

CHEM 3311
Dr. Minger

Hour Exam #2
June 21, 2022

Name Key
PRINT CLEARLY

Put a check by your recitation section:

- 111 Charlie
- 112 Joy
- 113 Alan
- 114 Claire
- 115 Garrett

Sign the Honor Code pledge:

I pledge that on my honor, as a University of Colorado at Boulder student, I have neither given nor received unauthorized assistance on this exam.

Signature

**Instructions and a periodic table are on the other side of this page.
Please read the instructions carefully!**

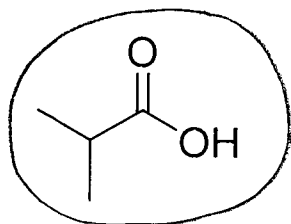
hydrogen 1 H 1.008																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.887	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	seelenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	* 57-70	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	* * 89-102	lanthanum 57 La [138.91]	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04							
			actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]							

* Lanthanide series

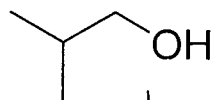
** Actinide series

General Instructions: There are 10 questions plus one extra credit question for a total of 11 questions (some have multiple parts). Be sure you have them all. Read each question carefully so that you know exactly what is being asked and what you need to write or draw. **DO NOT USE COLORED INK.** (You can use highlighters.) Your work on scratch pages will not be graded, so be sure everything you want graded is written on the exam itself and in the spaces provided for answers.

1. Circle the stronger acid. (Lone pairs are omitted; all atoms are neutral.) (5 pts)

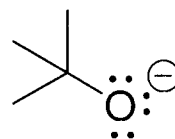
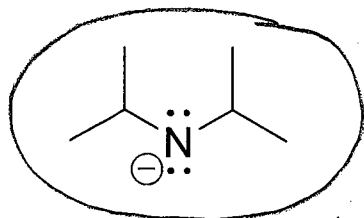


pKa 4-5



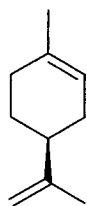
pKa 15-18

2. Circle the stronger base. (Lone pairs and charges are shown; counter ions have been omitted for clarity.) (5 pts)

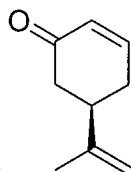


N is less electronegative than O - its e⁻ are more available for bonding

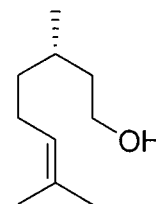
3. Determine the absolute configuration of the asymmetric carbon in each molecule. Write your answer in the box below each structure. (9 pts)



S

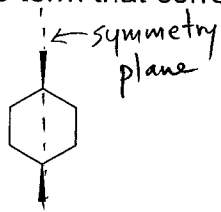


R



S

4. Circle the term that correctly describes each structure. (18 pts)

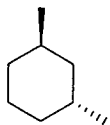


Chiral

Achiral

Achiral & meso

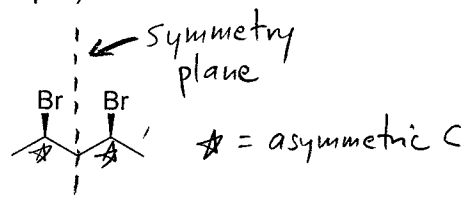
(no asymmetric C's)



Chiral

Achiral

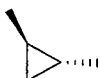
Achiral & meso



Chiral

Achiral

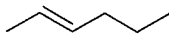
Achiral & meso



Chiral

Achiral

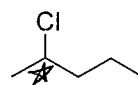
Achiral & meso



Chiral

Achiral

Achiral & meso



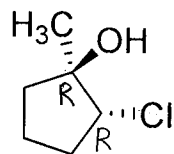
Chiral

Achiral

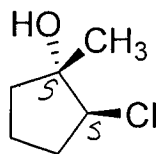
Achiral & meso

Has one asymmetric C; thus this constitution represents a chiral molecule (or racemic mixture)

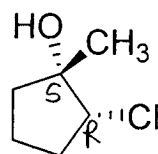
5. Circle the term that correctly describes the relationship between each pair of structures. (9 pts)



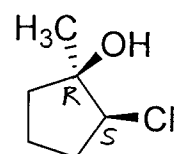
A



B



C



D

A and B	<u>enantiomers</u>	diastereomers	identical
B and C	enantiomers	<u>diastereomers</u>	identical
C and D	<u>enantiomers</u>	diastereomers	identical

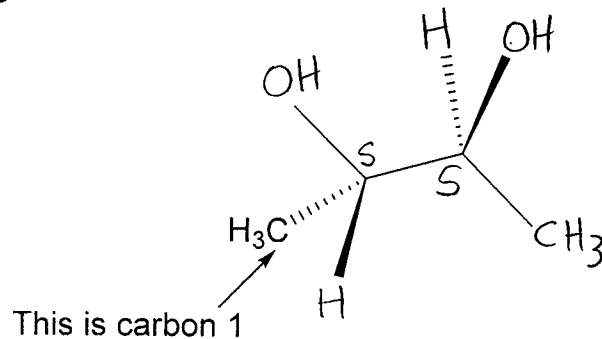
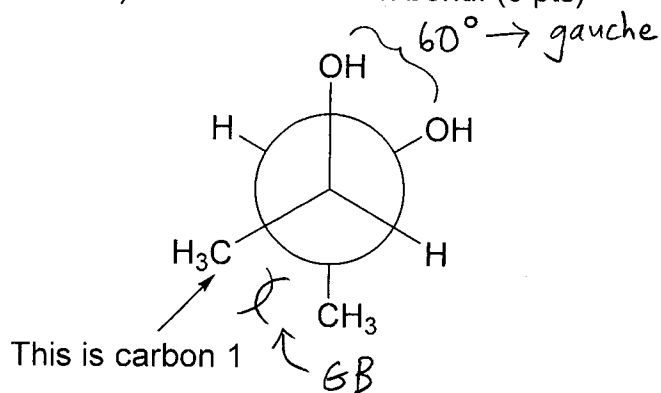
6. In structure A, what is the relationship (torsion angle) between the OH and the Cl? Circle your response. (3 pts)

Eclipsed

Gauche

Anti

- 7a. On the left is a Newman projection of one of the staggered conformations of 2,3-butanediol. Convert the Newman projection on the left to a wedge-and-dash ("perspective") drawing by writing the correct atom or group labels (e.g. H, CH₃, OH) at the end of each bond. (5 pts)



- 7b. Circle the term that correctly describes this molecule (2 pts):

Chiral

Achiral

Achiral & meso

- 7c. Circle the term that correctly describes the torsion angle between the two OH groups in this conformation (2 pts):

Anti

Eclipsed

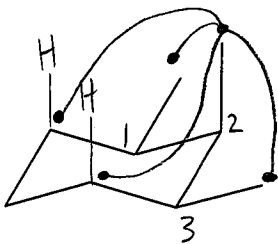
Gauche

- 7d. How many gauche butane interactions are present in this conformation? Write the number here (2 pts):

1

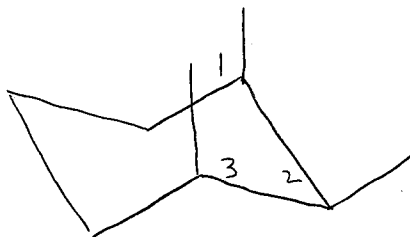
8. (10 pts for the following two questions)

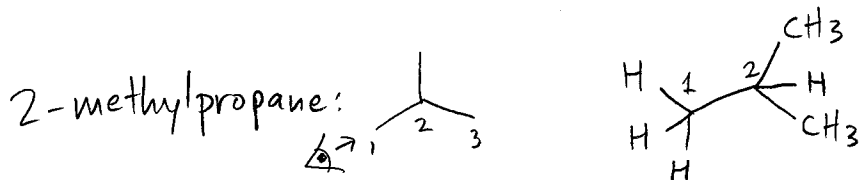
8a. How many gauche butane interactions exist in this chair? Circle your answer.



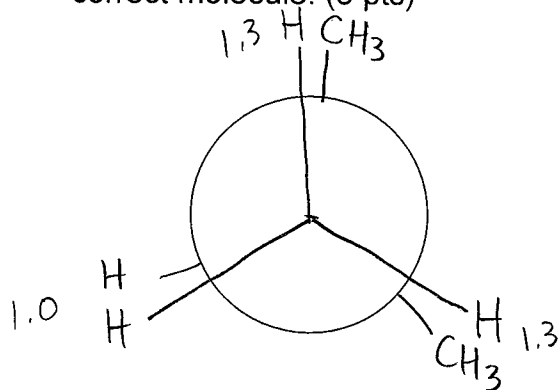
circle one: 0 1 2 3 4 5

8b. Draw the ring flip (the other chair conformation) of the molecule in 8a. Don't draw the hydrogens attached to the ring, just draw the three methyl groups. Be sure your chair is drawn properly according to the instructions given in class.



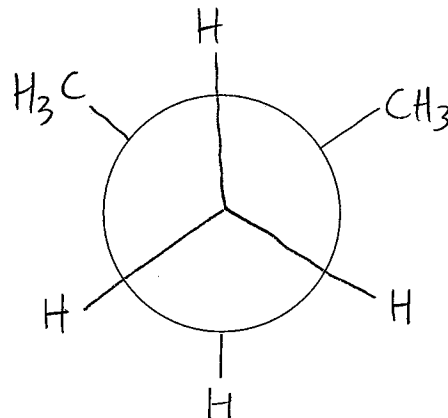


- 9a. Draw the least stable and most stable conformations of 2-methylpropane looking down the C1-C2 bond. Use the templates provided. Be sure you are drawing the correct molecule! (8 pts)



LEAST STABLE

$$\text{total strain } E = 3.6 \text{ kcal/mol}$$



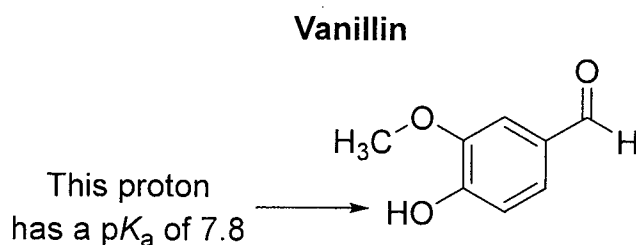
MOST STABLE

$$\text{no strain} \rightarrow 0 \text{ kcal/mol}$$

- 9b. Calculate the barrier to rotation, in kcal/mol, around the C1-C2 bond in 2-methylpropane (see #9a!). A table of strain energies is provided for you. (Me = Methyl) (3 pts)

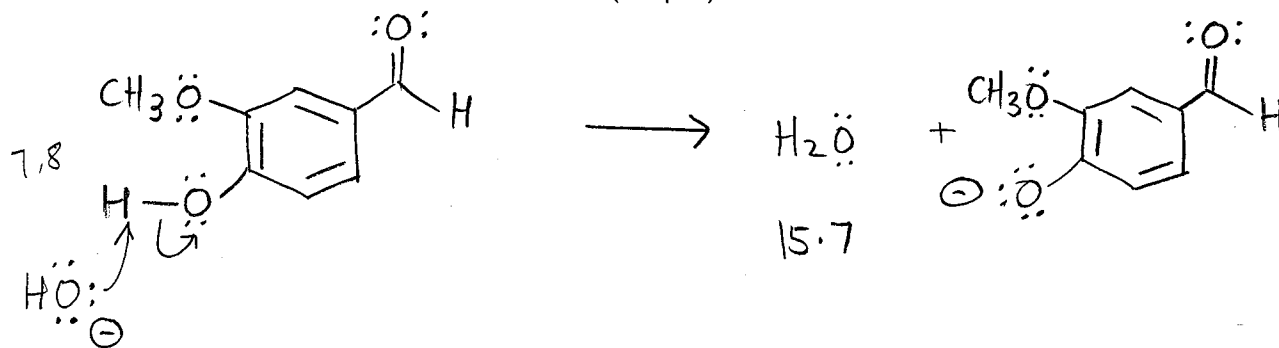
Interaction	Energy (kcal/mol)	Barrier to rotation = $3.6 - 0 = 3.6 \text{ kcal/mol}$
Me-Me gauche ("gauche butane interaction")	0.8	
H-H eclipse	1.0	
Me-H eclipse	1.3	
Me-Me eclipse	4.0	

10. A compound called vanillin is one of the major components of the extract of vanilla beans:

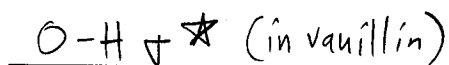


In the structure above, all atoms are neutral but lone pairs are not explicitly drawn.

- a. Using hydroxide ion as the Bronsted base, draw a mechanism to show the deprotonation of the OH group in vanillin. Include all necessary curved arrows, lone pair electrons and nonzero formal charges. Draw the products of the proton transfer reaction. You will need to redraw the structure of vanillin. (10 pts)



- b. Identify the orbital that is the LUMO in this reaction (3 pts):



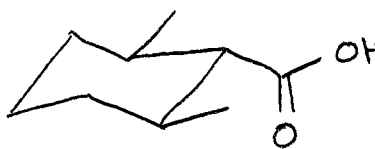
- c. Estimate the equilibrium constant for the proton transfer you drew in part "a" (3 pts):

$$K \approx 10^{(15.7 - 7.8)} \approx 10^{(16 - 8)} \approx 10^8$$

- c. Vanillin is an example of a phenolic compound. ("Phenol" is a term that describes a benzene ring with an OH group attached.) Which of the six factors that we discussed in class is responsible for the stabilization of the conjugate base of vanillin? (One or two words only; no explanation needed) (3 pts)

Resonance

- No GB interactions
 - Has a pKa ≈ 4



- Achiral & meso

11. **Extra credit.** World-famous pigeon chemist Professor Burblecoo, working with his research group, has been studying the properties of a mysterious Bronsted acid called "breadcrumb acid", which is a solid at room temperature.

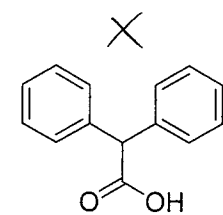
Unfortunately, the pigeon chemists in Prof. Burblecoo's research lab confuse "breadcrumb acid" with actual bread crumbs, and so supplies of this acid are generally gobbled up by the researchers before any experiments can happen. Fortunately, a different research group (one that does not have pigeon chemists) has determined the following information about breadcrumb acid:



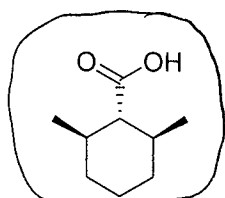
Professor Burblecoo (seated on assistant professor's head) with several research associates, discussing the properties of "breadcrumb acid"

- When breadcrumb acid is deprotonated by hydroxide ion, the equilibrium constant for the proton transfer is about 10^{12} .
 Allows us to estimate its pKa (see below)
- The most stable conformation of breadcrumb acid is a chair conformation.
 Structure must contain cyclohexane
- The LUMO of breadcrumb acid is an O-H σ^* orbital. Could be an alcohol or carboxylic acid
- A pure sample of breadcrumb acid does not rotate plane polarized light.
 → So it's achiral or achiral and meso
- The most stable conformation of breadcrumb acid does not have any gauche butane interactions, though steric strain is present.

Based on these statements, circle the structure that is **most likely** to be breadcrumb acid. (5 pts)

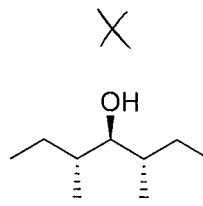
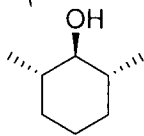


lacks , so no chairs

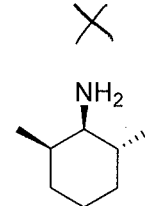


See top of page

pKa $\approx 15-18$



not so no chair



chiral

