



Final Examination
2017/2018 Academic Session

May/June 2018

JIK327 – Chemical Spectroscopy
[Spektroskopi Kimia]

Duration : 3 hours
[Masa : 3 jam]

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

Answer **FIVE (5)** questions. Answer the questions in English. You may also answer the questions in Bahasa Malaysia, but not a mix of both languages.

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 EMPAT** muka surat dan **Lampiran** yang bercetak sebelum anda memulakan peperiksaan ini.*

*Jawab **LIMA (5)** soalan. Jawab soalan-soalan dalam Bahasa Inggeris. Anda juga dibenarkan menjawab soalan dalam Bahasa Malaysia, tetapi campuran antara kedua-dua bahasa ini tidak dibenarkan.*

Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

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

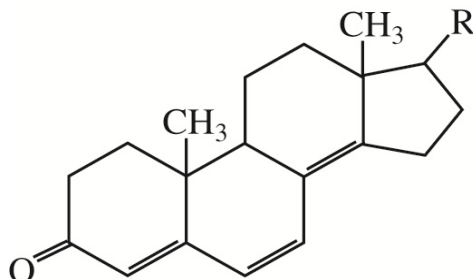
Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

- 2 -

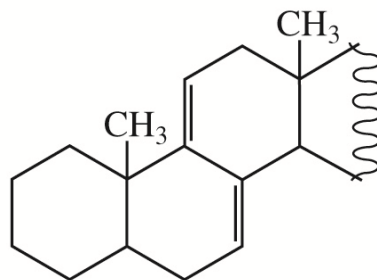
1. (a). Calculate λ_{max} for the compounds below.

Kirakan λ_{max} bagi sebatian di bawah.

(i).



(ii).



(6 marks/markah)

- (b). A solution containing the complex formed between Bi(III) and thiourea has a molar absorptivity of $9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 470 nm.
- (i). What is the absorbance of a $6.24 \times 10^{-5} \text{ M}$ solution of the complex at 470 nm in a 1.00 cm cell?
- (ii). What is the molar concentration of the complex in a solution that has the absorbance described in (i). when measured at 470 nm in a 5.00 cm cell.

Suatu larutan mengandungi kompleks yang terbentuk antara Bi(III) dan tiourea mempunyai keterserapan molar sebanyak $9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ pada 470 nm.

- (i). *Apakah nilai serapan bagi $6.24 \times 10^{-5} \text{ M}$ larutan kompleks pada 470 nm di dalam sel 1.00 cm?*
- (ii). *Apakah nilai kepekatan molar bagi kompleks di dalam larutan yang mempunyai nilai serapan di (i). apabila diukur pada 470 nm di dalam sel 5.00 cm.*

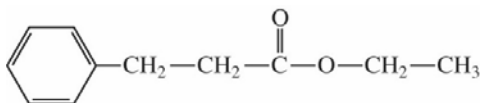
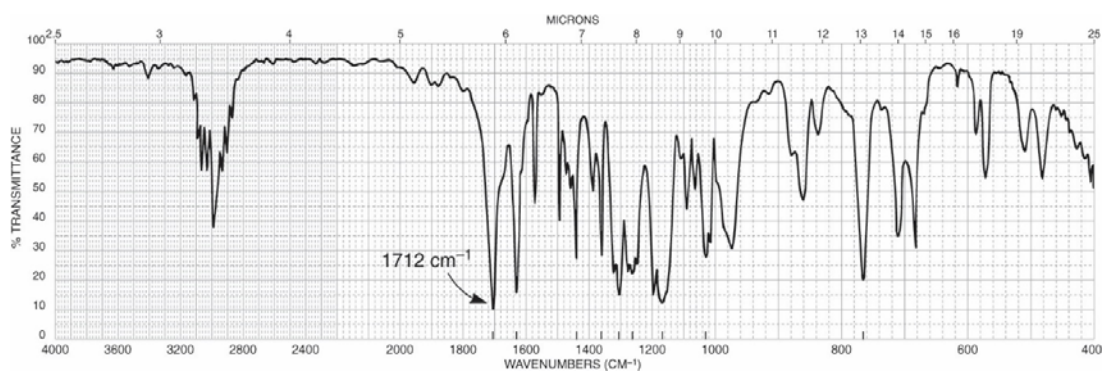
(4 marks/markah)

- 3 -

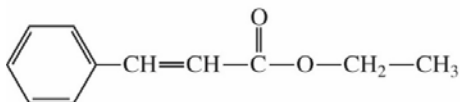
- (c). Based on the infrared spectrum shown below, choose the most suitable structure.

Berdasarkan spektrum inframerah yang ditunjukkan di bawah, pilih struktur yang paling sesuai.

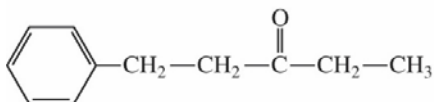
(i).



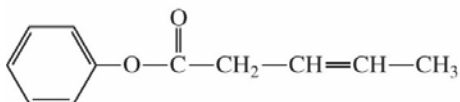
A



B



C

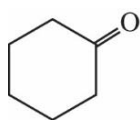
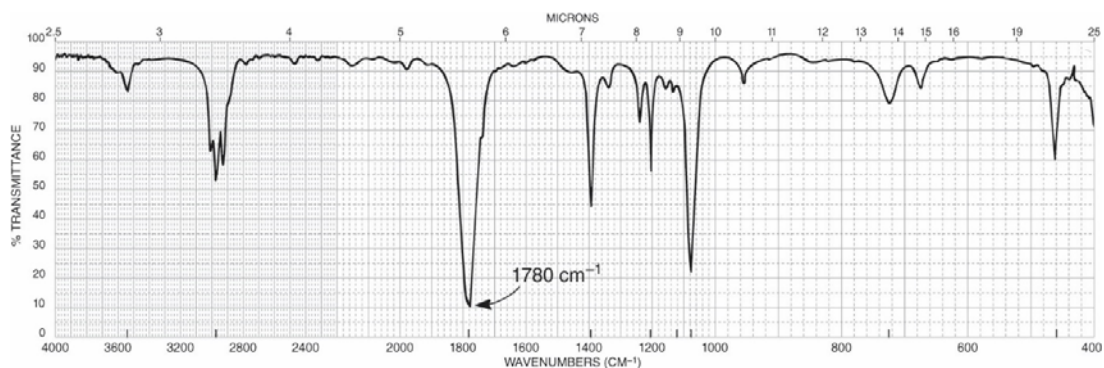


D

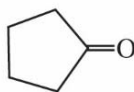
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- 4 -

(ii).



A



B



C



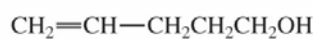
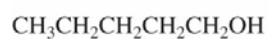
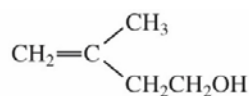
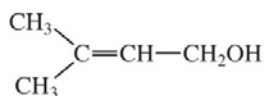
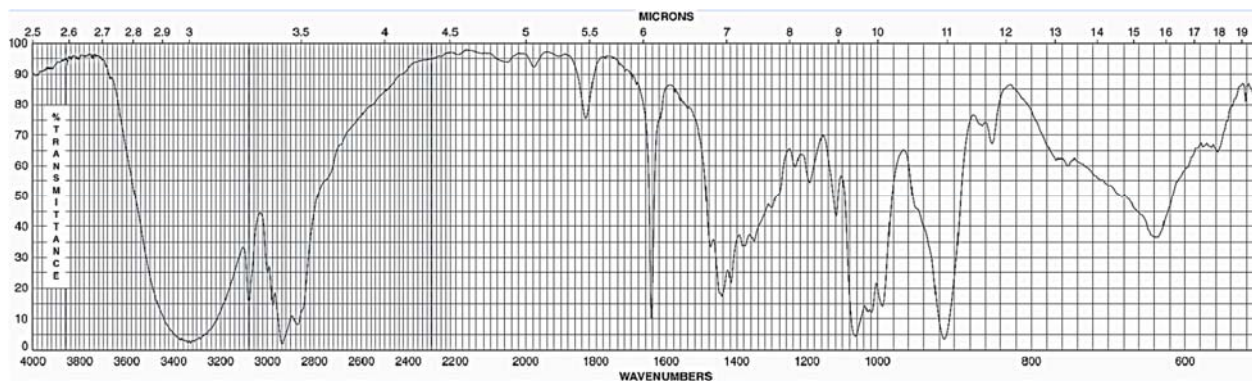
D

(4 marks/markah)

(d). Assign a structure to each of the following spectra.

Padankan struktur bagi setiap spektra yang ditunjukkan.

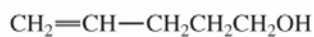
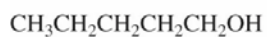
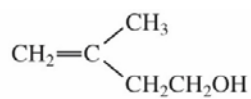
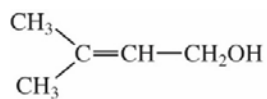
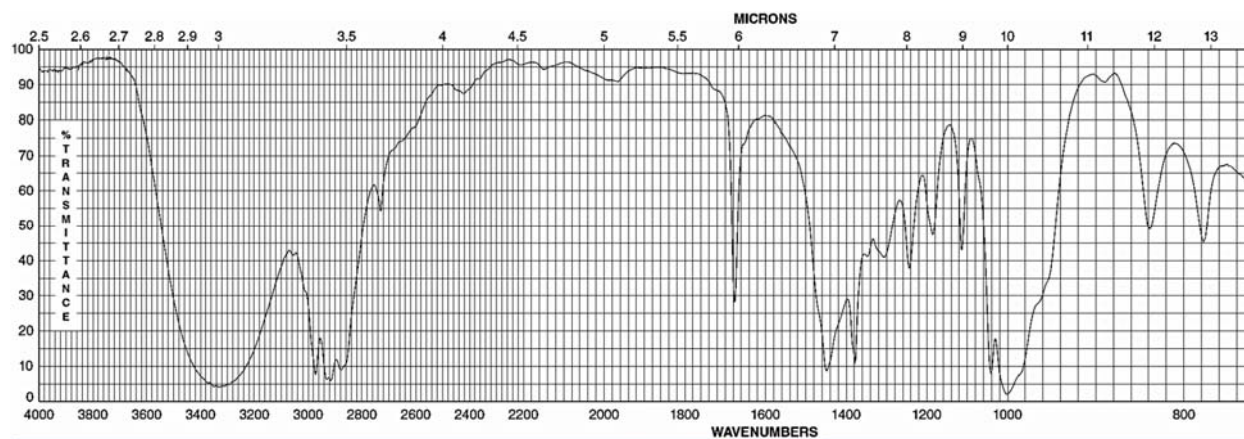
(i).



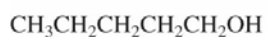
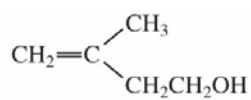
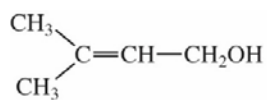
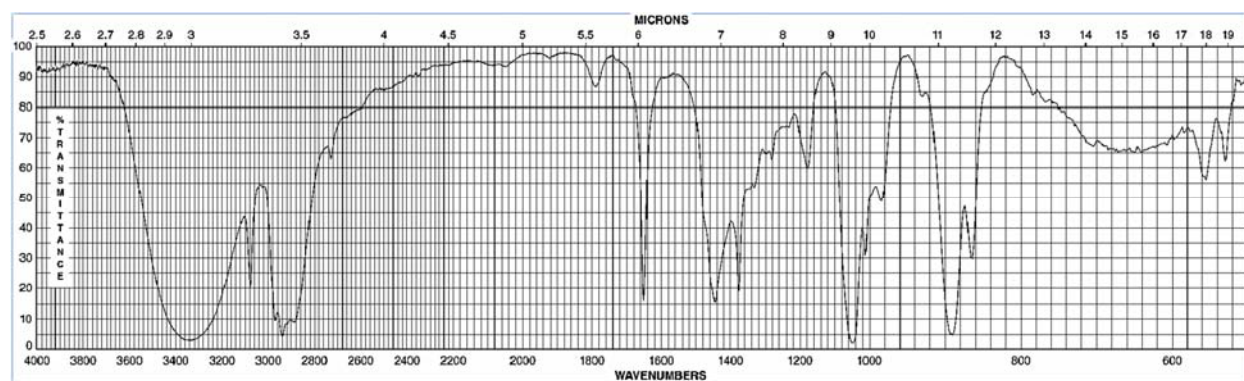
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- 5 -

(ii).



(iii).



(6 marks/markah)

...6/-

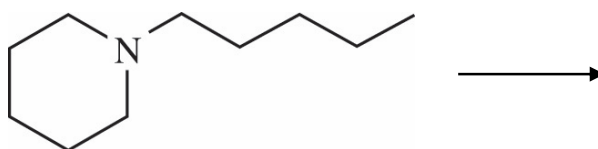
- 6 -

2. (a). For each structure shown below:
- Draw the structure of the ion indicated by m/z value(s).
 - Draw a fragmentation mechanism that accounts for the formation of that fragment ion.

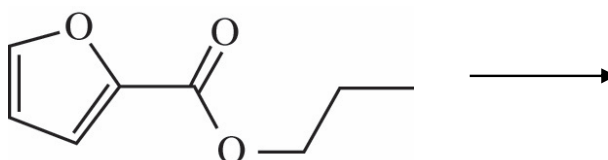
Bagi setiap struktur yang ditunjukkan di bawah:

- *Lukiskan struktur bagi ion yang memberikan nilai m/z .*
- *Lukiskan mekanisme penyerpihan yang bertanggungjawab bagi pembentukan serpihan ion berkenaan.*

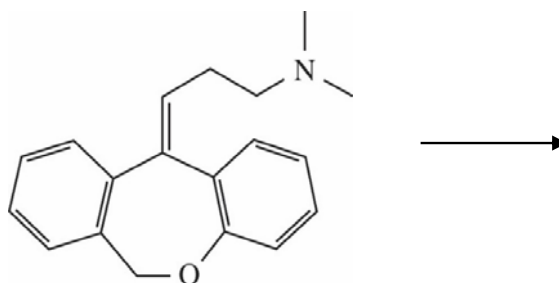
- (i). Fragment ion at $m/z = 98$ (base peak)
Ion serpihan pada $m/z = 98$ (puncak utama)



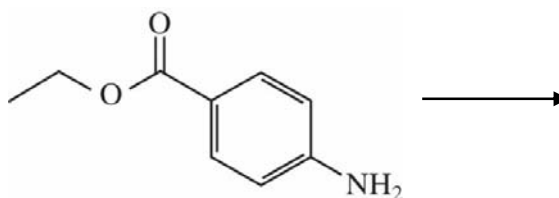
- (ii). Fragment ion at $m/z = 95$ (base peak)
Ion serpihan pada $m/z = 95$ (puncak utama)



- (iii). Fragment ion at $m/z = 58$ (base peak)
Ion serpihan pada $m/z = 58$ (puncak utama)



- (iv). Fragment ion at $m/z = 120$ (base peak)
Ion serpihan pada $m/z = 120$ (puncak utama)



(8 marks/markah)

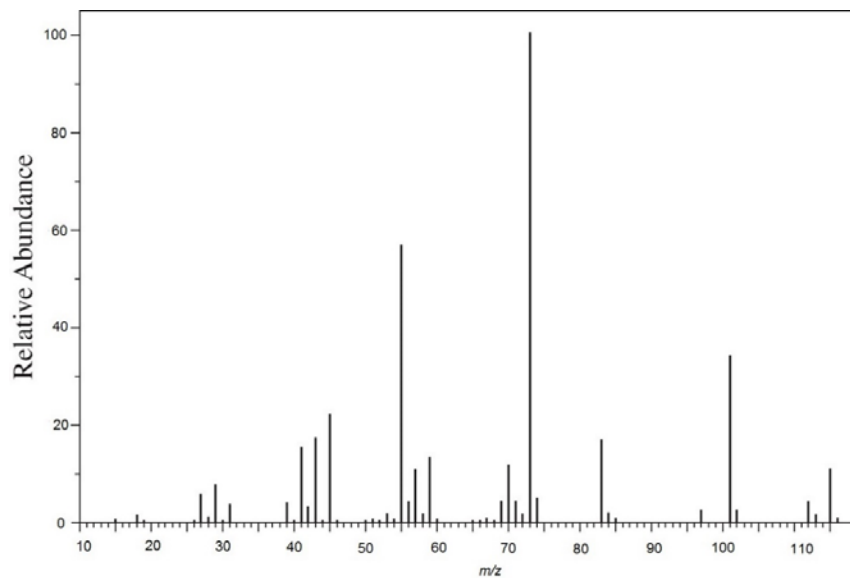
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- 7 -

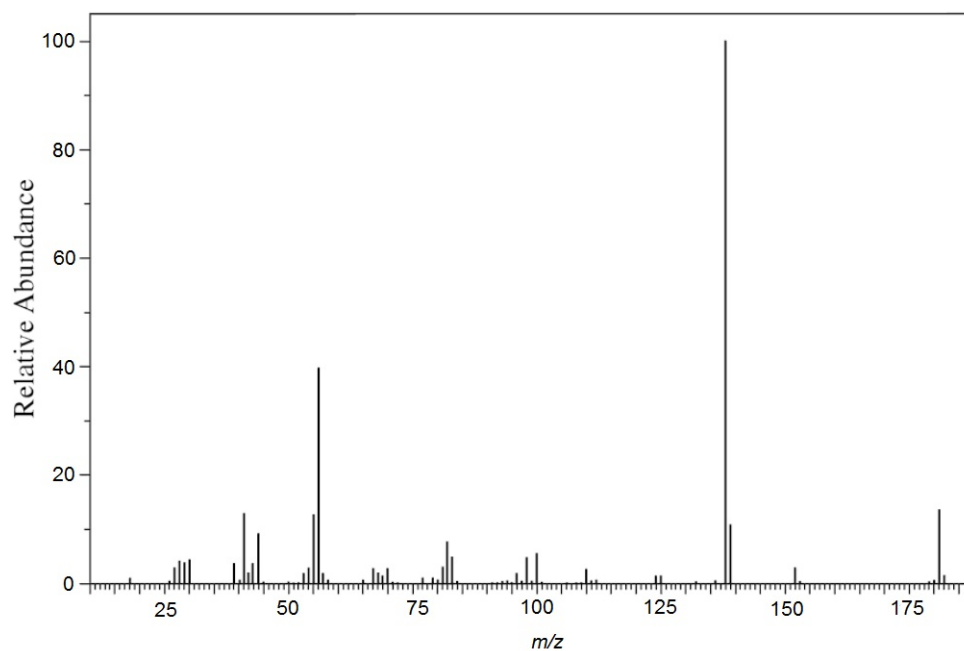
- (b). For each mass spectrum below, determine the structure of the prominent fragment ions and draw a fragmentation mechanism to explain their formation.

Bagi setiap spektrum jisim di bawah, tentukan struktur bagi ion serpihan utama dan lukiskan mekanisme penyerpihan bagi menerangkan pembentukkannya.

- (i). 3-methylheptan-3-ol
3-metilheptan-3-ol



- (ii). Dicyclohexylamine
Disikloheksilamina



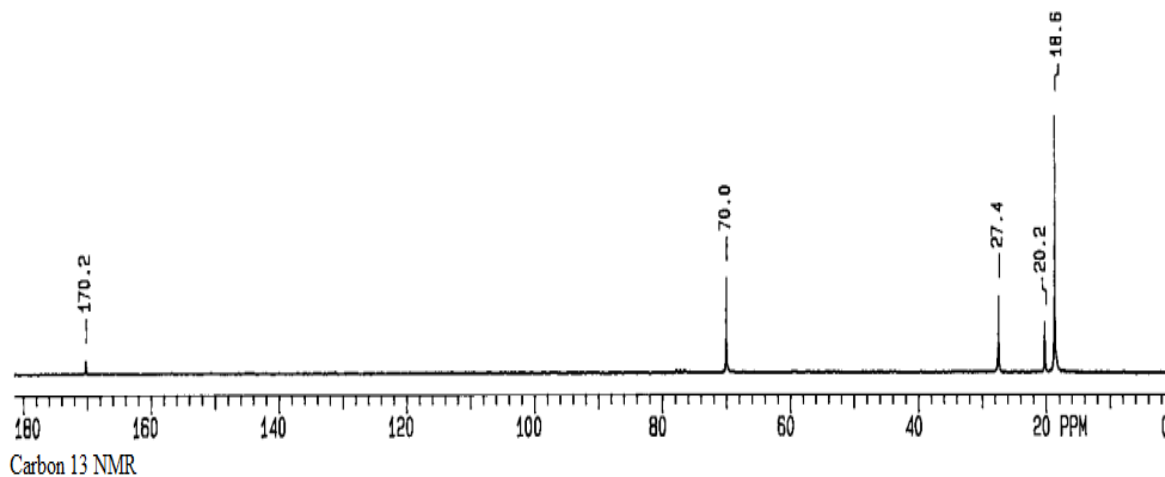
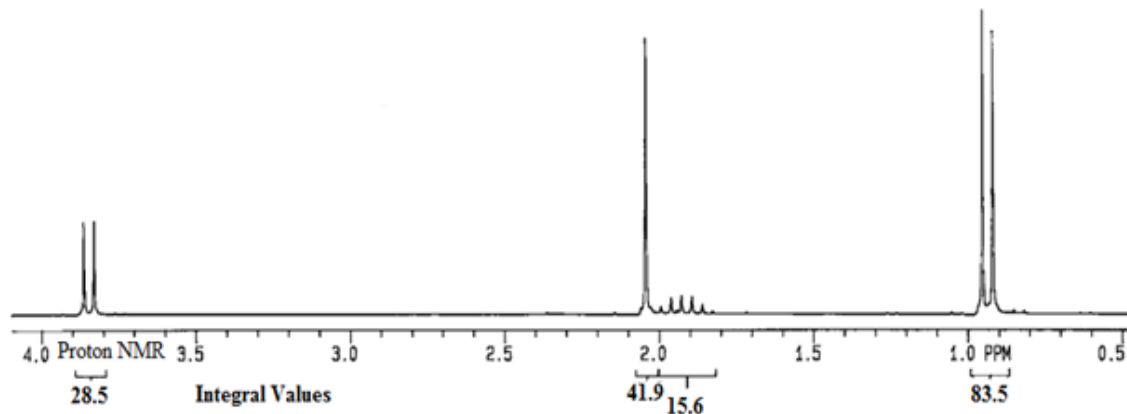
(12 marks/markah)

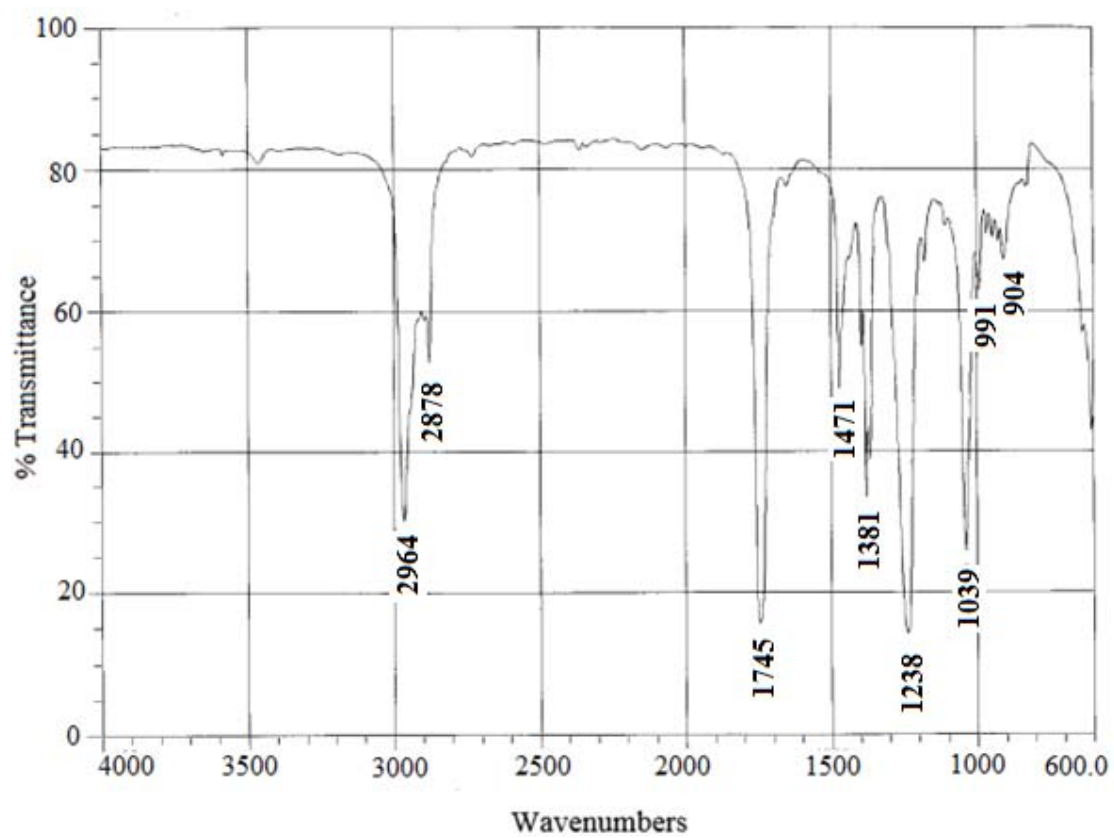
...8/-

3. (a). Draw the structure of each of the following unknown compounds based on its molecular formula and its ^1H NMR, ^{13}C NMR and IR spectra. Explain your answer.

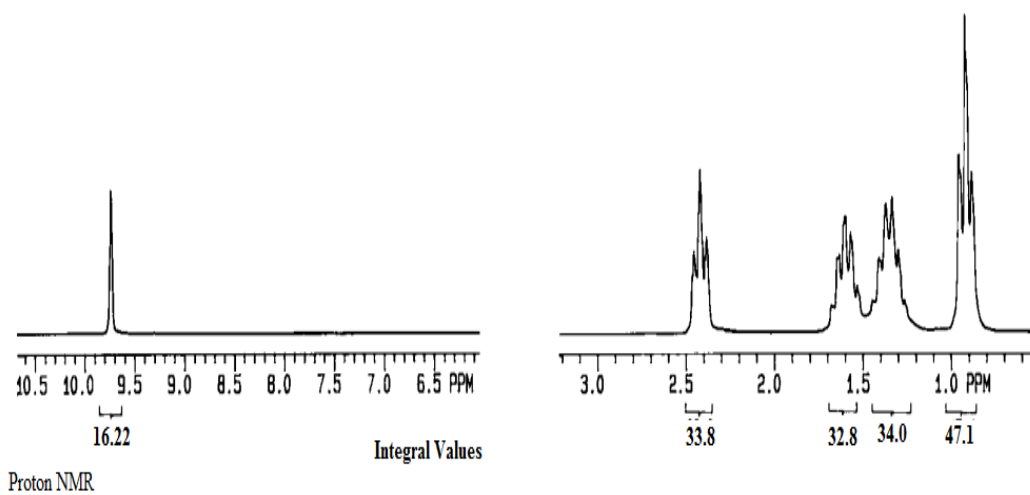
Lukiskan struktur untuk setiap sebatian yang tidak diketahui di bawah berdasarkan formula molekul dan spektrum ^1H NMR, ^{13}C NMR serta IR masing-masing. Jelaskan jawapan anda.

- (i). $\text{C}_6\text{H}_{12}\text{O}_2$

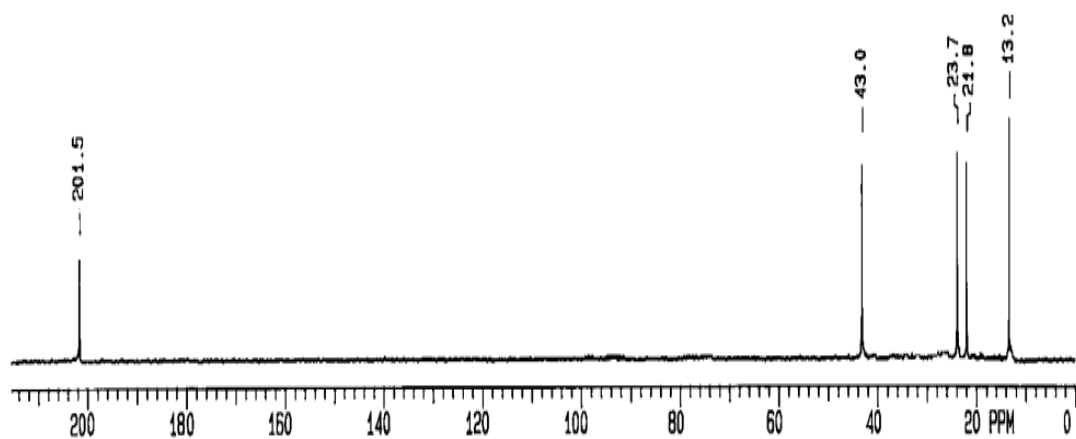




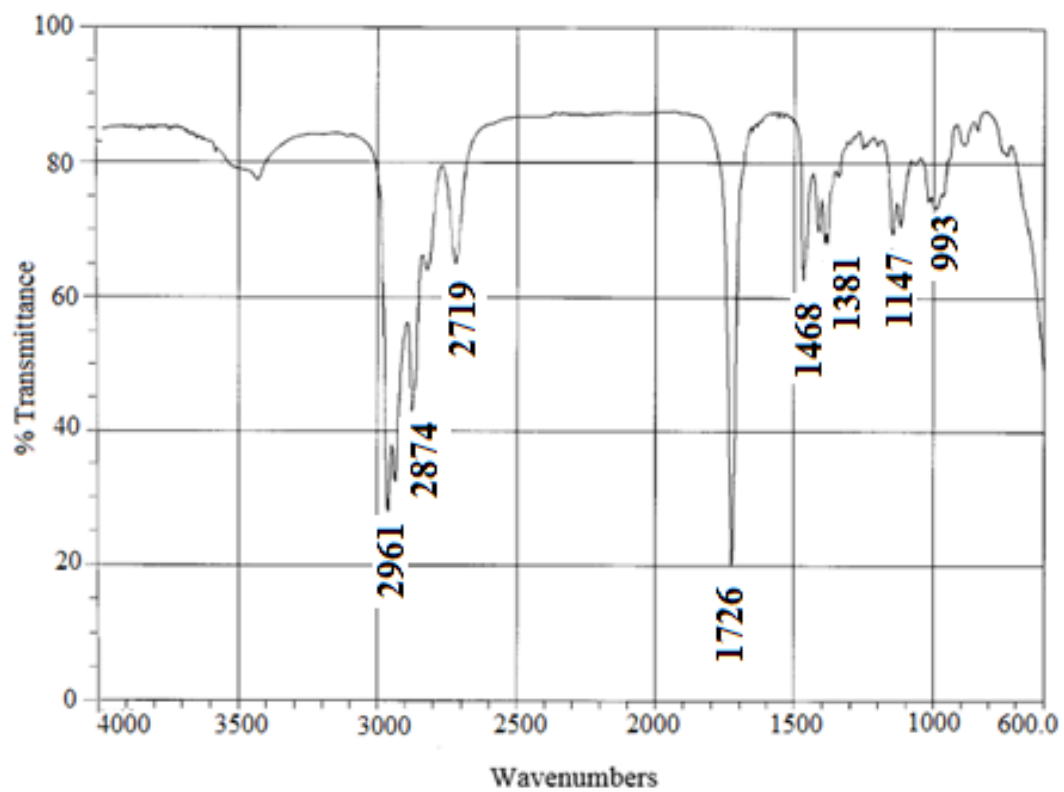
(ii). $C_5H_{10}O$



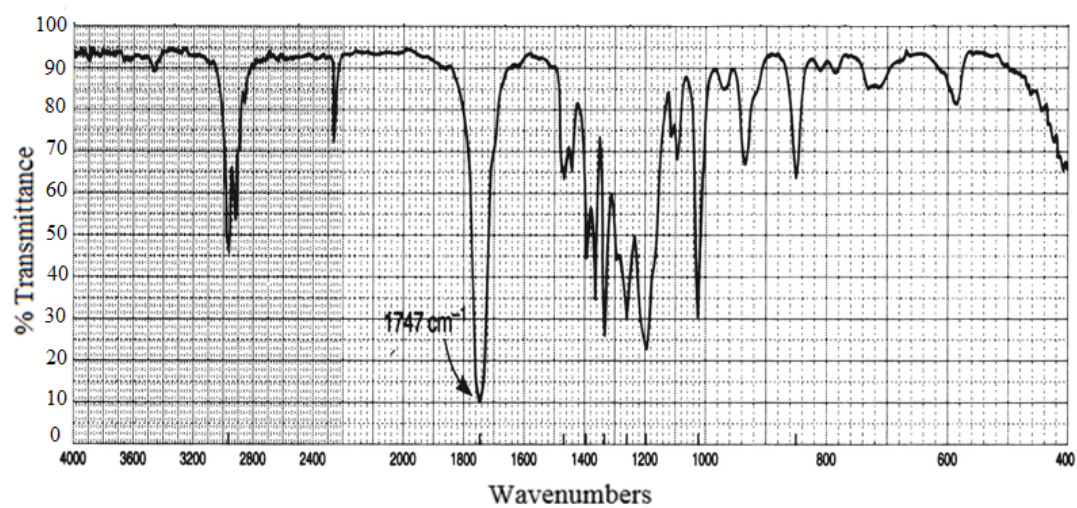
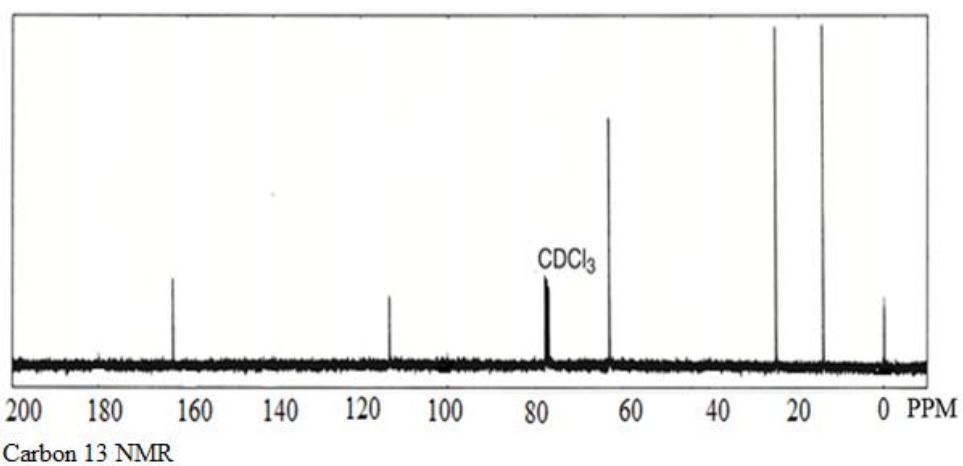
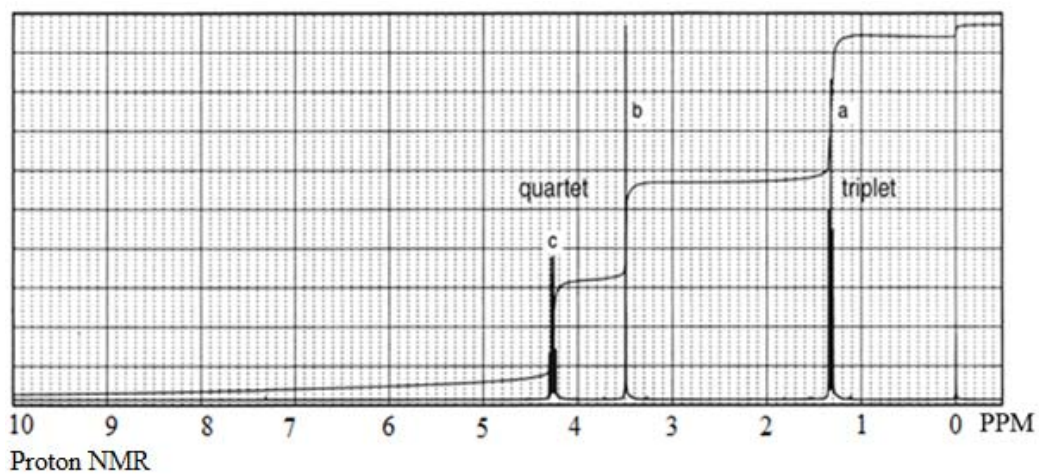
- 10 -



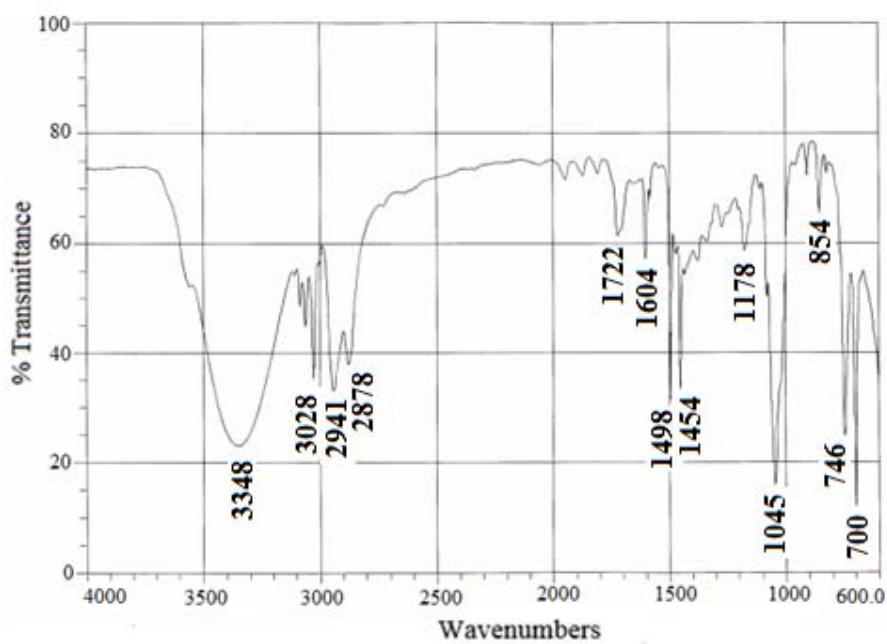
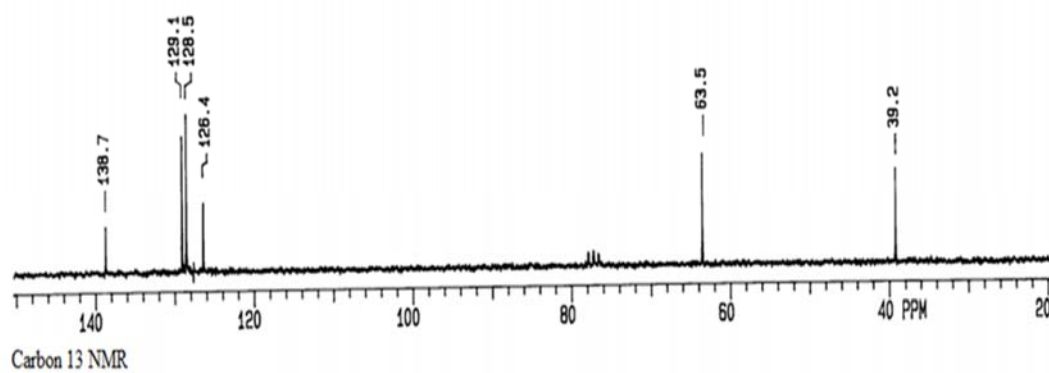
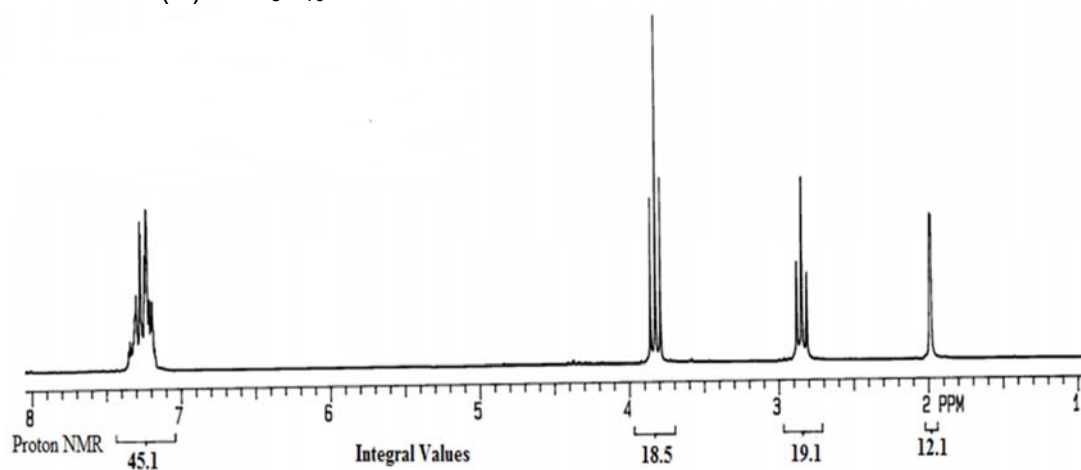
Carbon 13 NMR



...11/-

(iii). $C_5H_7NO_2$ 

- 12 -

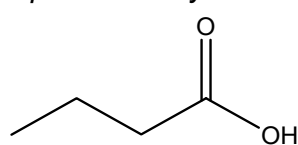
(iv). $C_8H_{10}O$ 

(20 marks/markah)

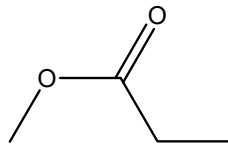
...13/-

4. (a). Explain how you would distinguish the three isomers below using NMR spectroscopy. Give specific examples of peaks, chemical shifts and splitting patterns that would illustrate the differences.

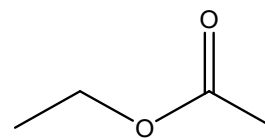
Terangkan bagaimana anda akan membezakan tiga isomer di bawah dengan menggunakan spektroskopi NMR. Berikan contoh spesifik bagi puncak, anjakan kimia dan pola pemecahan untuk menunjukkan perbezaannya.



butanoic acid
asid butanoik



methyl propanoate
metil propanoat



ethyl ethanoate
etil etanoat

(6 marks/markah)

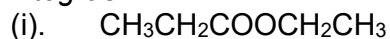
- (b). Determine the structure of $C_8H_{14}O$ from the NMR data below.
Tentukan struktur $C_8H_{14}O$ berpandukan data NMR di bawah.

Chemical shift (δ)	Number of hydrogen	Splitting pattern
9.72 ppm	1H	s
5.34 ppm	1H	t
3.21 ppm	1H	q
2.00 ppm	2H	m
1.82 ppm	3H	s
1.06 ppm	3H	t
0.83 ppm	3H	s

(4 marks/markah)

- (c). Draw the 1H -NMR spectrum you would expect for the following compounds. Show clearly the splitting pattern and the integration values.

Lukiskan spektrum 1H -NMR yang anda jangkakan untuk sebatian-sebatian di bawah. Tunjukkan dengan jelas pola pemecahan dan nilai integrasi.



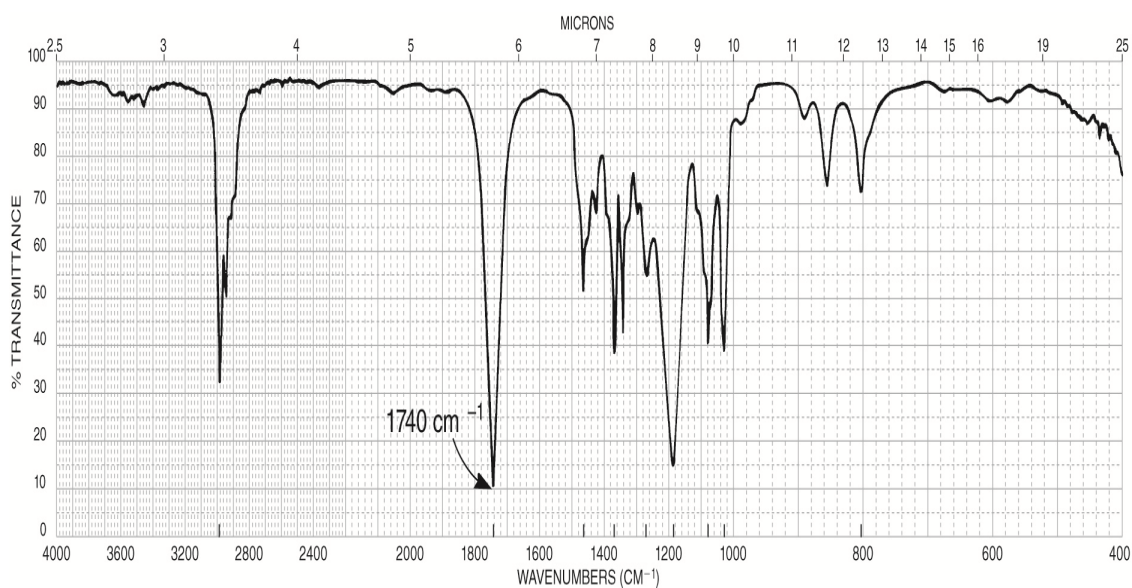
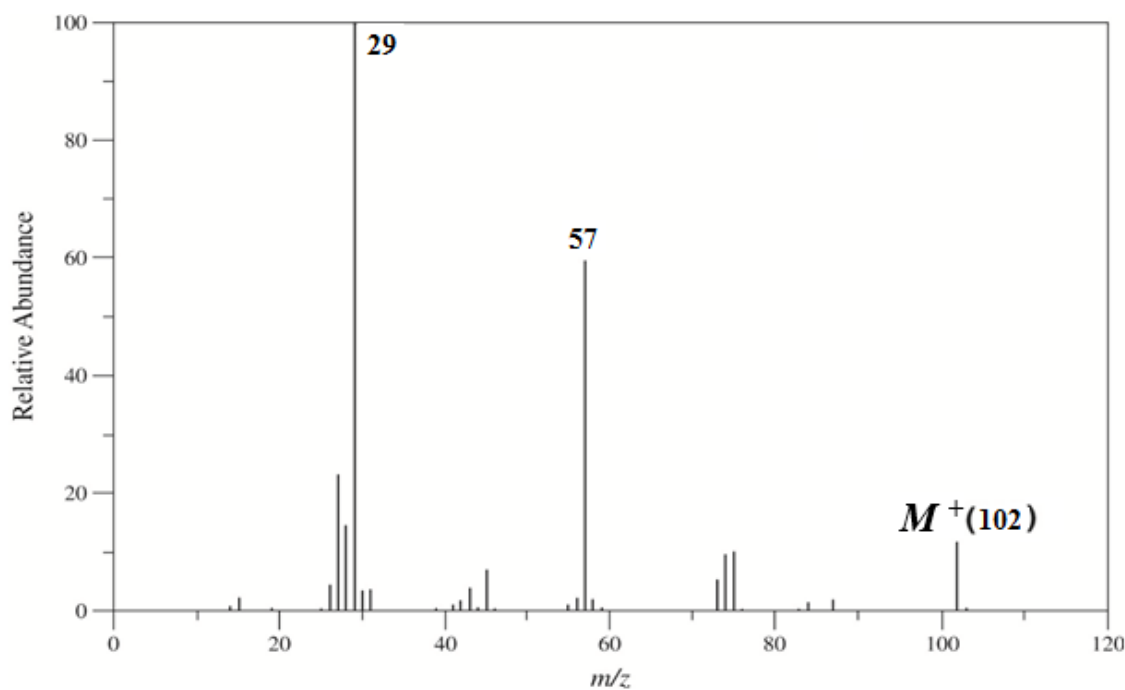
(10 marks/markah)

...14/-

- 14 -

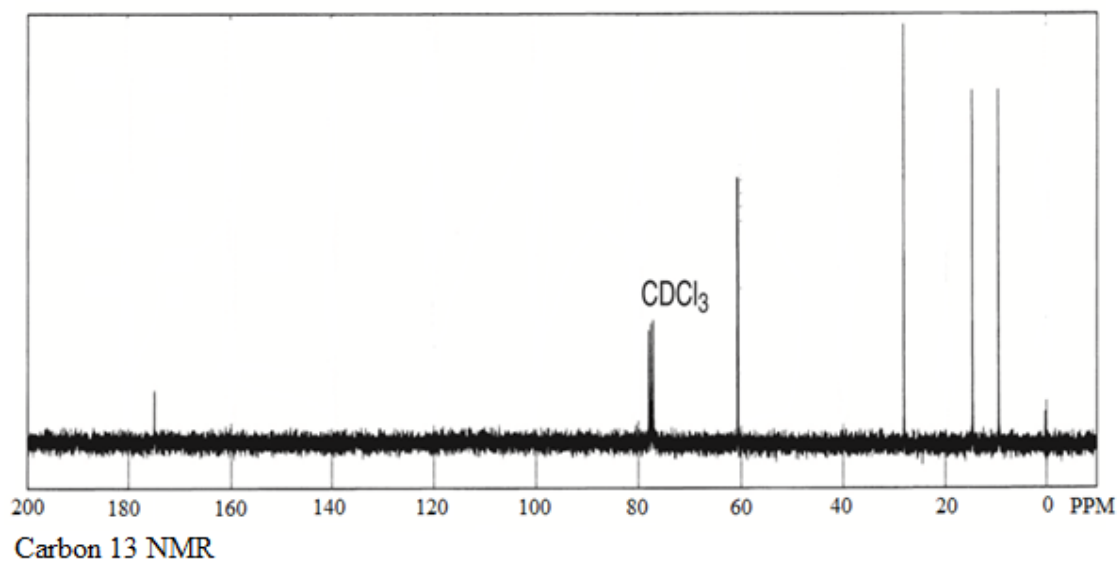
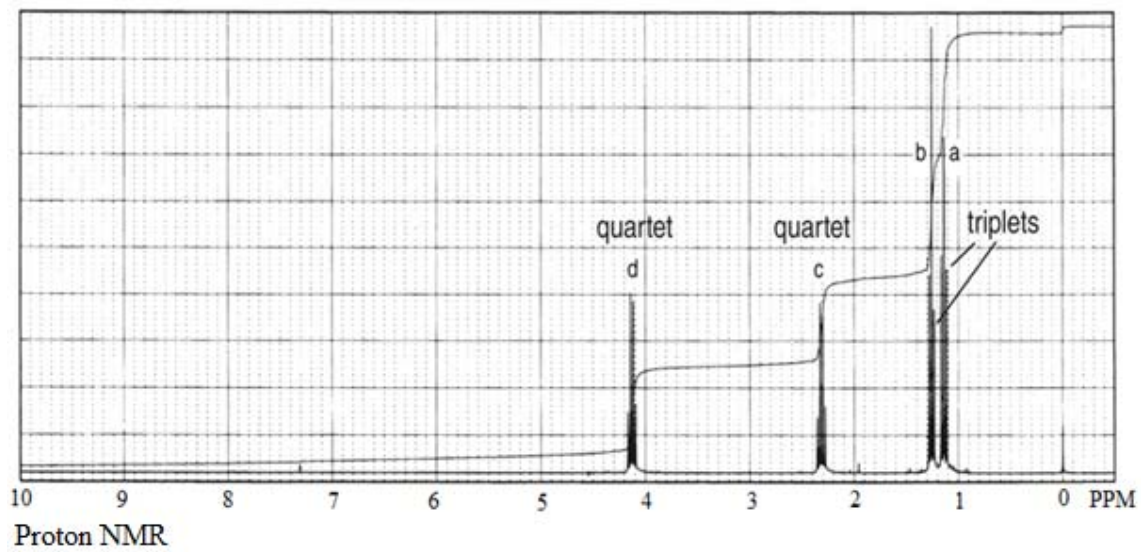
5. An unknown compound, **Y** has the following mass, IR, ^1H and ^{13}C NMR spectra. The UV spectrum of this compound shows only end absorption. Explain each spectrum individually and then consider them in relation to each other. Determine and draw the structure of compound **Y**.

Suatu sebatian yang tidak diketahui, Y mempunyai data jisim, spektrum IR, ^1H dan ^{13}C -NMRnya. Spektrum UV sebatian ini hanya menunjukkan penyerapan akhir. Jelaskan setiap spektrum secara berasingan dan kemudian pertimbangkan hubungan spektrum-spektrum antara satu sama lain. Tentukan dan lukiskan struktur sebatian Y.



...15/-

- 15 -



(20 marks/markah)

...16/-

6. (a). Determine the symmetry elements and assign the point group of the following molecules or ions.

Tentukan unsur-unsur simetri dan tetapkan kumpulan titik bagi molekul-molekul atau ion-ion berikut.

- (i). NH_3Cl^+
 (ii). BF_4^+
 (iii). PF_3
 (iv). SF_4
 (v). XeF_4

(10 marks/markah)

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

Dapatkan perwakilan tak terturunkan untuk data terturunkan berikut:

- (i).

C_{6v}	E	2C_6	2C_3	C_2	$3\sigma_v$	$3\sigma_d$
	4	-1	1	2	0	-2

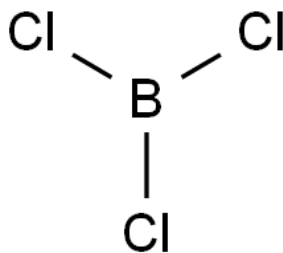
- (ii).

T_d	E	8C_3	3C_2	6S_4	$6\sigma_d$
	8	2	0	2	2

(6 marks/markah)

- (c). Predict the IR and Raman vibrations in boron trichloride (D_{3h}). Show your calculation.

Ramalkan getaran IR dan Raman dalam boron triklorida (D_{3h}). Tunjukkan pengiraan anda.



boron trichloride

(4 marks/markah)

APPENDIX

Rules of Diene Absorption	
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) ₂	+60
Solvent correction	+0
	<i>λ_{calc} = Total</i>

Rules of Enones Absorption	
Base values:	
Six-membered ring or acyclic parent enone	215
Five-membered ring parent enone	202
Acyclic dienone	245
Increments for:	
Double-bond-extending conjugation	+30
Alkyl group or ring residue	α +10 β +12 γ and higher +18
Exocyclic double bond	+5
Homocyclic diene component	+39
	<i>λ_{calc} = Total</i>

Reducing Formula

$$a_i = 1/h \sum X_R^s X_i^s N^s$$

h ; total number of operations in certain point group.

X_R^s ; Character (X) for reducible representation.

X_i^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 Γ_{3N}

R	$\chi(R)$
E	+3
i	-3
σ	+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.₁ : Irr. Rep is symmetry with respect to $C_2 \perp C_n$ (if no C_2), then

Irr. Rep. Is symmetry with respect to σ_v

Sub.₂ : Irr. Rep is antisymmetry under conditions as those in Sub.₁ of above.

Sub._g : (gerade) irr. rep. are symm. With respect to inversion at an i

Sub._u : (ungerade) irr. rep. are antisymm. with respect to an i

' : irr. Rep are symm with respect to reflection in a σ_h

'' : irr. Rep. Are antisymm with respect to reflection in a σ_h

The C_{nh} Groups

C_{2h}	C_2	C_s	C_i	C_{3h}	C_3	C_s
A_g	A	A'	A_g	A'	A	A'
B_g	B	A''	A_g	E'	E	$2A'$
A_u	A	A''	A_u	A''	A	A''
B_u	B	A'	A_u	E''	E	$2A''$

C_{4h}	C_4	S_4	C_{2h}	C_2	C_s	C_i	C_{5h}	C_5	C_s
A_g	A	A	A_g	A	A'	A_g	A'	A	A'
B_g	B	B	A_g	A	A'	A_g	E_1'	E_1	$2A'$
E_g	E	E	$2B_g$	$2B$	$2A''$	$2A_g$	E_2'	E_2	$2A'$
A_u	A	B	A_u	A	A''	A_u	A''	A	A''
B_u	B	A	A_u	A	A''	A_u	E_1''	E_1	$2A''$
E_u	E	E	$2B_u$	$2B$	$2A'$	$2A_u$	E_2''	E_2	$2A''$

The C_m Groups

C_{2v}	C_2	C_s	C_s	C_{3v}	C_3	C_s
A_1	A	A'	A'	A_1	A	A'
A_2	A	A''	A''	A_2	A	A''
B_1	B	A'	A''	E	E	$A' + A''$
B_2	B	A''	A'			

C_{4v}	C_4	C_{2v}	σ_v	σ_d	C_{2v}	C_2	C_s	σ_d	C_s
A_1	A	A_1	A_1	A_1	A_1	A	A'	A'	A'
A_2	A	A_2	A_2	A_2	A_2	A	A''	A''	A''
B_1	B	A_1	A_1	A_2	A	A	A'	A''	A''
B_2	B	A_2	A_2	A_1	A	A	A''	A'	A'
E	E	$B_1 + B_2$	$B_1 + B_2$	$B_1 + B_2$	2B	$A' + A''$	$A' + A''$	$A' + A''$	$A' + A''$

C_{5v}	C_5	C_s	σ_v	σ_d	$\sigma_v \rightarrow \sigma(zx)$	C_{3v}	C_3	C_2	C_s	σ_d	C_s
A_1	A	A'	A_1	A_1	A	A_1	A	A	A'	A'	A'
A_2	A	A''	A_2	A_2	A	A_2	A	A	A''	A''	A''
E_1	E_1	$A' + A''$	A_1	B_1	B	A_1	A	B	A'	A''	A''
E_2	E_2	$A' + A''$	A_2	B_2	B	A_2	A	B	A''	A'	A'
			E	$B_1 + B_2$	E_1	E	E	2B	$A' + A''$	$A' + A''$	$A' + A''$
			E_2	E_2	E_2	E	E	2A	$A' + A''$	$A' + A''$	$A' + A''$

The D_{nd} Groups

D_{2d}	$C_2 \rightarrow C_2(z)$			C_2	C_2'	C_s
	S_4	D_2	C_{2v}	C_2	C_2	
A_1	A	A	A_1	A	A	A'
A_2	A	B_1	A_2	A	B	A''
B_1	B	A	A_2	A	A	A''
B_2	B	B_1	A_1	A	B	A'
E	E	$B_2 + B_3$	$B_1 + B_2$	2B	$A + B$	$A' + A''$

D_{3d}	D_3	C_{3v}	S_6	C_3	C_{2h}	C_2	C_2	C_i
	A_{1g}	A_1	A_1	A_g	A	A_g	A	A'
A_{2g}	A_2	A_2	A_g	A	B_g	B	A''	A_g
E_g	E	E	E_g	E	$A_g + B_g$	$A + B$	$A' + A''$	$2A_g$
A_{1u}	A_1	A_2	A_u	A	A_u	A	A''	A_u
A_{2u}	A_2	A_1	A_u	A	B_u	B	A'	A_u
E_u	E	E	E_u	E	$A_u + B_u$	$A + B$	$A' + A''$	$2A_u$

D_{4d}	D_4	C_{4v}	S_8	C_4	C_{2v}	C_2	C_2'	C_s
						C_2	C_2	
A_1	A_1	A_1	A	A	A_1	A	A	A'
A_2	A_2	A_2	A	A	A_2	A	B	A''
B_1	A_1	A_2	B	A	A_2	A	A	A''
B_2	A_2	A_1	B	A	A_1	A	B	A'
E_1	E	E	E_1	E	$B_1 + B_2$	2B	$A + B$	$A' + A''$
E_2	$B_1 + B_2$	$B_1 + B_2$	E_2	2B	$A_1 + A_2$	2A	$A + B$	$A' + A''$
E_3	E	E	E_3	E	$B_1 + B_2$	2B	$A + B$	$A' + A''$

D_{5d}	D_5	C_{5v}	C_5	C_2	C_2	C_i
	A_{1g}	A_1	A_1	A	A	A'
A_{2g}	A_2	A_2	A	B	A''	A_g
E_{1g}	E_1	E_1	E_1	$A + B$	$A' + A''$	$2A_g$
E_{2g}	E_2	E_2	E_2	$A + B$	$A' + A''$	$2A_g$
A_{1u}	A_1	A_2	A	A	A''	A_u
A_{2u}	A_2	A_1	A	B	A'	A_u
E_{1u}	E_1	E_1	E_1	$A + B$	$A' + A''$	$2A_u$
E_{2u}	E_2	E_2	E_2	$A + B$	$A' + A''$	$2A_u$

The D_{nh} Groups

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	x^2, y^2, z^2
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	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	yz
B_{3g}	1	-1	-1	1	1	-1	-1	1	xy, yz
A_u	1	1	1	1	-1	-1	-1	-1	R_x
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	$2C_3$	$3C_2$	σ_h	$2S_6$	$3\sigma_v$	$x^2 + y^2, z^2$
A_1'	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	$(x^2 - y^2, xy)$
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 T_d Groups

T_d	D_{2d}	C_{3v}	S_4	D_2	C_{2v}	C_3	C_2	C_5
A_1	A_1	A_1	A	A	A_1	A	A	A'
A_2	B_1	A_2	B	A	A_2	A	A	A''
E	$A_1 + B_1$	E	$A + B$	$2A$	$A_1 + A_2$	E	$2A$	$A' + A''$
T_1	$A_2 + E$	$A_2 + E$	$A + E$	$B_1 + B_2 + B_3$	$A_2 + B_1 + B_2$	$A + E$	$A + 2B$	$A' + 2A''$
T_2	$B_2 + E$	$A_1 + E$	$B + E$	$B_1 + B_2 + B_3$	$A_1 + B_1 + B_2$	$A + E$	$A + 2B$	$2A' + A''$