

UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Kedua
Sidang Akademik 2004/2005

Mac 2005

JIK 319 – SPEKTROSKOPI KIMIA ORGANIK

Masa : 3 jam

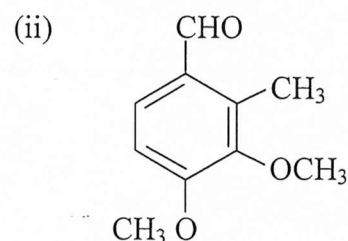
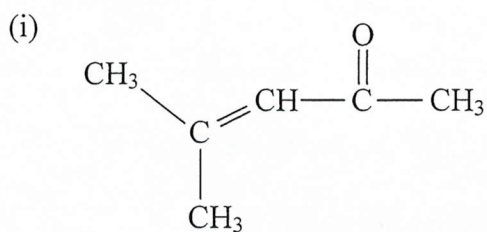
Sila pastikan bahawa kertas peperiksaan ini mengandungi **DUA PULUH TIGA** muka surat yang bercetak sebelum anda memulakan peperiksaan ini.

Jawab LIMA soalan.

Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

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

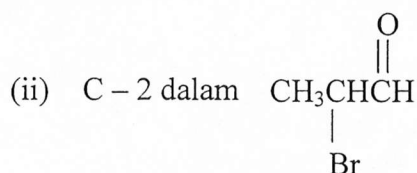
1. (a) Anggarkan λ_{\max} untuk sebatian berikut :



(6 markah)

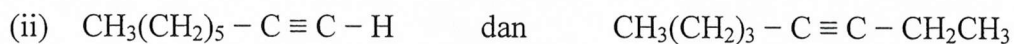
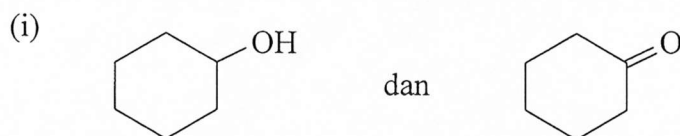
(b) Jelaskan corak pengkupelan yang dijangka untuk proton pada

(i) C - 2 dalam Z - 1, 3 - dikloropropena



(7 markah)

(c) Jelaskan ciri-ciri penyerapan IR yang dapat membezakan di antara pasangan sebatian berikut :



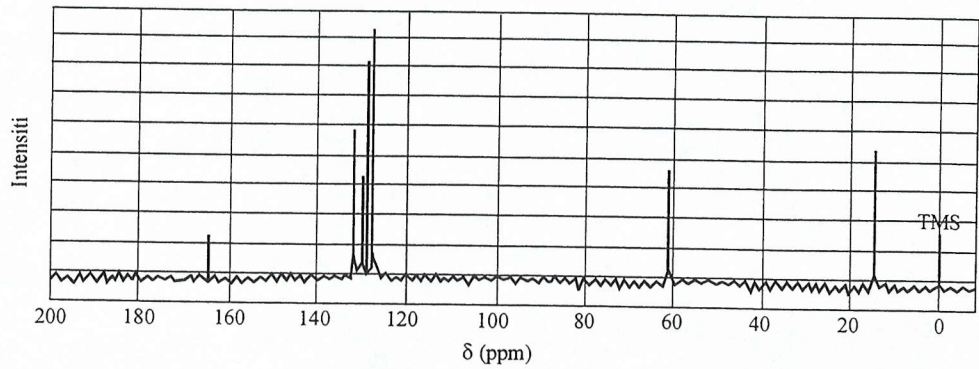
(7 markah)

2. (a) Apakah ciri yang dapat dicerap dengan senang pada spektrum MS jika ada kehadiran unsur berikut ?

- (i) Br
- (ii) Cl
- (iii) N
- (iv) S

(8 markah)

- (b) Kenalpasti puncak-puncak resonans, sebanyak mana yang anda boleh, kepada karbon-karbon tertentu dalam spektrum ^{13}C - NMR etil benzoat.

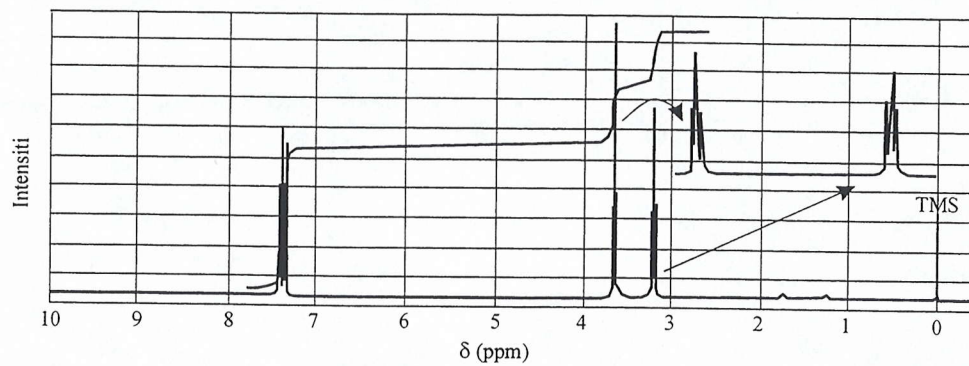


(7 markah)

- (c) Cadangkan struktur sebatian ($\text{C}_{10}\text{H}_{14}$) yang sesuai dengan data ^1H -NMR :
1.30 δ (9H , singlet)
7.30 δ (5H , singlet)

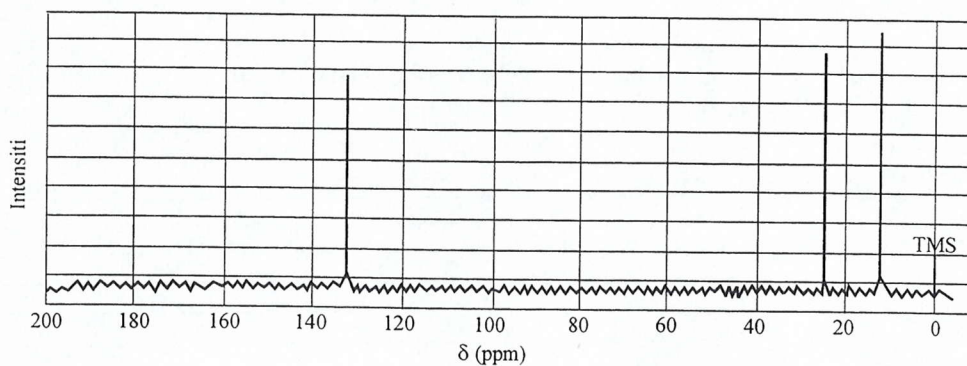
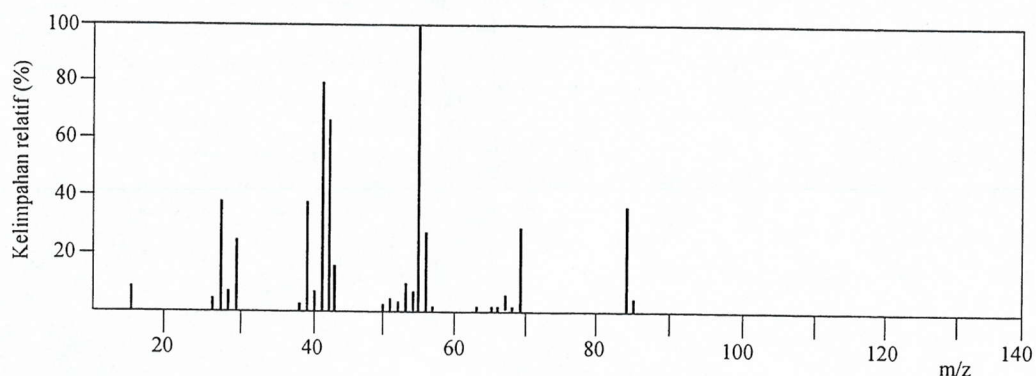
(5 markah)

3. (a) Cadangkan struktur sebatian, $\text{C}_8\text{H}_9\text{Br}$, yang mempunyai spektrum ^1H -NMR berikut :



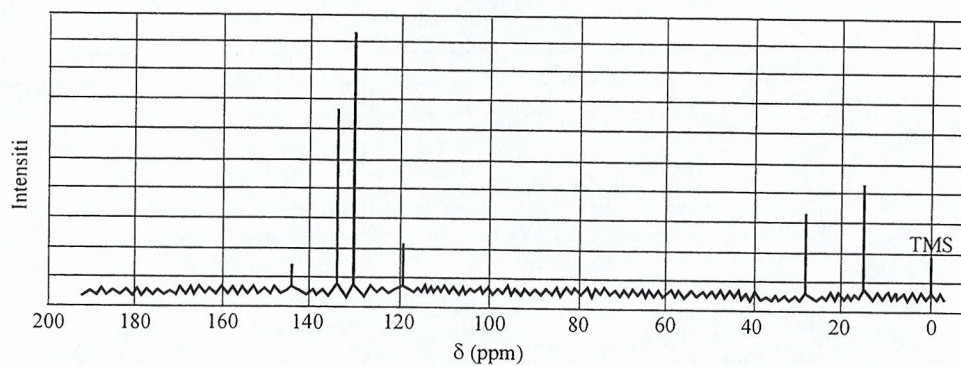
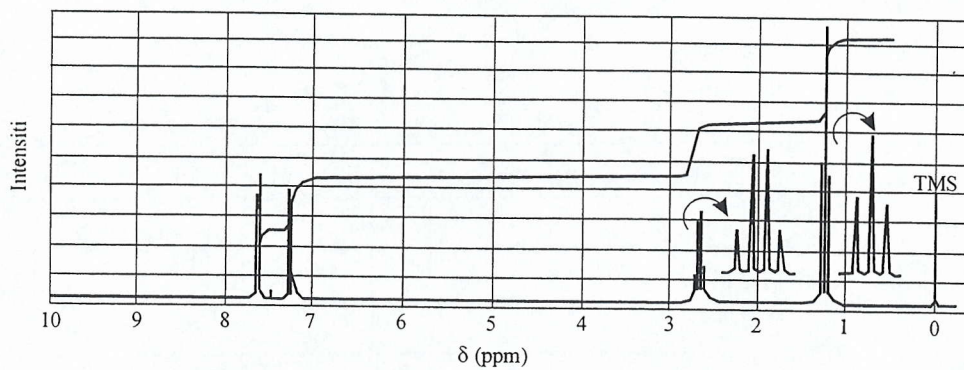
(5 markah)

- (b) Spektrum jisim dan spektrum ^{13}C -NMR suatu sebatian hidrokarbon diberikan di bawah. Cadangkan struktur hidrokarbon ini dan jelaskan data spektrum tersebut.



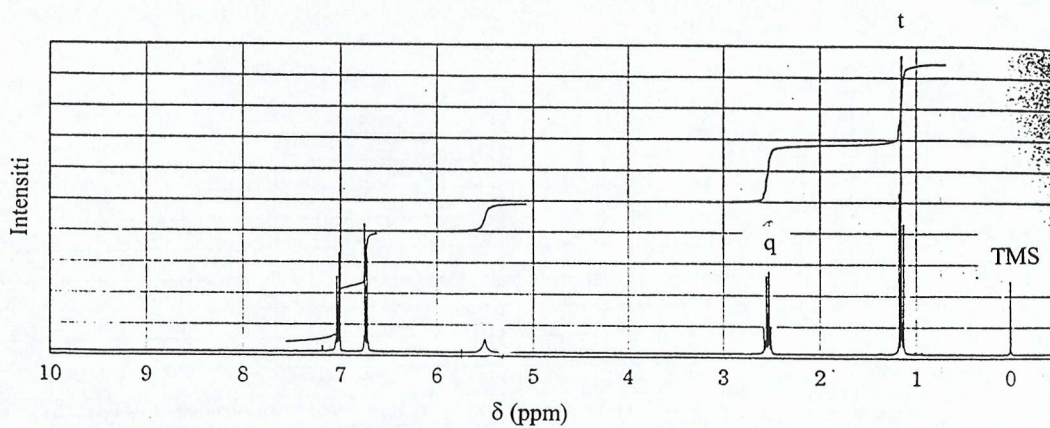
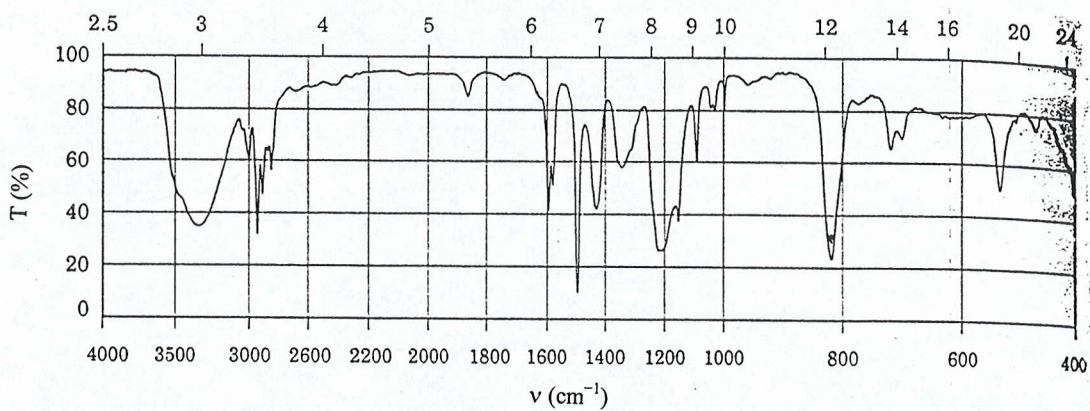
(8 markah)

- (c) Spektrum ^1H -NMR dan ^{13}C -NMR suatu sebatian $\text{C}_8\text{H}_9\text{Br}$, diberikan di bawah. Cadangkan struktur sebatian ini serta padankan data spektrum dengan struktur yang anda cadang.



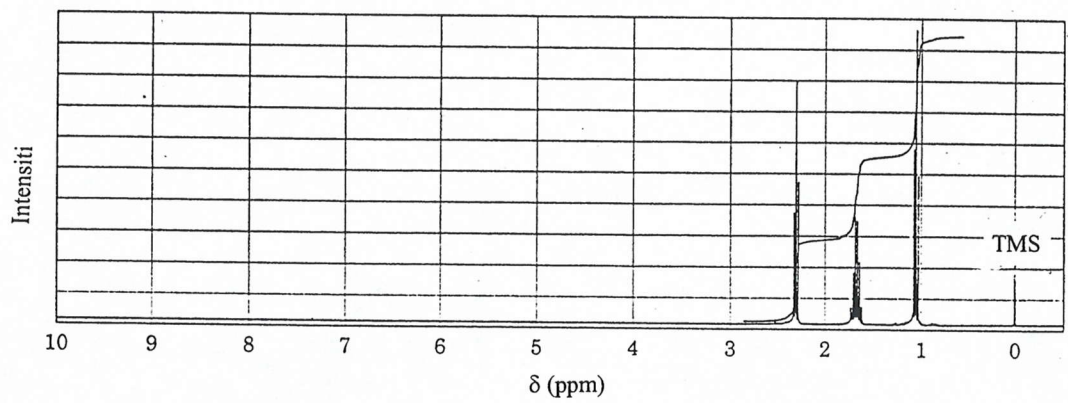
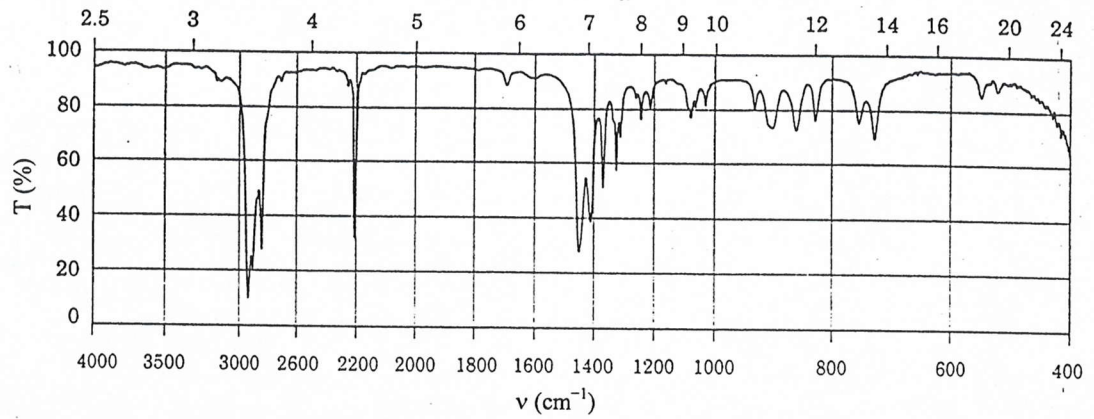
(7 markah)

4. (a) Sebatian A, $C_8H_{10}O$, mempunyai spektrum IR dan 1H -NMR di bawah. Cadangkan satu struktur yang sesuai dengan spektrum yang didapati dan tentukan kumpulan untuk setiap puncak NMR. Puncak pada 5.58 hilang apabila sampel ditambah D_2O .



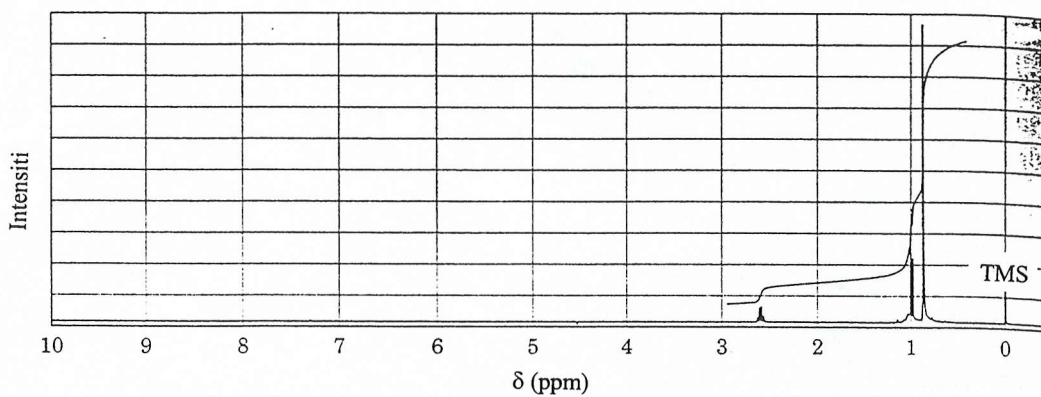
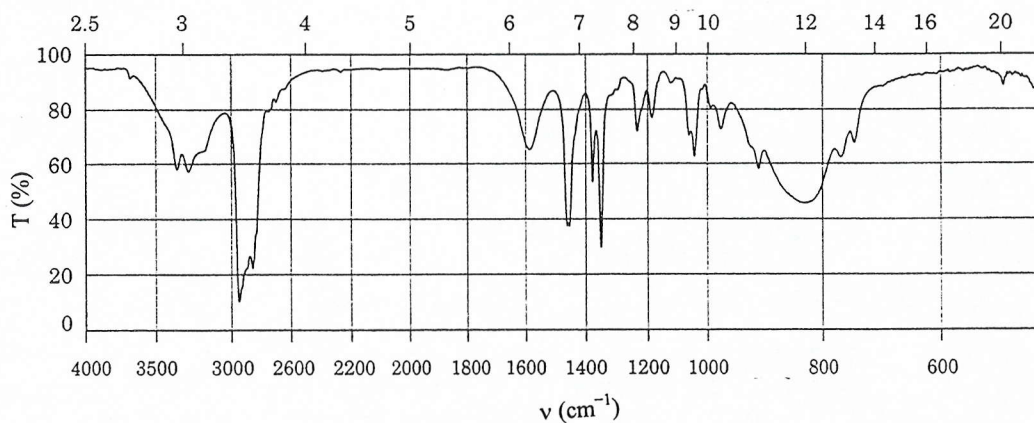
(12 markah)

- (b) Cadangkan struktur untuk sebatian, C_4H_7N , yang mempunyai spektrum IR dan 1H -NMR berikut :



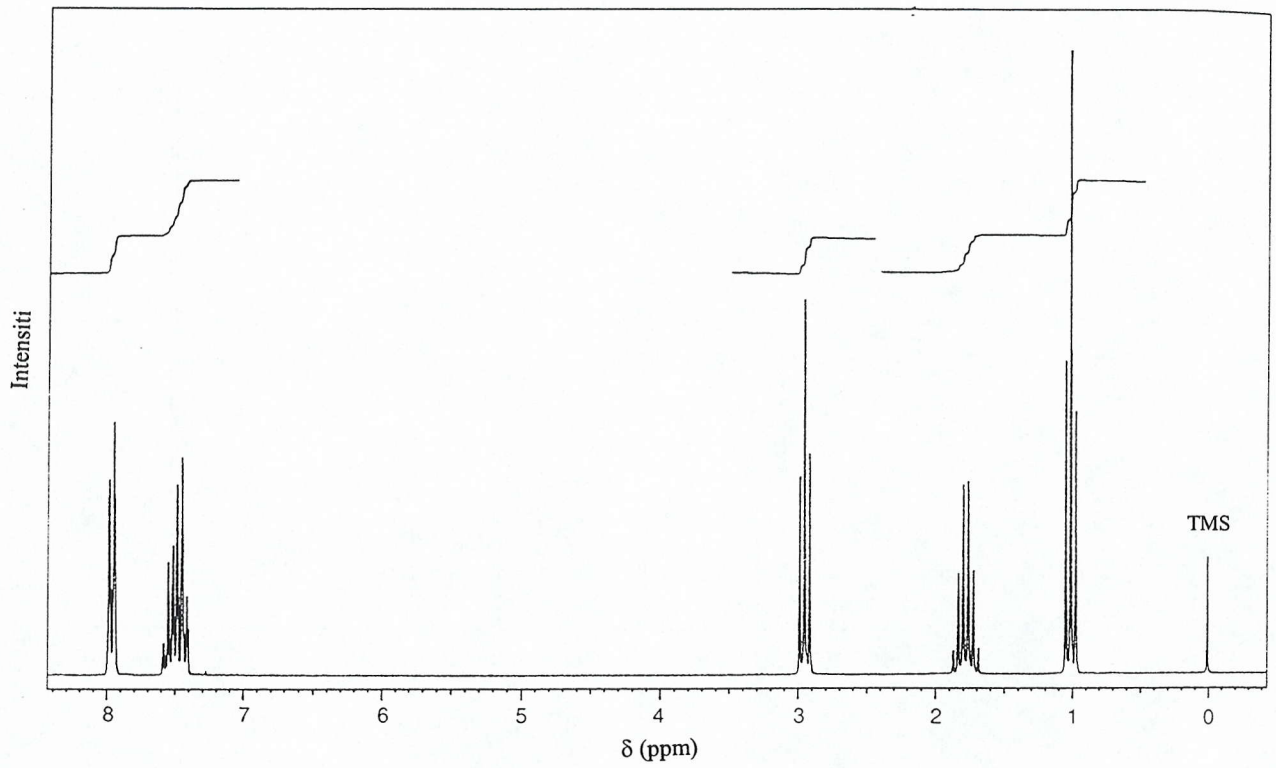
(8 markah)

5. (a) Sebatian A, $C_6H_{12}O$, mempunyai penyerapan IR pada 1715 cm^{-1} dan memberikan sebatian B, $C_6H_{15}N$, apabila diolah dengan ammonia dan diikuti dengan $NaBH_3CN$. Spektrum IR dan 1H -NMR sebatian B diberikan di bawah. Lukiskan struktur A dan B.



(13 markah)

- (b) Sebatian C, $C_{10}H_{12}O$, memberikan spektrum 1H -NMR yang ditunjukkan di bawah. Tentukan struktur sebatian ini dan tunjukkan bagaimana data spektrum ini menyokong struktur yang anda cadangkan itu.

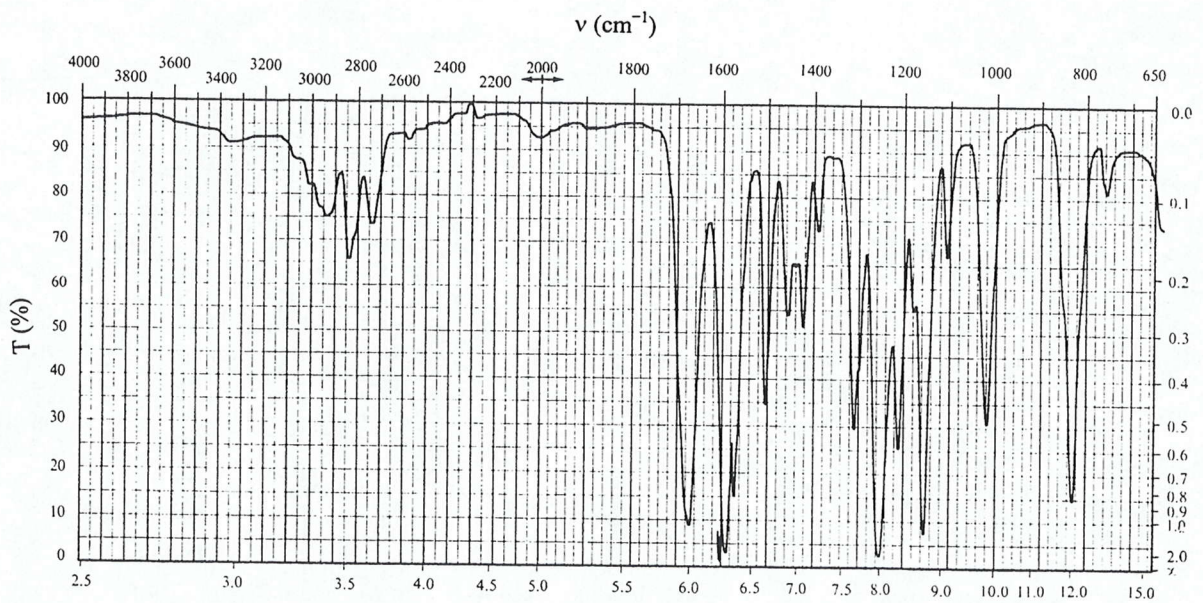
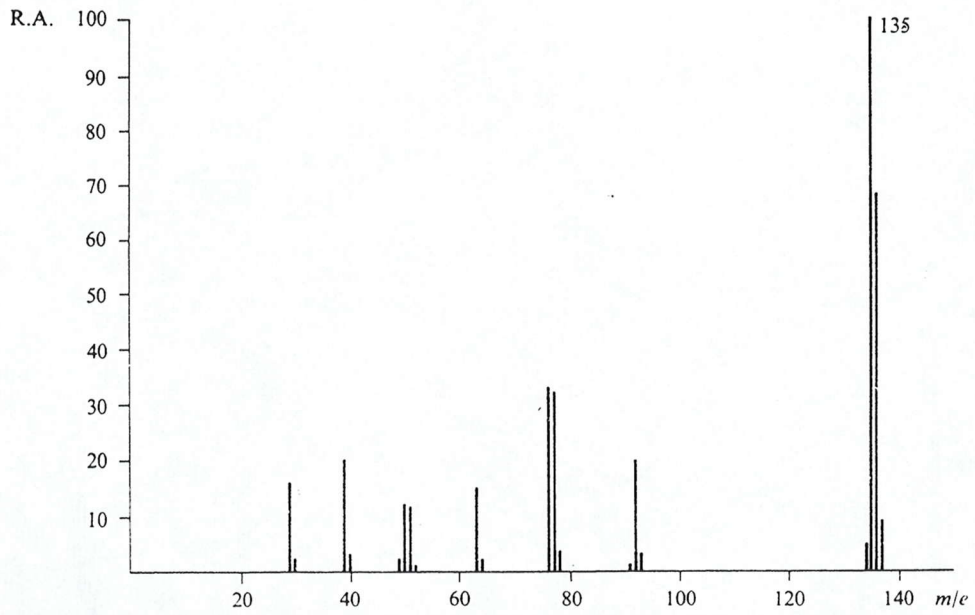


(7 markah)

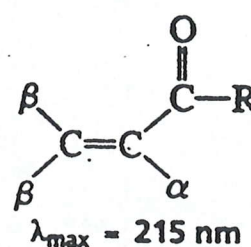
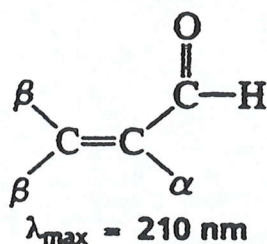
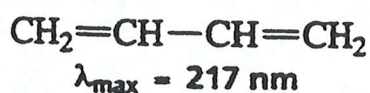
6. Cadangkan struktur suatu sebatian (t.d. 248°C) yang data spektrumnya diberikan di bawah :

UV : $\lambda_{\text{max}} = 250 \text{ nm}$

MS :

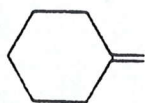


UV : Calculations of λ_{\max} --- Woodward-Fieser Rules

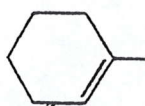


To the base number is added:

1. 30 for each extra conjugated double bond
2. 5 each time a conjugated double bond is an exocyclic double bond
3. 36 for each conjugated double bond that is frozen in the *s-cis* conformation
4. 5 for each alkyl group or halogen bonded to the conjugated system of a polyene
5. 10 for an α -substituent of a conjugated aldehyde or ketone
6. 12 for a β -substituent of a conjugated aldehyde or ketone



an exocyclic double bond



an endocyclic double bond




double bonds frozen in the *s-cis* conformation

IR Absorptions of Carbon-Hydrogen Bonds

IR Absorptions of Carbon-Hydrogen Bonds

Carbon-Hydrogen Stretching Vibrations	$\tilde{\nu}(\text{cm}^{-1})$
$\text{C}\equiv\text{C}-\text{H}$	~3300
$\text{C}=\text{C}-\text{H}$	3100-3020
$\text{C}-\text{C}-\text{H}$	2960-2850
$\begin{array}{c} \text{O} \\ \\ \text{C}-\text{C}-\text{H} \end{array}$	~2700
Carbon-Hydrogen Bending Vibrations	$\tilde{\nu}(\text{cm}^{-1})$
$\text{CH}_3-\text{---CH}_2-\text{---}\overset{ }{\text{CH}}-\text{---}$	1450-1420
$\text{CH}_3-\text{---}$	1385-1365
$\begin{array}{ccc} \text{H} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{R} & & \text{H} \end{array}$	trans 980-960
$\begin{array}{ccc} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	cis 730-675
$\begin{array}{ccc} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{R} & & \text{H} \end{array}$	trisubstituted 840-800
$\begin{array}{ccc} \text{R} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{R} & & \text{H} \end{array}$	terminal alkene 890
$\begin{array}{ccc} \text{R} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	terminal alkene 990 and 910

IR Stretching Frequencies

Important IR Stretching Frequencies		
Type of bond	$\bar{\nu}$ (cm ⁻¹)	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
	~1600 and ~1500	strong
C=O	1780–1650	strong
C–O	1250–1050	strong
C–N	1230–1020	medium
O–H (alcohol)	3650–3200	strong, broad
O–H (acid)	3300–2500	strong, very broad
N–H	3500–3300	medium, broad
C–H	3300–2700	medium

Isotopes

The Natural Abundance of Isotopes Commonly Found
in Organic Compounds

Element	Natural abundance		
carbon	^{12}C	^{13}C	
	98.89%	1.11%	
oxygen	^{16}O	^{17}O	^{18}O
	99.76%	0.37%	0.204%
nitrogen	^{14}N	^{15}N	
	99.63%	0.37%	
hydrogen	^1H	^2H	
	99.99%	0.01%	
fluorine	^{19}F		
	100%		
chlorine	^{35}Cl		^{37}Cl
	75.77%		24.23%
bromine	^{79}Br		^{81}Br
	50.69%		49.31%
iodine	^{127}I		
	100%		

The Exact Masses of Some Common Isotopes

^1H	1.007825	^{32}S	31.9721
^{12}C	12.00000	^{35}Cl	34.9689
^{14}N	14.0031	^{79}Br	78.9183
^{16}O	15.9949		

Mass Spectrometry

Common Fragment Ions*

<i>m/z</i>	Ion	<i>m/z</i>	Ion
14	CH ₂	46	NO ₂
15	CH ₃	47	CH ₂ SH, CH ₃ S
16	O	48	CH ₃ S + H
17	OH	49	CH ₂ Cl
18	H ₂ O, NH ₄	51	CHF ₂
19	F, H ₃ O	53	C ₄ H ₅
26	C≡N	54	CH ₂ CH ₂ C≡N
27	C ₂ H ₃	55	C ₄ H ₇ , CH ₂ =CHC=O
28	C ₂ H ₄ , CO, N ₂ , CH=NH	56	C ₄ H ₈
29	C ₂ H ₅ , CHO	57	C ₄ H ₉ , C ₂ H ₅ C=O
30	CH ₂ NH ₂ , NO		
31	CH ₂ OH, OCH ₃		
32	O ₂ (air)	58	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CCH}_2 \end{array} + \text{H}, \text{C}_2\text{H}_5\text{CHNH}_2, (\text{CH}_3)_2\text{NCH}_2, \\ \text{C}_2\text{H}_5\text{NHCH}_2, \text{C}_2\text{H}_2\text{S}$
33	SH, CH ₂ F		
34	H ₂ S		
35	Cl	59	$(\text{CH}_3)_2\text{COH}, \text{CH}_2\text{OC}_2\text{H}_5, \begin{array}{c} \text{O} \\ \\ \text{COCH}_3, \\ \text{CH}_2\text{C}=\text{O} + \text{H}, \text{CH}_3\text{OCHCH}_3, \\ \\ \text{NH}_2 \end{array}$
36	HCl		
39	C ₃ H ₃		
40	CH ₂ C=N		
41	C ₃ H ₅ , CH ₂ C=N + H, C ₂ H ₂ NH		
42	C ₃ H ₆	60	CH ₃ CHCH ₂ OH
43	C ₃ H ₇ , CH ₃ C=O, C ₂ H ₅ N		
44	CH ₂ CH=O + H, CH ₃ CHNH ₂ , CO ₂ , NH ₂ C=O, (CH ₃) ₂ N		
45	CH ₃ CHOH, CH ₂ CH ₂ OH, CH ₂ OCH ₃ , COOH, CH ₃ CHO + H		

*All of these ions have a single positive charge.

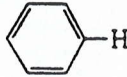
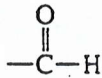
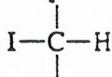
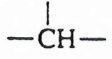
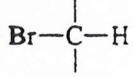
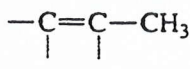
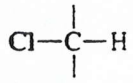
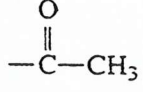
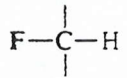
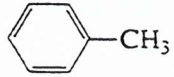
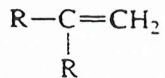
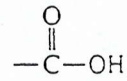
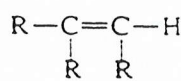
Mass Spectrometry

Common Fragment Lost

Molecular Ion Minus	Fragment Lost	Molecular Ion Minus	Fragment Lost
1	H		
15	CH ₃	43	$\overset{\text{O}}{\parallel}$ C ₃ H ₇ , CH ₃ C, CH ₂ =CHO, CH ₃ + CH ₂ =CH ₂ , HCNO
17	HO		
18	H ₂ O	44	CH ₂ =CHOH, CO ₂ , N ₂ O, CONH ₂ , NHCH ₂ CH ₃
19	F		
20	HF	45	CH ₃ CHOH, CH ₃ CH ₂ O, CO ₂ H, CH ₃ CH ₂ NH ₂
26	CH≡CH, C≡N		
27	CH ₂ =CH, HC≡N	46	H ₂ O + CH ₂ =CH ₂ , CH ₃ CH ₂ OH, NO ₂
28	CH ₂ =CH ₂ , CO, (HCN + H)	47	CH ₃ S
29	CH ₃ CH ₂ , CHO	48	CH ₃ SH, SO, O ₃
30	NH ₂ CH ₂ , CH ₂ O, NO	49	CH ₂ Cl
31	OCH ₃ , CH ₂ OH, CH ₃ NH ₂	51	CHF ₂
32	CH ₃ OH, S	52	C ₄ H ₄ , C ₂ N ₂
33	HS, (CH ₃ and H ₂ O)	53	C ₄ H ₅
34	H ₂ S	54	CH ₂ =CHCH=CH ₂
35	Cl	55	CH ₂ =CHCHCH ₃
36	HCl, 2 H ₂ O	56	CH ₂ =CHCH ₂ CH ₃ , CH ₃ CH=CHCH ₃
37	HCl + H	57	C ₄ H ₉
38	C ₃ H ₂ , C ₂ N, F ₂	58	NCS, NO + CO, CH ₃ COCH ₃
39	C ₃ H ₃ , HC ₂ N		
40	CH ₃ C≡CH	59	$\overset{\text{O}}{\parallel}$ CH ₃ OC, $\overset{\text{O}}{\parallel}$ CH ₃ CNH ₂
41	CH ₂ =CHCH ₂	60	C ₃ H ₇ OH
42	CH ₂ =CHCH ₃ , CH ₂ =C=O, $\overset{\text{CH}_2}{\diagup}$ CH ₂ -CH ₂ , NCO		

	<u>M + 1</u>	<u>M + 2</u>
84		
C ₂ H ₂ N ₃ O	3.38	0.24
C ₂ H ₄ N ₄	3.75	0.06
C ₃ H ₂ NO ₂	3.73	0.45
C ₃ H ₄ N ₂ O	4.11	0.27
C ₃ H ₆ N ₃	4.48	0.81
C ₄ H ₄ O ₂	4.47	0.48
C ₄ H ₆ NO	4.84	0.29
C ₄ H ₈ N ₂	5.21	0.11
C ₅ H ₈ O	5.57	0.33
C ₅ H ₁₀ N	5.95	0.15
C ₆ H ₁₂	6.68	0.19
136		
C ₃ H ₈ N ₂ O ₄	4.29	0.87
C ₃ H ₁₀ N ₃ O ₃	4.66	0.69
C ₃ H ₁₂ N ₄ O ₂	5.04	0.51
C ₄ H ₁₀ NO ₄	5.02	0.90
C ₄ H ₁₂ N ₂ O ₃	5.40	0.72
C ₅ H ₂ N ₃ O ₂	6.66	0.59
C ₅ H ₄ N ₄ O	7.03	0.42
C ₅ H ₁₂ O ₄	5.75	0.94
C ₆ H ₂ NO ₃	7.01	0.81
C ₆ H ₄ N ₂ O ₂	7.39	0.64
C ₆ H ₆ N ₃ O	7.76	0.46
C ₆ H ₈ N ₄	8.14	0.29
C ₇ H ₄ O ₃	7.75	0.86
C ₇ H ₆ NO ₂	8.12	0.69
C ₇ H ₈ N ₂ O	8.49	0.52
C ₇ H ₁₀ N ₃	8.87	0.35
C ₈ H ₈ O ₂	8.85	0.75
C ₈ H ₁₀ NO	9.23	0.58
C ₈ H ₁₂ N ₂	9.60	0.41
C ₉ H ₁₂ O	9.96	0.64
C ₉ H ₁₄ N	10.33	0.48
C ₁₀ H ₂ N	11.22	0.57
C ₁₀ H ₁₆	11.06	0.55
C ₁₁ H ₄	11.95	0.65

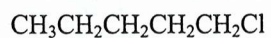
Approximate Values of Chemical Shifts for ^1H NMR

Approximate Values of Chemical Shifts for ^1H NMR ^a			
Type of proton	Approximate chemical shift (δ)	Type of proton	Approximate chemical shift (δ)
$(\text{CH}_3)_4\text{Si}$	0		6.5-8
$-\text{CH}_3$	0.9		9.7-10
$-\text{CH}_2-$	1.3		2-4
	1.4		2.5-4
	1.7		3-4
	2.1		4-4.5
	2.3	RNH_2	variable, 1.5-4
$-\text{C}\equiv\text{C}-\text{H}$	2.4	ROH	variable, 2-5
$\text{R}-\text{O}-\text{CH}_3$	3.3	ArOH	variable, 4-7
	4.7		variable, 10-12
	5.3		

^aThe values are approximate because they are affected by neighboring substituents



84.50



83.50




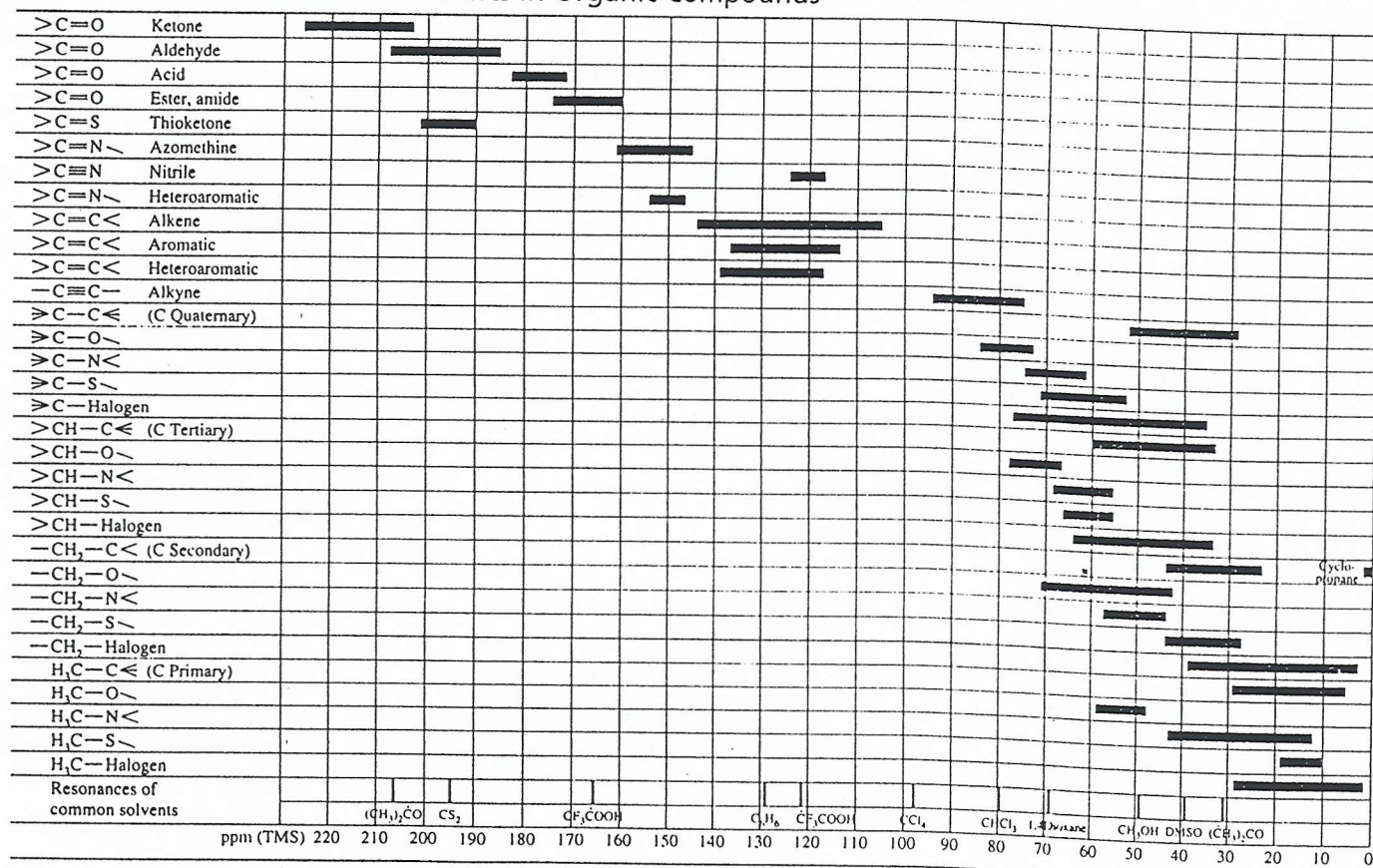
83.40



83.20

Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (δ)	Type of carbon	Approximate chemical shift (δ)
$(\text{CH}_3)_4\text{Si}$	0	$\text{C}-\text{I}$	0—40
$-\text{CH}_3$	8—35	$\text{C}-\text{Br}$	25—65
$-\text{CH}_2-$	15—50	$\text{C}-\text{Cl}$	35—80
$\begin{array}{c} \\ -\text{CH}- \end{array}$	20—60	$\text{C}-\text{O}$	50—80
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	30—40	$\text{C}=\text{O}$	170—210
$\equiv\text{C}$	65—85		110—170
$=\text{C}$	100—150		

¹³C Chemical Shifts in Organic Compounds*

*Relative to internal tetramethylsilane.

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