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UNIVERSITI SAINS MALAYSIA

Final Examination  
2015/2016 Academic Session

May/June 2016

**JIK 227 – Chemical Spectroscopy**  
*[Spektroskopi Kimia]*

Duration : 3 hours  
*[Masa : 3 jam]*

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Please ensure that this examination paper contains **TWENTY** printed pages and an **Appendix** before you begin the examination.

Answer **FIVE** questions. You may answer **either** in Bahasa Malaysia or in English.

All answers must be written in the answer booklet provided.

Each question is worth 20 marks and the mark for each sub question is given at the end of that question.

In the event of any discrepancies in the exam questions, the English version shall be used.

*Sila pastikan bahawa kertas peperiksaan ini mengandungi **DUA PULUH** muka surat dan **Lampiran** yang bercetak sebelum anda memulakan peperiksaan ini.*

*Jawab **LIMA** soalan. Anda dibenarkan menjawab soalan **sama ada** dalam Bahasa Malaysia atau Bahasa Inggeris.*

*Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.*

*Setiap soalan bernilai 20 markah dan markah subsoalan diperlihatkan di penghujung subsoalan itu.*

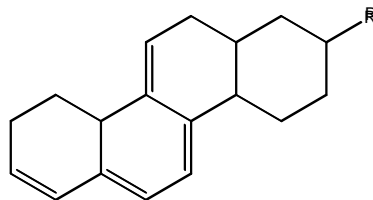
*Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.*

Answer **FIVE** (5) Question.

Jawab **LIMA** (5) Soalan.

1. (a) Calculate  $\lambda_{max}$  for the compound below where R is an alkyl side chain.

*Kira  $\lambda_{max}$  bagi sebatian di bawah (R ialah rantai alkil).*



(4 marks/markah)

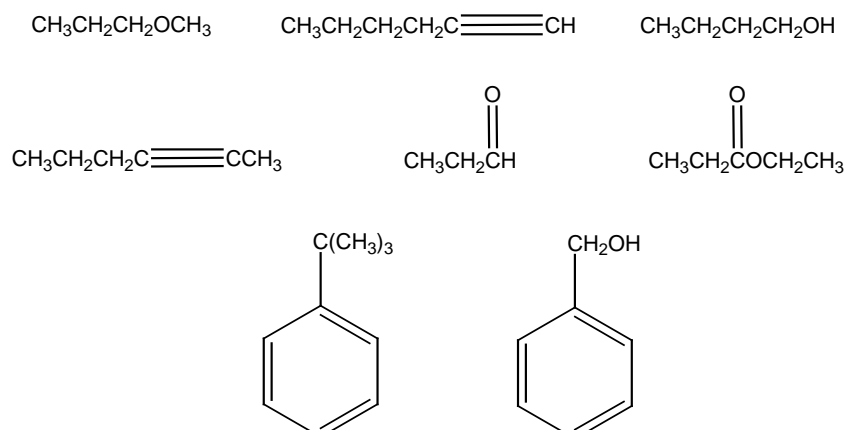
- (b) A solution of 4-methyl-3-penten-2-one in ethanol shows an absorbance of 0.52 at 236 nm in a cell with a 1 cm light path. Its molar absorptivity in ethanol at that wavelength is 12 600. What is the concentration, M, of the compound?

*Satu larutan 4-metil-3-penten-2-on dalam etanol menunjukkan serapan 0.52 pada 236 nm dalam satu sel dengan 1 cm laluan cahaya. Absorptiviti molarinya dalam etanol pada panjang gelombang tersebut ialah 12 600. Apakah kepekatan, M, untuk sebatian tersebut?*

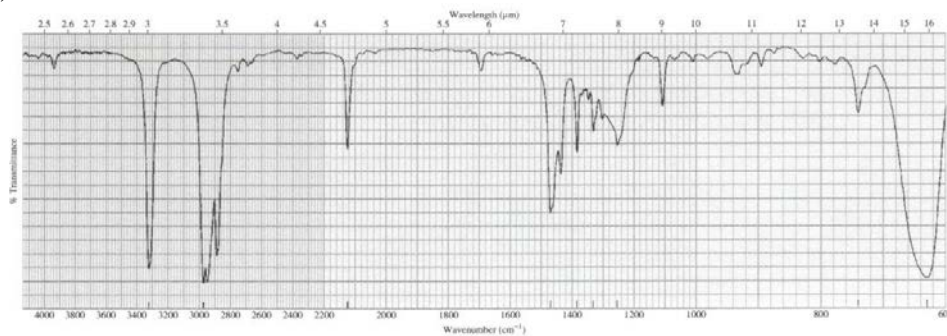
(4 marks/markah)

- (c) For each of the IR spectra below (i) to (iv), assign each IR to its correct compound.

*Bagi setiap spektrum IR di bawah (i) ke (iv), padankan setiap IR kepada sebatian yang betul.*

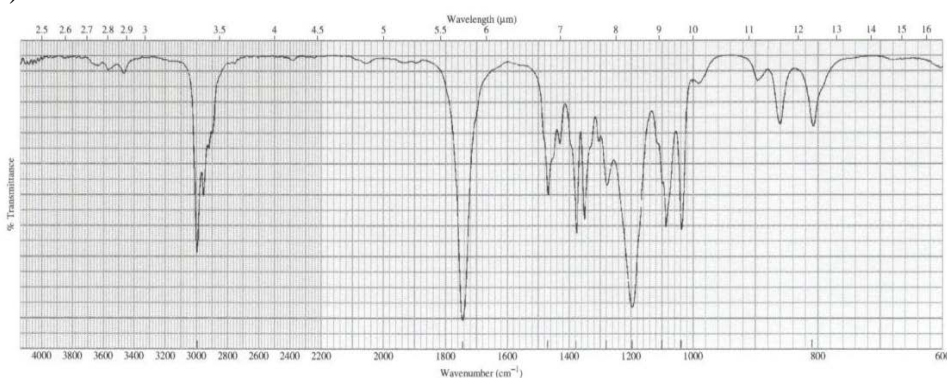


(i)



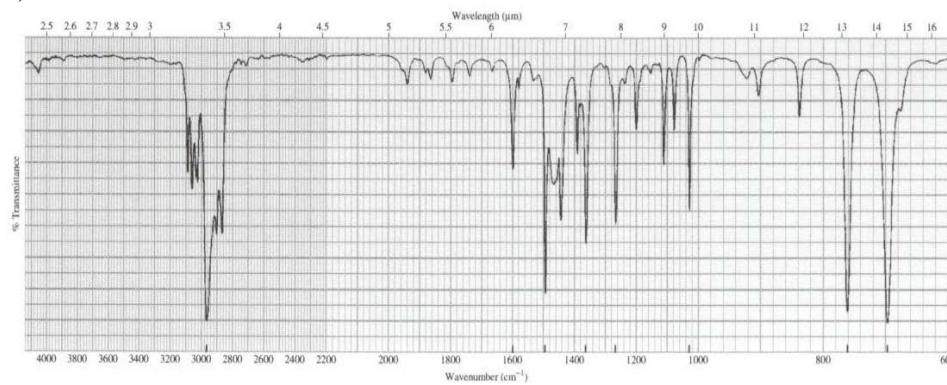
(2 marks/markah)

(ii)



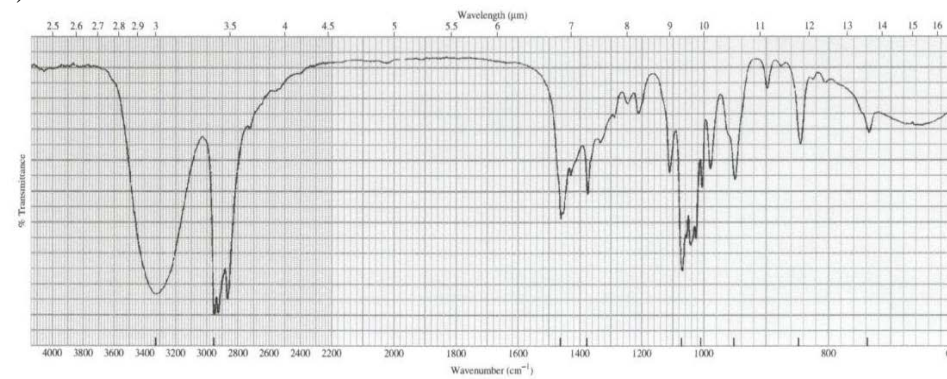
(2 marks/markah)

(iii)



(2 marks/markah)

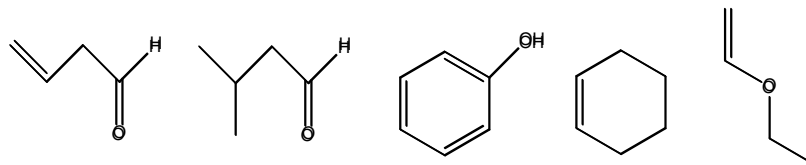
(iv)



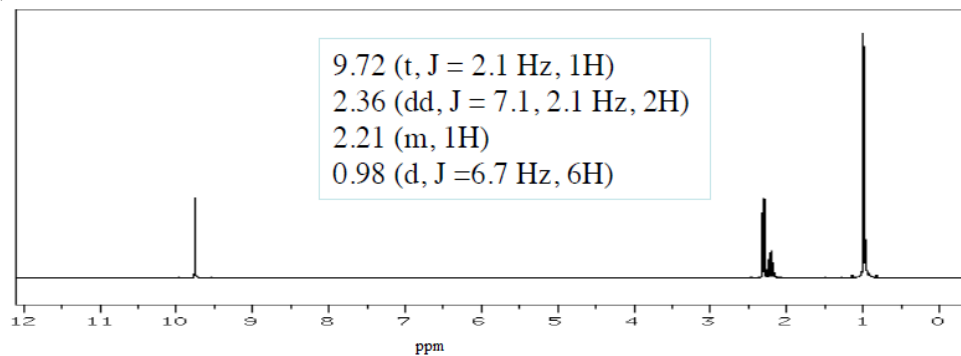
(2 marks/markah)

- (d) Match the following  $^1\text{H}$  NMR spectra (i) and (ii) with one of the following compounds.

*Padankan spektrum  $^1\text{H}$  NMR di bawah (i) dan (ii) kepada salah satu daripada sebatian di bawah.*

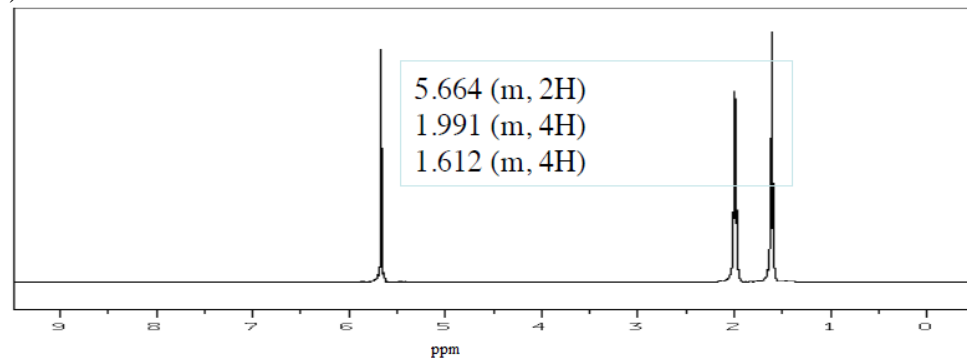


(i)



(2 marks/markah)

(ii)



(2 marks/markah)

2. (a) The mass spectrum of 2,6-dimethylheptan-4-ol gave peaks at  $m/z$  values of 87 and 126. Draw the structures for these two fragments.

*Spektrum jisim untuk 2,6-dimetilheptan-4-ol memberikan puncak-puncak pada  $m/z=87$  dan  $m/z=126$ . Lukiskan struktur-struktur untuk kedua-dua serpihan tersebut.*

(5 marks/markah)

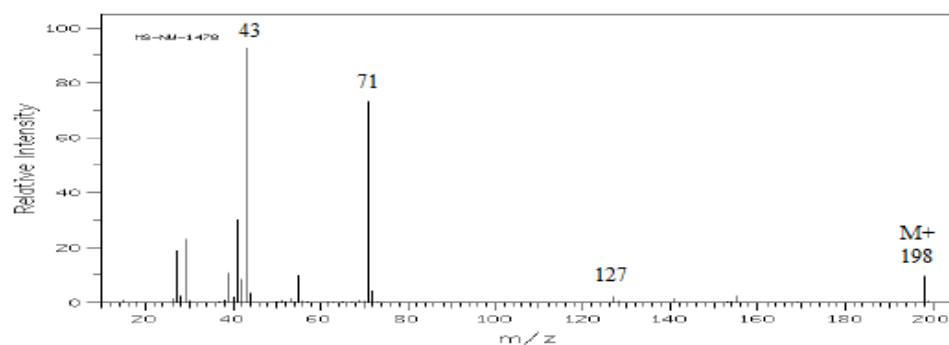
- (b) Show the fragmentations that accounts for the cation at  $m/z=57$  in the mass spectrum of 2-methylpentane. Explain why this ion is less abundant than those at  $m/z=71$  and  $m/z=43$ .

*Tunjukkan penyerpihan yang menyumbang kepada kation pada  $m/z=57$  dalam spektrum jisim 2-metilpentana. Jelaskan mengapa limpahan ion ini adalah kurang daripada  $m/z=71$  dan  $m/z=43$ .*

(5 marks/markah)

- (c) Provide a structure for the compound,  $C_5H_{11}I$ , represented in the following mass spectrum. Show the fragmentations that give rise to the important peaks below.

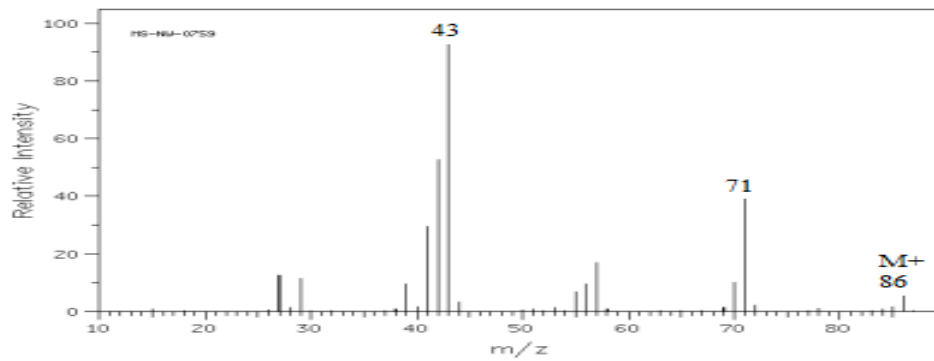
*Berikan satu struktur untuk sebatian,  $C_5H_{11}I$ , yang diwakili oleh spektrum jisim di bawah. Tunjukkan penyerpihan yang menyumbang kepada puncak-puncak penting di bawah.*



(5 marks/markah)

- (d) A saturated hydrocarbon,  $C_6H_{14}$ , gives the following mass spectrum. Provide a structure for the unknown hydrocarbon and show the fragmentations that give rise to the important peaks below.

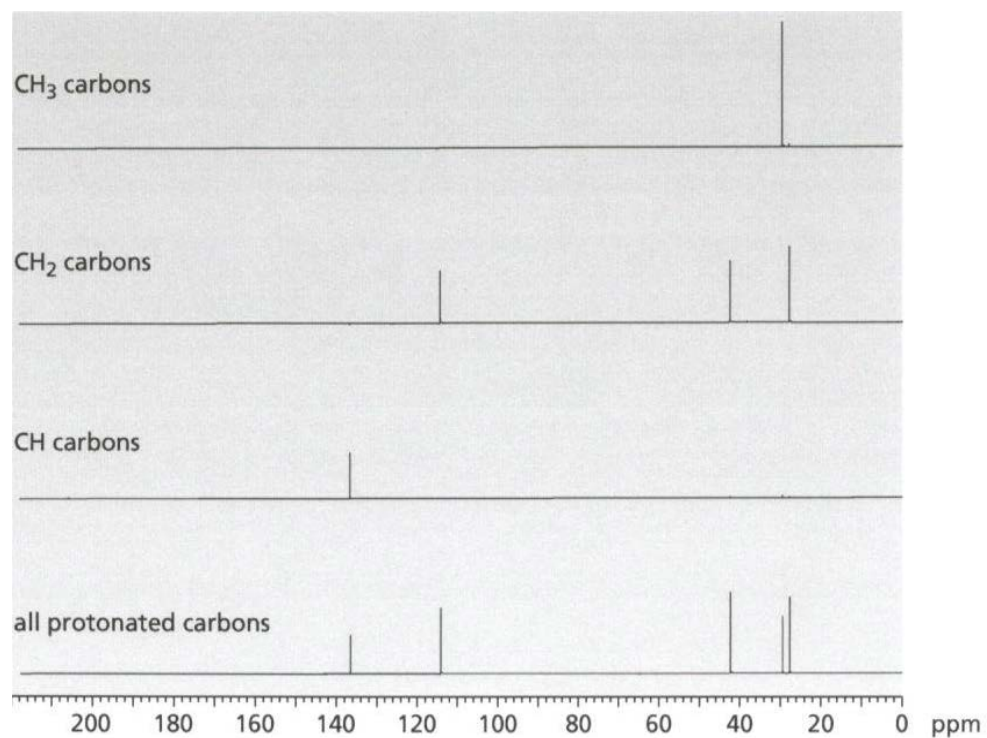
*Satu hidrokarbon tepu,  $C_6H_{14}$ , memberikan spektrum jisim seperti di bawah. Berikan satu struktur untuk hidrokarbon yang tidak diketahui ini dan tunjukkan penyerpihan yang menyumbang kepada puncak-puncak penting di bawah.*



(5 marks/markah)

3. (a) Identify the compound with molecular formula  $C_6H_{10}O$  that give rise to the following DEPT  $^{13}C$  NMR spectrum. Explain your answer.

*Kenal pasti sebatian dengan formula molekul  $C_6H_{10}O$  yang menyumbang kepada spektrum DEPT  $^{13}C$  NMR di bawah. Jelaskan jawapan anda.*



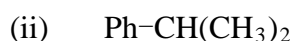
(5 marks/markah)

- (b) Draw the  $^1\text{H-NMR}$  spectrum you would expect for the following compounds. Show clearly the splitting pattern and the integration values.

*Lukiskan spektrum  $^1\text{H-NMR}$  yang anda jangkakan untuk sebatian-sebatian di bawah. Tunjukkan dengan jelas corak pengkupelan dan nilai integrasi.*



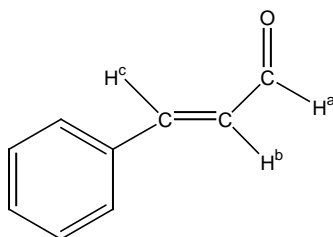
(5 marks/markah)



(5 marks/markah)

- (c) Draw a splitting tree to analyse the complex splitting of the  $\text{H}^b$  proton ( $\delta$  6.7) in the molecule below if  $J_{ab} = 8 \text{ Hz}$  and  $J_{bc} = 18 \text{ Hz}$ .

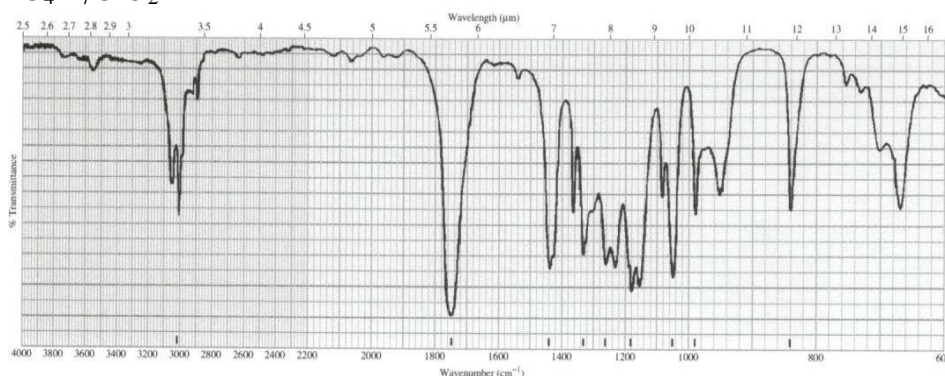
*Lukiskan satu pohon pengkupelan untuk menganalisa pengkupelan yang kompleks bagi proton  $\text{H}^b$  ( $\delta$  6.7) untuk molekul di bawah jika  $J_{ab} = 8 \text{ Hz}$  dan  $J_{bc} = 18 \text{ Hz}$ .*

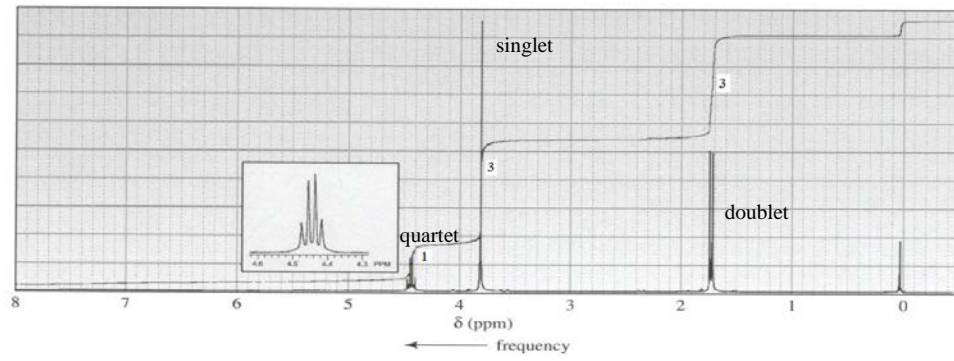


(5 marks/markah)

4. Draw the structure of each of the following unknown compounds based on its molecular formula and its IR and  $^1\text{H NMR}$  spectra. Explain your answer.

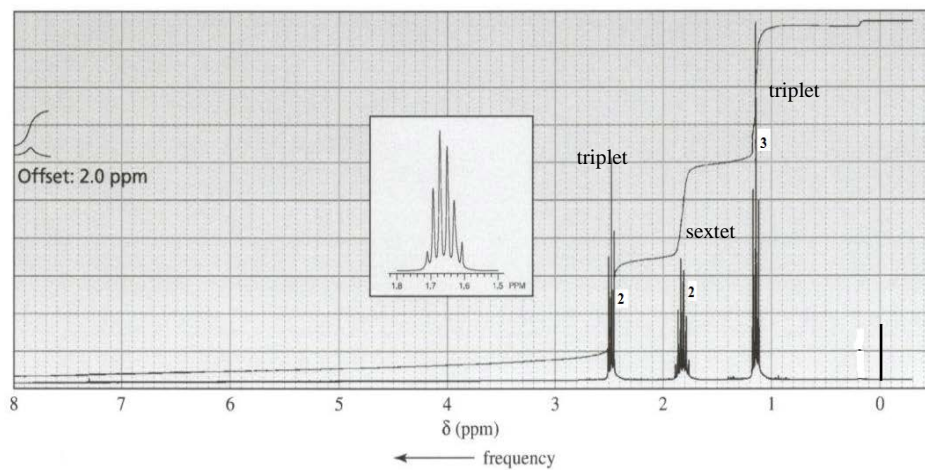
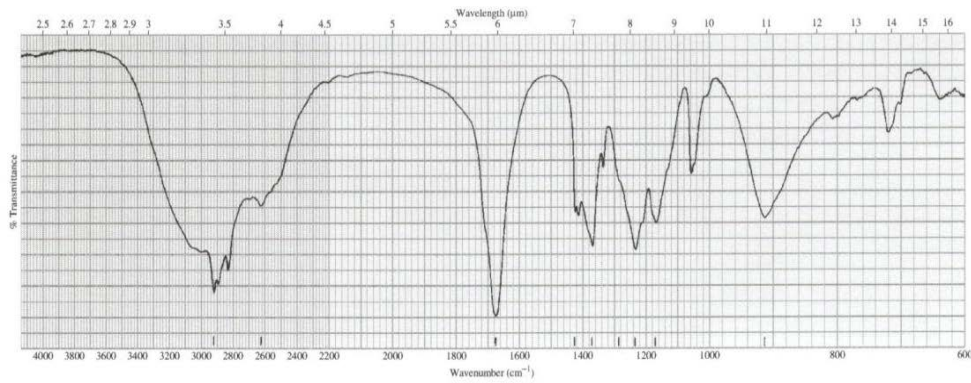
*Lukiskan struktur untuk setiap sebatian yang tidak diketahui di bawah berdasarkan formula molekul dan spektrum IR serta  $^1\text{H NMR}$  masing-masing. Jelaskan jawapan anda.*





(5 marks/markah)

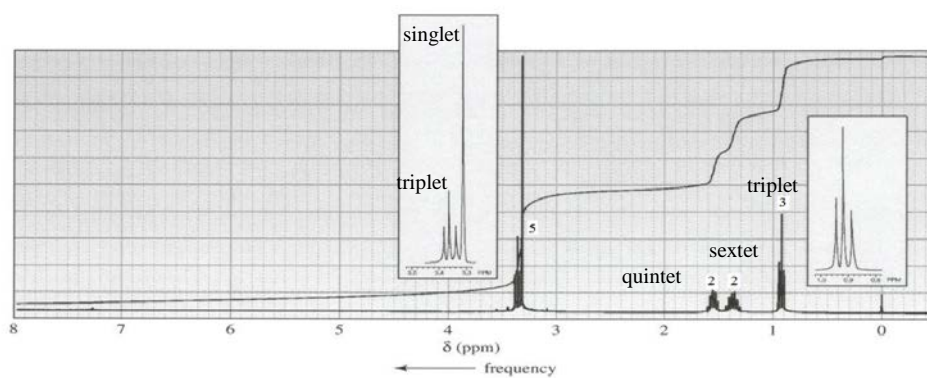
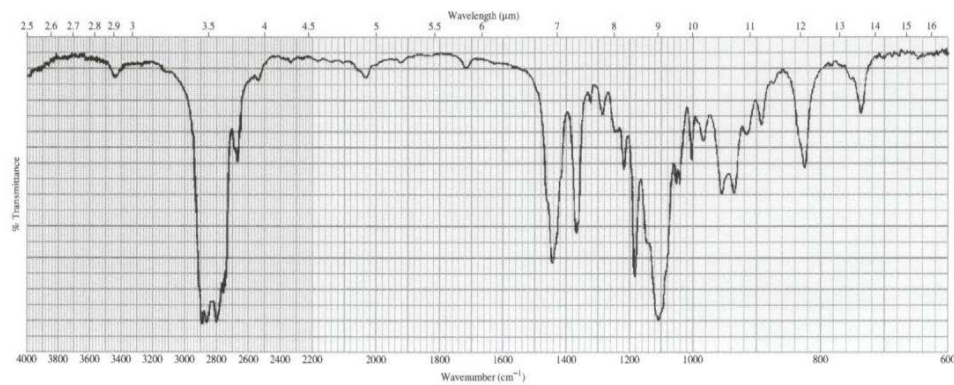
(b)  $C_4H_8O_2$



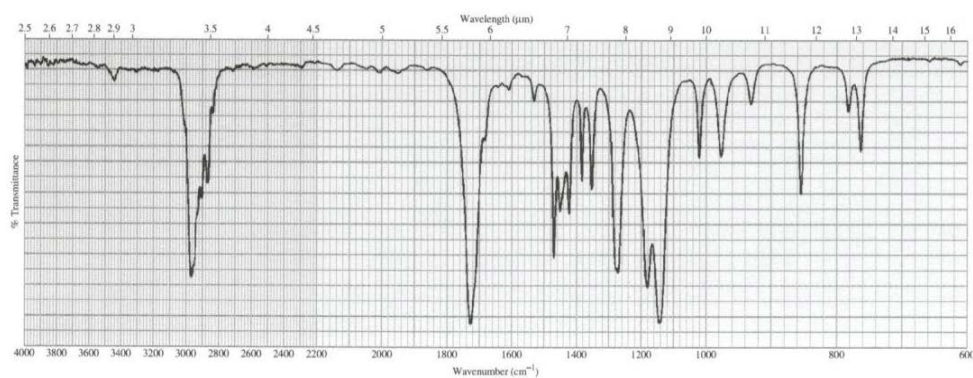
(5 marks/markah)



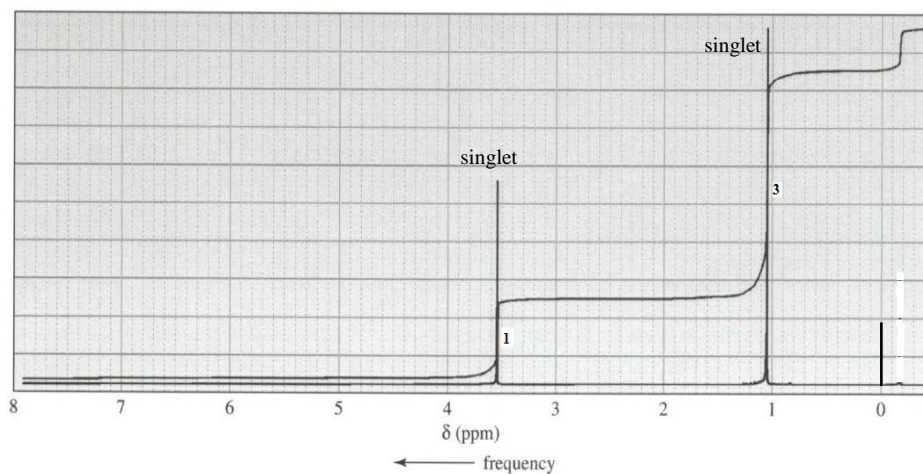
- 9 -

(c)  $C_5H_{12}O$ 

(5 marks/markah)

(d)  $C_6H_{12}O_2$ 

- 10 -

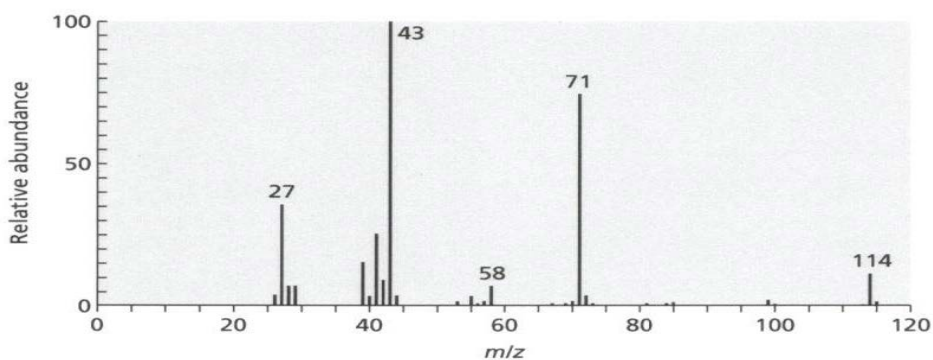


(5 marks/markah)

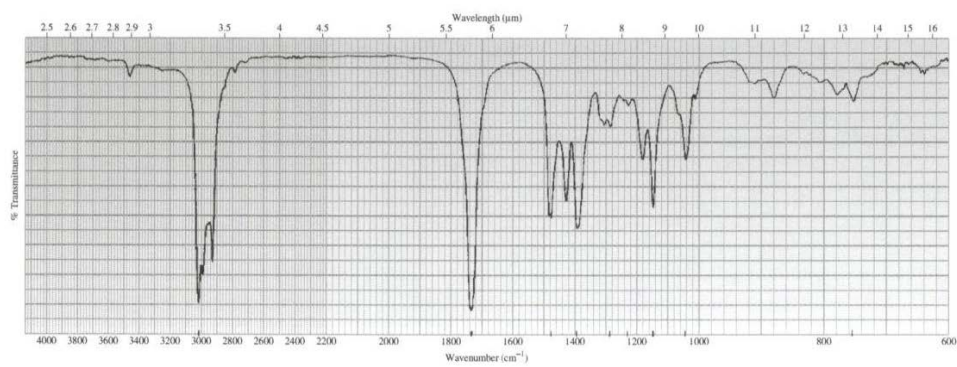
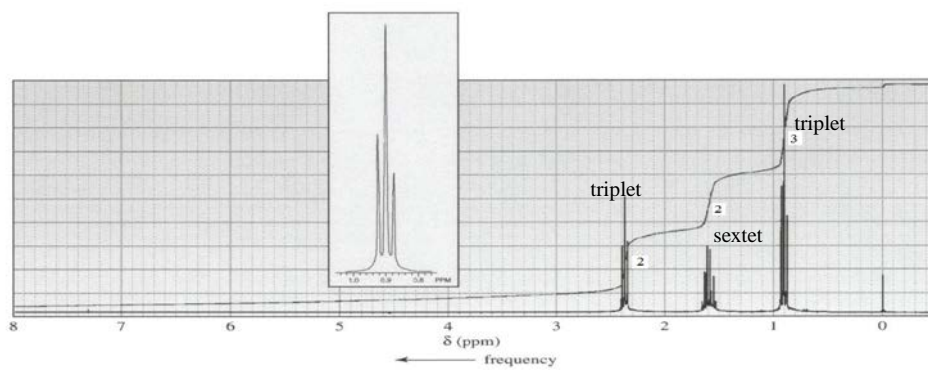
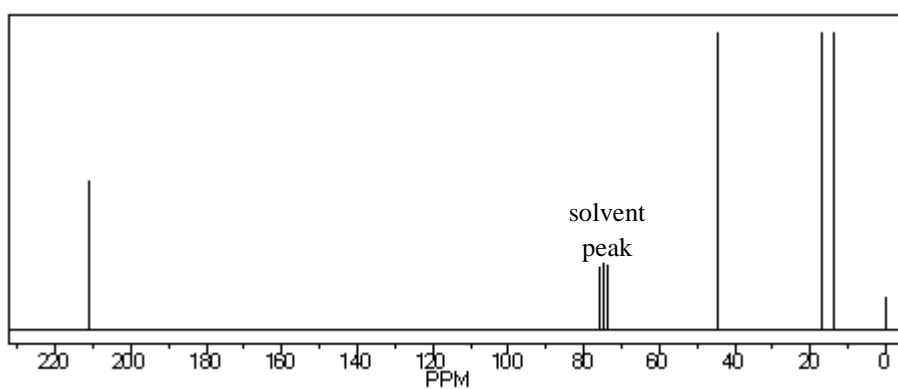
5. An unknown compound, X has the following mass, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Explain each spectrum individually and then consider them in relation to each other. Determine and draw the structure of compound X.

*Suatu sebatian yang tidak diketahui, X mempunyai data jisim, spektrum IR,  $^1\text{H}$  dan  $^{13}\text{C}$ -NMRnya. Jelaskan setiap spektrum secara berasingan dan kemudian pertimbangkan hubungan spektrum-spektrum antara satu sama lain. Tentukan dan lukiskan struktur sebatian X.*

### MS



## IR

<sup>1</sup>H-NMR<sup>13</sup>C-NMR

(20 marks/markah)

6. (a) Complete the multiplication table for the operations of the molecule *trans* but-2-ene.

*Lengkapkan jadual pendaraban di bawah sebagai operasi-operasi bagi trans-but-2-ena.*

<b>E</b>	<b>E</b>	<b>C<sub>2</sub></b>	<b>σ</b>	<b>i</b>
<b>C<sub>2</sub></b>				
<b>σ</b>				
<b>i</b>				

(2 marks/markah)

- (b) Find irreducible representation for the following reducible ones.

*Dapatkan perwakilan tak terturunkan untuk data berikut.*

(i)

<b>C<sub>2h</sub></b>	<b>E</b>	<b>C<sub>2</sub></b>	<b>i</b>	<b>σ<sub>h</sub></b>
<b>Γ</b>	<b>8</b>	<b>0</b>	<b>6</b>	<b>2</b>

(ii)

<b>C<sub>3v</sub></b>	<b>E</b>	<b>2C<sub>3</sub></b>	<b>3σ<sub>v</sub></b>
<b>Γ</b>	<b>6</b>	<b>0</b>	<b>-2</b>

(4 marks/markah)

- (c) Ethylene has D<sub>2h</sub> symmetry.

*Etilena mempunyai simetri D<sub>2h</sub>.*

- (i) List all the symmetry operations of ethylene.

*Senaraikan semua operasi simetri etilena.*

(2 marks/markah)

- (ii) Write a transformation matrix for each symmetry operation that describes the effect of that operation on the coordinates of a point  $x$ ,  $y$ ,  $z$ .

*Tuliskan matrik transformasi bagi setiap operasi simetri yang menerangkan kesan operasi yang ada pada koordinat titik  $x$ ,  $y$ ,  $z$ .*

(4 marks/markah)

- (iii) Using the characters of transformation matrices, obtain a reducible representation.

*Dengan menggunakan aksara matrik transformasi, dapatkan perwakilan terturun.*

(3 marks/markah)

- (d) Predict the IR and Raman vibrations in  $\text{BCl}_3$ , a  $D_{3h}$  molecule. Show your calculation.

*Ramalkan getaran IR dan Raman dalam  $\text{BCl}_3$ , suatu molekul  $D_{3h}$ . Tunjukkan pengiraan anda.*

(5 marks/markah)



Table V Rules of Diene Absorption<sup>2</sup>

Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
N(Alk) <sub>2</sub>	+60
Solvent correction	+0
	$\lambda_{\text{calc}} = \text{Total}$

**Reducing Formula**

$$a_i = 1/h \sum X_R^S X_1^S N^S$$

$h$  ; total number of operations in certain point group.

$X_R^S$  ; Character ( $X$ ) for reducible representation.

$X_1^S$  ; Character ( $X$ ) for reducible representation (from the character Table)

$N^S$  ; Number of symmetry operation for each type or class of operation.

**Contribution for the Character,  $\chi(R)$ , for each unshifted atom in  $\Gamma_{3N}$**

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R	$\chi(R)$
E	+3
i	-3
$\sigma$	+1
$C_2$	-1
$C_3^1, C_3^2$	0
$C_4^1, C_4^3$	+1
$C_6^1, C_6^5$	+2
$S_3^1, S_3^5$	-2
$S_4^1, S_4^3$	-1
$S_6^1, S_6^5$	0



Notations of the Character Table

a	b		
f	c	d	e

- a. Schoenflies symbols for point group
- b. lists the symmetry operations (by classes) for that group
- c. lists all the characters, for all irreducible representations, of each class of each operation
- d. shows the irreducible representations for which the six vectors,  $T_x, T_y, T_z, R_x, R_y, R_z$ , provide the bases
- e. shows the functions which are binary combinations of  $x, y, z$  (e.g.  $xy, z^2$ ) provide bases for certain irreducible representations
- f. lists conventional symbols for the irreducible representations called *Mulliken symbols*. All one-dimensional irreducible rep. are labelled as A or B, all two-dimensional as E, all three-dimensional as T (in certain texts it is given the label F), four-dimensional as G and five-dimensional as H.

In addition to the letter, most Mulliken symbols possess certain subscripts and/or superscripts. For two- and higher-dimensional irreducible representations they can be regarded as labels. For one-dimensional representations, they have the following specifications.

- A : One-dimensional irreducible rep. if it is symmetry about  $C_n$  axis, i.e. ( $\chi = +1$ )
- B : " " " antisymm. " ( $\chi = -1$ )

- Sub.<sub>1</sub> : Irr. Rep is symmetry with respect to  $C_2 \perp C_n$  (if no  $C_2$ ), then  
Irr. Rep. Is symmetry with respect to  $\sigma_v$
- Sub.<sub>2</sub> : Irr. Rep is antisymmetry under conditions as those in Sub<sub>1</sub> of above.

- Sub.<sub>g</sub> : (gerade) irr. rep. are symm. With respect to inversion at an i
- Sub.<sub>u</sub> : (ungerade) irr. rep. are antisymm. with respect to an i

- ' : irr. Rep are symm with respect to reflection in a  $\sigma_h$
- '' : irr. Rep. Are antisymm with respect to reflection in a  $\sigma_h$

The  $D_{nh}$  Groups

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
$A_g$	1	1	1	1	1	1	1	1		$x^2, y^2, z^2$
$B_{1g}$	1	1	-1	-1	1	1	-1	-1	$R_z$	$xy$
$B_{2g}$	1	-1	1	-1	1	-1	1	-1	$R_y$	$zx$
$B_{3g}$	1	-1	-1	1	1	-1	-1	1	$R_x$	$yz$
$A_u$	1	1	1	1	-1	-1	-1	-1		
$B_{1u}$	1	1	-1	-1	-1	-1	1	1	$T_z$	
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	$T_y$	
$B_{3u}$	1	-1	-1	1	-1	1	1	-1	$T_x$	

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	1	1	1	1	1	1	$x^2+y^2, z^2$
$A_2'$	1	1	-1	1	-1	-1	$R_z$
$E'$	2	-1	0	2	-1	0	$(T_x, T_y)$
$A_1''$	1	1	1	-1	-1	-1	$T_z$
$A_2''$	1	1	-1	-1	-1	1	$(R_x, R_y)$
$E''$	2	-1	0	-2	1	0	$(yz, zx)$

The  $C_{nh}$  Groups

$C_{2h}$	E	$C_2$	i	$\sigma_h$	
$A_g$	1	1	1	1	$x^2, y^2, z^2, xy$ $yz, zx$
$B_g$	1	-1	1	-1	
$A_u$	1	1	-1	-1	
$B_u$	1	-1	-1	1	
					$R_z$ $R_x, R_y$ $T_z$ $T_x, T_y$

$C_{3h}$	E	$C_3$	$C_3^2$	$\sigma_h$	$S_3$	$S_3^2$	$\epsilon = \exp(2\pi i/3)$
$A'$	1	1	1	1	1	1	$x^2 + y^2, z^2$
$E'$	1	$\epsilon$	$\epsilon^*$	1	$\epsilon$	$\epsilon^*$	$(x^2 - y^2, xy)$
		$\epsilon^*$	$\epsilon$	1	$\epsilon^*$	$\epsilon$	
$A''$	1	1	1	-1	-1	-1	$(yz, zx)$
$E''$	1	$\epsilon$	$\epsilon^*$	-1	$-\epsilon$	$-\epsilon^*$	
		$\epsilon^*$	$\epsilon$	-1	$-\epsilon^*$	$-\epsilon$	

$C_{4h}$	E	$C_4$	$C_2$	$C_4^3$	i	$S_4^3$	$\sigma_h$	$S_4$
$A_g$	1	1	1	1	1	1	1	1
$B_g$	1	-1	1	-1	1	-1	1	-1
$E_g$	1	i	-1	i	1	-i	-1	-i
		-i	-1	-i	1	i	-1	i
$A_u$	1	1	1	1	-1	-1	-1	-1
$B_u$	1	-1	1	-1	-1	1	-1	1
$E_u$	1	i	-1	i	-1	-i	1	-i
		-i	-1	-i	-1	i	1	i
								$R_z$ $(R_x, R_y)$ $T_z$ $(T_x, T_y)$
								$x^2 + y^2, z^2$ $x^2 - y^2, xy$ $(yz, zx)$

*The C<sub>nv</sub> Groups*

C <sub>2v</sub>	E	C <sub>2</sub>	σ <sub>v</sub> (xz)	σ <sub>v</sub> (yz)	
A <sub>1</sub>	1	1	1	1	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	-1	xy
B <sub>1</sub>	1	-1	1	-1	zx
B <sub>2</sub>	1	-1	-1	1	yz
					T <sub>z</sub> R <sub>z</sub> T <sub>x</sub> , R <sub>y</sub> T <sub>y</sub> , R <sub>x</sub>

C <sub>3v</sub>	E	2C <sub>3</sub>	3σ <sub>v</sub>	
A <sub>1</sub>	1	1	1	x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	
E	2	-1	0	(x <sup>2</sup> -y <sup>2</sup> , xy), (yz, zx)
				T <sub>z</sub> R <sub>z</sub> (T <sub>x</sub> , T <sub>y</sub> ), (R <sub>x</sub> , R <sub>y</sub> )

C <sub>4v</sub>	E	2C <sub>4</sub>	C <sub>2</sub>	2σ <sub>v</sub>	2σ <sub>d</sub>	
A <sub>1</sub>	1	1	1	1	1	x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	1	-1	-1	
B <sub>1</sub>	1	-1	1	1	-1	x <sup>2</sup> -y <sup>2</sup>
B <sub>2</sub>	1	-1	1	-1	1	xy
E	2	0	-2	0	0	(yz, zx)
						T <sub>z</sub> R <sub>z</sub> (T <sub>x</sub> , T <sub>y</sub> ), (R <sub>x</sub> , R <sub>y</sub> )