Final Examination
2018/2019 Academic Session

June 2019

JIK327 – Chemical Spectroscopy
(Spektroskopi Kimia)

Duration : 3 hours
(Masa : 3 jam)

Please check that this examination paper consists of **NINETEEN (19)** pages of printed material before you begin the examination.

*[Sila pastikan bahawa kertas peperiksaan ini mengandungi **SEMBILAN BELAS (19)** muka surat yang bercetak sebelum anda memulakan peperiksaan ini].*

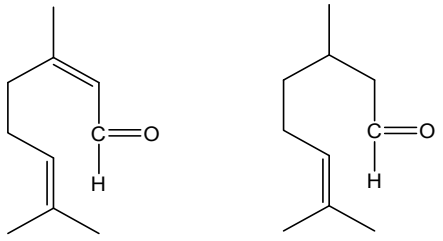
Instructions : Answer **FIVE (5)** questions. Answer the questions in English. You may also answer the questions in Bahasa Malaysia, but not a mix of both languages.

*[**Arahan** : 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].*

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

[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah digunapakai].

1. (a). Ants emit an alarm pheromone to warn other ants in the vicinity to evacuate a dangerous area. Several components of the pheromone in one species have been identified, and two of the components are citral and citronellal.
Semut mengeluarkan feromon penggera untuk memberi amaran kepada semut lain yang berada dekat dengannya untuk menjauhi kawasan berbahaya. Beberapa komponen feromon telah dikenalpasti dan antara duanya ialah sitral dan sitronelal.



Citral Citronellal

(i). How do you distinguish citral and citronellal using infrared spectroscopy.
Bagaimana sitral dan sitronelal dapat dibezakan menggunakan spektroskopi inframerah.

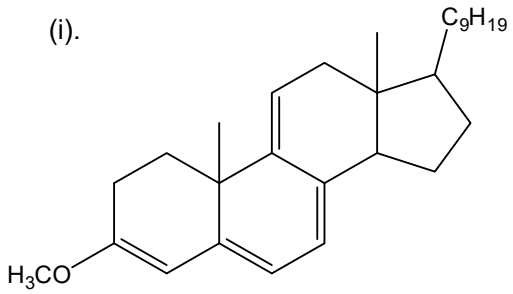
(ii). Explain the significant differences of their ^{1}H and ^{13}C NMR spectra.
Jelaskan perbezaan ketara spektrum-spektrum ^{1}H dan ^{13}C NMR mereka.

(iii). The reduction of both compounds will produce citronellol. How do you confirm that the reaction goes to completion?
Penurunan kedua-dua sebatian akan menghasilkan sitronelol. Bagaimana anda dapat mengesahkan tindak balas telah lengkap sepenuhnya?

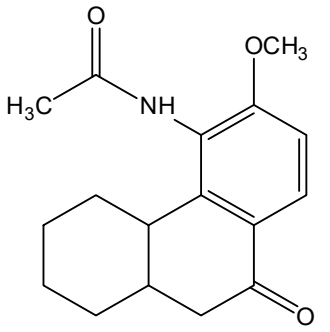
(6 marks/*markah*)

(b). Calculate the λ_{max} for the following compounds.
Kirakan λ_{maks} bagi sebatian di bawah.

(i).



(ii).

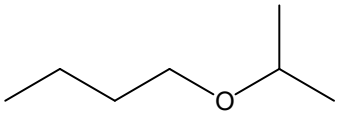


(6 marks/*markah*)

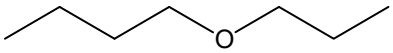
(c). Compounds **A** and **B** give prominent peaks at *m/z* 116, 73, 57 and 43. However, one compound gives a distinctive strong peak at *m/z* 87 and the other compound at *m/z* 101.
*Sebatian **A** dan **B** menghasilkan puncak utama pada m/z 116, 73, 57 dan 43. Walaubagaimanapun, satu sebatian menunjukkan puncak yang kuat pada m/z 87 dan satu sebatian lagi pada m/z 101.*

(i). Determine which compound gives the peak at *m/z* 87 and which one gives the peak at *m/z* 101.
Tentukan sebatian yang mana yang memberikan puncak pada m/z 87 dan m/z 101.

(ii). Propose fragmentations to account for the ions at *m/z* 116, 101, 87 and 43 for compounds **A** and **B**.
*Cadangkan penyerpihan yang bertanggungjawab untuk ion pada m/z 116, 101, 87 dan 43 untuk sebatian **A** dan **B**.*



Compound **A**



Compound **B**

(8 marks/*markah*)

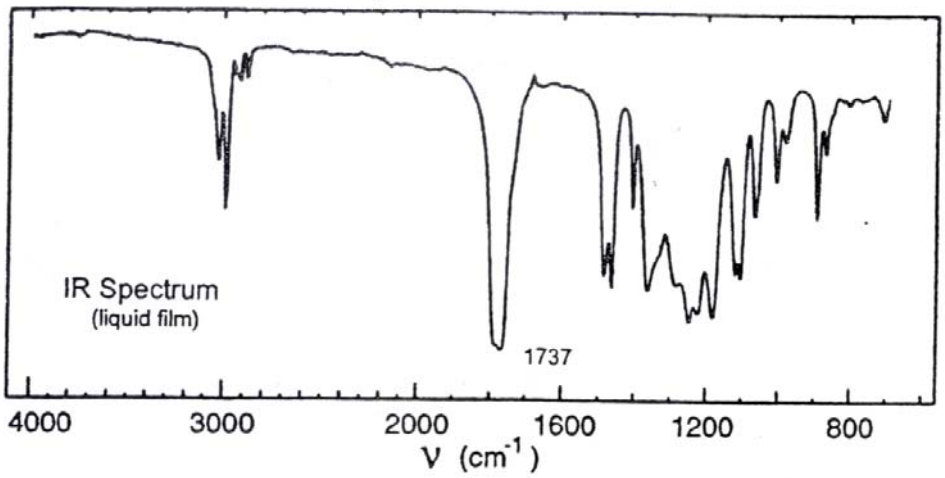
...4/-

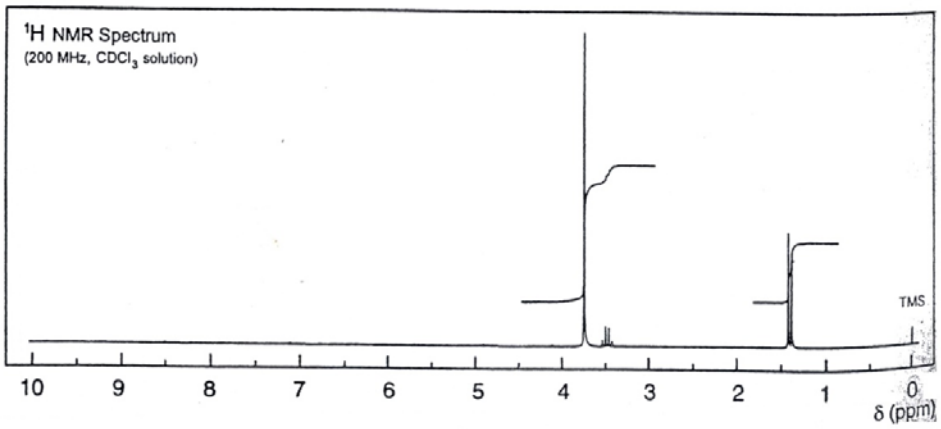
2. (a). An unknown compound **E** with molecular formula $C_6H_{10}O_4$ shows the following IR, ^1H and ^{13}C NMR and mass spectra. The elemental analysis gives the percentage composition of the compound: C, 75.00% and H, 8.33%.

*Suatu sebatian tak diketahui **E** dengan formula molekul $C_6H_{10}O_4$ menunjukkan spektrum IR, ^1H dan ^{13}C NMR dan jisim berikut. Analisis unsur memberikan peratus komposisi sebatian C, 75.00% dan H, 8.33%.*

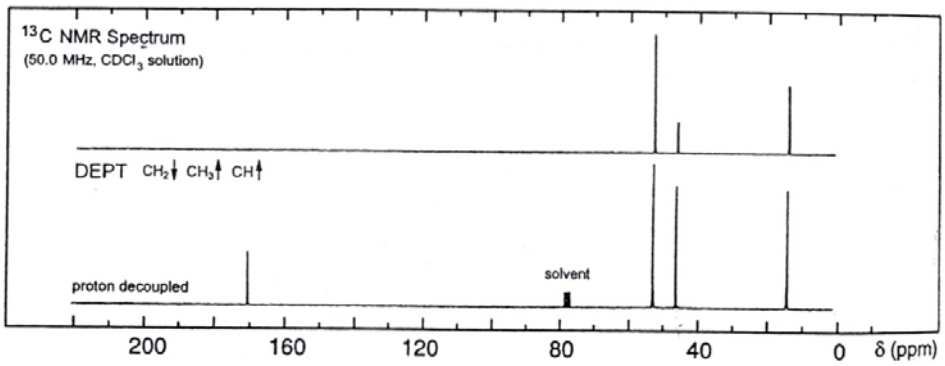
(i). Analyse and elaborate all the spectra.
Analisiskan dan jelaskan semua spektrum.

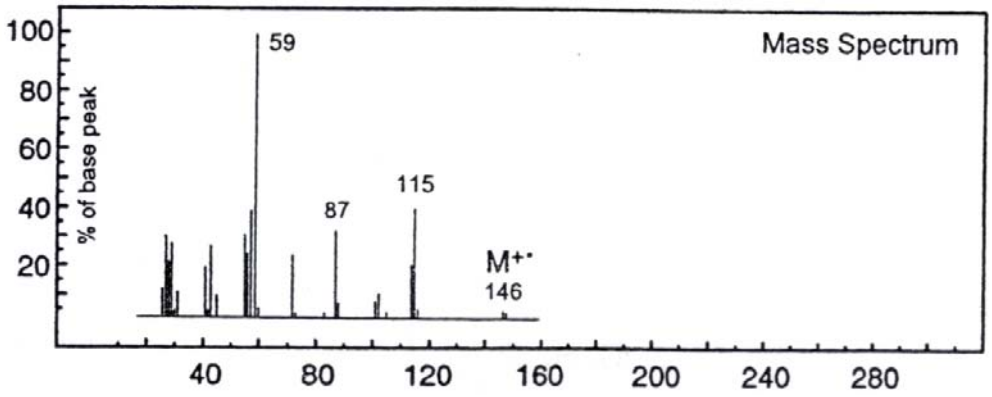
(ii). Propose the most plausible structure of compound **E.**
*Cadangkan struktur yang paling tepat untuk sebatian **E.***





...5/-





(8 marks/*markah*)

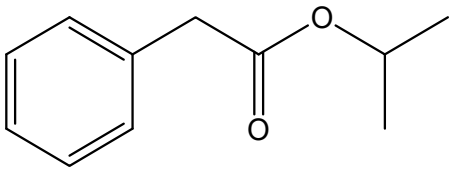
(b). Provide a mechanism and fragment structure that lead to the formation of the base peak at *m/z* 59.
Sertakan mekanisme dan struktur serpihan yang mendorong penghasilan puncak asas pada m/z 59.

(6 marks/*markah*)

(c). Propose fragmentations to account for the ions at *m/z* 115 and 87.
Cadangkan penyerpihan yang bertanggungjawab untuk ion pada m/z 115 dan 87.

(6 marks/*markah*)

3. (a). Consider the structure of compound **F**.
*Pertimbangkan struktur sebatian **F**.*



Compound **F**

(i). Give the absorption frequencies and the functional groups present.
Berikan frekuensi penyerapan dan kumpulan berfungsi yang hadir.

(ii). Give the chemical shifts, integral ratios, multiplicity and type of protons for each signal in the ^{1}H NMR.
Berikan nilai anjakan kimia, kadar kamiran, kemultipelan dan jenis proton untuk setiap isyarat dalam spektrum ^{1}H NMR.

(iii). Draw the ^{1}H and ^{13}C NMR spectrum you would expect for compound **F**. Show clearly the splitting pattern and the integration values.
*Lukiskan spektrum ^{1}H dan ^{13}C NMR yang anda jangkakan bagi sebatian **F**. Tunjukkan dengan jelas pola pemecahan dan kadar kamiran.*

(12 marks/*markah*)

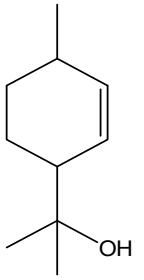
(b). Explain why 4-nitroaniline gives greater red shifts than 3-nitroaniline and 1,4-dinitroaniline.
Jelaskan mengapa 4-nitroanilina memberikan anjakan merah lebih besar berbanding 3-nitroanilina dan 1,4-dinitroanilina.

(3 marks/*markah*)

(c). Dehydration of tertiary alcohol **G** using H_2SO_4 can give four possible dienes **H**-**K**, in which three of them are conjugated dienes **I**, **J** and **K**.
*Pendehidratan alkohol tertier **G** menggunakan H_2SO_4 akan menghasilkan empat diena **H**-**K** yang mungkin di mana tiga daripadanya adalah diena berkonjugat **I**, **J** dan **K**.*

(i). Give the structures of dienes **H** to **K**
Berikan struktur diena **H** hingga **K**

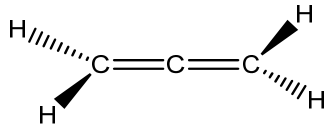
(ii). Can the three conjugated dienes be distinguished by the UV. Give reasons.
Bolehkah ketiga-tiga diena berkonjugat dibezakan menggunakan UV. Berikan sebab.



Compound **G**

(5 marks/*markah*)

4. (a). Find all the possible symmetry operations for 1, 2-propadiene.
Kenal pasti semua operasi simetri yang berkemungkinan berlaku pada 1, 2-propadiena:



(10 marks/*markah*)

(b). What are the symmetry elements and point groups for the following molecules:

Apakah unsur-unsur simetri dan titik kumpulan untuk molekul-molekul berikut:

(i). $CH_2FC\ell$

(ii). ClSb=O

(iii). O=C=C=C=C=O

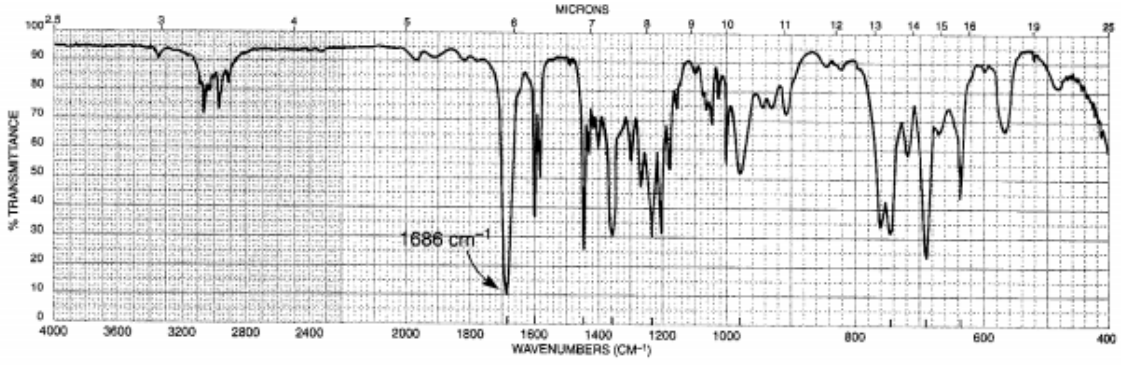
(iv). HI

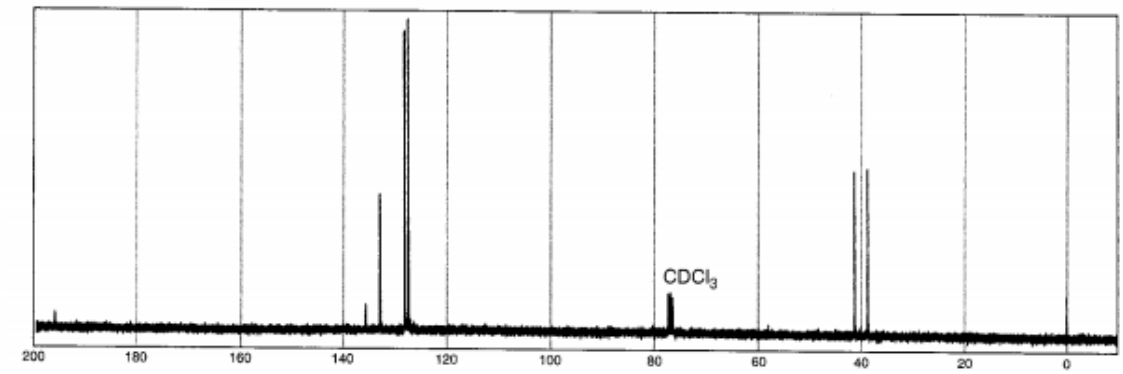
(v). $TeC\ell_4$

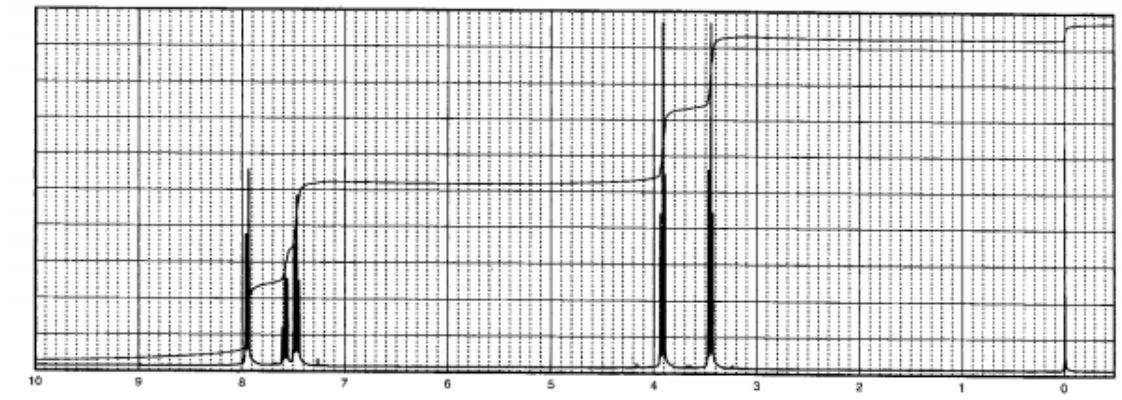
(10 marks/*markah*)

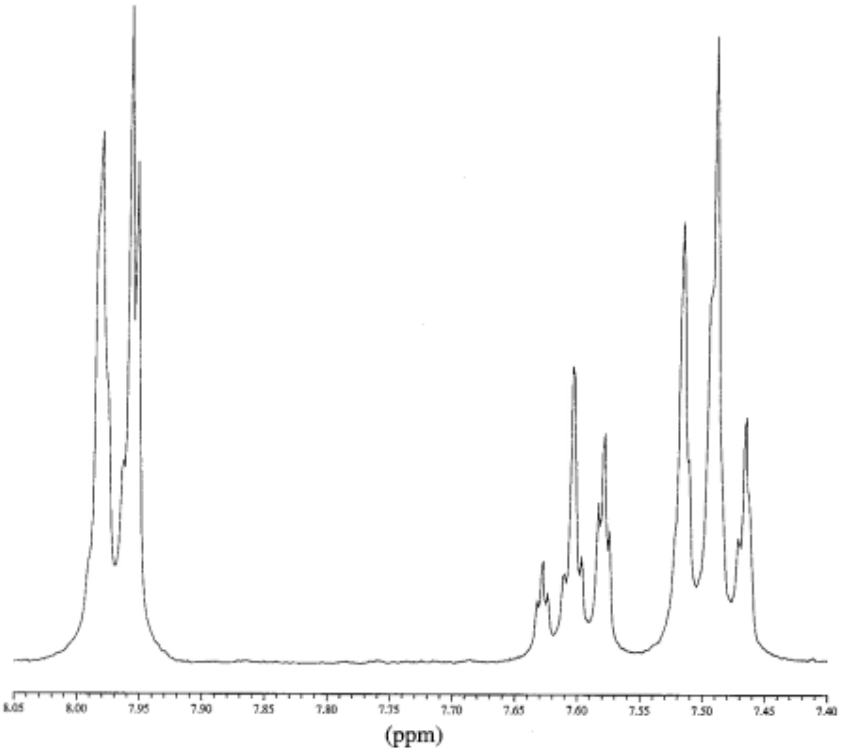
5. (a). Predict the structure of the compound $C_9H_9C\ell O$ given IR, ^{1}H NMR and ^{13}C NMR the spectra below. Show all the interpretations and assign all the peaks involved.

Ramalkan struktur sebatian $C_9H_9C\ell O$ berdasarkan spektra IR ,^{1}H NMR dan ^{13}C NMR *di bawah. Sila tunjukkan semua tafsiran dan labelkan semua puncak yang terlibat.*

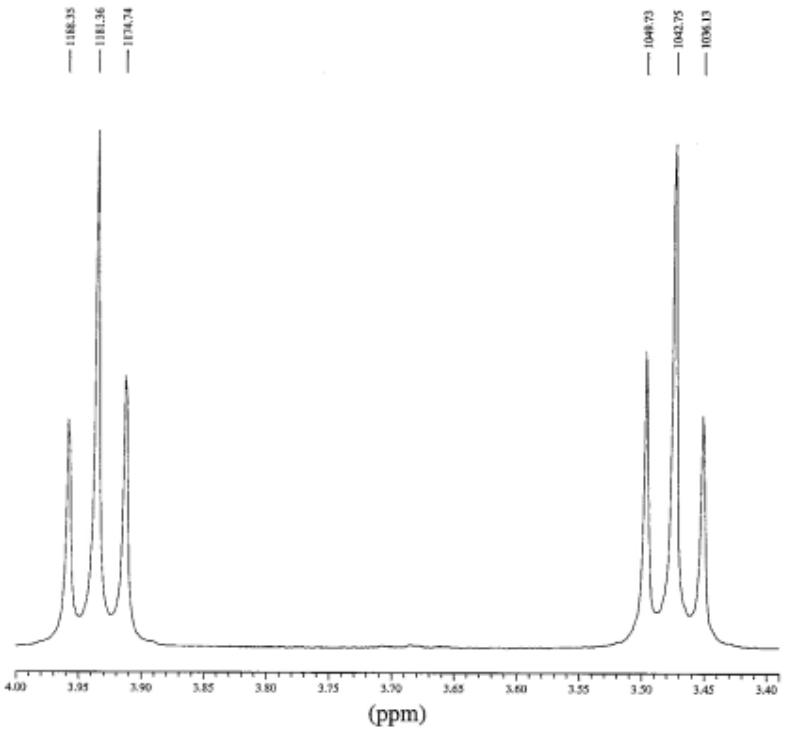



CDCl3
200
180
160
140
120
100
80
60
40
20
0


10
9
8
7
6
5
4
3
2
1
0


8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
(ppm)

...10/-



(20 marks/*markah*)

6. (a). State the main components in Fourier Transform Nuclear Magnetic Resonance (FT-NMR) spectrometer.
Nyatakan komponen utama dalam spektrometer "Fourier Transform Resonance Magnetic Nuclear Resonance (FT-NMR)".

(5 marks/*markah*)

(b). Explain how NMR signals are obtained by FT-NMR spectrometer.
Terangkan bagaimana isyarat NMR diperolehi oleh spektrometer FT-NMR.

(5 marks/*markah*)

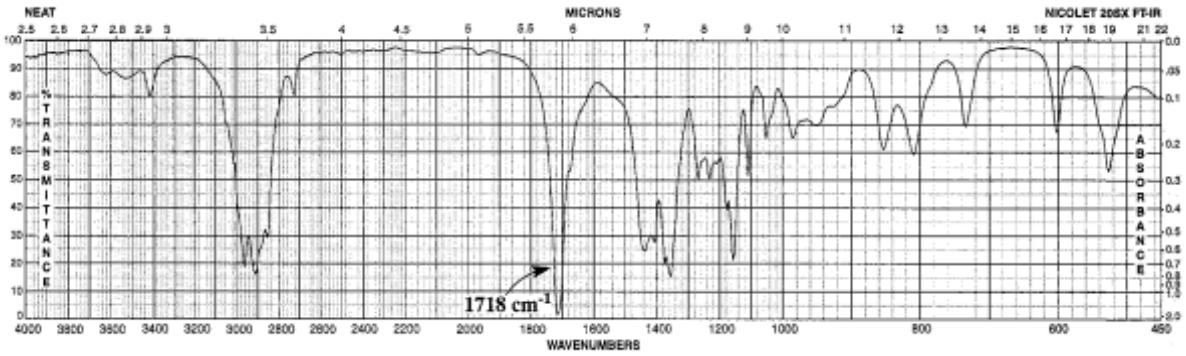
(c). Give two reasons why tetramethylsilane (TMS), $(CH_3)_4Si$ is used as standard reference in ^1H and some ^{13}C NMR analyses.
Berikan dua sebab mengapa tetrametilsilana (TMS), $(CH_3)_4Si$ digunakan sebagai rujukan piawai dalam analisis ^1H dan sesetengah ^{13}C NMR.

(2 marks/*markah*)

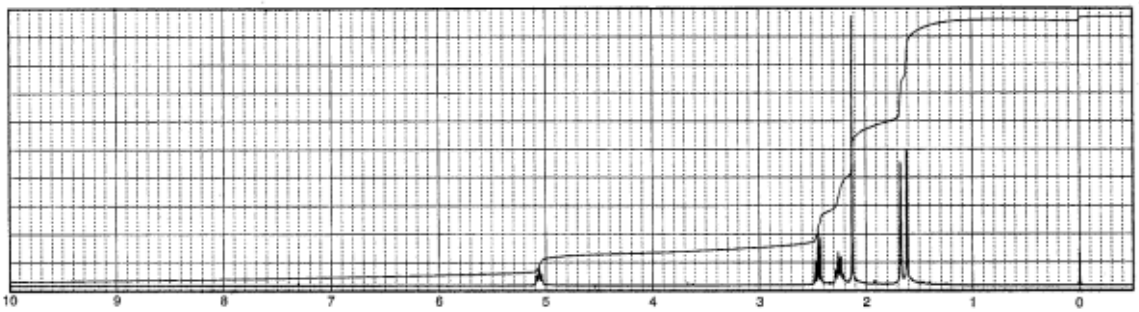
...11/-

(d). Predict the molecular structure of an unknown compound with a molecular formula of $C_8H_{14}O$. The IR, ^1H NMR and ^{13}C NMR spectra of the compound are given below. Identify the unknown compound based on the information given and assign all of the protons and carbons for the predicted structure as well as in the spectrums.

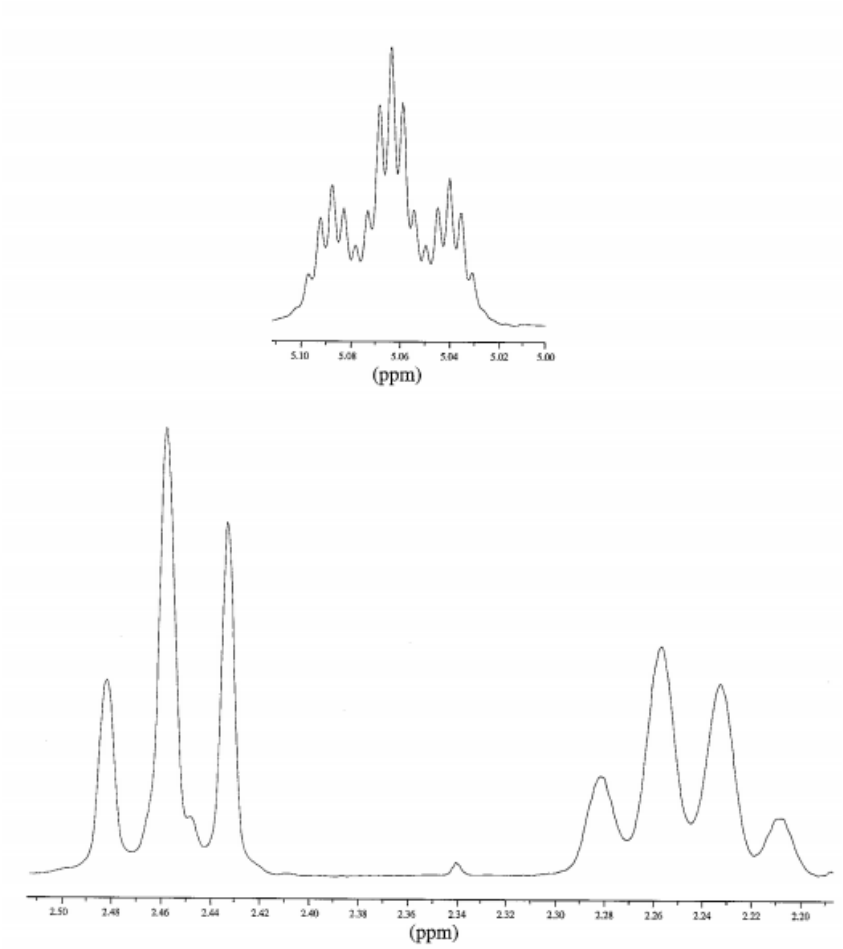
Ramalkan struktur molekul sebatian yang tidak diketahui dengan formula molekul iaitu $C_8H_{14}O$. Spektra IR, ^1H NMR dan ^{13}C NMR untuk sebatian tersebut diberikan dibawah. Kenal pasti sebatian yang tidak diketahui berdasarkan maklumat yang diberikan dan tujukan semua proton dan karbon terhadap struktur yang diramalkan serta dalam spektrum tersebut.



Normal Carbon (ppm)	DEPT-135	DEPT-90
18	Positive	No peak
23	Negative	No peak
26	Positive	No peak
30	Positive	No peak
44	Negative	No peak
123	Positive	Positive
133	No peak	No peak
208	No peak	No peak



...12/-



(8 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
	λcalc = Total

Rules of Enones Absorption	
Base values: Six-membered ring or acyclic parent enone Five-membered ring parent enone Acyclic dienone	 215 202 245

Increments for: Double-bond-extending conjugation Alkyl group or ring residue	 +30 α +10 β +12 γ and higher +18
Exocyclic double bond	+5
Homocyclic diene component	+39
	λcalc = Total

...14/-

Reducing Formula

$a_i = 1/h \sum X^S{}_R X^S{}_i N^S$

h ; total number of operations in certain point group.

$X^S{}_R$; Character (X) for reducible representation.

$X^S{}_i$; 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, χ(R), for each unshifted atom in Γ_{3N}

R	χ(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 ,Tx, Ty, Tz, Rx, Ry, Rz, provide the bases

e. shows the funtions 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 –dimentional irreducible rep. Are labelled as A or B, all two-dimentional as E, all three-dimentional as T (in certain texts it is given the label F), four-dimentional as G and five-dimentional as H.

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

A : One-dimentional irreducible rep. if it is symmetry about Cn axis, i.e.($\chi = +1$)

B : „ „ „ antisymm. „ ($\chi = -1$)

Sub.$_1$: Irr. Rep is symmetry with respect to $C_2 \perp Cn$ (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

...16/-

The C_{nh} Groups

C_{2h}	C_2	C_s	C_i
A_g	A	A′	A_g
B_g	B	A″	A_g
A_u	A	A″	A_u
B_u	B	A′	A_u

C_{3h}	C_3	C_s
A′	A	A′
E′	E	2A′
A″	A	A″
E″	E	2A″

C_{4h}	C_4	S_4	C_{2h}	C_2	C_s	C_i
A_g	A	A	A_g	A	A′	A_g
B_g	B	B	A_g	A	A′	A_g
E_g	E	E	$2B_g$	2B	2A″	$2A_g$
A_u	A	B	A_u	A	A″	A_u
B_u	B	A	A_u	A	A″	A_u
E_u	E	E	$2B_u$	2B	2A′	$2A_u$

C_{5h}	C_5	C_s
A′	A	A′
E_1'	E_1	2A′
E_2'	E_2	2A′
A″	A	A″
E_1''	E_1	2A″
E_2''	E_2	2A″

The C_{nv} 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′			

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

			σ_v	σ_d	$\sigma_v \rightarrow \sigma(zx)$			σ_v	σ_d
C_{5v}	C_5	C_s	C_{6v}	C_6	C_{3v}	C_{3v}	C_{2v}	C_3	C_2	C_s	C_s
A_1	A	A′	A_1	A	A_1	A_1	A_1	A	A	A′	A′
A_2	A	A″	A_2	A	A_2	A_2	A_2	A	A	A″	A″
E_1	E_1	A′ + A″	B_1	B	A_1	A_2	B_1	A	B	A′	A″
E_2	E_2	A′ + A″	B_2	B	A_2	A_1	B_2	A	B	A″	A′
			E_1	E_1	E	E	$B_1 + B_2$	E	2B	A′ + A″	A′ + A″
			E_2	E_2	E	E	$A_1 + A_2$	E	2A	A′ + A″	A′ + A″

The D_{nd} Groups

	$C_2 \rightarrow C_2(z)$			C_2	C_2'	
D_{2d}	S_4	D_2	C_{2v}	C_2	C_2	C_s
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_s	C_i
A_{1g}	A_1	A_1	A_g	A	A_g	A	A′	A_g
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″	$2A_u$

						C_2	C_2'	
D_{4d}	D_4	C_{4v}	S_8	C_4	C_{2v}	C_2	C_2	C_s
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_s	C_i
A_{1g}	A_1	A_1	A	A	A′	A_g
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	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
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	$2C_3$	$3C_2$	σ_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)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	T_z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(yz, zx)

The T_d Groups

T_d	D_{2d}	C_{3v}	S_4	D_2	C_{2v}	C_3	C_2	C_s
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″

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