UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Kedua
Sidang Akademik 2002/2003

Februari/Mac 2003

JIK 319 – Spektroskopi Kimia Organik

Masa : 3 jam

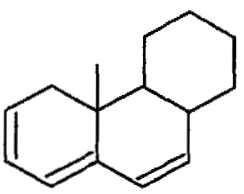
Sila pastikan bahawa kertas peperiksaan ini mengandungi ENAM BELAS muka surat yang bercetak sebelum anda memulakan peperiksaan ini.

Jawab LIMA soalan sahaja.

Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

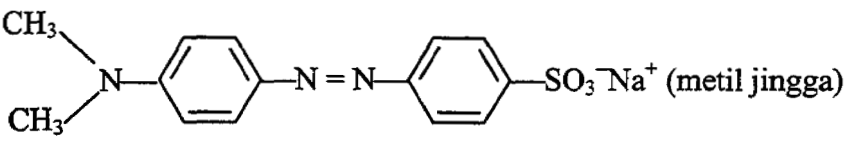
Setiap soalan bernilai 20 markah dan markah subsoalan diperlihatkan di penghujung subsoalan itu.

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



(5 markah)

(b) Metil jingga (sruktur di bawah) adalah penunjuk asid-bes. Dalam larutan yang mempunyai pH < 4 warnanya kuning, dan dalam larutan yang mempunyai pH > 4 warnanya merah. Jelaskan perubahan warna ini.

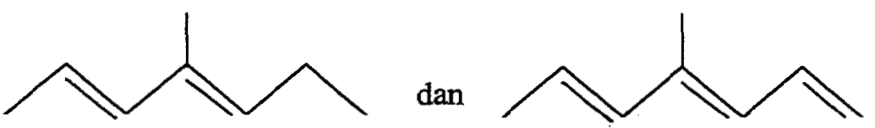


(metil jingga)

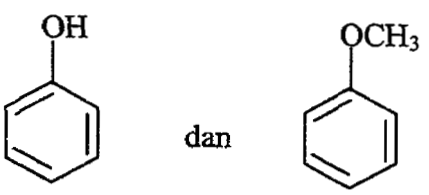
(5 markah)

(c) Bagaimanakah anda dapat bezakan di antara pasangan-pasangan sebatian berikut dengan menggunakan spektroskopi UV?

(i)

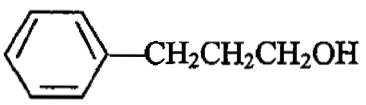


(ii)



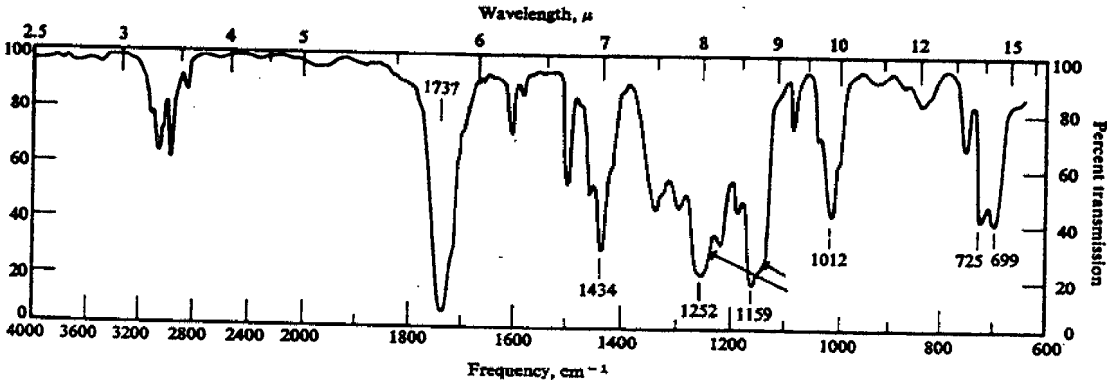
(10 markah)

2. (a) Berikan frekuensi penyerapan (cm^{-1}) serta ciri penyerapan (kuat, lemah, tajam, dan lain-lain) dalam spektrum IR untuk sebatian berikut:



(10 markah)

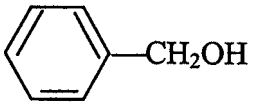
(b) Jelaskan spektrum IR berikut serta cadangkan kumpulan-kumpulan berfungsi yang hadir.



(10 markah)

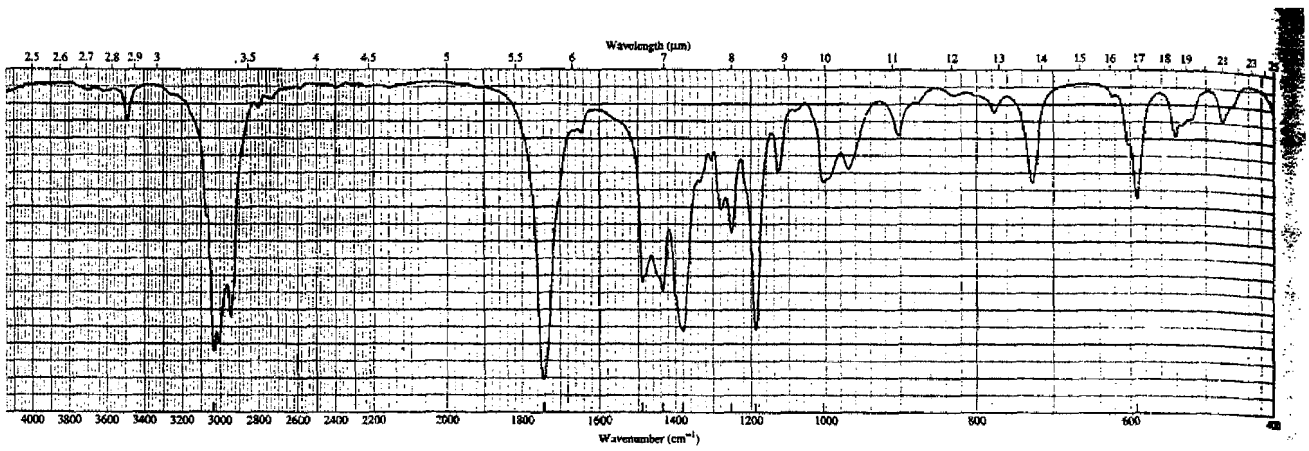
3. (a) Tunjukkan serpihan-serpihan utama yang dapat dicerap dalam spektrum jisim sebatian-sebatian berikut:

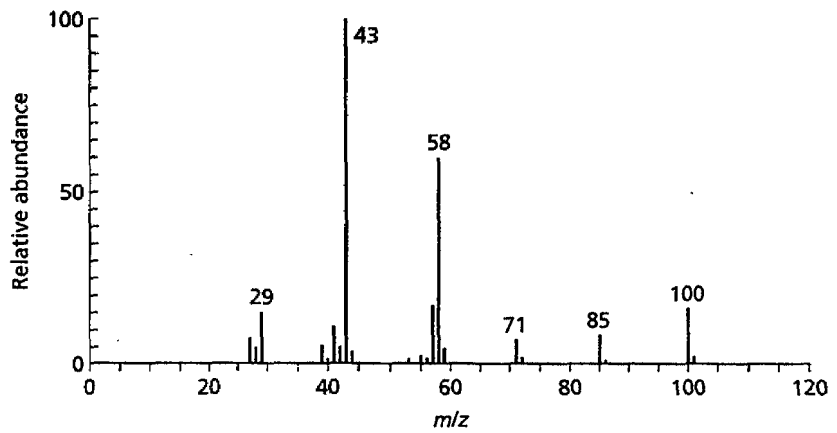
(i) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_3$

(ii) 

(10 markah)

(b) Kenalpasti struktur sebatian yang mempunyai spektrum jisim dan IR berikut:

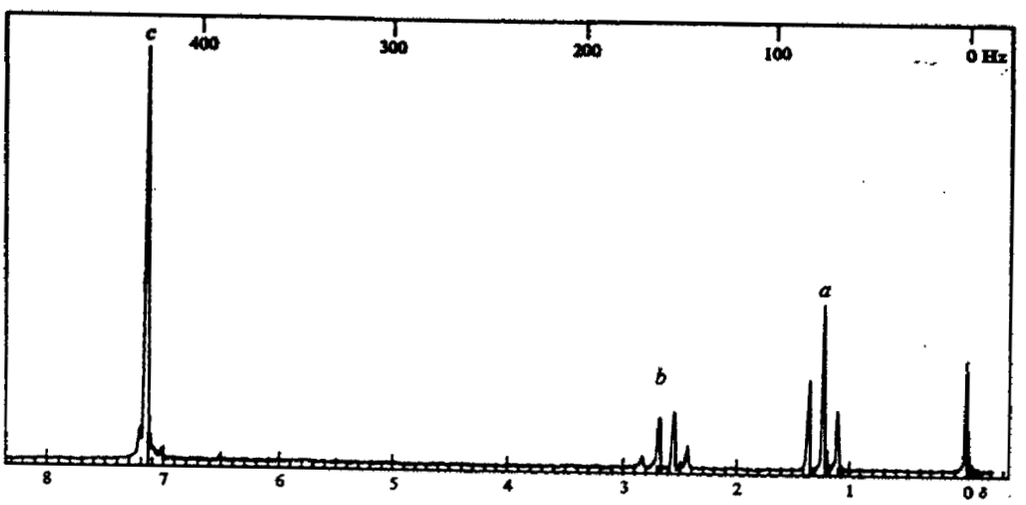




(10 markah)

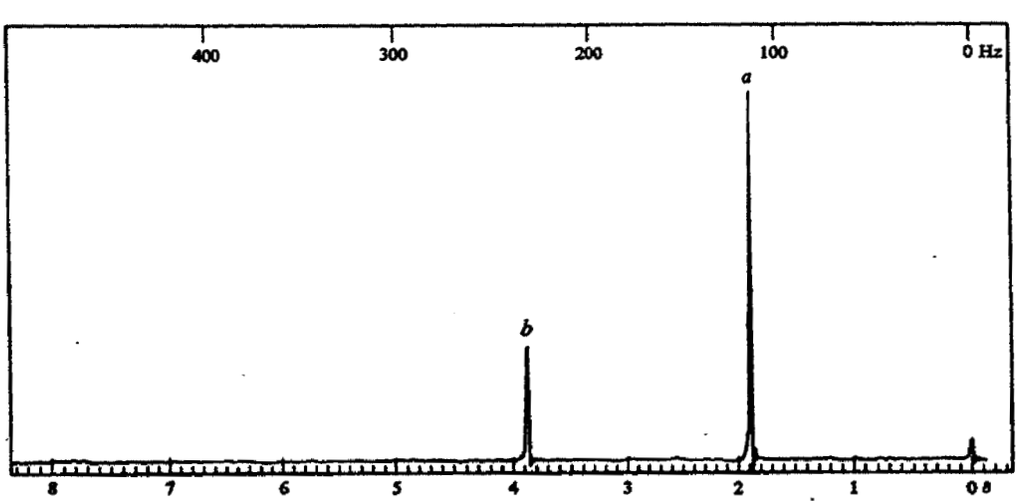
4. Dengan memberikan penjelasan kenalpasti struktur sebatian-sebatian berikut daripada spektrum ^{1}H-nmr yang diberikan.

(a) formula molekul C_8H_{10}



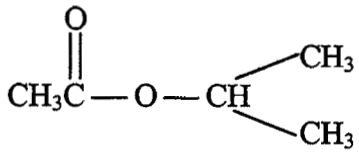
(10 markah)

(b) formula molekul $C_4H_8Br_2$



(10 markah)

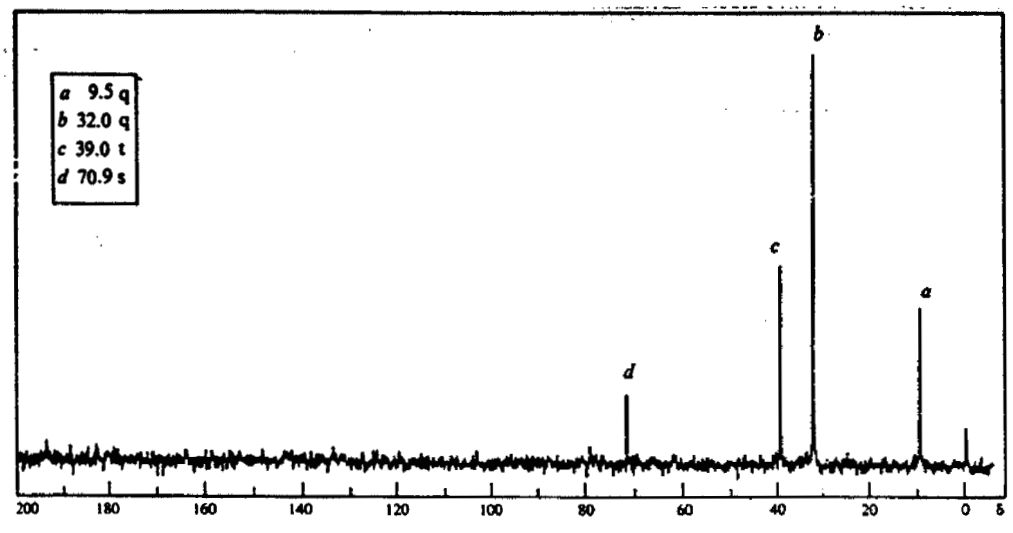
5. (a) Cadangkan anjakan kimia dalam ^{13}C-nmr terdekupel untuk isopropil asetat:



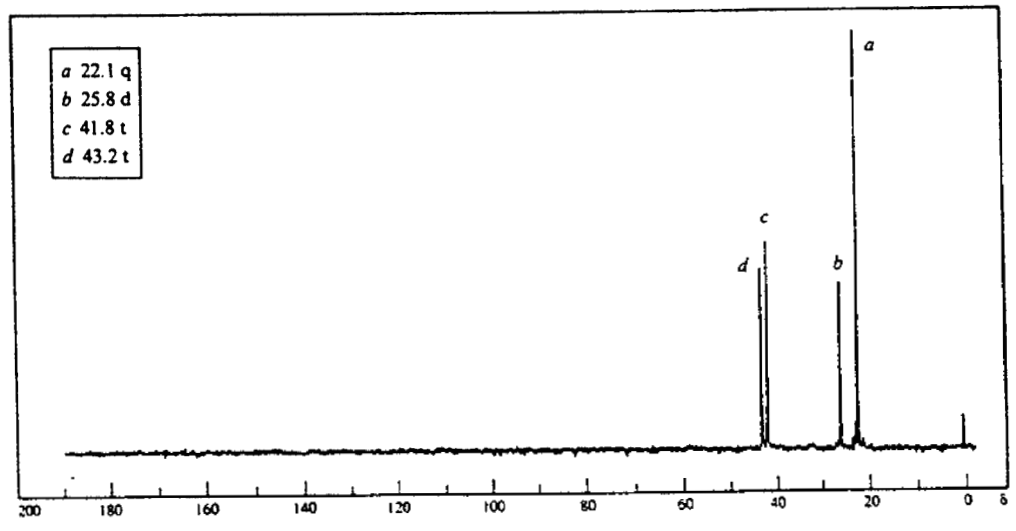
(5 markah)

(b) Cadangkan struktur isomer yang munasabah untuk alkil klorida ($C_5H_{11}Cl$) jika spektrum ^{13}C-nmr adalah seperti berikut:

(i)

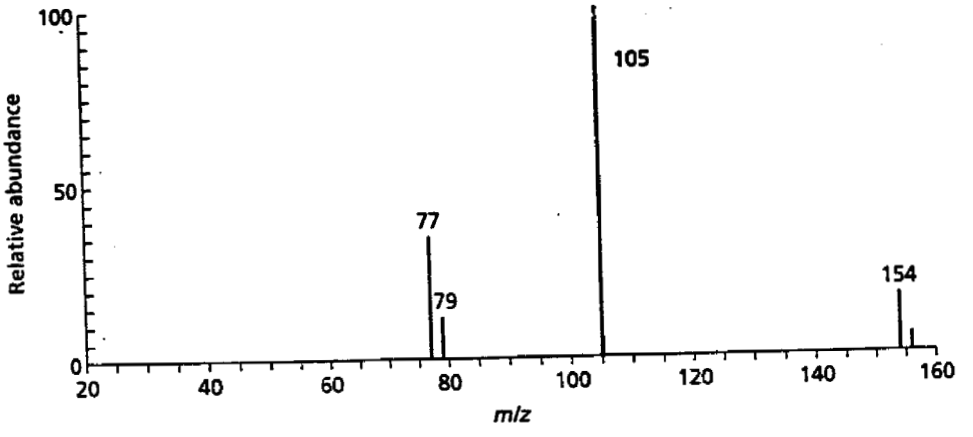


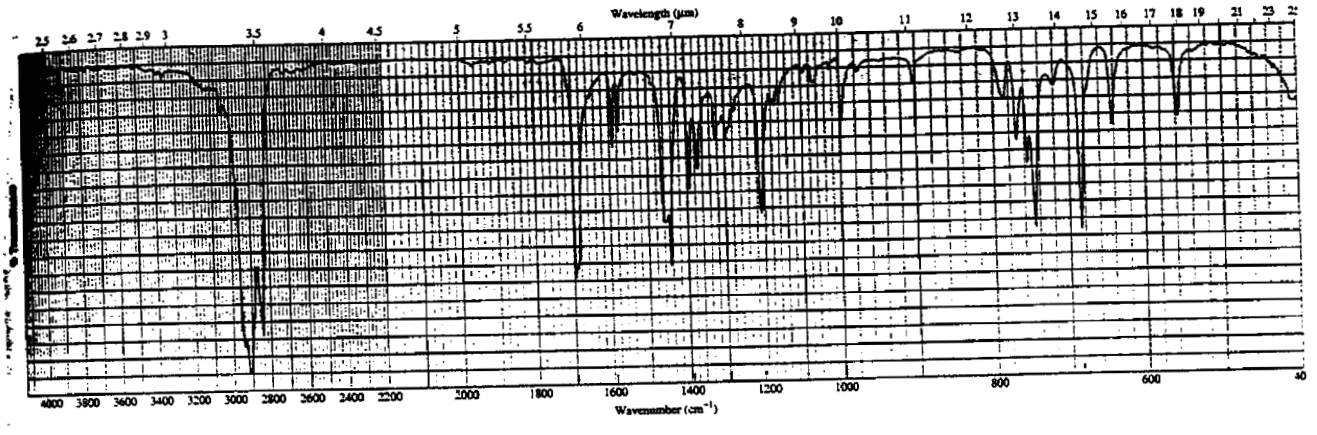
(ii)

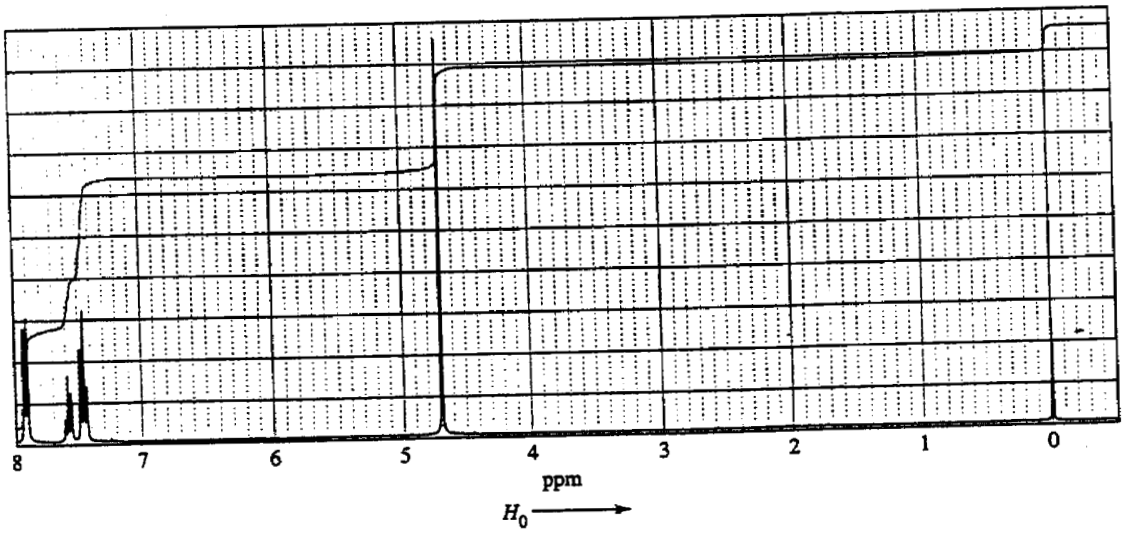


(15 markah)

6. Dengan memberikan penjelasan kenalpasti struktur sebatian yang mempunyai spektrum jisim, IR dan ^{1}H-nmr berikut:

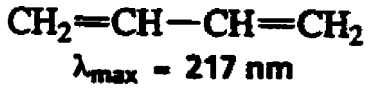




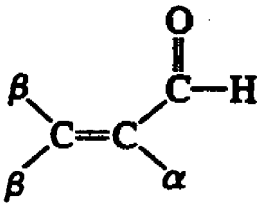


(20 markah)

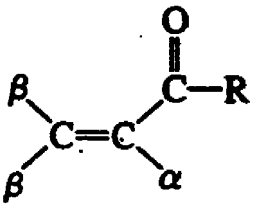
UV : Calculations of λ_{max}---Woodward-Fieser Rules



λ_{max} = 217 nm



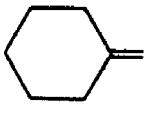
λ_{max} = 210 nm



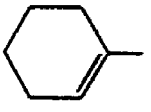
λ_{max} = 215 nm

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

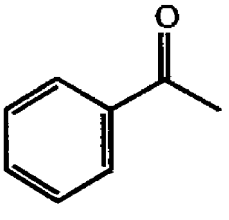


an endocyclic double bond

double bonds frozen in the *s*-cis conformation

7. 3 for an alkyl substitution at *ortho* position.

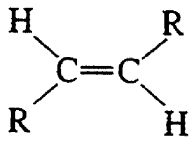
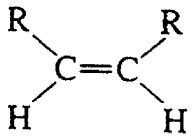
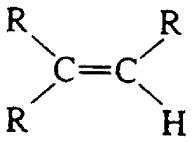
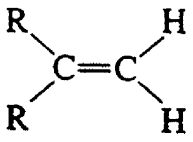
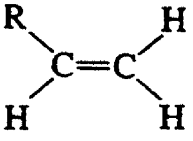
8. 25 for an alkoxy substitution at *para* position.



λ_{max} = 246

IR Absorptions of Carbon-Hydrogen Bonds

TABLE 12.6 IR Absorptions of Carbon–Hydrogen Bonds

Carbon–Hydrogen Stretching Vibrations		$\tilde{\nu}$ (cm^{-1})
C≡C—H		~3300
C=C—H		3100–3020
C—C—H		2960–2850
O ‖ C—C—H		~2700
Carbon–Hydrogen Bending Vibrations		$\tilde{\nu}$ (cm^{-1})
CH_3— —CH_2— —CH(—)		1450–1420
CH_3—		1385–1365
	trans	980–960
	cis	730–675
	trisubstituted	840–800
	terminal alkene	890
	terminal alkene	990 and 910

IR Stretching Frequencies

TABLE 12.4 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

TABLE 12.2 The Natural Abundance of Isotopes Commonly Found in Organic Compounds

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

TABLE 12.3 The Exact Masses of Some Common Isotopes

^{1}H	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*

m/z	Ion
14	CH_2
15	CH_3
16	O
17	OH
18	H_2O, NH_4
19	F, H_3O
26	$C{\equiv}N$
27	C_2H_3
28	C_2H_4, CO, N_2, $CH{=}NH$
29	C_2H_5, CHO
30	CH_2NH_2, NO
31	CH_2OH, OCH_3
32	O_2 (air)
33	SH, CH_2F
34	H_2S
35	Cl
36	HCl
39	C_3H_3
40	$CH_2C{=}N$
41	C_3H_5, $CH_2C{=}N$ + H, C_2H_2NH
42	C_3H_6
43	C_3H_7, $CH_3C{=}O$, C_2H_5N
44	$CH_2CH{=}O$ + H, CH_3CHNH_2, CO_2, $NH_2C{=}O$, $(CH_3)_2N$
45	CH_3CHOH, CH_2CH_2OH, CH_2OCH_3, COOH, CH_3CHO + H
46	NO_2
47	CH_2SH, CH_3S
48	CH_3S + H
49	CH_2Cl
51	CHF_2
53	C_4H_5
54	$CH_2CH_2C{\equiv}N$
55	C_4H_7, $CH_2{=}CHC{=}O$
56	C_4H_8
57	C_4H_9, $C_2H_5C{=}O$
58	$CH_3\overset{\overset{O}{\|}}{C}CH_2$ + H, $C_2H_5CHNH_2$, $(CH_3)_2NCH_2$, $C_2H_5NHCH_2$, C_2H_2S
59	$(CH_3)_2COH$, $CH_2OC_2H_5$, $\overset{\overset{O}{\|}}{C}OCH_3$, $CH_2\underset{\underset{NH_2}{\|}}{C}{=}O$ + H, CH_3OCHCH_3, CH_3CHCH_2OH
60	CH_2COOH + H, CH_2ONO

*All of these ions have a single positive charge.

Mass Spectrometry

Common Fragment Lost

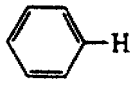
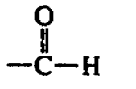
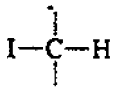
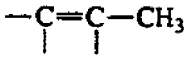
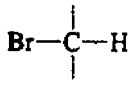
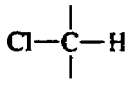
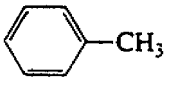
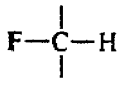
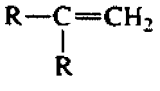
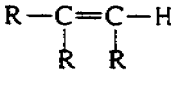
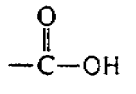
Molecular Ion Minus	Fragment Lost	Molecular Ion Minus	Fragment Lost
1	H	43	C_3H_7, $CH_3\overset{O}{\overset{\|}{C}}$, $CH_2{=}CHO$, CH_3 + $CH_2{=}CH_2$, HCNO
15	CH_3		
17	HO		
18	H_2O	44	$CH_2{=}CHOH$, CO_2, N_2O, $CONH_2$, $NHCH_2CH_3$
19	F		
20	HF	45	CH_3CHOH, CH_3CH_2O, CO_2H, $CH_3CH_2NH_2$
26	$CH{\equiv}CH$, $C{\equiv}N$		
27	$CH_2{=}CH$, $HC{\equiv}N$	46	H_2O + $CH_2{=}CH_2$, CH_3CH_2OH, NO_2
28	$CH_2{=}CH_2$, CO, (HCN + H)	47	CH_3S
29	CH_3CH_2, CHO	48	CH_3SH, SO, O_3
30	NH_2CH_2, CH_2O, NO	49	CH_2Cl
31	OCH_3, CH_2OH, CH_3NH_2	51	CHF_2
32	CH_3OH, S	52	C_4H_4, C_2N_2
33	HS, (CH_3 and H_2O)	53	C_4H_5
34	H_2S	54	$CH_2{=}CHCH{=}CH_2$
35	Cl	55	$CH_2{=}CHCHCH_3$
36	HCl, 2 H_2O	56	$CH_2{=}CHCH_2CH_3$, $CH_3CH{=}CHCH_3$
37	HCl + H	57	C_4H_9
38	C_3H_2, C_2N, F_2	58	NCS, NO + CO, CH_3COCH_3
39	C_3H_3, HC_2N		$\overset{O}{\overset{\|}{C}}H_3O$, $CH_3\overset{O}{\overset{\|}{C}}NH_2$
40	$CH_3C{\equiv}CH$	59	
41	$CH_2{=}CHCH_2$	60	C_3H_7OH
42	$CH_2{=}CHCH_3$, $CH_2{=}C{=}O$, $\overset{CH_2}{\diagup\diagdown}$ $CH_2{-}CH_2$, NCO		

...14/-

	M+1	M+2
100		
$C_2H_2N_2O_2$	3.42	0.45
$C_2H_4N_4O$	3.79	0.26
$C_3H_2NO_3$	3.77	0.65
$C_3H_4N_2O_2$	4.15	0.47
$C_3H_6N_2O$	4.52	0.28
$C_3H_8N_4$	4.90	0.10
$C_4H_4O_3$	4.50	0.68
$C_4H_6NO_2$	4.88	0.50
$C_4H_8N_2O$	5.25	0.31
$C_4H_{10}N_3$	5.63	0.13
$C_5H_6O_2$	5.61	0.53
$C_5H_{10}NO$	5.98	0.35
$C_5H_{12}N_2$	6.36	0.17
$C_6H_{12}O$	6.72	0.39
$C_6H_{14}N$	7.09	0.22
C_7H_2N	7.98	0.28
C_7H_{16}	7.82	0.26
C_8H_4	8.71	0.33
154		
$C_5H_2N_2O_4$	6.35	0.97
$C_5H_4N_3O_3$	6.73	0.80
$C_5H_6N_4O_2$	7.10	0.62
$C_6H_4NO_4$	7.09	1.02
$C_6H_6N_2O_3$	7.46	0.84
$C_6H_8N_3O_2$	7.83	0.67
$C_6H_{10}N_4O$	8.21	0.50
$C_7H_6O_4$	7.82	1.07
$C_7H_8NO_3$	8.19	0.90
$C_7H_{10}N_2O_2$	8.57	0.73
$C_7H_{12}N_3O$	8.94	0.56
$C_7H_{14}N_4$	9.31	0.39
$C_8H_2N_4$	10.20	0.47
$C_8H_{10}O_3$	8.92	0.95
$C_8H_{12}NO_2$	9.30	0.79
$C_8H_{14}N_2O$	9.67	0.62
$C_8H_{16}N_3$	10.05	0.46
$C_9H_2N_2O$	10.56	0.70
$C_9H_4N_3$	10.93	0.54
$C_9H_{14}O_2$	10.03	0.85
$C_9H_{16}NO$	10.40	0.69
$C_9H_{18}N_2$	10.78	0.53
$C_{10}H_2O_2$	10.92	0.94
$C_{10}H_4NO$	11.29	0.78

Approximate Values of Chemical Shifts for ^{1}H NMR

TABLE 13.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

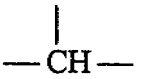
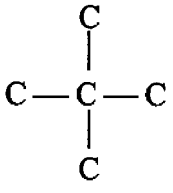
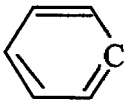
Type of proton	Approximate chemical shift (δ)	Type of proton	Approximate chemical shift (δ)
$(CH_3)_4Si$	0		6.5–8
$-CH_3$	0.9		
$-CH_2-$	1.3		9.7–10
	1.4		2–4
	1.7		
			2.5–4
	2.1		
			3–4
	2.3		
			4–4.5
$-C\equiv C-H$	2.4		
$R-O-CH_3$	3.3	RNH_2	variable, 1.5–4
	4.7	ROH	variable, 2–5
		ArOH	variable, 4–7
	5.3		variable, 10–12

[a]The values are approximate because they are affected by neighboring substituents.

$CH_3CH_2CH_2CH_2CH_2F$ $CH_3CH_2CH_2CH_2CH_2Cl$ $CH_3CH_2CH_2CH_2CH_2Br$ $CH_3CH_2CH_2CH_2CH_2I$

δ 4.50 δ 3.50 δ 3.40 δ 3.20

Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (δ)	Type of carbon	Approximate chemical shift (δ)
$(CH_3)_4Si$	0	C — I	0 — 40
— CH_3	8 – 35	C — Br	25 — 65
— CH_2 —	15 – 50	C — Cl	35 — 80
	20 – 60	C — O	50 — 80
	30 – 40	C═O	170 — 210
≡C	65 – 85		110 — 170
═C	100 – 150		

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