UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

Version

01

November 8th, 2017 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.**

14% PART 1: RELATIVE PROPERTIES

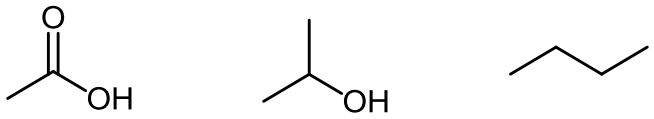
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

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.

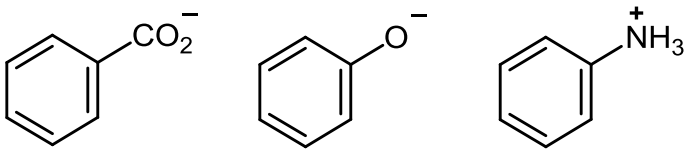
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

1. The relative boiling points of the compounds shown below:



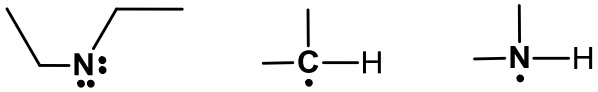
i **ii** **iii**

2. The relative basicity of the following:



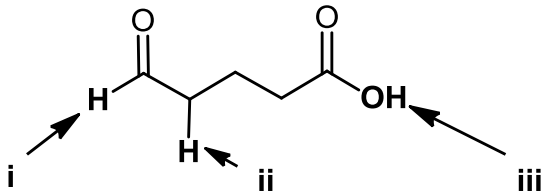
i **ii** **iii**

3. The relative charge on the **bold** atoms in each of the following:



i **ii** **iii**

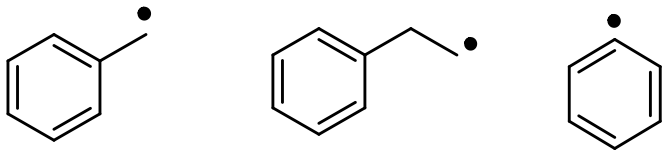
4. The relative acidity of each of the following:



Use the following code to indicate your answers.

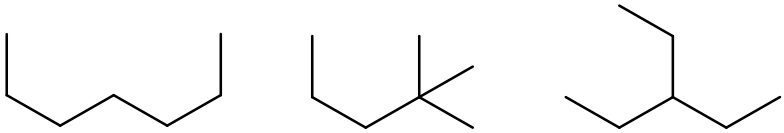
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

5. The relative stability of the following radicals:



i **ii** **iii**

6. The relative stability of the following isomers:

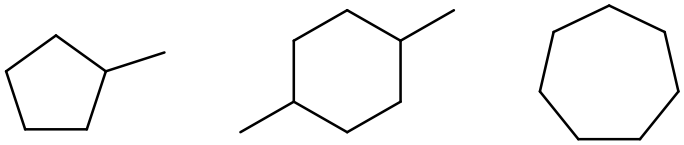


i **ii** **iii**

7. The relative bond length of the **C2-C3** bond in each of the following:

i 2-butene **ii** 1-butene **iii** butane

8. The number of different monochlorinated constitutional isomers produced when each of the following undergo a uv light catalysed reaction with chlorine:



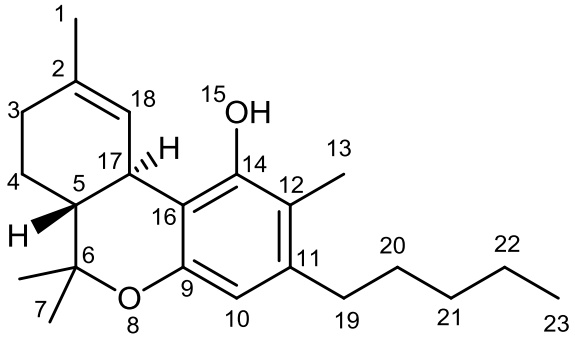
i **ii** **iii**

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.

Use the structure of **Tetrahydrocannabinol,** an active ingredient from Marijuana, shown below, to answer the questions **9-12.**



Tetrahydrocannabinol (THC)

9. Which of the following bonds is the weakest ?

A. C1-H **B. C3**-H **C. C5**-H **D. C7**-H **E. C13**-H **AB**. **C17**-H

10. Which of term(s) describe the functional group involving **C19** ?

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

11. Which of the following bonds is the strongest ?

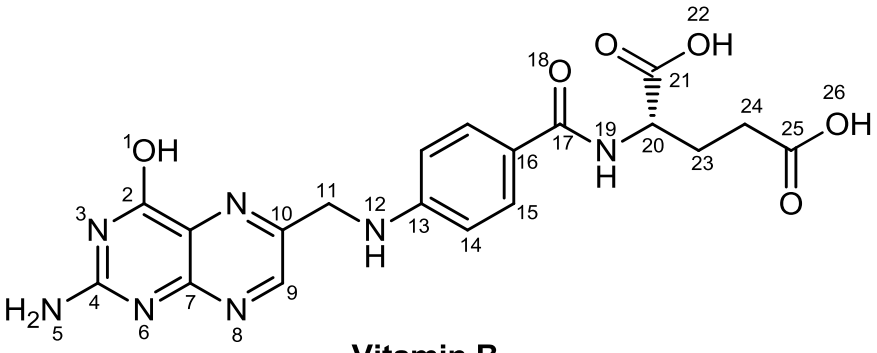
A. C1-C2 **B. C2-C18** **C. C5-C6** **D. C9-C10** **E. C12-C14**

12. Which configurational term best describes the situation at **C5** ?

A. R **B.** S **C.** E **D.** Z

Use the structure of **Vitamin B9,** shown below, to answer the questions **13-17**.

In some cases more than one selection may be required for full credit.



Vitamin B_9

13. What is the index of hydrogen deficiency (IHD) of **Vitamin B_9** (above) ?

A. 12 **B.** 13 **C.** 14 **D.** 15 **E.** 16 **AB**. 17

14. What is the oxidation state of **C2** ?

A. -4 **B.** -3 **C.** -2 **D.** -1 **E.** 0 **AB**. +1 **AC**. +2 **AD** +3 **BC**. +4

15. Which of the following protons is the *most* acidic in **Vitamin B_9** (above) ?

A. N5-**H** **B.** N12-**H** **C.** N19-**H** **D.** O1-**H** **E.** O22-**H** **AB.** O26-**H**

16. What type of orbital do the lone pairs of electrons on **N3** and **N19** occupy respectively ?

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

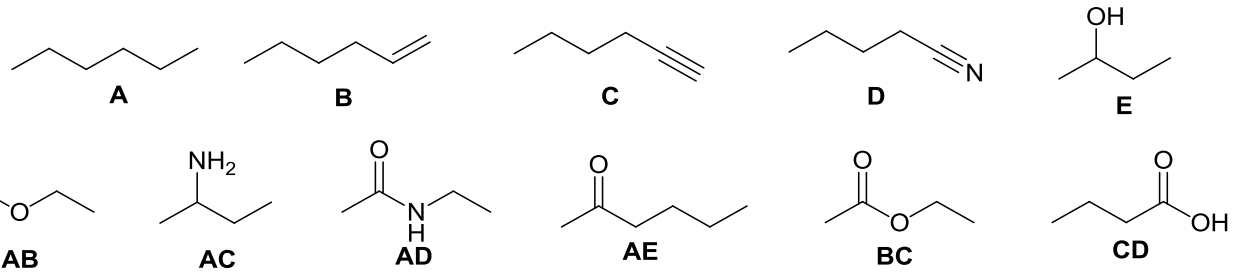
17. Which of the following atoms in **Vitamin B9** (above) is the *least* basic ?

A. O1 **B.** O18 **C.** N3 **D.** N5 **E.** N12 **AB.** N19 **AC.** C24

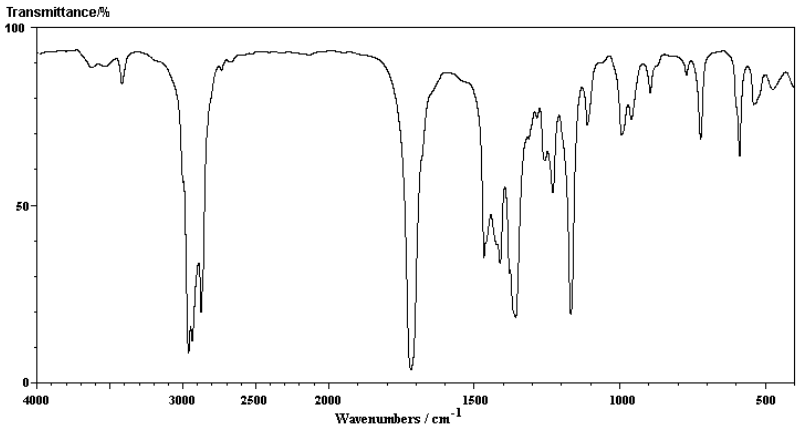
15% **PART 3: SPECTROSCOPY**

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

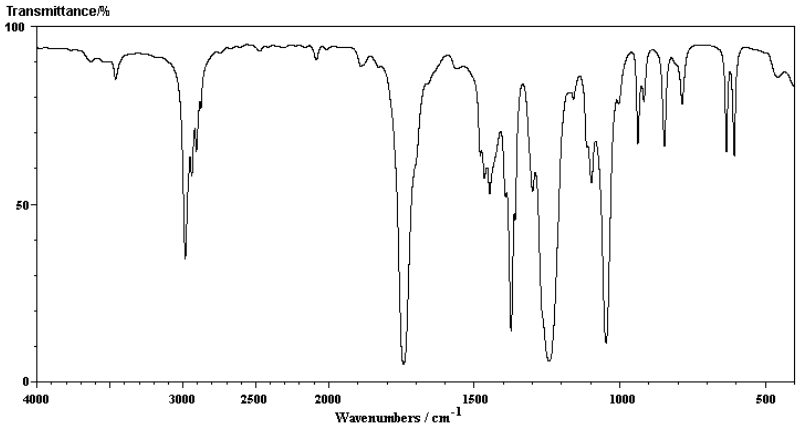
For each of the questions 18-23, match the IR spectra to a structure in the list below:



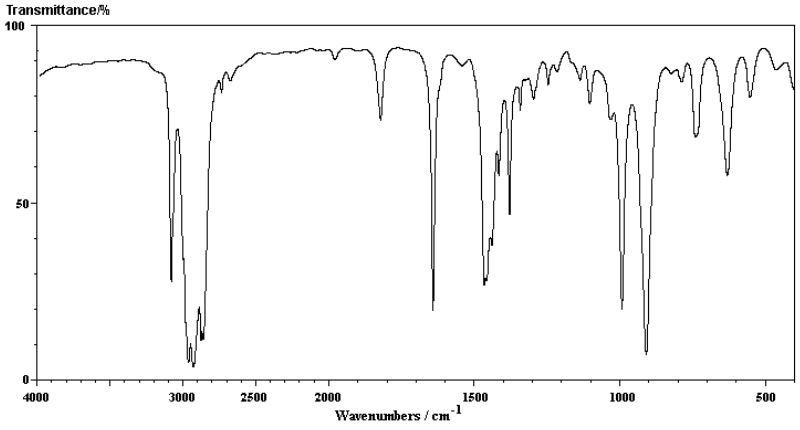
18.

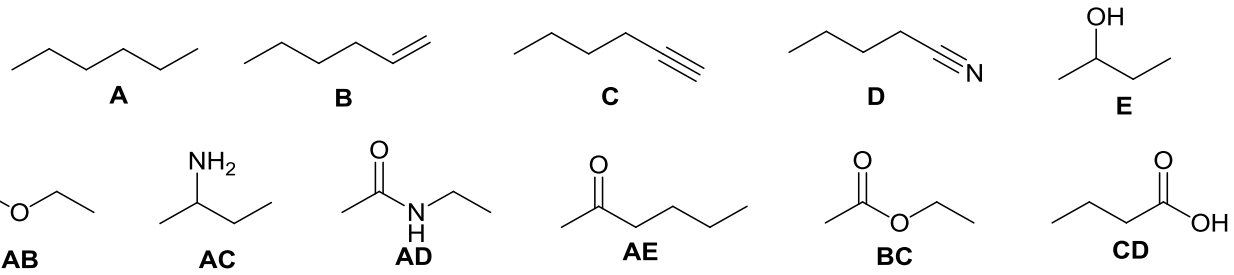


19.

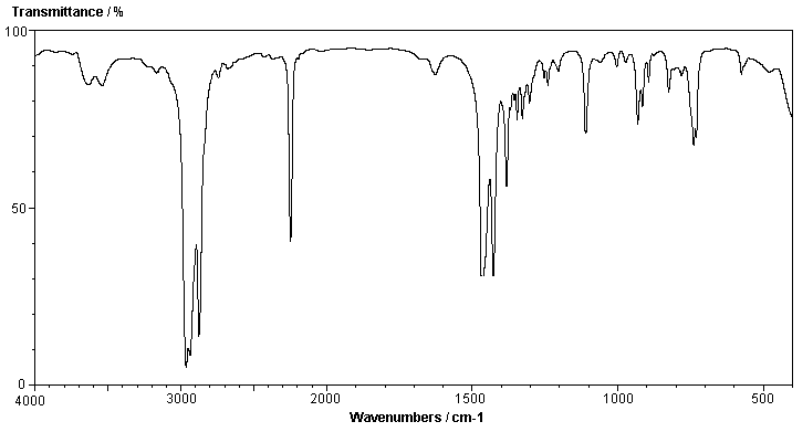


20.

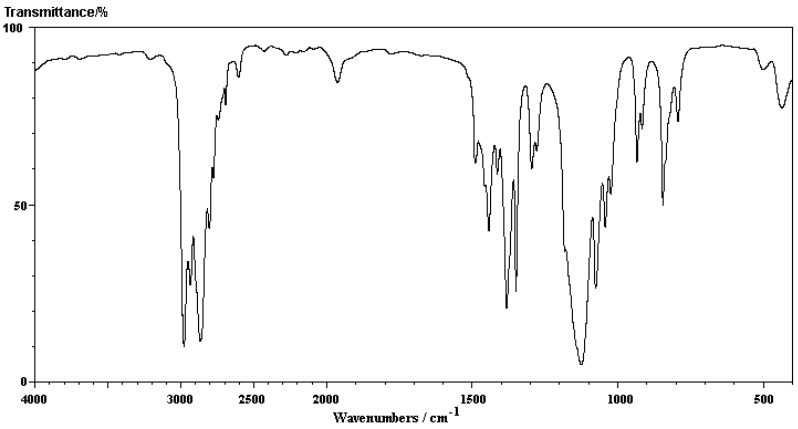




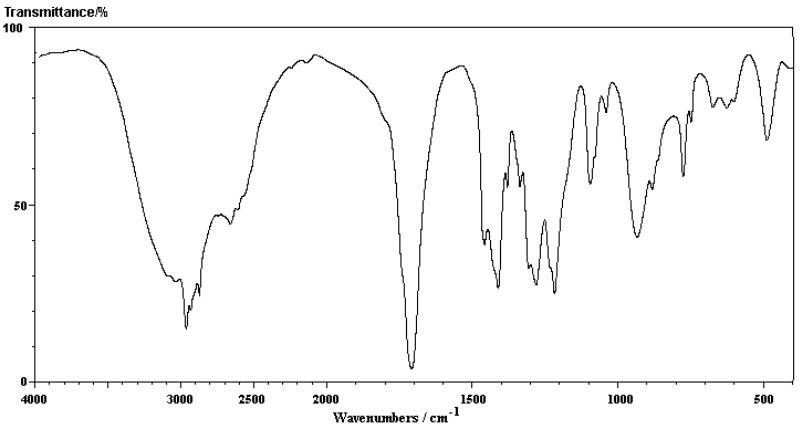
21.



22.



23.



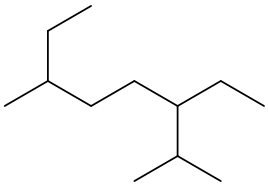
Cont'd

14% **PART 4: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question).

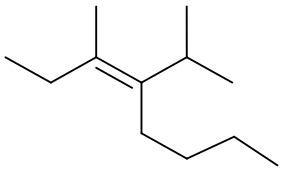
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



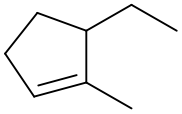
A. 3-isopropyl-6-ethylheptane
B. 2,6-dimethyl-3-ethyloctane
C. 3,7-dimethyl-6-ethyloctane
D. 2-ethyl-5-isopropylheptane
E. 3-ethyl-2,6-dimethyloctane
AB. 6-ethyl-3-isopropylheptane

25.



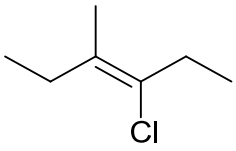
A. (Z)-3-methyl-4-isopropyloct-3-ene
B. (E)-3-methyl-4-isopropyloct-3-ene
C. (Z)-4-isopropyl-3-methyloct-3-ene
D. (E)-4-isopropyl-3-methyloct-3-ene
E. (Z)-4-butyl-3,5-dimethylhex-3-ene
AB. (E)-4-butyl-3,5-dimethylhex-3-ene

26.



A. 2-ethyl-1-methylcyclopentene
B. 2-methyl-1-ethylcyclopentene
C. 1-ethyl-2-methylcyclopentene
D. 3-ethyl-2-methylcyclopentene
E. 1-methyl-5-ethylcyclopentene
AB 5-ethyl-1-methylcyclopentene

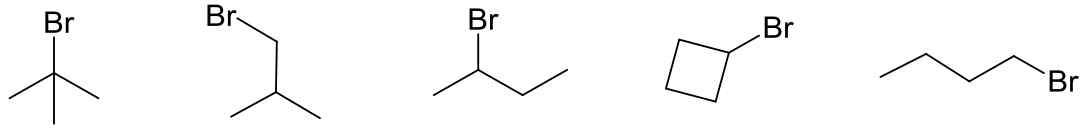
27.



A. *trans*-3-methyl-4-chlorohex-3-ene
B. *cis*-3-methyl-4-chlorohex-3-ene
C. *trans*-3-chloro-4-methylhex-3-ene
D. *cis*-3-chloro-4-methylhex-3-ene
E. *trans*-4-chloro-3-methylhex-3-ene
AB. *cis*-4-chloro-3-methylhex-3-ene

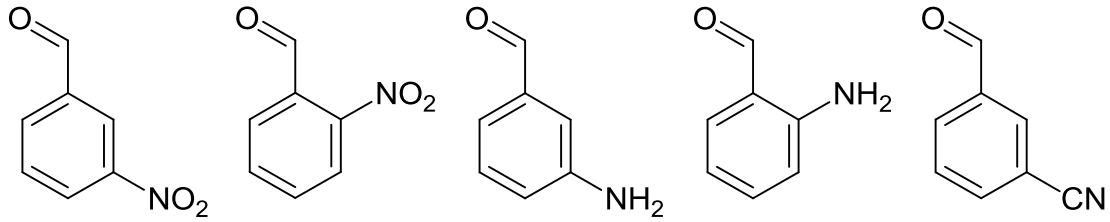
For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

28. isobutyl bromide



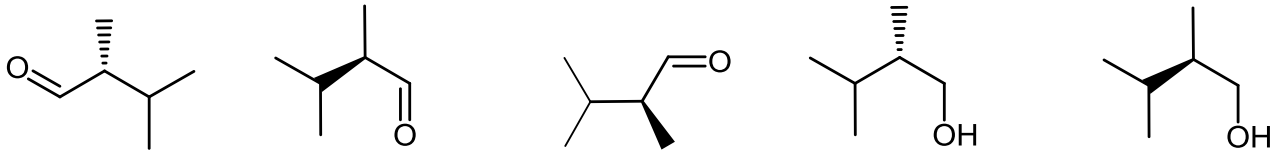
A. **B.** **C.** **D.** **E.**

29. m-nitrobenzaldehyde



A **B** **C** **D** **E**

30. (S)-2,3-dimethylbutanal



A. **B.** **C.** **D.** **E.**

31. 6-methylbicyclo[3.2.1]oct-2-ene:

A **B** **C** **D** **E**

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.

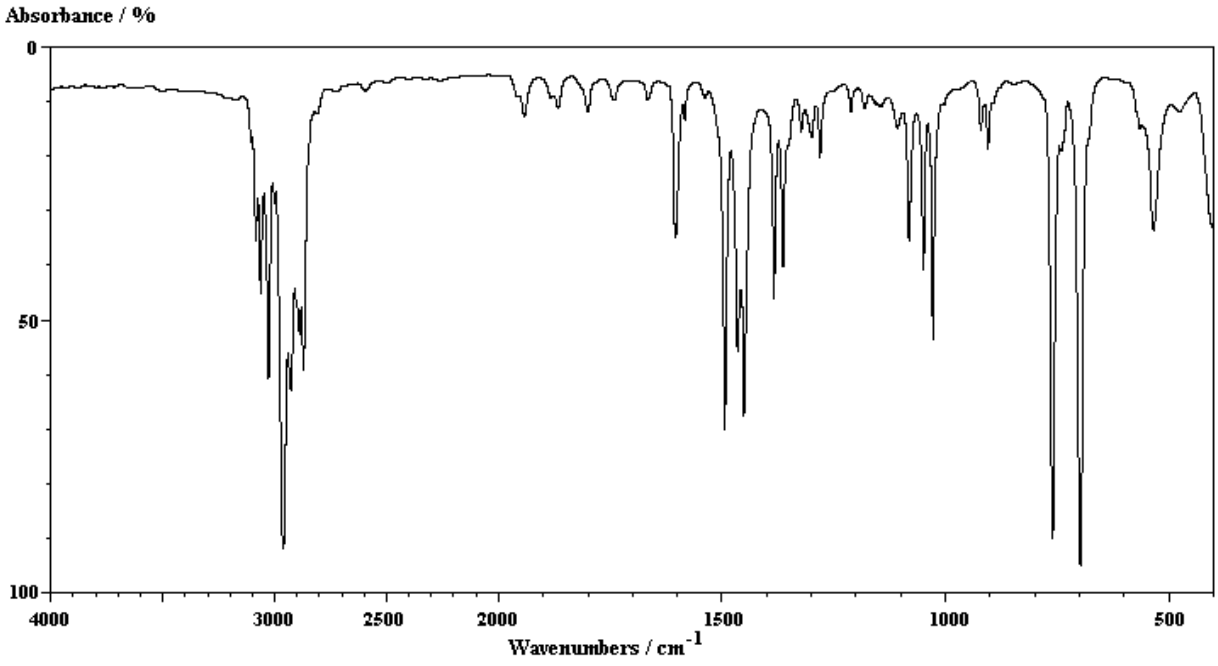
A hydrocarbon "**X**" was found to have 89.94% carbon and 10.06% hydrogen by weight. The mass spectrum revealed that the compound had a molecular weight = 120.19 g/mol.

a) What is the empirical formula ?

b) What is the molecular formula ?

c) What is the index of hydrogen deficiency ?

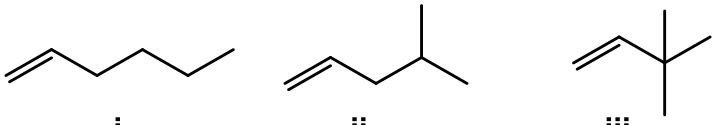
d) The infra-red spectra of **X** is shown below. **X** was found to have 5 types of H and 6 types of C. **X** gave two different monochlorination products when reacted with Cl_2 / uv light. Draw a structure for **X** consistent with this data. Provide an IUPAC name for **X**.



13% **PART 6: THERMODYNAMICS**

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

The structures of three isomers are shown below:



i **ii** **iii**

a) Write a balanced reaction equation for the complete combustion of isomer **i**.

b) Given the thermodynamic data below, calculate the heats of formation for isomer **i** and the heat of combustion for isomer **ii** 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 (kcal mol^{-1})		
Compound	**ΔH_C^o**	**ΔH_f^o**
Isomer i	-964.3	**?**
Isomer ii	**?**	-11.0
Isomer iii	**-**960.0	-14.3

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

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

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

f) A fourth isomer **iv** (not shown above) which has no sp^2 C atoms, reacts with chlorine and UV light to give only one monochlorinated product. Draw the structure of isomer **iv**.

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 single reaction sequence described verbally by the following points in which an alkyne, 3-methylbut-1-yne, is alkylated using iodoethane in the presence of a base, sodium amide ($NaNH_2$), to give 2-methylhex-3-yne.

Step 1.

An acid / base reaction of the amide ion from sodium amide ($NaNH_2$), where it deprotonates 3-methylbut-1-yne to give a nucleophilic carbanion and ammonia.

Step 2.

Reaction of the nucleophilic carbanion with the electrophilic carbon in iodoethane to form a new carbon–carbon bond with the simultaneous loss of an iodide ion as a leaving group to give 2-methylhex-3-yne and sodium iodide.

b) Briefly comment on the feasibility of the following three proposed alternate methods for preparing 2-methylhex-3-yne:

i) Replacing the sodium amide base used in the above reaction with sodium hydroxide.

ii) Alkylating 4-methylpent-2-yne with iodomethane in the presence of the sodium amide base.

iii) Alkylating but-1-yne with 2-iodopropane in the presence of the sodium amide base.

c) Based on the information provided in this question, what materials would you use if you wanted to prepare 6-methylhept-2-yne ?

**** THE END ****

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		ca. 3500	ca. 2.86	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

Cont'd

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	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)