2009

M.Sc. Part-II Examination

CHEMISTRY

PAPER—VII

Full Marks : 75

Time : 3 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *five* questions
taking at least *two* from each group.

Group—A

1. (a) Deduce the working formula for the determination of Einstein co-efficient of induced absorption using a UV-vis spectrophotometer. 10

   (b) Write short notes on :

   (i) Mirror image relationship.

   (ii) Kasha's rule. $2\frac{1}{2} \times 2$

2. (a) Show that for a diatomic molecule obeing the laws of Simple Harmonic Oscillator :

(i) Transition occurs between two consecutive vibrational level.

(ii) There must be fluctuation in dipole moment during molecular vibration.

Given below the Hermite polynomial identity i.e.

$$\xi H_v(\xi) = vH_{v-1}(\xi) + \frac{1}{2} H_{v+1}(\xi).$$ 8

(b) Write a short note on the loss of energy through radiative process in electronic spectroscopy. 7

3. (a) Write a short note on the environmental effect on electronic absorption and emission spectra. 5

(b) Describe the principle involved for the determination of excited state dipolemoment of a fluorophore. 10

4. (a) Give a qualitative discussion on the origin of hyperfine splitting in epr spectral line. 6

(b) Predict the esr spectra of the following radicals. (i) $^{\cdot}CH_3$, (ii) $^{\cdot}[CF_2H]$, (iii) $^{\cdot}[CClH_2]$, (iv) $^{\cdot}CPh_3$. 4

(c) How do you calculate 'g' of a sample from ESR spectroscopy if 'g' of a reference substance is known. 5

5. (a) Describe how molar polarisation vary with frequency applied. When molar polarisation becomes equal to molar refraction? Give reasons.

(b) Describe what are meant by ferro and antiferro-magnetism. (6+3)+(3+3)

Group—B

6. It has been observed experimentally that 3-hydroxyflavone shows intramolecular proton transfer in its first excited singlet state, whereas in the ground state the reverse proton transfer (from keto to end tautomer) is a spontaneous one.

(i) Draw a schematic potential energy diagram for both the ground and first excited singlet state for 3-hydroxyflavone w.r.t the proton transfer co-ordinate.

(ii) How do you obtain the excited state acidity constant $\left(pK_a^*\right)$ of 3-hydroxyflavone using fluorescence spectrophotometer?

(iii) From the above potential energy diagram, show, that 3-hydroxyflavone can be used as proton transfer dye laser. 3+3+9

7. (a) Write down the steps involved and the rate of each steps for the Enimolecular photophysical processes. Show that,

$$\frac{\phi_P}{\phi_f} = K_{ISC}\tau_f^\circ$$

Assume that ϕ_P is large and $\phi_P + \phi_f \simeq 1$
(Here symbols have their usual significance). 3+5

(b) Write a short note on TICT emission. 7

8. (a) What do you mean by static and dynamic quenching of a fluorophore? How do you determine the rate constant for both static and dynamic quenching of a fluorophore which undergoes quenching via both static and dynamic quenching mechanism. 2+8

(b) Give an outline of TCSPC method for the measurement of excited state lifetime of a fluorophore. 5

9. Write notes on (any *three*) : 5×3

(i) Nuclear overhauser effect

(ii) FT-NMR spectroscopy.

(iii) Spin lattice and spin-spin relaxation in NMR spectroscopy.

(iv) Second order NMR spectra.

(v) Electron electron double resonance (EEDOR) in NMR spectroscopy.

10. (a) When does a nucleus show NMR spectra ? How do you obtain resonance condition for NMR ? 4

(b) What are the broad similarities and dissimilarities in NMR and ESR ? 7

(c) Discuss the spectrum of ethyl alcohol under high resolution (i) when it is ordinarily pure, (ii) when it is extra pure. 4

(Inorganic Special)

Answer any *five* questions
taking at least *two* from each group.

Group—A

1. (a) Considering ϕ_{T_1} and ϕ_{T_2} are the quantum yields of a photochemical reaction at temperature T_1 and T_2, respectively, establish the relation between true activation energy (E_a) and apparent activation energy (E_{app}). 7

(b) Write notes on :

(i) Charge transfer excited states.

(ii) Non-radiative transition. 4+4

2. (a) When photochemical reaction of $[Mn_2(CO)_{10}]$ is performed in CCl_4 solvent the isolated product is $[Mn(CO)_5Cl]$. Explain the formation of this product. 4

(b) State the conditions that should be followed for getting a practical photochemical energy storage cycles. 4

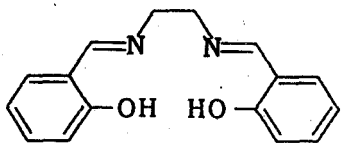
(c) $$Mn_2(CO)_{10} + PPh_3 \xrightarrow{h\nu} [Mn_2(CO)_9(PPh_3)] \text{ (minor product)} + [Mn_2(CO)_8(PPh_3)_2] \text{ (major product)}$$

Explain the product formation. 5

(d) How photodecomposition of NOCl occur? 2

3. (a) Describe the three broad classes of DNA adducts that can be made by bifunctional platinum complexes. 5

(b) (i) $[Os(salen)O_2] \xrightarrow[\text{stir, } 50^\circ C]{\text{isopropanol}}$ product (with structure)

salen = 

3

(ii) $K_2[Pt(NO_2)_4] \cdot H_2O \xrightarrow[HClO_4,\ \text{stir 3h, heat}]{\text{Glacial acetic acid}}$ product (with structure)

3

(c) What are the biological consequences of platinum-DNA binding? 4

4. (a) Explain the principle of thermogravimetric analysis with example. 3

(b) Define retention time (t_R), retention factor (k) and dead time (t_M) in separation by column chromatography. How they are related to each other? 1+1+1+1

(c) Explain the cyclic voltammetric responses for an EC and ECE type reactions with appropriate examples. 3+3

(d) Write the relation between distribution ratio and distribution coefficient of an organic acid between aqueous and organic phase in separation by solvent solvent extraction methods. Use it to show the effect of pH on such separation. 1+1

5. (a) Prove that $\sigma = \frac{Ne^2\tau}{2m}$

where, σ = conductivity
N = number of electrons
m = man of the electron
τ = relaxation time/collision time/mean free time.

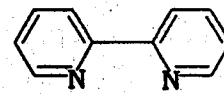
5

(b) Give brief account of semiconductor and exciton. 7+3

Group—B

6. (a) What happen when photolysis of $[W_2(\eta^5 - C_5H_5)_2(CO_6)]$ is performed in presence of Ph_3CCl. Explain the reaction mechanism. 4

(b) Describe the photochemical reduction and oxidation of H_2O molecules using $[Ru(bPy)_3]^{2+}$ as photosensitizer. 9

bPy = 

(c) What do you mean by DOSENCO state? 2

7. (a) Explain the mechanism of conversion of NO_3^- to nitrogeneous organic compounds by phytoplankton. 4

(b) What do you mean by corrosion. Describe one experiment with explanation to show that the corrosion is an electrochemical phenomenon. 2+4

(c) Describe briefly the following :

(i) Elements present in sea-water.

(ii) Underground corrosion. $2\frac{1}{2}\times2$

8. (a) "The absorption spectrum and the electrochemical properties of the dendrimer are practically 'sum' of the spectra and redox patterns of the constituent units"—discuss. 5

(b) What do you mean by convergent and divergent approach of formation of dendrimers? Describe with one example of in each case. (Metal = Ru, OS etc. Ligand = 2, 3-dipyridyl pyrazine ; 2, 5-dipyridyl pyrazine ; 2, 2'-bipyridyl ; 2, 3-methyldipyridyl pyrazine). 3+3

(c) What is intramolecular interligand exchange of electron between coordinated catechol and semiquinone. Explain with an example. 4

9. (a) Give examples of synthetic cation exchange resin and anion exchange resin. What is the role of cross-linking in their structures ? State one application of ion-exchange chromatography. 1+1+1+1

(b) Explain the principle of Differential Thermal Analysis (DTA) and indicate the physico-chemical origin of DTA curves. 3+1

(c) Draw a schematic representation of the set up of a cyclic voltammetric apparatus. What is the role of the supporting electrolyte ? 3+1

(d) What do you mean by "tailing" and "fronting" in chromatography. Mention its significance. 1+1+1

10. (a) "When KCl crystal is heated in excess K atom, a colour is observed"—Explain the phenomenone. 6

(b) Define atomic scattering factor and scattering factor curve. $1\frac{1}{2}+1\frac{1}{2}$

(c) "A sudden drop in the quantum yield is observed for the reaction $2F \rightarrow F'$ in the beginning of the irradiation with F light at temperatures below 140K"—Explain. 3

(d) Calculate the geometrical structure factor, F_{hkl}, for a simple cubic lattice and hence interprete the result. 3

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(Organic Special)

Answer any *five* questions
taking at least *two* from each group.

Group—A

1. (a) Write down the retrosynthetic steps for the construction of the non-Nitrogenous part of the alkaloid yohimbine.

(b) Show that all cinchona alkaloids possess the same stereochemistry at C-3 and C-4 and that is in cis relationship. 7+8

2. (a) Show that caryophyllene is macrocyclic sesquiterpene containing two rings and determine their ring size.

(b) "Although structurally altogether different, quinine alkaloids originate from the same precursor as that of indoe alkaoids". Justify the statement with proper biogenetic steps. 8+7

3. How can you carry out the following conversions and write down the plausible mechanism where necessary. 3×5

(a) Quinine ⟶ Quinidine
(b) Yohimbine ⟶ Yohimbine Oxindole
(c) Yohimbone ⟶ Yohimbine
(d) Pseudo-yohimbine ⟶ Yohimbine
(e) Caryophyllene ⟶ Clovanediol

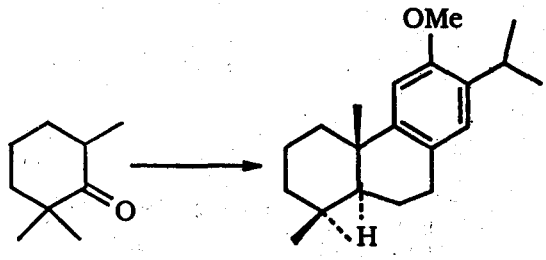
4. (a) How were the positions of isopropyl group, the double bonds and the stereochemistry of A/B ring juncture in abietic acid determined? 3+2+3

(b) How can you chemically prove that abietic acid and podocarpic acid have opposite configuration of –COOH group? 4

(c) How was the absolute stereochemistry of the –OH group at C-17 in yohimbine established? 3

5. (a) Carry out the following synthesis : $3\frac{1}{2} \times 2$

(i)



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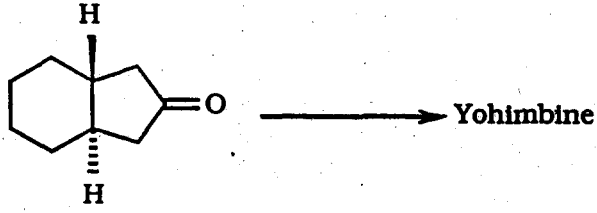
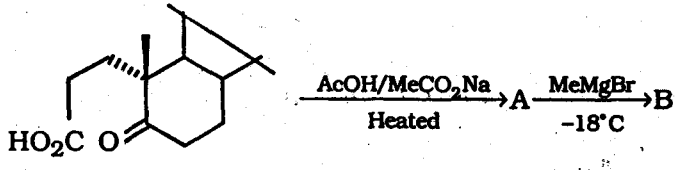
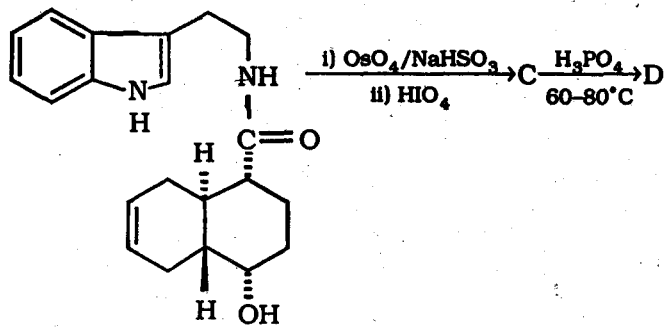


(b) Identify the product expected (A, B, C, D) in the following reactions : 2×4

(i)



(ii)

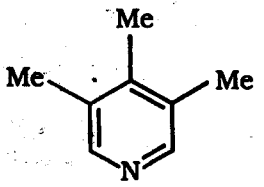


(Continued)

Group—B

6. (a) Draw the possible configurations of the geometrical isomers of dimethylmuconate having the general structural formula $MeO_2C-CH = CH-CH=CH-CO_2Me$. Indicate how you would ascertain their stereochemistry from the chemical shifts of their olefinic protons. 3

(b) How would you distinguish between the following pairs of isomeric compounds from their proton chemical shifts? Indicate only the distinguishing feature(s). Answer any *three*. 2×3

(i) 

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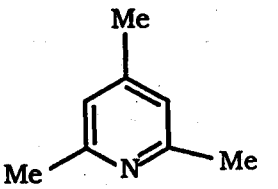
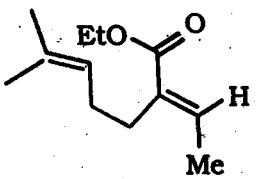


(ii) 

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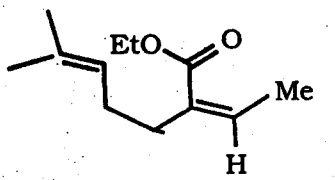
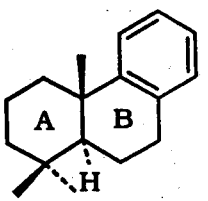


(iii) *Trans*-stibene and *Cis*-stilbene

(iv) 

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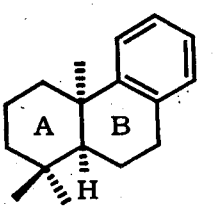
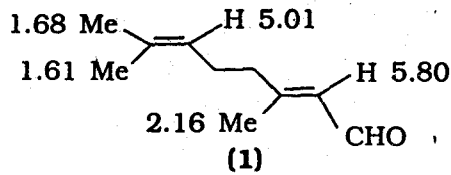


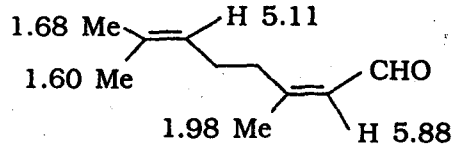
(c) What is the relative order of J_{gem}, J_{cis} and J_{trans} in a monosubstituted olefin of the type R–CH=CH_2 ? Give reasons for your answer. 3

(d) What are shift reagents ? For what purpose are they used in NMR spectroscopy ? Give one example to illustrate your answer. 3

7. (a) What is Nuclear Overhauser Effect ? Explain the reason for this effect. The chemical shifts (in δ_{ppm}) of the vinylic methyls and the olefinic protons of citral-a(**1**) and citral-b(**2**) are shown on their structural diagrams. How would you confirm their indicated stereochemistry and the assignments of the chemical shifts of the vinylic methyl protons at δ 1.68, 1.61 and 1.60 by Nuclear Overhauser Effect ? 6

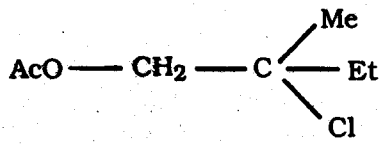


(1)



(2)

(b) Indicate the multiplicity of the signal of the protons of the methylene group attached to the acetoxy function in the compound 3. Give reasons for your answer. What changes in the multiplicity of the signals of the above protons would you observe, if the chlorine atom in 3 is replaced by (i) a methyl group and (ii) a hydrogen atom ? 4



(3)

(c) How does the equatorial proton of a rigid cyclohexane derivative differ from its axial counterpart linked to the same carbon atom ? Give reason for your answer. Cite one specific example. 5

8. (a) Answer any *one*. 6

(i) Suggest a structure for the compound A, $C_{10}H_{12}O_2$, from its following spectral data :

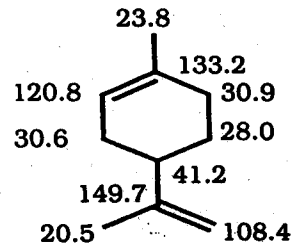
UV : λ_{max} (pH = 7) 263 and 300nm (log € 4.2 and 3.6); λ_{max} (pH = 13) 288 and 315nm (log € 4.0 and 3.8).

IR : √max 3510(s), 3030(w), 1600(s), 1430(s) and 965cm–1; series of short peaks below 900cm–1.

^{1}H NMR : δ 6.0(1H, octet, J_1 = 16Hz and J_2 = 7Hz), 6.2(1H, d, J = 16Hz), 5.60 (1H, br. s; disappears on deuterium exchange), 6.70(3H, m; showing an ABX type of splitting pattern), 1.81(3H, d, J = 7Hz) and 3.75(3H, s)

(ii) Compound B, $C_6H_{10}O_2$, shows two ^{1}H NMR signals at δ 2.2(6H, s) and 2.7(4H, s); Compound C, C_8H_6, also shows two ^{1}H NMR signals at δ 3.08(s) and 7.4(m) in the ratio of 1:5; Compound D, $C_{12}H_{18}$, exhibits only one ^{1}H NMR signal at δ 2.2(s). Suggest probable structures for all the three compounds.

(b) What are the full versions of the terms SFORD, DEPT and APT? What information do they provide? Draw the DEPT and APT spectra of the compound **4** having its δ_C values shown on its structural diagram. 3



(4)

(c) Calculate the δ_C values of C–9 and C–10 of *trans*- and *cis*- decalins from the given additive parameters and show how the stereochemistry of the ring juncture of the two isomers can be ascertained from the above δc values. [Additive parameters in ppm : Base value = 27.7, α-ax-Me = +1.1, β-ax-Me = +5.2, γ-ax-Me = –5.4, δ-ax-Me = –0.1, α-equate-Me = +5.6, β-equat-Me = +8.9, γ-equat-Me = 0.0, δ-equat-Me = –0.3, vic-diequat = –2.3 and vic-ax-equat = –3.1]. 6

9. (a) What are the full names of the terms COSY, HMQC and HMBC? What informations do they provide? Draw the expected COSY and HMBC spectra of ethyl *trans*-crotonate having the following ^1H and ^{13}C NMR spectral data. 5

^1H NMR : δ 1.24(2H, t, J = 7.0 Hz), 1.88(3H, dd, J_1 = 6.8 Hz and J_2 = 1.7 Hz), 4.13 (2H, q, J = 7.0Hz), 5.81(1H, dq, J_1 = 16Hz and J_2 = 1.7Hz) and 6.90(1H, dq, J_1 = 16Hz and J_2 = 6.8Hz).

^{13}C NMR: δ_C 15.2 and 60.1(OEt), 18.1(Me–CH=), 124.5(C–2), 145.3(C–3) and 168.0(C=0).

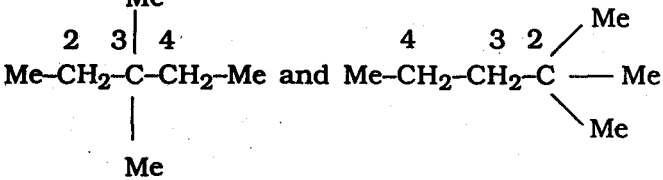
(b) How would you distinguish between the following isomeric compounds from their calculated carbon chemical shifts? Answer any *three*. 2×3

(i) $Me–CH_2–CH_2–CH_2–CH_2–OH$ and

$Me–CH_2–CH(OH)–CH_2–Me$

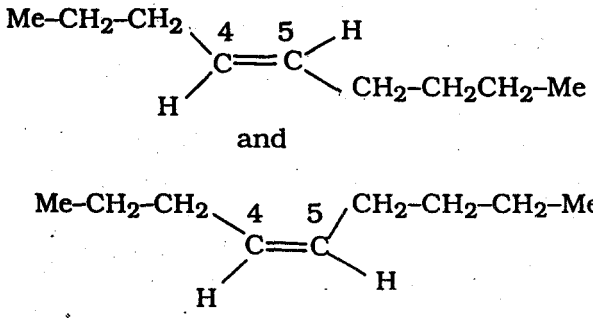
[For terminal alcohol : Effect on the α-carbon atom : +48.0 ppm; Effect on the β-carbon atom : +10.0 ppm ; Effect on the γ-carbon atom : –5ppm; For internal alcohol : Effect on the α-carbon atom : +41.0 ppm ; Effect on the β-carbon atom : +8.0 ppm ; Effect on the γ-carbon atom : –5 ppm; α-, β-, γ- and δ-effects for the parent hydrocarbon have usual values.]

(ii)

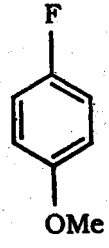


[Calculate the δc values of only C–2 and C–3. Usual additive parameters for α-, β-, γ- effects. 2°(4°) = –7.2ppm, 4°(2°) = –8.4ppm; 4°(1°) = –1.5ppm]

(iii)



[Calculate the δc values of only C–4 and C–5. Base value : 122.2ppm; Additive parameters in ppm : α-effect = +11.0, β^{o} = +6.0, β^{m} = –7.1, γ^{m} = –1.9, γ^{o} = –1.0, δ^{m} = +1.1, δ^{o} = +0.7, *cis*-effect = –1.2]

(iv) 

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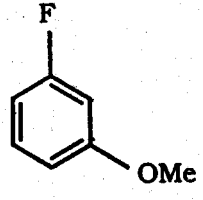
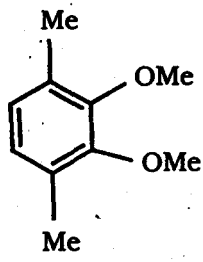


[Calculate only the δc values of the protonated aromatic carbons of *p*-fluoroanisole and those of C–2, C–4 and C–6 of *m*-fluoroanisole. Additive parameters in ppm : Base value = 128.7, *ortho* to F = –14.1, *meta* to F =+1.6, *para* to F = –4.4, *ortho* to OMe = –15.5, *meta* to OMe = 0.0, *para* to OMe = –8.9]

(c) (i) Indicate the more important mass spectral fragmentation(s) of the following Compounds : 3

$Me–CH_2–CH_2—O–CH_2–CH_2–Me$ and 

(ii) How would you distinguish between the following oxygenated substitution patterns in the following isomeric compounds from their methoxyl carbon resonances ? 1



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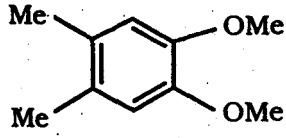
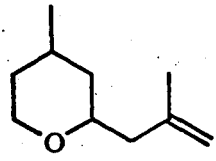


10. (a) What is McLafferty rearrangement in the mass spectral fragmentations of some organic compounds? Give direct evidence for the mechanism of this rearrangement using appropriate deuterium labelled compounds. 4

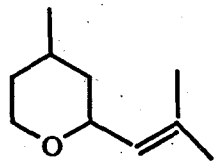
(b) How would you distinguish between the following isomeric compounds from their mass spectral fragmentations? Answer any *three*. 2×3

(i)



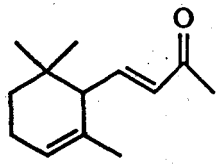
M^+ 154

and



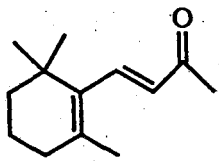
M^+ 154

(ii)



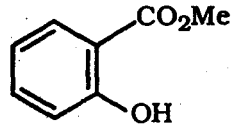
M^+ 192

and

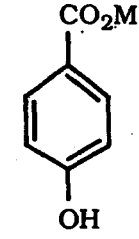


M^+ 192

(iii)



and



M^+ 152 M^+ 152

(iv) Me–CH_2–CH_2–CH_2–CH_2–Me and

M^+ 86

Me–$CH(CH_3)$–$CH(CH_3)$–Me

M^+ 86

(c) An organic compound (M.W. 108) is not an acid, can be easily oxidised to a crystalline compound (m.p. 122°C). It gives the following spectral data :

UV : λ_{max} 255nm (ϵ_{max} 202)

IR : $\bar{\nu}_{max}(cm^{-1})$: 3402(s, br), 3056(w), 2888(m), 1499(w, sh), 1455(m)

^1H NMR : δ :	3.90	4.60	7.26
Multiplicity :	s	s	s
Intensity ratio :	1	2	5

Deduce the structure of the compound and predict the principal ions in its mass spectrum. 5