UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

Version

01

November 2nd, 2022 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.

ENTER **VERSION NUMBER 01** ON THE **COMPUTER ANSWER SHEET**

The examination consists of Parts 1 - 7, each of which should be attempted. Note that some parts provide you with a choice of questions, *e.g*. answer 4 out of 5. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. Parts 1 - 4 will be computer graded, and only Parts 5, 6, and 7 are to be answered in the blue booklet provided.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 31 which are to be answered on your computer answer sheet (no extra time is provided for "bubbling" in the score sheet). Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a ***pencil only*** and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***. **Absolutely no other electronic devices are allowed.**

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14% PART 1: RELATIVE PROPERTIES

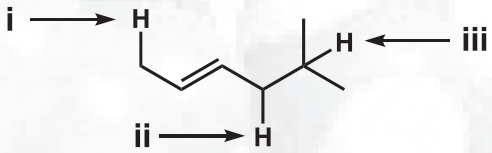
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most etc. first) with respect to the indicated property.

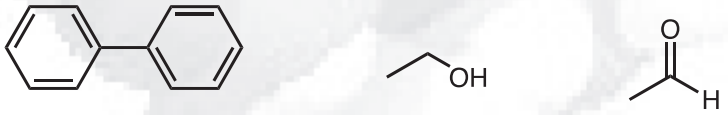
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

1. The strengths of the **C-H** bonds indicated below:

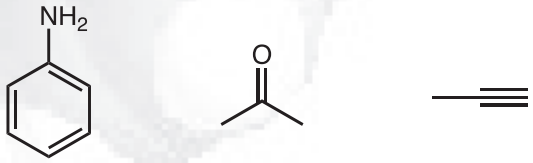


2. The boiling point for each of the compounds shown below:



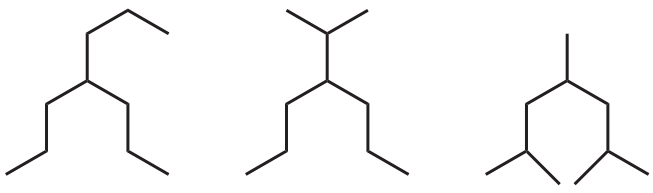
i **ii** **iii**

3. The relative acidities of each of the following:



i **ii** **iii**

4. The relative stability of each of the following isomers:

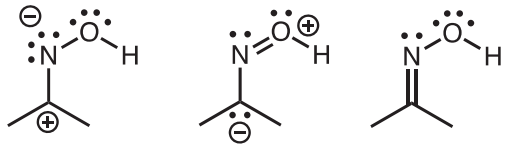


i **ii** **iii**

Use the following code to indicate your answers.

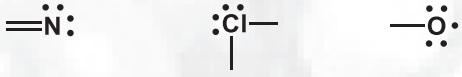
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

5. The relative importance of the following resonance contributors:



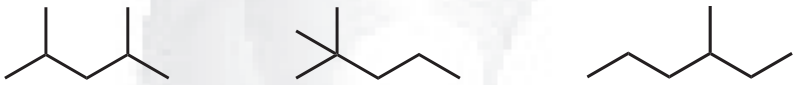
i **ii** **iii**

6. The formal charge on each of the atoms indicated in bold from most positive to negative (all electrons are shown):



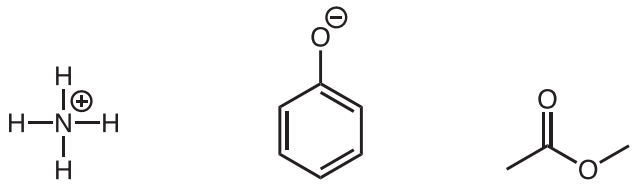
i **ii** **iii**

7. The number of different monochlorinated constitutional isomers formed by the reaction of each of the following molecules with chlorine in the presence of uv light.



i **ii** **iii**

8. The relative basicity of the following:



i **ii** **iii**

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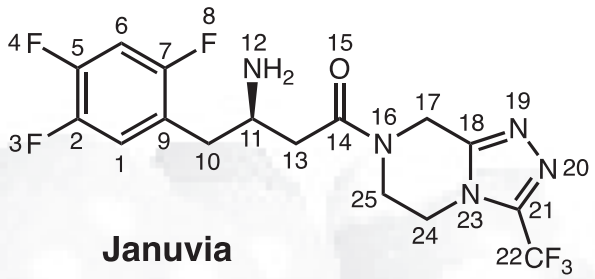
18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 9 – 17

For each of the questions 9 - 17 select the appropriate answer(s) from the answers provided. In some cases more than one selection may be required for full credit.

Questions 9-17 all refer to Januvia, a treatment for type II diabetes (structure shown below):



Januvia

9. Which atom is the most basic?

A. N19 **B.** O15 **C.** N23 **D.** F8 **E.** N12

10. Which bond is the strongest?

A. C5-F4 **B.** C6-C7 **C.** C14-O15 **D.** C14-N16 **E.** C24-C25

11. What are the hybridisations of **N16** and **N23** respectively?

A. sp^2, sp^2 **B.** sp^3, sp^2 **C.** sp^3, sp^3 **D.** sp^2, sp **E.** sp^2, sp^3

12. What is the IHD of Januvia?

A. 6 **B.** 7 **C.** 8 **D.** 9 **E.** 10

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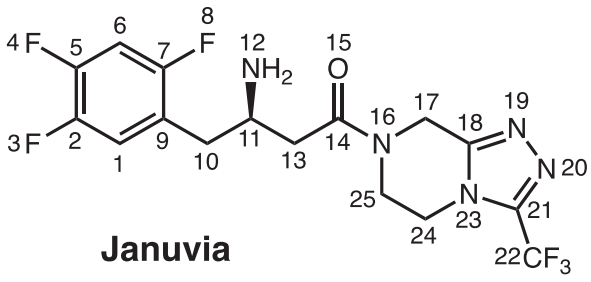

Januvia

13. The lone pair on N19 is found in what type of orbital**?**

A. s **B.** p **C.** sp **D.** sp^2 **E.** sp^3

14. Which of the following functional groups are found in Januvia?

A. amine **B.** alkyne **C.** ketone **D**. ether **E**. arene

15. Which of the following term(s) apply to the C-H bonds found at C10?

A. allylic **B.** primary **C.** secondary **D.** tertiary **E.** benzylic

16. Which of the following properly described the configuration of Januvia

A. R **B.** S **C.** R, R **D.** S, S **E.** None apply

17. Which value is closest to the C11-C13-C14 bond angle?

A. 60º **B.** 90º **C.** 109.5º **D.** 120º **E.** 180º

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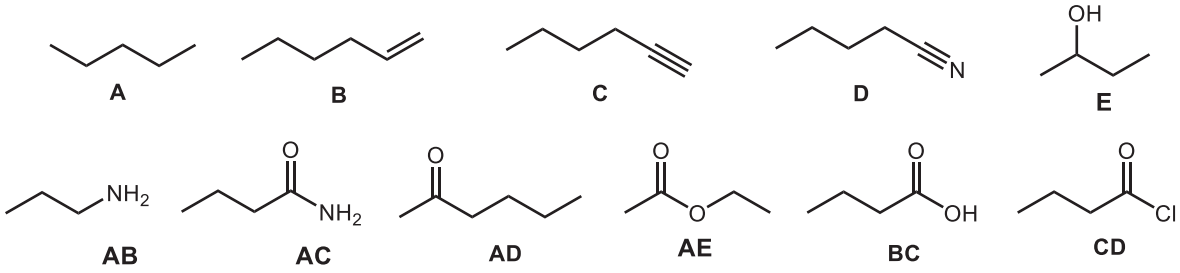
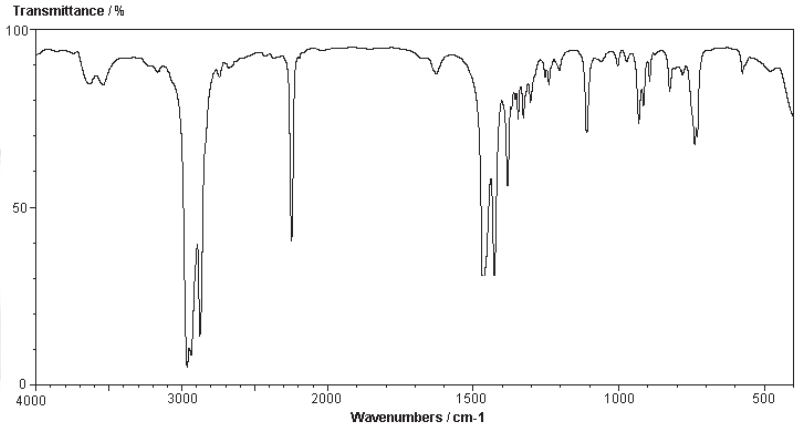
15% **PART 3: SPECTROSCOPY**

ANSWER ALL SIX (6) OF QUESTIONS 18 – 23 (2.5 marks per question).

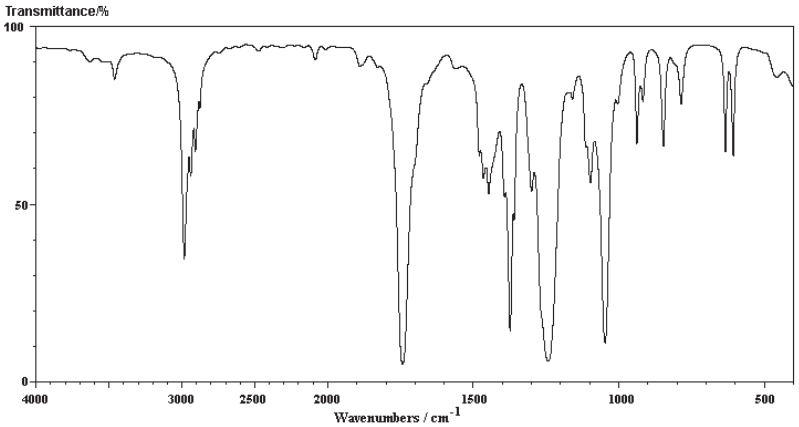
For each of the questions 18-23, match the IR spectra to a structure in the list below:



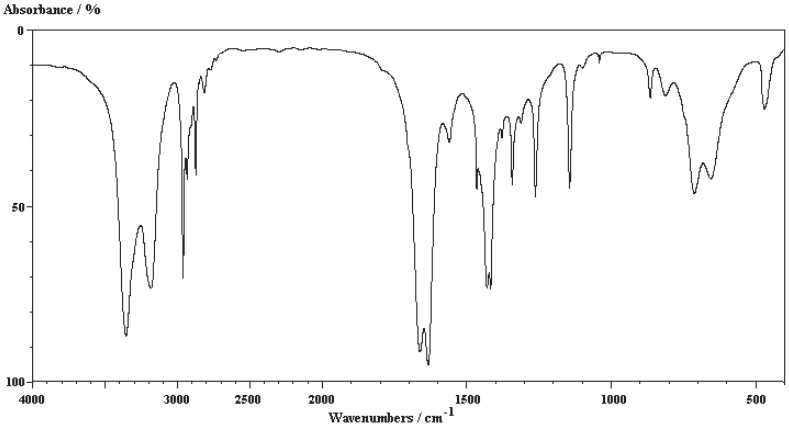
18.

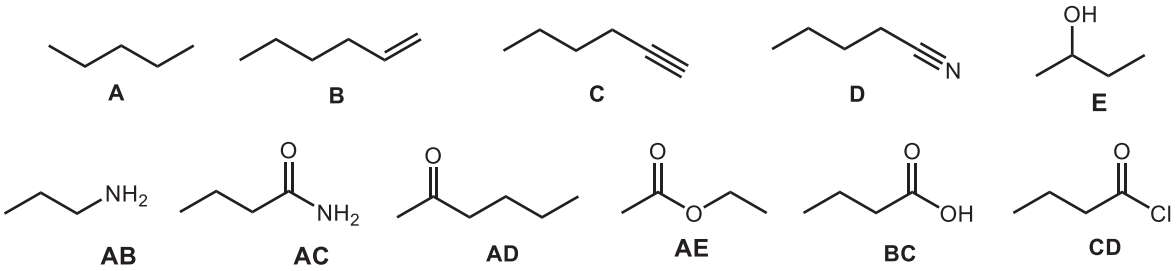


19.

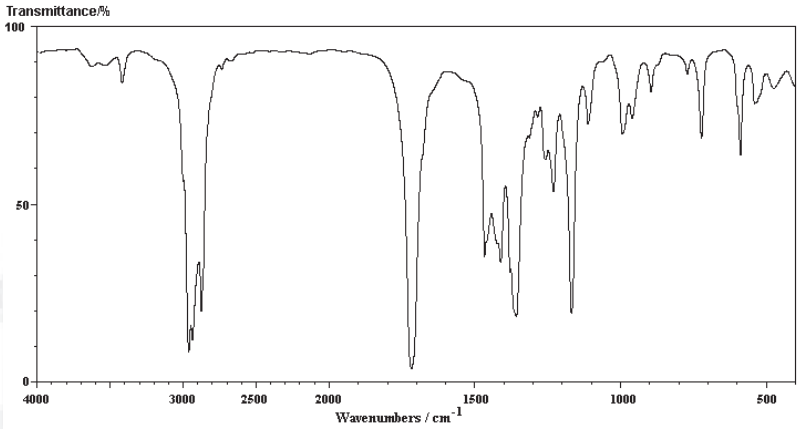


20.

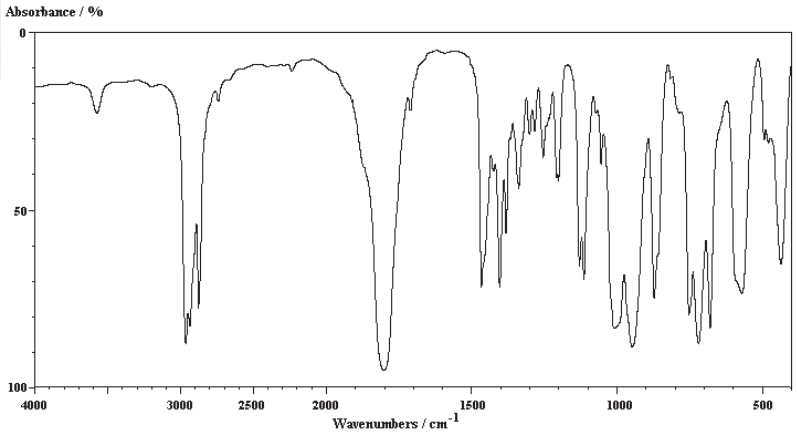



A
B
C
D
OH
N
E
NH2
AB
O
NH2
AC
O
AD
O
O
AE
O
OH
BC
O
Cl
CD

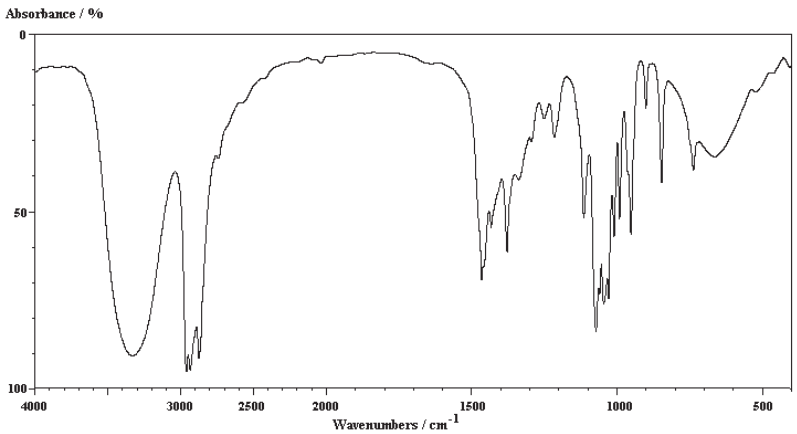
21.


Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

22.


Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

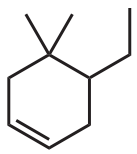
23.


Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

14% PART 4: NOMENCLATURE

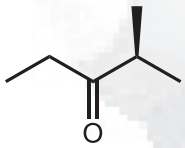
ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question). For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



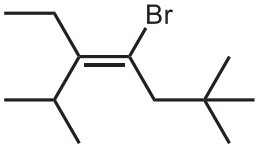
A. 1,1-dimethyl-2-ethylcyclohex-4-ene
B. 2-ethyl-1,1-dimethylcyclohex-4-ene
C. 4-ethyl-5,5-dimethylcyclohex-1-ene
D. 5-ethyl-4,4-dimethylcyclohexene
E. 4-ethyl-3,3-dimethylcyclohexene
AB. 4,4-dimethyl-3-ethylcyclohex-1-ene

25.



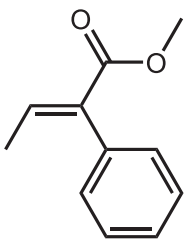
A. (R)-2-methylpentan-3-one
B. (S)-2-methylpentan-3-one
C. (R)-4-methylpentan-3-one
D. (S)-4-methylpentan-3-one
E. 4-methylpentan-3-one
AB. 2-methylpentan-3-one

26.



A. (E)-4-bromo-5-ethyl-2,2,6-trimethylhept-4-ene
B. (Z)-4-bromo-5-ethyl-2,2,6-trimethylhept-4-ene
C. (Z)-4-bromo-3-ethyl-2,6,6,6-tetramethylhex-3-ene
D. (E)-4-bromo-3-ethyl-2,6,6,6-tetramethylhex-3-ene
E. (E)-4-bromo-3-ethyl-2,6,6-trimethylhept-3-ene
AB. (Z)-4-bromo-3-ethyl-2,6,6-trimethylhept-3-ene

27.



A. methyl *cis* 4-phenylhex-2-enoate
B. methyl *trans* 2-phenylbut-2-enoate
C. methyl *cis* 2-phenylbut-2-enoate
D. methyl 2-phenylbut-2-enoate
E. methyl *trans* 3-phenylbutenoate
AB. methyl *cis* 3-phenylbutenoate

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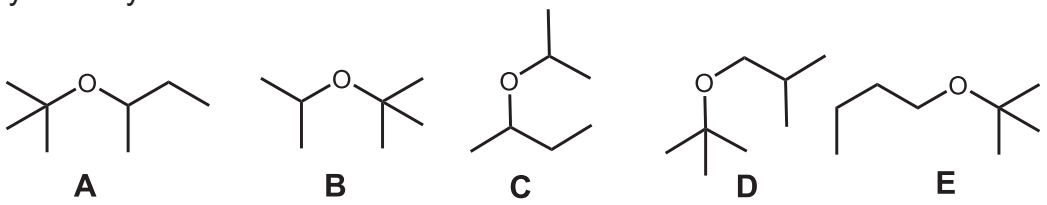
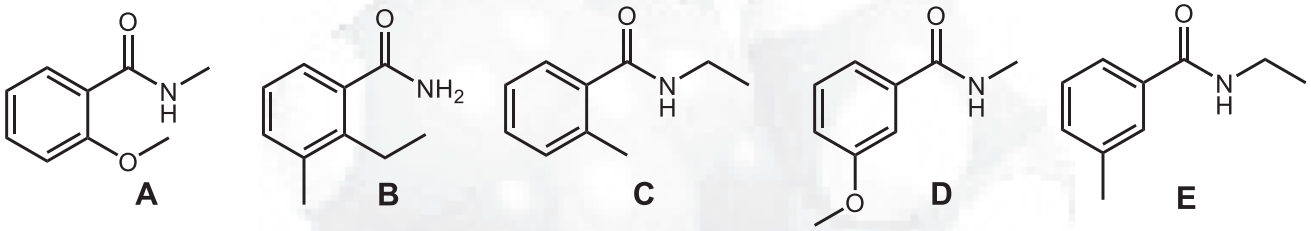
ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question). For each of questions 28 to 31, select the correct structure for the name provided:

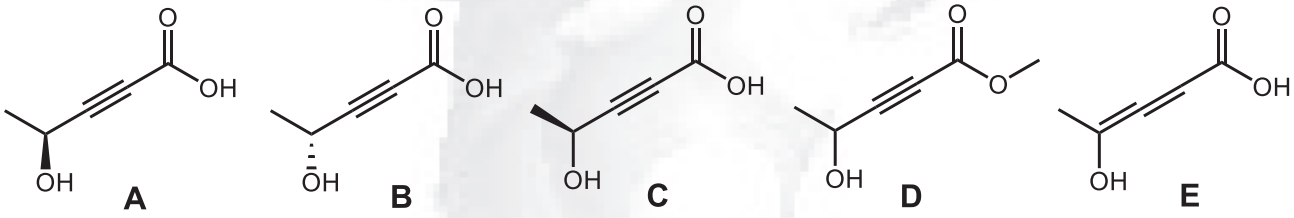
28. t-butyl isobutyl ether



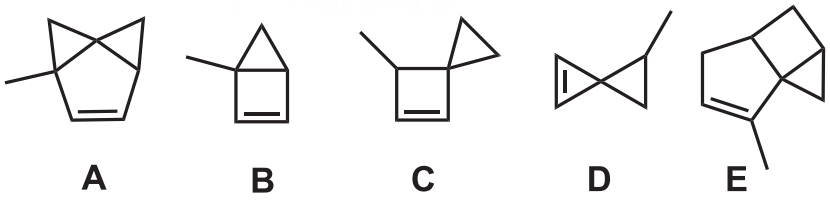
29. N-ethyl o-methyl benzamide



30. (R)-4-hydroxypent-2-ynoic acid



31. 1-methylbicyclo[2.1.0]pent-2-ene



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13% PART 5: STRUCTURE DETERMINATION

Write your answer in the booklet provided. For FULL marks you MUST show your work. PARTIAL marks will be awarded.

Each of the following questions needs to be answered based on compound **Q** which has the molecular formula $C_6H_{10}O_2$.

a) What is the molecular weight of compound **Q**?

b) What is the index of hydrogen deficiency of compound **Q**?

c) Draw a structure for **Q** where the most acidic hydrogen has a pKa of 25.

d) Draw a structure for **Q** that would have a broad IR peak at 3300 cm^{-1}, would be soluble in NaOH, and contains five types of carbon.

e) Draw a structure for **Q** that has no IR peak between 3350–3150 cm^{-1} but a peak between 2300–2100 cm^{-1}

f) **i.** Draw a structure for **Q** that has an ester functional group, an alkene, and a chiral center.

ii. Show how to assign priority groups around the chiral center in **i.** above.

iii. What is the chirality of this structure?

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13% **PART 6: THERMODYNAMICS**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

All of the questions in this section are based on three constitutional isomers **X**, **Y** and **Z** with the chemical formula C_5H_{12}.

a) Write a balanced reaction equation for the complete combustion of one of the isomers.

b) Given the thermodynamic data below, calculate the heat of formation for isomer **X** and the heat of combustion for isomer **Y** using the following heats of combustion: ΔH_c^o (graphite) = -94.05 kcal mol^{-1}, ΔH_c^o (H_2) = -68.32 kcal mol^{-1}.

	Thermodynamic Data in kcal mol^{-1}	
Compound	**ΔH_c^o**	**ΔH_f^o**
Isomer X	-840.03	**?**
Isomer Y	**?**	-36.73
Isomer Z	-845.09	-35.08

c) Draw the three isomers and match them to **X**, **Y**, and **Z**.

d) Draw an energy diagram (with clearly labeled reactants, products, **X**, **Y** and **Z**, and all ΔH values) to illustrate the relative energy difference between these three isomers.

e) On your energy diagram, compare the three isomers by **clearly indicating** which one is the most stable and which one is the least stable.

f) Use the principles of bonding to briefly explain the observed trend in their relative stability.

g) One of the isomers undergoes radical chlorination when reacted with Cl_2 and uv light to give 3 isomeric mono-chlorinated products. Draw the structure and name the major mono-chlorinated product of that reaction.

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13% **PART 7: MECHANISM**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

a) Draw a mechanistic sequence using double headed (*i.e.* electron pair) curly arrows that represents the reaction sequence described verbally by the following points in which an alkyl nitrile, butanenitrile, is hydrolyzed using a catalytic amount of hydrochloric acid.

Step 1. Protonation of the most basic atom in butanenitrile with hydrochloric acid to make an organic cation and a chloride anion.

Step 2. Attack of water as a nucleophile on the most electrophilic carbon of the organic cation to create a new C-O bond and an oxonium ion.

Step 3. Removal of a proton from the oxonium ion by chloride to regenerate the hydrochloric acid catalyst. The organic product from this reaction sequence will have a functional group that you most likely have not seen before.

b) The product of this reaction is an *isomer* of butanamide. Draw the structure of butanamide, and clearly label the most acidic proton in butanamide. What is the pKa of this proton?

c) To both the final organic product from part (a), and to butanamide, add a proton to the most basic atom in each molecule to create the conjugate acid. For the two new molecules you have just drawn, what is the relationship between the molecules?

**** THE END ****

IRH / ERS / JVH F2022

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INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
$-CH_3$		(bend)	1450 and 1375	6.90 and 7.27	m
$-CH_2-$		(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		3500-3100	2.86-3.23	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R–NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad

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Cont'd

PERIODIC TABLE

1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008	2 2A																2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											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	3	4	5	6	7	8	9	10	11	12	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** 47.88	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** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	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** 183.9	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** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	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
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	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** (260)

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