Delta T \quad (\text{any ideal gas})$$

$$w = \int -pdV$$

$$q_{\text{isotherm}} = -w$$

$$q_{\text{isobar}} = nc_p \Delta T$$

$$q_{\text{isochore}} = nc_v \Delta T$$

$$c_p = c_v + R \quad (\text{any ideal gas})$$

Along the isotherm (1-2):

$$q_{12} = nRT_1 \ln\left(\frac{V_2}{V_1}\right) = p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$w_{12} = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) = -p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U_{12} = 0$$

Along the isobar (2-3):

$$q_{23} = nc_p (T_3 - T_2) = \frac{c_p}{R} (p_3 V_3 - p_2 V_2) = \frac{c_p}{R} (p_2 V_1 - p_2 V_2)$$

$$w_{23} = -p_2 (V_3 - V_2) = -p_2 (V_1 - V_2)$$

$$\Delta U_{23} = nc_v (T_3 - T_2) = \frac{c_v}{R} (p_3 V_3 - p_2 V_2) = \frac{c_v}{R} (p_2 V_1 - p_2 V_2)$$

Along the isochore (3-1)

$$q_{31} = nc_v (T_1 - T_3) = \frac{c_v}{R} (p_1 V_1 - p_3 V_3) = \frac{c_v}{R} (p_1 V_1 - p_2 V_1)$$

$$w_{31} = 0$$

$$\Delta U_{31} = q_{31} = \frac{c_v}{R} (p_1 V_1 - p_2 V_1)$$

The following table summarizes the results:

Path	$q$	$w$	$\Delta U$
1–2 (isotherm)	$p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$	$-p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$	0
2–3 (isobar)	$\frac{c_p}{R}(p_2 V_1 - p_2 V_2)$	$-p_2(V_1 - V_2)$	$\frac{c_v}{R}(p_2 V_1 - p_2 V_2)$
3–1 (isochore)	$\frac{c_v}{R}(p_1 V_1 - p_2 V_1)$	0	$\frac{c_v}{R}(p_1 V_1 - p_2 V_1)$

Note that the problem statement did not specify a monatomic gas. We'll be nice and not deduct if you used a monatomic gas (see the end of part b for why). If you assumed  $c_v=3R/2$ , you would obtain the following table:

Path	$q$	$w$	$\Delta U$
1–2 (isotherm)	$p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$	$-p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$	0
2–3 (isobar)	$\frac{5}{2}(p_2 V_1 - p_2 V_2)$	$-p_2(V_1 - V_2)$	$\frac{3}{2}(p_2 V_1 - p_2 V_2)$
3–1 (isochore)	$\frac{3}{2}(p_1 V_1 - p_2 V_1)$	0	$\frac{3}{2}(p_1 V_1 - p_2 V_1)$

(5 pts per correct value. No credit for answers that contain  $p_3$ ,  $V_3$ ,  $T_1$ ,  $T_2$ , or  $T_3$ . Accept answers from either table.)

The overall  $\Delta U_{TOT}$  is (keeping in mind that  $p_1 V_1 = p_2 V_2$ )

$$\Delta U_{TOT} = 0 + \frac{c_v}{R}(p_2 V_1 - p_2 V_2) + \frac{c_v}{R}(p_1 V_1 - p_2 V_1)$$

$$\Delta U_{TOT} = 0 + \frac{c_v}{R}(p_2 V_1 - p_1 V_1) + \frac{c_v}{R}(p_1 V_1 - p_2 V_1)$$

$$\Delta U_{TOT} = 0$$

(5 pts for showing math leading to  $\Delta U_{TOT}=0$ . OK if student wrote  $3/2$  instead of  $c_v/R$ )

b) The efficiency of the engine is given by

$$\mathcal{E} = \frac{-w_{TOT}}{q_{in}} \quad (5 \text{ pts})$$

The only paths with positive  $q$  are the isotherm (1–2) and the isochore (3–1).

$$\mathcal{E} = \frac{p_1 V_1 \ln\left(\frac{V_2}{V_1}\right) + p_2(V_1 - V_2) + 0}{p_1 V_1 \ln\left(\frac{V_2}{V_1}\right) + \frac{c_v}{R} V_1(p_1 - p_2)} \quad (10 \text{ pts for correct algebraic substitution})$$

Plugging in our given values,

$$\varepsilon = \frac{(5.00 \text{ atm})(1.00 \text{ L}) \ln\left(\frac{2.00 \text{ L}}{1.00 \text{ L}}\right) + (2.50 \text{ atm})(1.00 \text{ L} - 2.00 \text{ L})}{(5.00 \text{ atm})(1.00 \text{ L}) \ln\left(\frac{2.00 \text{ L}}{1.00 \text{ L}}\right) + \frac{c_v}{R}(1.00 \text{ L})(5.00 \text{ atm} - 2.50 \text{ atm})} \quad (5 \text{ pts for substitution})$$

$$\varepsilon = \frac{3.47 \text{ L atm} - 2.50 \text{ L atm}}{3.47 \text{ L atm} + (2.50 \text{ L atm})\left(\frac{c_v}{R}\right)} = \frac{0.97 \text{ L atm}}{3.47 \text{ L atm} + (2.50 \text{ L atm})\left(\frac{c_v}{R}\right)}$$

This is as far as you can go without assuming a monatomic gas. If you did substitute  $c_v/R=3/2$ , then we'll accept your simplified answer (see below for why):

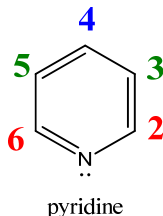
$$\varepsilon = \frac{0.97 \text{ L atm}}{7.22 \text{ L atm}} = 0.13 \quad (\text{limited to two sigfigs by the numerator})$$

(5 pts for either the algebraic expression or the numeric answer, no credit for an answer with incorrect sigfigs.)

That's not a very good engine! And if you look at the algebraic expression, the efficiency gets worse for a diatomic ( $c_v/R=5/2$ ) or a non-linear polyatomic ( $c_v/R=3$ ). This is why we didn't deduct points for assuming a monatomic gas; who in their right mind would use more complex molecule?

## Closed Book Problem 4 – Determination of Structure by IR and NMR

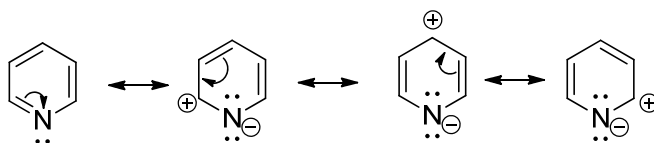
a)



Peak size: protons 2 and 6 are at  $\delta=8.50$  ppm, proton 4 is at 7.46 ppm, and protons 3 and 5 are at 7.06 ppm; grouped by equivalent protons (molecule is symmetric)

Splitting: 1) protons 2 and 6 are adjacent to 1 other proton (2 and 5 respectively) = doublet, 2) proton 4 is adjacent to 3 and 5, which are chemically equivalent = triplet, 3) proton 3 is adjacent to 2 protons that are not equivalent, same for proton 5 = multiplet

Chemical shifts:

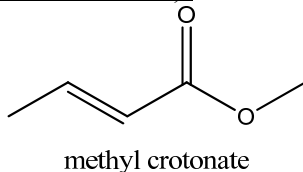


From the resonance structures we see that protons 6, 2, and 4 are more deshielded (less electron density, carry positive charge in resonance structures) than protons 3 and 5. This explains why they have a larger chemical shift. Protons 6 and 2 are more deshielded because they are directly next to the electron withdrawing nitrogen.

(10 pts for correct assignment, 5 pts for reasonable justification of areas and splitting, 5 pts for using resonance to explain the relative chemical shifts. No credit for resonance structures missing lone pairs, formal charges, or curved arrows)

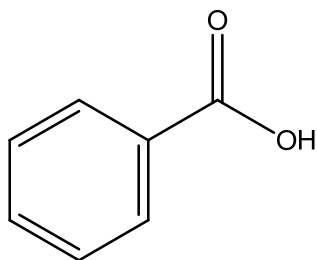
b) IR: we observe a strong peak at  $1720\text{ cm}^{-1}$ , indicative of a carbonyl group. (5 pts) We also observe a strong peak at  $1650\text{ cm}^{-1}$ , indicative of a C=C group. (5 pts) These two groups account for our two degrees of unsaturation, so our structure must be acyclic.

NMR: The relative areas of the peaks are 1:1:3:3 (6.90, 5.76, 3.67, 1.88 ppm). The peak at 1.88 ppm is a doublet with area 3, so it belongs to a  $\text{CH}_3\text{-CH}$  group. (5 pts) The peaks at 6.90 and 5.76 ppm have area 1, and have a chemical shift consistent with vinyl hydrogens. ( $\text{-CH=CH-}$ ). (5 pts) Finally, the peak at 3.67 ppm is a singlet with area 3, so it must be  $\text{CH}_3\text{-O-}$  (if it was  $\text{CH}_3\text{-(C=O)-}$ , it would appear closer to 2 ppm). (5 pts) Putting it all together, we obtain the structure of methyl crotonate (methyl 2-butenate). Shown below is the E isomer.

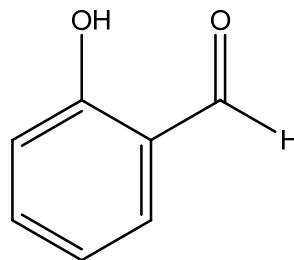


(10 pts for structure. Award full credit for any alternate reasonable justification, including if the entire structure was correctly derived from only the NMR. Accept both E and Z isomers. Award partial credit if portions of analysis are correct, but final structure is not. No need for name)

c) Consider the structures of benzoic acid and 2-hydroxybenzaldehyde:



benzoic acid



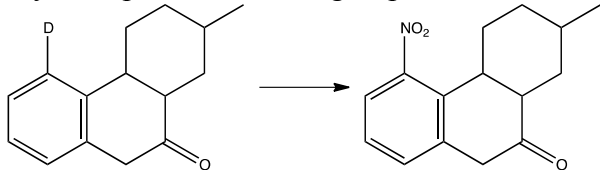
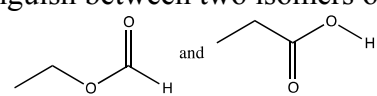
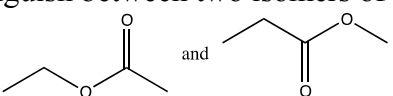
2-hydroxybenzaldehyde

NMR: The most deshielded proton will be located at  $\delta \sim 11$  ppm for an acid and  $\delta \sim 9$  ppm for an aldehyde. Additionally, 2-hydroxybenzaldehyde will exhibit an additional singlet from the  $-\text{OH}$  group in the range  $\delta \sim 3\text{--}6$  ppm, whereas benzoic acid will not. Finally, benzoic acid only has 4 distinct peaks, whereas 2-hydroxybenzaldehyde has six peaks. (5 pts for any one of these explanations)

IR: 2-hydroxybenzaldehyde will have a characteristic aldehyde  $\text{C-H}$  stretch ( $2700\text{ cm}^{-1}$ ), whereas benzoic acid will not. (Note that both molecules have an  $\text{OH}$  stretch and a  $\text{C=O}$  stretch, so those peaks cannot be used to differentiate between the two) (5 pts for aldehyde  $\text{C-H}$  stretch. -3 if aldehyde stretch is mentioned in conjunction with either the  $\text{OH}$  stretch or  $\text{C=O}$  stretch. No credit otherwise.)

## Closed Book Problem 5 – The Spectroscopy Variety Pack

a) (3.5 points per correct answer. Either answer acceptable for part e)

Scenario	Choice of Spectroscopy
(a) Lacaille 9352 is a star 10.7 light-years away and you want to know what elements are in it.	UV-Vis
(b) $\text{O}=\text{C}=\text{S}$ is a simple gaseous molecule. How do you determine its bond lengths?	ROT
(c) Designing a drug, you need to verify whether or not the following reaction actually incorporated an $\text{NO}_2$ group into the molecule: 	IR
(d) You are working on the same drug as in (c), but now you need to verify the connectivity of atoms in the molecule.	NMR
(e) You need to distinguish between two isomers of $\text{C}_3\text{H}_6\text{O}_2$ : 	IR or NMR
(f) You need to distinguish between two isomers of $\text{C}_4\text{H}_8\text{O}_2$ : 	NMR
(g) You have multiple solutions with different amounts of a protein and you need to know the exact concentrations.	UV-Vis
(h) The Grubbs group has been working hard on a Z-selective metathesis catalyst that makes long polymer chains with cis double bonds (instead of trans). How do they tell between cis and trans?	NMR

b)

$$A = \epsilon \ell c$$

$$\epsilon = \frac{A}{\ell c} = \frac{1.50}{(2.00 \text{ cm})(0.00240 \text{ M})} = 312.5 \text{ M}^{-1} \text{ cm}^{-1} \longrightarrow 313 \text{ M}^{-1} \text{ cm}^{-1}$$

(4 pts formula, 4 pts answer. No credit for an answer with incorrect sigfigs or units)

c)

$$A = -\log T = \epsilon \ell c$$

$$T = 10^{-\epsilon \ell c} = 10^{-(312.5 \text{ M}^{-1} \text{ cm}^{-1})(2.00 \text{ cm})(0.00480 \text{ M})}$$

$$T = 10^{-3.00} = 0.0010$$

(5 pts for transmittance equation, 4 pts for answer. No credit for an answer with incorrect sigfigs. While you should use  $312.5 \text{ M}^{-1} \text{ cm}^{-1}$  since it's an intermediate value, we will not deduct for using  $313 \text{ M}^{-1} \text{ cm}^{-1}$ )