M. Sc DEGREE END SEMESTER EXAMINATION - OCTOBER 2022
SEMESTER 3 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY
COURSE : **16P3CHET12/16P3CPHT12 : SPECTROSCOPIC METHODS IN CHEMISTRY**
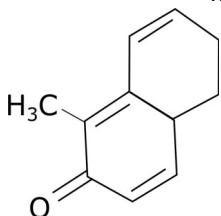*(For Supplementary - 2016/2017/2018/2019/2020 Admissions)*

Time : Three Hours   Max. Marks: 75

PART A
Answer any 10 (2 marks each)

1. Name any two solvents used in UV spectroscopy. Why they are used?

2. Calculate the λ_{max} of the following compound .

3. Explain Multiple Cotton effect curves in the ORD spectrum of a molecule.

4. The IR spectrum of ethylene glycol has two bands around 3600 cm^{-1}. Explain this observation.

5. How can you distinguish acetophenone and benzyl methyl ketone using IR spectroscopy?

6. An organic compound having molecular formula $C_3H_6O_2$ shows two singlets in the proton NMR spectrum. The chemical shift values are 2.2 and 4.1. Predict the structure of the compound.

7. An organic compound with molecular formula $C_4H_{10}O$ gives one triplet and one quartet in proton NMR spectrum (1.0 and 4.0). The carbon-13 NMR spectrum show only two signals, one is positive and other negative in DEPT-135 spectrum. Predict the structure of the compound.

8. The ortho protons of methyl phenyl ether exhibits a chemical shift value δ 6.8. Justify the low chemical shift value.

9. Phenol shows CO loss on EI analysis. Show the mode of fragmentation.

10. Ethanal shows an ion of *m/z*-29 in its EI mass spectrum. Explain.

11. An organic compound (C_4H_9Br) shows only one signal in proton NMR spectrum. The base peak in the EI mass spectrum is an ion of m/z 57. What is the structure of the compound.

12. Predict the proton NMR spectrum of 1-bromo-3-methylbut-2-ene

13. A compound with molecular formula $C_5H_{10}O_2$ shows two positive and two negative signals in DEPT-135 experiment. The HETCOR spectrum show four correlations and ^{1}H-^{1}H cosy showed only one correlation. Identify the structure.

(2 x 10 = 20)

14. In the absorption spectrum of ketones, λmax (n-π* transition) depends on several variables. Consider the absorption spectrum of *cyclohexanone*. Predict the change observed when a) solvent polarity is changed; b) a chlorine substituent is introduced at the α-position.

15. Compare the C = 0 stretching frequencies in the following pairs and explain.
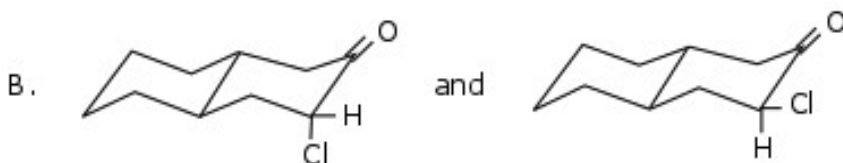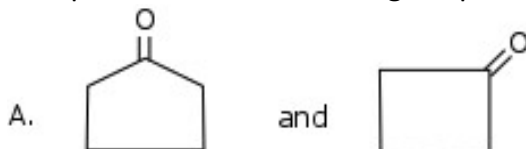
16. Explain how the wave number of C=C stretch vary with the ring size in cyclo alkenes. Explain with examples. Give their approximate values and rationalise your answer.

17. Label the spin system in 1-nitropropane. Predict the proton and carbon-13 NMR spectra of the compound and sketch the heterocosy spectrum.

18. An organic compound having molecular formula $C_8H_8O_2$ showed the following NMR data: Proton: δ 3.8, 6.9, 7.5, 7.75 and 10.4. Carbon-13: δ 55.5, 111, 120, 125, 128, 136, 161, 189. Identify the molecule, assign the data and predict the DEPT-135 and DEPT-90 spectra.

19. Give a brief note on GC-MS. What are its advantages?

20. An organic compound ($C_{10}H_{10}O_3$) showed the following spectral data: Proton NMR δ 3.8(s), 6.4(d, J=16Hz), 6.9(m), 7.1(m), 7.2(m), 7.4(m), 7.7(d, J=16Hz), 12.5. Carbon NMR spectrum showed 58, 114, 117, 118, 121, 130, 135, 148, 160, 172. DEPT-90 show 6 signals and DEPT-135 show seven signals. Predict the structure.

21. Identify a suitable structure using the following data. Rationalise your answer
    MS data: m/z -150 (molecular ion), 91(base peak), 43
    IR Spectrum in cm^{-1}: 3030, 2970, 1720, 1100
    NMR spectrum: δ ppm 2.0 (3H,s), 5.1 (2H,s), 7.3(5H,s)

(5 x 5 = 25)

PART C
Answer any 2 (15 marks each)

22. What is vicinal coupling ? Discuss AX, AX3, A2X2, A2X3 and AMX coupling systems taking one example for each.

23. Discuss in detail various methods of mass analysers of ions and explain the principles involved.

24. A compound molecular formula, C_5H_8O, showed the following spectral data. IR spectrum show bands at 2937, 1644. Proton NMR spectrum show signals at δ 1.9, 2.0,

4.0, 4.65 (m J=9Hz, J=6Hz), 6.3 (m, J=9Hz, J=2Hz). Carbon-13 NMR spectrum show signals at δ 19, 22, 65, 100, 144. There two positive signals and three negative signals in DEPT-135 spectrum. The HETCOR spectrum of the compound showed correlations (1.9-19), (2.0-22), (4.0-65), (4.65-100) and (6.3-144). EI mass spectrum show ions of m/z 84, 83, 56. On irradiation of the signal at δ 4.65 enhances the signal at δ 6.3. Identify the structure and explain the data. Sketch the HETCOR spectrum

25. An organic compound, molecular formula $C_6H_{12}O$, showed the following spectra data: IR spectrum a broad band at 3420, 2940 cm-1, proton NMR spectrum showed signals at δ 0.9(t), 1.35(m), 1.8(disappears on adding D_2O to the sample), 2.05(m), 4.1(m), 5.6(m). Irradiation of the proton at δ 2.05 enhances the intensity of the protons at δ 4.1. Carbon-13 NMR spectrum showed signals at δ 13, 23, 29, 59, 129, 133. HETCOR spectrum showed correlations (0.9-13), (1.35-23), (2.05-29), (4.1-59), (5.6-129) and (5.6-133). DEPT-135 show positive signals at δ 13, 129, 133 and negative signals at 23, 29, 59. EI mass spectrum showed peaks at m/z 100, 82, 71. Identify the molecule and assign the data.

(15 x 2 = 30)