PG/IIIS/CH - 2103/09

2009

CHEMISTRY

PAPER — CH-2103

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks
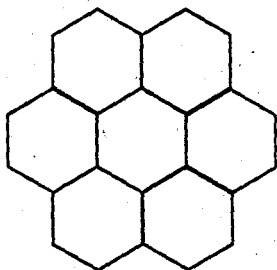

(*Inorganic*)

Answer any *four* questions

1. (*a*) Explain the defect in crystal in thermodynamic
aspect. 3

(*b*) Show that number of Schottky defect increases
exponentially with absolute temperature. 4

(*c*) AgCl shows Frenkel defect, but not NaCl
although both Ag^+ and Na^+ are monovalent
cations. Explain. 3

2. (a) Write short note on Hopping semiconductor. 4

   (b) What is the disadvantage of using oxidized NiO as a semiconductor ? How it is used ? 3

   (c) Discuss p-type semiconductor briefly. 3

3. (a) When KCl is heated in presence of K-vapour or Na-vapour , it shows violet colour in both the cases ? Explain. 4

   (b) NaCl shows yellow colour after bombardment with X-ray. Explain. 2

   (c) How the existance of F-centre is determined ? 2

   (d) What is R-centre ? 2

4. (a) What are the two types of coulometric processes used in analysis ? Depict the experimental set up in a coulometric measurement. 2 + 3

(b) Cite examples of the application of cyclic voltametry in the coordination chemistry of cobalt and ruthenium system. 5

5. (a) Write the Ilkovic equation for limiting diffusion current in polarography. Explain the terms involved in the equation. $1 + 2$

(b) Show the basic instrumental set up in cyclic voltametry. 3

(c) Define half-wave potential. How can you determine the half-wave potential for reversible redox process from a cyclic voltammogram. $2 + 2$

6. (a) How can you represent the cyclic voltammogram of ferrocene, specify $E_{p_a}, E_{p_c}, i_{p_a}, i_{p_c}$ and $E_{1/2}$ in the diagram. Comment on the nature of the redox process involved in ferrocene from the voltammogram. $2 + 1$

(b) How do strong and weak synthetic ion-exchange resins differ in structure ? Show with examples.   3

(c) Describe the equilibrium process involved in the extraction of metal chelates.   4

7. (a) What is crystal engineering ?   2

(b) Show the formation of hexagonal sheets by benzene 1, 3, 5-tricarboxylic acid via hydrogen bonding.   2

(c) What do you mean by techtons ?   2

(d) What is a "network" ? Predict the Well's symbol for the following 2D net —   2 + 2
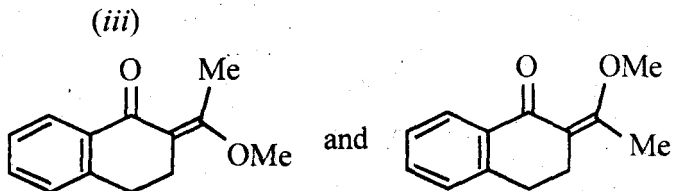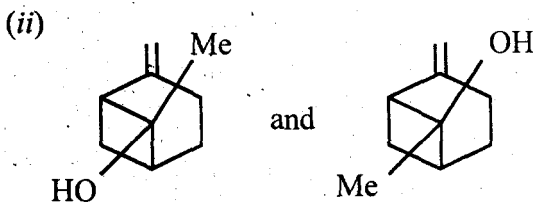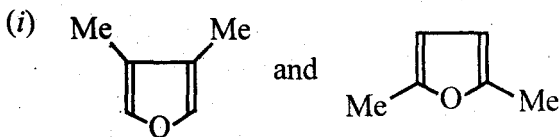

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(5)

(Organic)

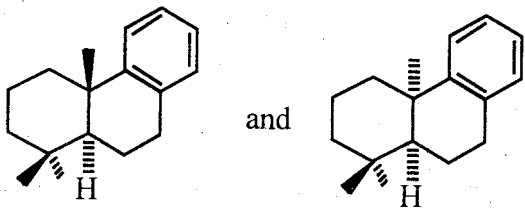Answer any *five* questions taking atleast *two*
from each Group

GROUP — A

1. (a) How would you distinguish between the
isomeric compounds in each of the following
pairs from their ^{1}H spectral data. Indicate only
the distinguishing feature. Answer any *three*:

2×3
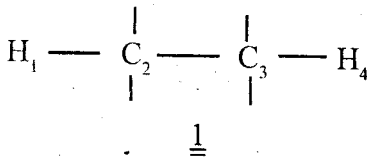
(i)

and

(ii)

and

(iii)

and

(iv)

and

(b) How is the coupling constant (J) for two non-equivalent vicinal protons in a substitued ethane of the type $\underline{1}$ related to their dihedral angle ϕ ?   2

$$H_1 — \overset{|}{\underset{|}{C_2}} — \overset{|}{\underset{|}{C_3}} — H_4$$
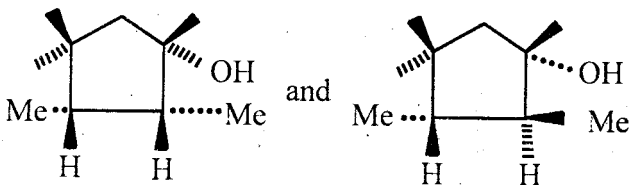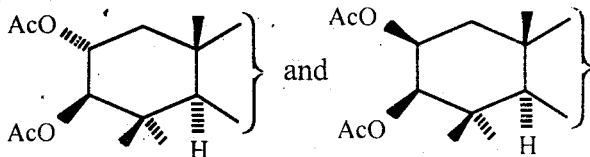
$$\underline{1}$$

2. (a) How would you distinguish between the following pairs of isomeric compounds using the Karplus equation ? $1\frac{1}{2} \times 2$

(i)

and

(Continued)

(ii)

(b) What is meant by spin-decoupling between two interacting protons (or groups of protons)? How is this carried out? Indicate the changes in the multiplicity of the signals of the protons of pure ethanol on successive spin-decoupling of the methyl, methylene and the hydroxyl protons. $1 + 1 + 3$

3. (a) What is Nuclear Overhauser Effect (NOE) Explain the reason for this effect. Give one example of the application of this effect.
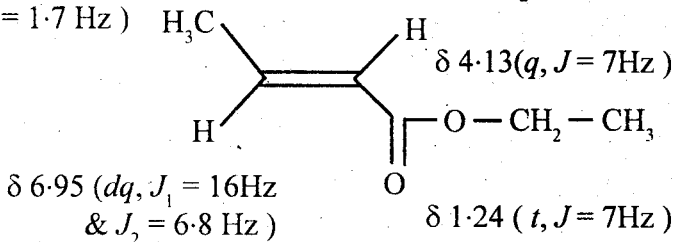
$$1 + 2\frac{1}{2} + 1\frac{1}{2}$$

(b) What are the full names of COSY, HMQC and HMBC spectra? Draw the expected COSY

spectrum of ethyl *trans*-crotonate having the proton chemical shifts given on its structural diagram :

$$1\frac{1}{2} + 1\frac{1}{2}$$

δ 1·88 (*dd*, J_1 = 6·8Hz & J_2 = 1·7 Hz)

δ 5·81 (*dq*, J_1 = 16Hz & J_2 = 1·7 Hz)

δ 4·13 (*q*, *J* = 7Hz)

δ 6·95 (*dq*, J_1 = 16Hz & J_2 = 6·8 Hz)
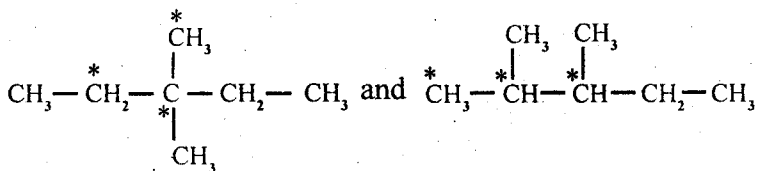
δ 1·24 (*t*, *J* = 7Hz)

4. (*a*) How would you distinguish between a primary, secondary and tertiary alcohols from their ^{1}H NMR spectra run in a particular solvent ? 2

(*b*) Compound A, $C_6H_{10}O_2$, shows two ^{1}H NMR signals at δ 2·2 (6H, s) and 2·7 (4H, s); compound B, 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, while compound C, $C_{12}H_{18}$, exhibits only one ^{1}H NMR signal at δ 2·2 (s). Suggest probable structures for all the three compounds. 6
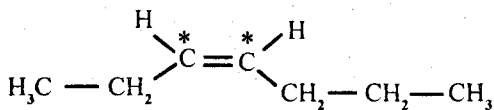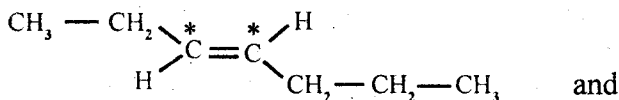
(*Continued*)

5. (a) Calculate the δ_c values of the carbon atoms marked with asterisk ($*$) of the following pairs of isomeric compounds using the given additive parameters and show how they can be distinguished from each other. Answer any *three*: 2×3

(i)

$$CH_3 - \overset{*}{C}H_2 - \underset{\underset{CH_3}{\overset{*}{|}}}{\overset{\overset{*}{CH_3}}{\overset{|}{C}}} - CH_2 - CH_3 \quad \text{and} \quad \overset{*}{CH_3} - \underset{\overset{*}{|}}{\overset{\overset{CH_3}{|}}{CH}} - \underset{\overset{*}{|}}{\overset{\overset{CH_3}{|}}{CH}} - CH_2 - CH_3$$

[Additive parameters in ppm: Base value: -2·5; α-effect: +9·1; β-effect: +9·4; γ-effect: -2·5; δ-effect: +0·3; 2°(4°): -7·2; 4°(2°): -8·4; 4°(1°): -1·5; 1°(4°): -3·4; 1°(3°): -1·1; 3°(3°): -9·5; 3°(2°): -3·7]

(ii)

$$CH_3 - CH_2 \underset{H}{\overset{}{\diagdown}} \overset{*}{C} = \overset{*}{C} \underset{CH_2 - CH_2 - CH_3}{\overset{H}{\diagup}} \quad \text{and}$$

$$H_3C - CH_2 \underset{}{\overset{H}{\diagdown}} \overset{*}{C} = \overset{*}{C} \underset{CH_2 - CH_2 - CH_3}{\overset{H}{\diagup}}$$

(*Turn Over*)

[Additive parameters in ppm: Base value: 122·2; α-effect: +11·0; β^σ-effect: +6·0; β^π-effect: -7·1; γ^σ: -1·0; γ^σ: -1·9; δ^π: +1·1; *cis*-effect: -1·2].

(*iii*)

$\overset{*}{C}H_3 - \overset{*}{C}H_2 - \overset{*}{C}H_2 - \overset{*}{C}H_2 - OH$ and $\overset{*}{C}H_3 - \overset{*}{C}H - \overset{*}{C}H_2 - \overset{*}{C}H_3$
                                                          |
                                                         OH
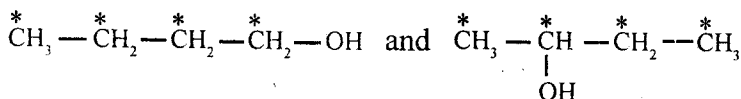
[Additive parameters in ppm: For terminal alcohol— α to OH: +48·0; β to OH: +10·0; γ to OH: -5·0. For internal alcohol— α to OH: +41·0; β to OH: +8·0 and γ to OH: -5·0].
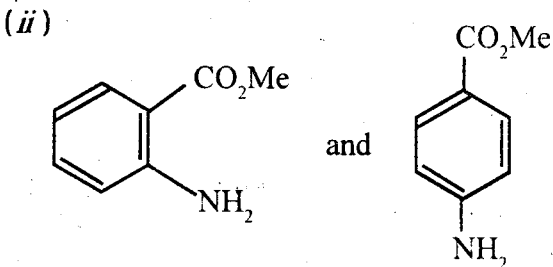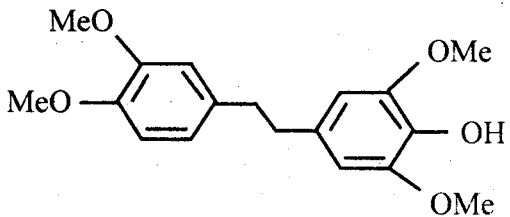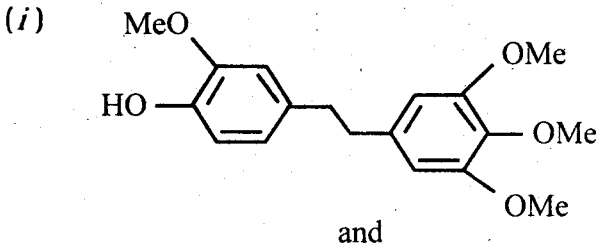
(*iv*)

and
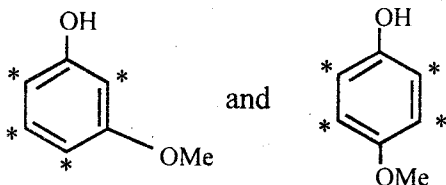
[Additive parameters in ppm: Base value = 128·7; *ortho* to OH: -12·6; *meta* to OH: +1·8; *para* to OH: -7·9; *ortho* to OMe: -15·5; *meta* to OMe: 0·0; *para* to OMe: -8·9].

(b) How would you distinguish between the following pairs of isomeric compounds from their mass spectral fragmentations ? Answer any *one* : 2

(i)

and

(ii)

and

GROUP—B

6. (a) The three isomeric (*ortho*, *meta* and *para*) xylenes give identical mass spectra, all showing the base peak at $m/z\,91$. Explain.   4

   (b) Briefly discuss the basic principle of Fast Atom Bombardment (FAB) mass spectrometry or the basic principle of Matrix Assisted Laser Desorption Ionisation (MALDI) mass spectrometry.   4

7. (a) Explain the formation of the following significant peaks observed in the MS of the following compounds (answer any *two*): $2 + 2$

   (i) $PhCH_2CH(Me)CHMe_2 \rightarrow m/z\,92$

   (ii) $CH_3(CH_2)_3CH_2OH \rightarrow m/z\,42$

   (iii) 2–Methylbenzyl alcohol $\rightarrow m/z\,104$.

(*Continued*)

(b) Briefly explain any *two* of the following:

$2 + 2$

(i) Retro Diels-Alder cleavage.

(ii) Even-electron Rule

(iii) Soft Ionisation Techniques in MS.

8. (a) Mark the statements (any *four*) as *True* (T) or *False* (F): 1×4

(i) If a compound contains *n* number of chlorine or bromine atoms in it, its Mass Spectrum will record "$(n + 1)$" number of molecular ion-peaks.

(ii) The Mass Spectrum of a mixture of methyl esters of saturated fatty acids will record a peak at *m/z* 74.

(iii) A Mass Spectrometer capable of resolving the two peaks at *m/z* 500·00 and 499·99 is a Low Resolution instrument.

(*iv*) Polar macromolecules of biological origin may be successfully subjected to EI-MS.

(*v*) A moving ionic species induces a secondary magnetic field.

(*b*) Answer any *one* of the following two questions : 4×1

(*i*) Derive the equation $m/z = B^2r^2/2V$ that governs the movement of ions inside a low resolution electron–impact mass spectrometer.

(*ii*) What are the sources of energy in PD–MS, SIMS, LD–MS and FAB–MS ?

9. Identify the following compounds from the IR, ^{1}H NMR and MS data.

(*a*) A compound, $C_6H_{12}O_2$ (MW 116) recorded the following important spectroscopic data : 4

IR : 2924, 1745 and 1456 cm^{-1}; ^{1}H NMR : δ 1·97, 3 H, s and 1·45, 9H, s; MS : m/z 116, 73, 57, 43.

(*Continued*)

(b) An aromatic compound C_9H_{12} (MW 120) recorded the following data: IR: 3067–2907, 1608, 1473 cm^{-1}; ^{1}H NMR: δ 2·26, 9H, s and 6·79, 3H, s; MS: m/z 120, 119, 40.   4

(*Physical Spl.*)

Answer any *four* questions taking *one* from each Group

GROUP—A

Answer any *one* of the following

1. General expression of wavefunction for a two level system is given by

$$\psi = a_l\psi_l + a_m\psi_m$$

where, ψ_l and ψ_m are the stationary state wavefunction for lower and upper state and a_l and a_m are the weight factor of lower and upper state towards the total wave function. Show that,

$$\frac{d}{dt}(a_m^* \, a_m) = \frac{8\pi^3}{3h^2}|\mu_{lm}|^2 \varrho$$

where symbols have their usual significance.   10

    (*Turn Over*)

2. (a) Deduce the relation between Einstein co-efficient of induced emission and spontaneous emission. 5

(b) Show that, for a two level system obeing Beer – Lambert's law,

$$\in_\gamma = B_{lm} \frac{Nh\gamma_{max}}{2303\, C}$$

where $\in_\gamma$ = molar absorptivity at frequency, γ

B_{lm} = Einstein co-efficient of induced absorption.

N = Avogadro's number

h = Plank's constant

γ_{max} = frequency of maximum absorption

C = velocity of light in the medium. 5

GROUP—B

Answer any *one* of the following

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

$$K_{ISC} = \frac{1}{\tau_f^\circ} \left(\frac{1 - \phi_f}{\phi_f} \right)$$

(where symbols have their usual significance.) 5

(b) Write short notes on E-type and P-type delayed fluorescence. $2\frac{1}{2} \times 2$

4. What do you mean by static and dynamic quenching of a fluorophore ? How do you obtain the rate constant for both static and dynamic quenching of a fluorophore when it undergoes quenching via both static and dynamic quenching mechanism. $2 + 8$

GROUP—C

Answer any *one* of the following

5. (a) Inversion of population is an essential criterian for a system to show lasing activity. Justify. Show that inversion of population can not be achieved for a two level system. 2 + 5

   (b) How can one obtain shorter laser pulses using mode locking techniques ? 3

6. (a) Write short notes on semi-conductor laser and dye laser. 3 + 3

   (b) How do you obtain second and third Harmonic frequency from a given frequency of laser radiation ? 4

GROUP—D

Answer any *one* of the following

7. (a) Write the spin wave function for an $A_2\left(I=\dfrac{1}{2}\right)$ system. Classify them according to their symmetry property with respect to interchange of identical particles. Also, identify the function, when the total spin quantum number is 1. 4

(b) Show that the primary condition for a NMR transition is that the magnetic field of radio frequency should be perpendicular to the external magnetic field. 3

(c) Consider an AX system and write down the possible spin eigenfunctions when both A and X have $I=\dfrac{1}{2}$. 3

8. Write down the non-interactive and interactive Hamiltonian for a nuclear spin system of AB type. How do you account for the observation of multiplates in such system? $2+8$