PG/IIIS/CEM-303/14

M.Sc. 3rd Semester Examination, 2014

CHEMISTRY

PAPER—CEM-303

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Organic Special*)

Answer Q. No. 1 and any four from the rest

1. Answer any *eight* of the following : 1 × 8

(*a*) Which of the following nuclei will be NMR active : $_1H^2$, $_6C^{13}$, $_9F^{19}$, $_7N^{14}$, $_3B^{10}$, $_8O^{16}$, $_{16}S^{34}$?

(*b*) State the reason why sensitivity increases with increasing applied magnetic field strength.

(*c*) Show pictorially the change in spin state of a spinning nucleus on absorption of resonance frequency.

(*d*) Which radio frequency is needed for ^1H nucleus at an applied magnetic field B_0 of 9·40 Tesla : 100 MHz, 200 MHz, 400 MHz ?

(*e*) NMR is an absorption spectroscopy : True or False ?

(*f*) Write two differences between CW and FT NMR techniques.

(*g*) Show pictorially the result of a short (μs) and powerful 270° RF pulse application.

(*h*) What is spin-lattice relaxation ?

(*i*) What is a metastable ion peak in Mass spectroscopy ?

(*j*) Why TMS is used as a reference compound in NMR ?

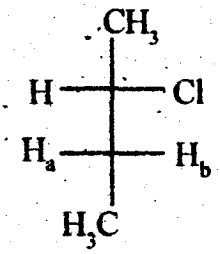
(*k*) Which reference compound is used for NMR in D_2O ? Write its structure.

(*l*) Coupling constant J is independent of the applied magnetic field : True of False ?

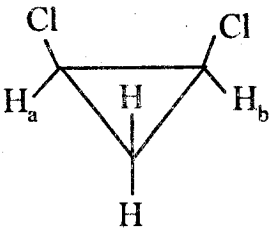
2. (*a*) Two lines of a doublet in 400 MHz ^{1}H-NMR spectrum appear at 2.32 and 2.36 ppm. Calculate the coupling constant. (*b*) What will be the separation (in ppm) between the two lines in 200 MHz and 800 MHz ^{1}H-NMR ? (*c*) Show qualitatively how a complex NMR spectrum recorded in a lower magnetic field can be simplified in a higher magnetic field. (*d*) What are NMR shift reagents ? Give examples and write the mechanism of their activity.

2 + 1 + 2 + 3

(*i*)



(*ii*)



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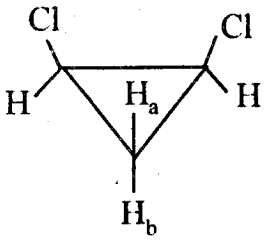


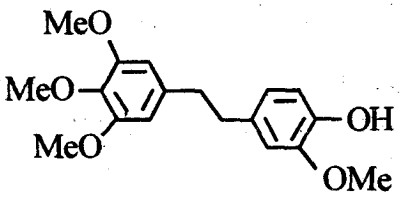
3. (*a*) What is Karplus equation ? Give an example.

(*b*) What are the stereochemical relationships between the H_a and H_b of the compounds (*i*) – (*iii*) ?

(*c*) Write the possible configurations of dimethyl muconate having the general structure $MeO_2C-CH=CH-CH=CH-CO_2Me$ and assign their stereochemistry using olefenic protons in ^1H NMR. 2 + 2 + 4

4. (*a*) How mass spectral analysis can be used to distinguish the structural isomers. Explain with the help of suitable examples. (*b*) Prove that in the benzylic system the mass spectral fragmentation is not straight forward rather it passes through stable tropylium cation intermediate. (*c*) Differentiate the following compounds with the help of mass spectroscopy (any *four*) ? 2 + 2 + 4

(*i*)



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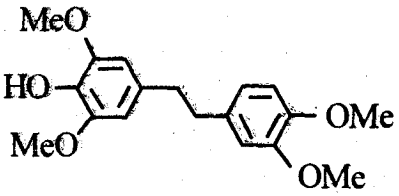

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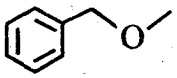

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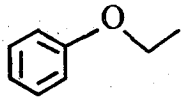
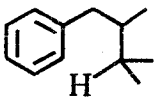
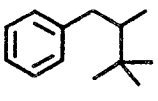
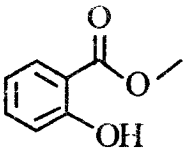
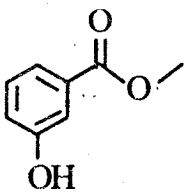
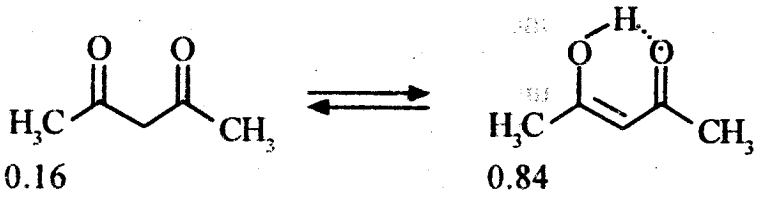


(*iii*)  and 

(*iv*) *cis*-methyl crotonate and *trans*-methyl crotonate.

(*v*)  and 

5. (*a*) What is chemical exchange ? (*b*) Calculate the percentage of keto and enol forms of acetyl acetone from the integral data given below ?



(*c*) A compound $C_9H_{10}O_2$ compound has strong infrared absorption at 1695 cm^{-1}. The ^1H NMR spectrum has five sets of line : a triplet at δ 1.3 (3H), a quartet at δ 4.1 (2H), a

doublet at δ 7.0 (2H), a doublet at δ 7.8 (2H) and a singlet at δ 9.8 (1H) ppm. Suggest a structure for this compound. 2 + 2 + 4

6. (*a*) Compound A, $C_8H_8O_3$, shows the following spectral data :

UV : λ_{max} (EtOH) 215, 235, 285 and 320 nm; λ_{max} (EtOH–NaOH) 260, 303 and 355 nm.

^{1}H-NMR (δ) : 9.80 (s, 1H), 7.40 (m, 2H), 7.10 (s, 1H, disappeared on deuterium exchange), 7.0 (1H, d, J = 8 Hz), 3.95 (s, 3H)
MS (m/z) : 152 (M^+, 100%), 151 (96%), and 123 (8%).

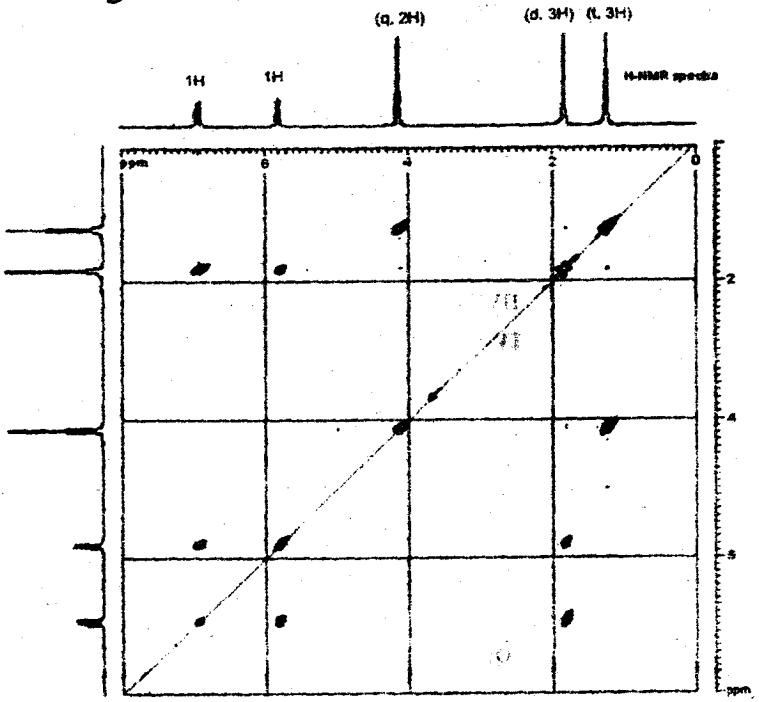
Suggest a probable structure for the compound.

(*b*) Compound B, $C_9H_{11}NO$, shows the following spectral data.

UV : λ_{max} 235(ε 8650) and 320(ε 28300)
FTIR (cm^{-1}) : 1695, 1600 (s), 1567, 1526, 808, 720 and bands immediately above and below 3000 cm^{-1}, well-defined doublets at 2820 and 2740 cm^{-1}.
^{1}H-NMR (δ) : 9.72 (s, 1H), 7.75 (d, 2H,

J = 9 Hz), 6.70 (d, 2H, J = 9 Hz), 2.98 (s, 6H)
MS (m/z) : 149 (M^+), 148 (base peak) and 120. 4 + 4

7. (*a*) What are the full forms of DEPT, DQF COSY, HMQC and HMBC ? (*b*) A compound having molecular formula $C_6H_{10}O_2$ shows the following 2D COSY NMR spectrum. Assign the structure. 8



8. (*a*) What is the Mc Lafferty rearrangement in the mass spectral fragmentation of organic compounds ? (*b*) Give examples. (*c*) Using appropriate deuterium labelled compound prove that in Mc Lafferty rearrangement always γ-hydrogen transfers. (*d*) What are the basic differences between soft ionization and hard ionization techniques ? Write down the name of different types of ionization techniques. 1 + 1 + 3 + 3

(*Inorganic Special*)

Answer any **five** questions taking at least **two** from each Group

GROUP – A

1. (*a*) State the essential criteria for developing a photochemical energy storage cycle. 3

(*b*) Distinguish between fluorescence and phosphorescence. 3

(*c*) The parity selection rule for radiationless transitions is precisely opposite to the selection rule for radiative transitions. Explain. 2

2. (*a*) What do you mean by thexi state ? Write the characteristics of this state. 3

(*b*) Write down the product(s) of the following photochemical reactions and suggest plausible mechanism : 2 + 2

(*i*) $Re_2(CO)_{10} \xrightarrow{I_2, h\nu}$

(*ii*) $Mn_2(CO)_{10} \xrightarrow{h\nu, PPh_3}$

(*c*) How cerium salt function in the process of photochemical splitting of H_2O molecule ? 1

3. Answer any *four* : 4 × 2

(*a*) What is the difference between chemisorption and physi-sorption ?

(*b*) Differentiate 1D materials and 2D materials.

(*c*) Nano materials behave quantum mechanically– Justify.

(*d*) Surface to volume ratio in nanomaterials is low. True or false ? Justify.

(*e*) What is meant by V.L.S technique of CNT preparation.

(*f*) Give the basic principle of probemicroscope.

4. (*a*) What is three electrode system ? Describe the mechanism of three electrode system using $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple. 1 + 2

(*b*) What is role of supporting electrolyte in voltametry and coulometry ? 2

(*c*) Give the name of six thermal methods indicating abbriviation, instrument used and parameter measured. 3

GROUP – B

5. (*a*) Why ligands with high absorption properties are essential for showing luminescence behaviour of lanthanide complexes ? Explain the luminescence properties of lanthanide complexes with qualitative energy level diagram. 2 + 3

   (*b*) Discuss thermodynamic and kinetic limitation on the photochemical conversion and storage of sun light. 3

6. (*a*) Write short notes on : 3 + 3

   (*i*) Oscillator strength and radiative life time

   (*ii*) Spontaneous emission.

   (*b*) What do you mean by "photosensitization" ? 2

7. (*a*) Describe the method of C.V.D. 3

   (*b*) What is the advantage of neutron diffraction ? How it is different from X-ray diffraction ? 3

   (*c*) How does the neuclear magnetic resonance originate ? 2

8. (*a*) Discuss the principle of TG analysis. 3

(*b*) What is the advantage of using DMF in polarography ? Define limiting and residual current ? 2 + 2

(*c*) What is the principle of cyclic voltametry ? 1

(*Physical Special*)

Answer any **five** questions taking at least **two** from each Group

GROUP – A

1. First order coefficient of transition from state 'ψ_n' to state ψ_k (two level system) in presence of weak perturbing field, H′ is given by,

$$a_k^{(1)}(t) = \frac{1}{i\hbar}\int_{t'=0}^{t'=t} e^{iw_{kn}t'} H'_{kn}\,dt'$$

where $H'_{kn} = \langle \psi_k \mid H' \mid \psi_n \rangle$ and all other symbols have their usual significances. Assume H′ as periodic function of time and explain the phenomena of stimulated absorption and emission processes. 8

2. Deduce the selection rule of vibrational transition and also show that it is the fluctuation of dipole moment during molecular vibration and not the permanent dipole moment which is responsible for vibrational transition. Given, the Hermite polynomial identity relation. 8

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

3. What is Doppler broadening in spectral transition ? Deduce an expression to calculate temperature of a gas from its spectral broadening data. (Assume Doppler effect is the only operative mechanism for spectral broadening). For potassium D-line (7681·94 Å) the Doppler broadening is 770 MHz. Calculate the temperature of potassium vapour. 5 + 3

4. (*a*) Define the term Dispersion (F) for nano-materials. Show that for a cubic nanocrystal having 'N' number of atoms, 1 + 3

$$F \simeq \frac{6}{N^{y_3}}$$

(*b*) "It is generally observed that the edge and in particular corner atoms are often missing on nanocrystals"– Explain. 2

(*c*) "Melting temperature for a given nano-material decreases as its size decreases."– Explain. 2

GROUP – B

5. Why does spin relaxation so important in NMR spectroscopy ? "The net effect of spin lattice relaxation is to depopulate the higher level rather than to populate it." Explain. 3 + 5

6. Write down the magnetic interaction Hamiltonian and the spin wavefunctions for A_2 spin system. Obtain the zero order energy and the frequency of possible transition. 2 + 4 + 2

7. (*a*) Define chemical shift (δ_H) is NMR transition. Show that the separation between two absorption lines for the chemical shift scale is independent of the applied magnetic field. 2 + 4

(*b*) "Chemical shift of a given proton decreases with the increase in shielding constant."– Explain. 2

8. (*a*) Draw a schematic potential energy diagram for nanoparticles whose overall potential is given by,

$$V = \frac{B}{R^n} - \frac{C}{R^6} + \frac{N^2.e^2}{\in_m .R}$$

where 'R' is the centre to centre distance between two spherical nanoparticle, 'N' is the number of particle carrying electronic charge 'e'. '$\in_m$' is the dielectric constant of the medium; 'B' and 'C' are the characteristic constant of nanoparticle. 4

(*b*) What is surface Plasmon Resonance (SPR) for metal nanoparticle ? How do you explain the appearence of two resonance absorption band for anisotropic (say rod shaped) gold nanoparticle ? 4
