

**Department of Chemistry  
Cumulative Examinations  
September 23, 2006**

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% *would not* yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains *five* examinations.

- 1) Analytical Cumulative Examination, Pages 1-2
- 2) Biochemistry Cumulative Examination, Pages 3-4
- 3) Inorganic Cumulative Examination, Pages 5-7
- 4) Organic Cumulative Examination, Pages 8-9
- 5) Physical Cumulative Examination, Pages 10-11

On your examination booklet:

- 1) Print your student ID number.
- 2) Print this Exam Booklet number: \_\_\_\_\_
- 3) Print the question number you are answering.
- 4) Print the Exam Date.

**Do not write your name anywhere on the examination booklet.** Each exam will be scored anonymously. If you attempt more than one exam, you must use a separate examination booklet for each examination.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

**PURDUE**  

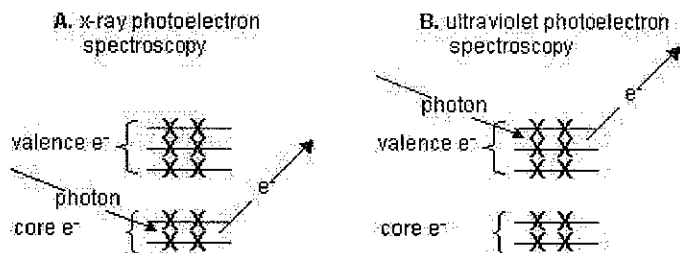
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**U N I V E R S I T Y**

Many analytical techniques rely on the interaction of light with matter. Given in the table below are the regions of the electromagnetic spectrum.

$$h = 6.63 \times 10^{-34} \text{ J sec}$$

Type	$\lambda$	Transition(s)	Example(s)
$\gamma$ -rays	$\sim < 1 \text{ pm}$	Nuclear	$\gamma + \text{nucleus} \rightarrow \text{nucleus} + e^- + e^+$
x-rays	$\sim 1 \text{ pm} - 1 \text{ nm}$	Inner electron	See A below
UV	$\sim 1 \text{ nm} - 400 \text{ nm}$	Outer electron/ ???	See B below UV Vis spectroscopy
Visible	$400 - 700 \text{ nm}$	???	UV Vis spectroscopy
Near IR	$700 - 2500 \text{ nm}$	???	
IR	$2500 - 25000 \text{ nm}$	molecular vib.	IR spectroscopy/ Raman
Microwaves	$25000 - 1000000 \text{ nm}$	molecular rot./  $e^-$ spin flips	EPR
Radio waves	$> 1000000 \text{ nm}$	???	NMR



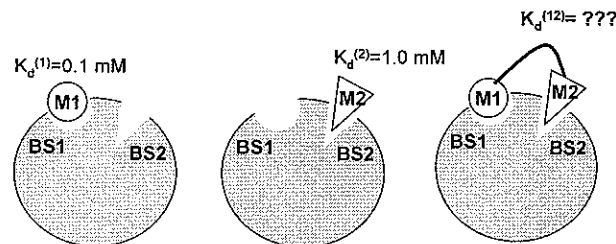
1. (10 pts.) Explain why x-ray photoelectron spectroscopy can be used for elemental analysis. (Hint: Recall that energy must be conserved).
2. (10 pts.) When you use a UV-vis spectrophotometer what transition are you interrogating? (Drawing an energy level diagram may help.)
3. (5 pts.) A molecule absorbs light at 400 nm. Determine the energy of this transition. Compare it to an energy that you know and comment.
4. (10 pts.) In a UV-vis spectrophotometer the absorbance is linearly related to three things, name them.
5. (20 pts.) Molecular vibrations and rotations are typically examined using infrared or Raman spectroscopy. Compare and contrast these two techniques.
6. (5 pts) Rotations are typically only observed in molecules in the gas phase. Why?
7. (10 pts) When you use a NMR what transition are you interrogating?
8. (30 pts) Pick two wavelength regions. For each region, give a technique that is used in that region and (a) explain how the light source in the technique works and (b) explain how the detector used in the technique works. (For many techniques there is more than one option for both the light sources and the detector, pick just one and be clear about which one you have chosen.)

## CUMULATIVE EXAMINATION IN BIOCHEMISTRY

Sep 23, 2006

It is expected that the answer should contain 1-4 succinct straight-to-the-point sentences. If you feel like elaborating, please stay within an 8 sentence limit anyway. All questions carry the same weight.

1. The Protein Databank coordinate set 1MBO shows the structure of myoglobin with an  $O_2$  molecule bound to the heme group. Close inspection of the structure reveals that there is no path available to  $O_2$  to leave myoglobin. If so, then how can myoglobin unload  $O_2$ ?
2. In order to study folding kinetics, a stopped-flow fluorescence experiment has been performed on a small protein domain. In doing so, 1 part of a denatured protein solution was rapidly mixed with 9 parts of a refolding buffer; then a fluorescence signal (mainly from a single tryptophan present in the protein) was monitored as a function of time. Predict the shape of the experimental curve (fluorescence intensity vs. time).
3. A protein sample was dissolved in  $D_2O$  and left on a bench for 10 mins. Then the sample was rapidly digested and the obtained peptide mixture was used to take a MALDI-TOF mass spectrum. The result: loop regions in the protein showed a higher level of deuteration than  $\alpha$ -helices. Why?
4. A small protein contains three tryptophan residues. In order to identify the NMR signals of these residues (specifically, three well resolved lines from indole  $^1H$ ) we rely on a site-directed mutagenesis strategy. What is the minimum number of mutants that need to be prepared in order to assign all three spectral lines?
5. Briefly describe the principle of 'western blotting' technique.
6. A protein has two binding sites, BS1 and BS2, located close to each other on the surface. Small molecule M1 binds to BS1 with dissociation constant  $K_d^{(1)}=0.1$  mM. Small molecule M2 binds to BS2 with  $K_d^{(2)} = 1.0$  mM.



We now make a construct where M1 and M2 are covalently linked through a tether

(assume that the tether is sufficiently long and flexible and does not interact with the protein). This construct, M1-M2, binds to the protein such as shown in the figure (right portion). Estimate the dissociation constant of the construct,  $K_d^{(12)}$ , and briefly describe your reasoning.

7. How many PCR cycles are needed to obtain  $\sim 10^6$ -fold DNA amplification?
8. Vectors used for bacterial expression of proteins carry genes for resistance to antibiotics (e.g. ampicillin). What is the purpose of inserting these genes there?
9. What is the difference between “native” gel and SDS gel?
10. To confirm the result of protein expression, amino acid analysis is performed. Briefly, the protein is hydrolyzed into individual amino acids, the products are run through HPLC, and the resulting chromatogram is used to determine the content of different amino acids. Write the reaction of hydrolysis of peptide bond (you do not need to specify intermediates, catalytic species, etc.).
11. What is the main difference between a conventional fluorescence microscope and a *confocal* fluorescence microscope?
12. Consider a certain protein for which both X-ray and NMR structure is available. The resolution of the X-ray structure is 1 Å. The precision of the NMR structure (backbone heavy atom rmsd) also happens to be 1 Å. Which structure is more accurate?

Part I. Lithium nitride,  $\text{Li}_3\text{N}$ , can be used as a solid electrolytes in electrochemical cells. Consider an electrochemical cell with a solid lithium electrode, a solid lithium nitride electrolyte, and a solid  $\text{CoO}_2$  electrode.

1. Sketch such an electrochemical cell and indicate the cathode and anode as the cell produces an electric current.
2. Write the half cell reactions that occur as the cell produces an electric current. Label the anode reaction and the cathode reaction.
3. Describe the role of the lithium nitride electrolyte and how it functions.

Part II. A compound resulting from the reaction of lithium nitride and lithium chloride has been considered for use as a solid electrolyte.

4. The compound of lithium, nitrogen, and chlorine is analyzed and found to contain 18.0 percent nitrogen and 45.87 percent chlorine. Use these percentages and determine the empirical formula of this compound. (At Wt: Li, 6.94; N, 14.01; Cl, 35.45)

Part III. A compound prepared from the reaction of lithium nitride with lithium chloride crystallizes in a hexagonal rhombohedral unit cell with  $a_0 = 366$  pm and  $c_0 = 1977$  pm, space group  $R\bar{3}m$ , #166. The atom positions are

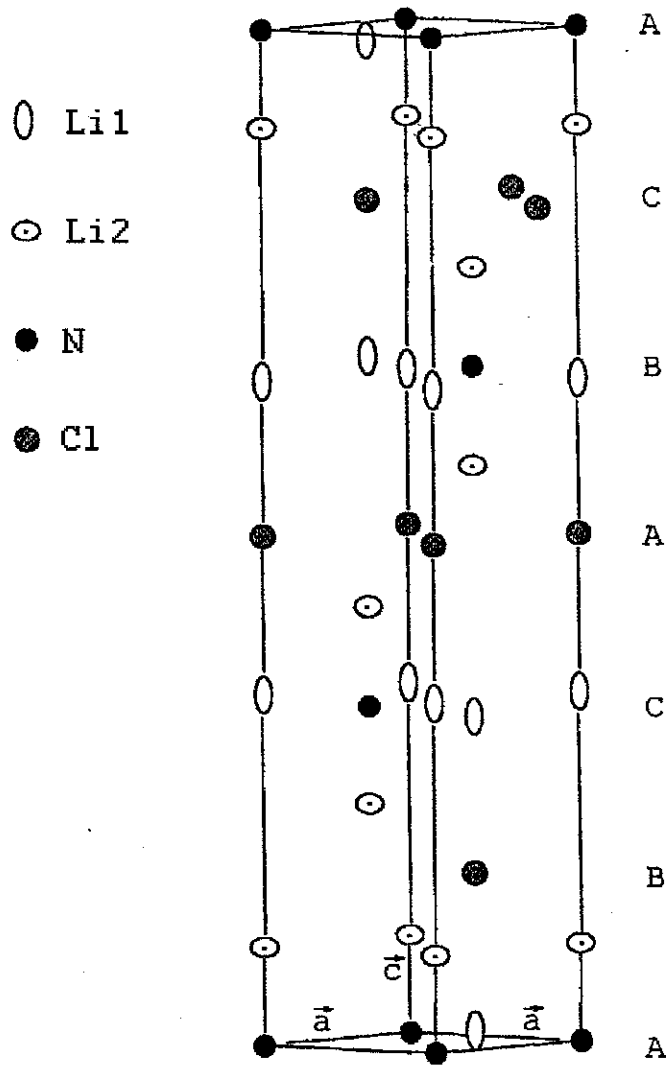
	x/a	y/b	z/c
Li(1)	0	0	0.6547
Li(2)	0	0	0.0970
N	0	0	0
Cl	0	0	0.5

A sketch the unit cell contents and a copy of the space group information is attached..

5. Count the number of atoms of each type in a unit cell. Could this be the same compound described in Part II? Explain your reasoning.
6. Calculate the shortest Li-Cl and Li-N distances parallel to the c axis of the unit cell. Using these distances and your knowledge of ionic size, which is the larger ion, the lithium ion, the chloride ion, or the nitride ion? Explain your reasoning.

Part IV. Lithium nitrides react with water.

7. Write the ionic equation for the reaction of lithium nitride with water
8. Write the ionic equation for the reaction of the compound described in Part II with water.
9. A 0.500 g sample of lithium nitride is added to enough water to give 750. mL of solution.
  - A. What is the concentration of hydroxide ion in the solution? Show calculations.
  - B. What is the ammonium ion concentration in the solution? Show calculations. (At. Wts.: H, 1.008; Li, 6.94; N, 14.01; O, 16.00)  $K_b$  for  $\text{NH}_3 = 1.8 \times 10^{-5}$



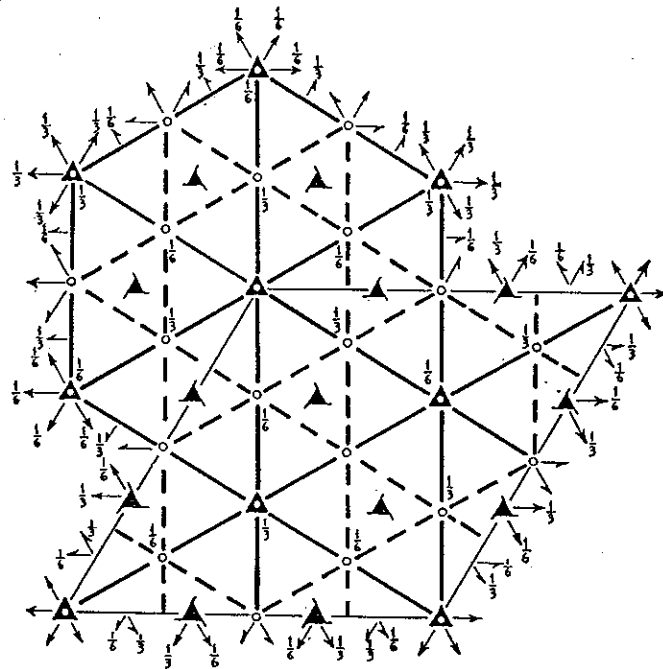
Unit Cell from Part III

Trigonal  $\bar{3}m$

$R\bar{3}2/m$

No. 166

$R\bar{3}m$   
 $D_{3d}^5$   
 (continued)



Origin at centre ( $\bar{3}m$ )

Number of positions,  
 Wyckoff notation,  
 and point symmetry

Co-ordinates of equivalent positions

Conditions limiting  
 possible reflections

(2) HEXAGONAL AXES:

$$(0,0,0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}) +$$

General:

$$hkl: -h+k+l=3n$$

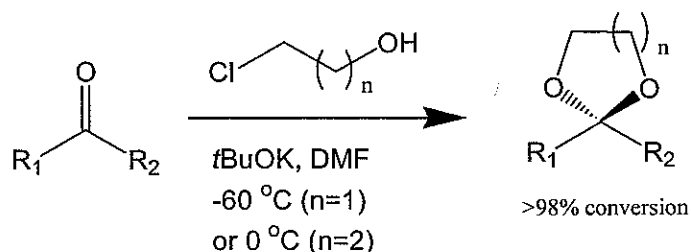
$$hh2\bar{h}l: (l=3n)$$

$$h\bar{h}0l: (h+l=3n)$$

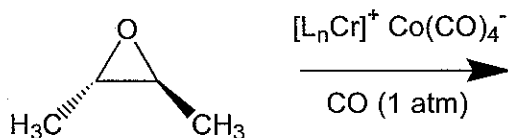
Special: as above only

36	<i>i</i>	1	$x, y, z; \bar{y}, x-y, z; y-x, \bar{x}, z;$ $\bar{x}, \bar{y}, \bar{z}; y, y-x, \bar{z}; x-y, x, \bar{z};$ $\bar{y}, \bar{x}, z; x, x-y, z; y-x, y, z;$ $y, x, \bar{z}; \bar{x}, y-x, \bar{z}; x-y, \bar{y}, \bar{z}.$
18	<i>h</i>	<i>m</i>	$x, \bar{x}, z; x, 2x, z; 2\bar{x}, \bar{x}, z;$ $\bar{x}, x, \bar{z}; \bar{x}, 2\bar{x}, \bar{z}; 2x, x, \bar{z}.$
18	<i>g</i>	2	$x, 0, \frac{1}{2}; 0, x, \frac{1}{2}; \bar{x}, \bar{x}, \frac{1}{2}; \bar{x}, 0, \frac{1}{2}; 0, \bar{x}, \frac{1}{2}; x, x, \frac{1}{2}.$
18	<i>f</i>	2	$x, 0, 0; 0, x, 0; \bar{x}, \bar{x}, 0; \bar{x}, 0, 0; 0, \bar{x}, 0; x, x, 0.$
9	<i>e</i>	$2/m$	$\frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, 0.$
9	<i>d</i>	$2/m$	$\frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$
6	<i>c</i>	$3m$	$0, 0, z; 0, 0, \bar{z}.$
3	<i>b</i>	$\bar{3}m$	$0, 0, \frac{1}{2}.$
3	<i>a</i>	$\bar{3}m$	$0, 0, 0.$

1. (25 pts.) Aldehydes and ketones are usually converted into acetals under acidic conditions. Barbasiewicz and Małkosza have developed a useful alternative for preparing cyclic acetals using basic conditions (*Org. Lett.* **2006**, *8*, 3745-48).

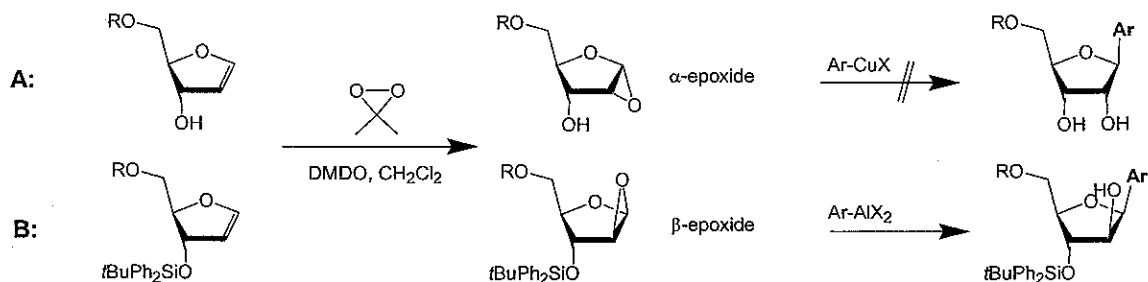


- a) Propose a mechanism for this transformation.
- b) In the experimental procedure, *t*BuOK is added last (and slowly) to the reaction mixture. Why?
- c) The formation of 5-membered cyclic acetals (1,3-dioxolanes) requires 1.5 equiv of chloroethanol at  $-60\text{ }^\circ\text{C}$  for efficient conversion, whereas the formation of 6-membered cyclic acetals (1,3-dioxanes) only requires 1.05 equiv. of 1,3-chloropropanol and can be performed at  $0\text{ }^\circ\text{C}$ , making the latter more tractable for scaleup. Provide reason(s) for the difference in reaction conditions.
2. (30 pts.) Coates and coworkers have developed a bimetallic Cr-Co ionic complex which can catalyze the formation of  $\beta$ -lactones from epoxides and CO in very high yields (*Org. Lett.* **2006**, *8*, 3709-12). The reaction is remarkable because the CO insertion can be performed at atmospheric pressure (1 atm). The reaction proceeds with inversion of configuration of one stereocenter, which becomes the  $\alpha$ -carbon of the  $\beta$ -lactone.



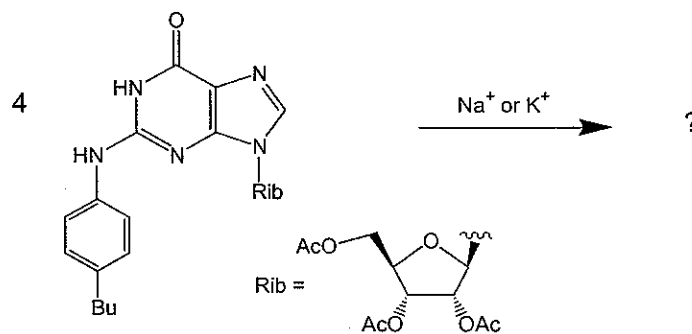
- a) Draw the expected product of this reaction.
- b) A ketone is produced as a minor product of the reaction above, with the same MW as the starting material. What is its structure?
- c) Propose a reaction mechanism with a catalytic cycle that can generate the products in (a) and (b).  
*Hint:*  $\text{Co(CO)}_4^-$  is a good nucleophile.

3. (20 pts.) In their efforts to make unnatural *C*-nucleosides, Singh and Seitz have developed a methodology from furanoid glycols (*Org. Lett.* **2006**, *8*, 4319-22). These compounds were stereoselectively epoxidized by dimethyl dioxirane (DMDO), followed by addition of organometallic reagents:



- (a) Provide a reasonable explanation for the stereoselective epoxidations in reactions **A** and **B**.
- (b) The organocuprate addition in reaction **A** failed, whereas the organoaluminum addition in reaction **B** produced the  $\beta$ -*C*-aryl furanoside in high yield and stereoselectivity. Give an explanation for each of these reaction outcomes.

4. (25 pts.) Liu *et al.* have synthesized a triacetylated guanosine derivative with an aryl substituent at N2 (*Org. Lett.* **2006**, *8*, 3685-88). When exposed to  $\text{Na}^+$  or  $\text{K}^+$ , four of these molecules can self-assemble into a planar, hydrogen-bonded tetramer known as a *G-quartet* (the metal ion acts as a template). Draw the  $C_4$ -symmetric *G*-quartet.



# Physical Chemistry Cumulative Exam

September 23, 2006

**Part 1:** Having a firm grasp of energy conversion factors and fundamental molecular properties is important. Sometimes it is necessary to do “back of the envelope” calculations (For instance: when you’re stuck at Shoney’s with your in-laws) to get a rough idea of signal-to-noise, or to just sound intelligent at a seminar or conference. Answer each of the following questions, they are worth two points apiece. Please write legibly, if I can’t read it it’s wrong.

- 1.) What is  $kT$  at room temperature? in kcal/mol?
- 2.) What is the  $H_2$  bond energy in kJ/mol and kcal/mol?
- 3.) How many  $cm^{-1}$  in 1 eV?
- 4.) How many  $cm^{-1}$  in 1 kcal/mol?
- 5.) How many molecules in 1 torr?
- 6.) How many GHz in 1  $cm^{-1}$ ?
- 7.) Is the absorption coefficient bigger for an IR transition or UV transition?
- 8.) What is a typical UV fluorescence lifetime? IR fluorescence lifetime?
- 9.) What is a typical rotational period for a diatomic? For a bigger molecule?
- 10.) What is a typical vibrational period for torsional motion? For stretching motion?

**Part 2:** The following questions deal with spectroscopic techniques. Answer each of the following questions.

- (2 pts) 1.) Draw the electromagnetic spectrum (Make sure you label the x-axis)
- (10 pts) 2.) Show where the following techniques are used in the EM spectrum: EPR, Electronic spectroscopy, NMR, Vibrational spectroscopy, Rotational spectroscopy.
- (10 pts) 3.) What are the expected natural excited state lifetimes for each of these measurements?
- (5 pts) 4.) Based on your answer above, what is the natural linewidth for each measurement?
- (6 pts) 5.) List at least one intramolecular mechanism that will shorten the excited state lifetime for the following processes. State explicitly the physical process responsible.
- a. Infrared excitation
  - b. Electronic excitation
- What effect does this shortening have on the lineshape? Do you need to worry about these processes in techniques at the low frequency end of the EM spectrum? Why or why not?
- (10 pts) 6.) List at least three mechanisms that will lead to broadened lineshapes that are caused by experimental conditions (not necessarily molecular processes). Propose experimental conditions that will minimize each effect.

**Part 3:** The following questions deal with the time-energy relationship in spectroscopy. Answer each of the following questions.

- (4 pts) 1.) What is the difference between  $T_1$  and  $T_2$  when used in spectroscopic jargon?
- (4 pts) 2.) Two peaks are separated in the frequency domain by  $10 \text{ cm}^{-1}$ . If these peaks are anharmonically coupled what is the lifetime of the bright state?
- (5 pts) 3.) What requirements or constraints would need to be imposed on the excitation source in order to coherently prepare these two levels? Fundamentally (i.e. quantum mechanically) what does it mean when we talk about coherence in spectroscopy?
- (6 pts) 4.) Assume the two levels above are coherently prepared, sketch the following (label the axes):
- The evolution of the bright state in time when  $T_1 \gg T_2$
  - The evolution of the dark state in time when  $T_1 \gg T_2$
  - The evolution of the bright state in time when  $T_1 = 3 * T_2$
- (8 pts) 5.) Does the rotation of the molecule influence how you drew the sketches from #4? Why or why not?
- (10 pts) 6.) Assume the measurement is performed in a dilute gas (1 torr) at room temperature. Do you expect collisions to be important i.e. do you expect them to influence the results, why or why not? If collisions were important how would that change the sketch of 10a?

