



III Semester M.Sc. Examination, December 2016
(CBCS)
CHEMISTRY
303 – OC : Organic Spectroscopy

Time : 3 Hours

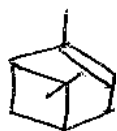
Max. Marks : 70

Instruction : Answer question No. 1 and **any five** of the remaining questions.

1. Answer **any ten** of the following : **(2×10=20)**
- a) What are different types of transitions involved in UV-Vis spectroscopy ? Arrange them as per their decreasing order of energy level.
 - b) Using UV-Vis spectroscopy how you will distinguish the cis-and trans-stilbenes ?
 - c) Give the range of finger print and function group regions in IR spectrum. Mention its significance for the interpretation of a spectrum.
 - d) Why esters of O-chlorobenzoic acid show two $>C=O$ stretching frequencies in its IR spectrum ?
 - e) In the PMR of cyclohexane the vicinal coupling constant 'J' between diaxial protons is larger than the diequatorial protons. Why ?
 - f) What information will you get from HETCOR spectrum of a compound ?
 - g) Which relaxation process is responsible for NMR phenomenon and why ?
 - h) Why the chemical shift range in CMR is very wide as compared to PMR spectroscopy ?
 - i) Write the structure of a base-ion peak at m/z 56 observed in the mass spectrum of 1-hexanol.
 - j) How can you use the information of ortho effect to explain the formation of ion at m/z 149 in the ester of phthalic acid ?
 - k) Why IR absorption due to carbonyl stretching occurs at higher frequency than C-C double bond ?
 - l) Sketch the off-resonance decoupled CMR of the following compound and assign the chemical shift values :
 $CH_3 - C \equiv C - CH_2 - CO NH_2$



2. a) Explain the Woodward-Fieser rules to predict the λ_{max} of conjugated dienes using suitable examples.
- b) How will you distinguish the following pairs of compounds using IR spectroscopy ?
- Anthranilic acid and 4-amino benzoic acid
 - Hexan-2, 4-dione and hexane – 2, 5 – dione.
- c) Write a note on complementarity of IR and Raman spectroscopy. **(3+4+3=10)**
3. a) What is magnetic anisotropy in NMR ? Explain using benzene as an example.
- b) What is deuterium exchange technique in PMR spectroscopy ? Explain its applications with appropriate examples.
- c) The following monoterpene, α -pinene has three methyl groups in different environments, as revealed by their chemical shift values at δ 0.85, 1.27 and 1.63. Assign the values and justify your answer.

**(3+4+3=10)**

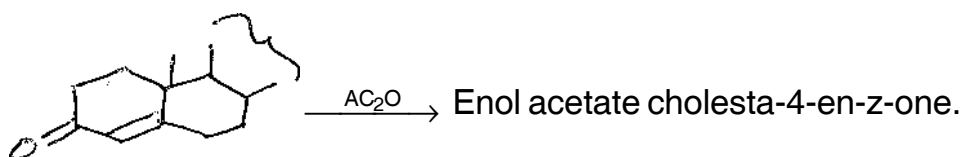
4. a) Explain the HETCOR technique used in 2D NMR. Mention its applications with suitable examples.
- b) Discuss the NOE phenomenon with the help of suitable example. Using this technique how will you distinguish the E-and Z-citral.
($\text{Me}_2\text{C} = \text{CH} - \text{CH}_2\text{CH}_2\text{C}(\text{Me}) = \text{CH} - \text{CHO}$).
- c) How the number and position of CMR signals can help in the identification of the four isomeric alcohols with the mol. formula $\text{C}_4\text{H}_{10}\text{O}$? **(3+3+4=10)**
5. a) How will you differentiate 3-methyl-and 4-methyl-cyclohexenes by mass-spectral fragmentation pattern ?
- b) Explain the differences observed in the EI and CI mass spectra of n-butyl propenoate.
- c) An organic compound with the molecular formula $\text{C}_7\text{H}_5\text{OCl}$ showed the following spectral data :
- IR(cm^{-1}) : 3070, 1730, 1595 and 830
- ^1H NMR (δ , ppm) : 9.0 (s, 1H), 7.6 (d, 2H) and 8.2(d, 2H)
- Mass (m/z : 140 (M^+), 142 ($\text{M}^+ + 2$)).
- Deduce the structure of compound and assign the values. **(3+3+4=10)**



6. a) Explain with suitable examples, effect of the following factors on the IR absorption frequency of carbonyl group :
- i) Conjugation
 - ii) Bond angle.
- b) Discuss the effect polarity of solvents on the UV-Vis absorption of α, β -unsaturated carbonyl compounds.
- c) Deduce the structure of an organic compound having molecular formula $C_{10}H_{13}O_2N$ with help of following spectral data : Assign the values :
- IR (CM^{-1}) : 3400, 3200, 1500, 830
- 1H NMR (δ , ppm) : 7.9 (bs, 1H), 4.0 (9, 2H, $J = 8Hz$), 2.1 (s, 3H), 1.3 (f, 3H, $J = 8Hz$), 6.8 (d, 2H) and 7.5(d, 2H)
- ^{13}C NMR (δ , ppm) : 15(q), 24(q), 64(f), 115 (d), 123(s), 157(s) and 171(s) .
- (3+3+4=10)**
7. a) What is the mass of the 'McLafferty ion' from the following compounds :
- i) Butanal
 - ii) Heptanal
 - iii) 2-Octanone
 - iv) 2-pentanone.
- b) With suitable example, discuss 2D-homonuclear correlation experiment for 1H NMR. Explain the importance of 'cross peaks' and diagonal peaks.
- c) Deduce the structure of an organic compound having molecular formula $C_8H_{11}N$ with the help of following spectral data :
- IR(cm^{-1}) : 3400 (s), 3040, 2880, 1400, 1500, 1600, 700(s), 750(s).
- 1H NMR (δ , ppm) : 6.5-7.5(m, 5H), 3.3(s, 1H), 3.1 (quartet, 2H) and 1.2 (f, 3H)
- M_s (m/z) : 106 (Base peak).
- (4+3+3=10)**



8. a) Explain the CIDNP technique in NMR spectroscopy. Discuss its application using appropriate examples.
- b) Discuss any two methods for the simplification of complex spectra ^1H NMR spectroscopy.
- c) Cholesta-4-en-3-one gives an enol acetate which has λ_{max} at 238 nm. Suggest the structure for the enol acetate.



(3+4+3=10)

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