

Reg. No .....

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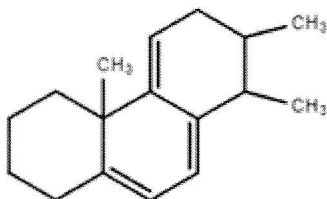
**M. Sc DEGREE END SEMESTER EXAMINATION - OCTOBER 2019****SEMESTER 3 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY****COURSE : 16P3CHET12/16P3CPHT12 : SPECTROSCOPIC METHODS IN CHEMISTRY***(For Regular - 2018 Admission and Supplementary - 2016/2017 Admissions)*

Time : Three Hours

Max. Marks: 75

**Section A****Answer any 10 (2 marks each)**

1. Name any two solvents used in UV spectroscopy. Why they are used?
2. Explain Multiple Cotton effect curves in the ORD spectrum of a molecule.
3. Use the woodward rule to calculate  $\lambda_{\max}$  for the compound



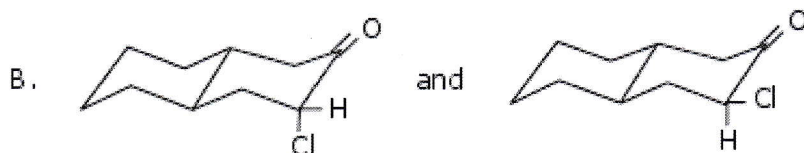
4. What is the difference between the IR spectrum of methanol and methanol in the vapour state.
5. How can you differentiate between benzaldehyde and acetophenone using IR spectroscopy?
6. What is the type of coupling present in the proton NMR spectrum of 1,1-dichloroethane? How is it labelled?
7. How will you distinguish between methyl acetate and propanoic acid using NMR spectroscopy.
8. The ortho protons of methyl phenyl ether exhibits a chemical shift value  $\delta$  6.8. Justify the low chemical shift value.
9. Explain rule of thirteen in mass spectrometry.
10. *Meta*-tolualdehyde gave an abundant ion of  $m/z$ - 91 in its EI mass spectrum. Explain.
11. An aromatic compound with molecular formula  $C_{14}H_{14}$  shows only two signals in the proton NMR spectrum in the ratio 5:2. The chemical shift values are 7.2(s) and 2.4(s). Identify the structure
12. 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.
13. A Compound with molecular formula  $C_4H_8O$  gives 3 signals in proton and 4 signals in carbon NMR. What is its structure ?

(2 x 10 = 20)

**Section B****Answer any 5 (5 marks each)**

14. Using Octant rule, predict the sign of the ORD curve of Trans-10-methyl-2-decalone.
15. How can you distinguish between intermolecular H-bonding and Intramolecular H-bonding using IR Spectroscopy? Justify your answer.

16. Compare the C = O stretching frequencies in the following pairs and explain.



17. What is the condition for getting first order spectrum? Assign the chemical shift values of the protons of acrylonitrile, 6.20(dd J=17Hz, J=2 Hz), 6.08(dd, J=10Hz, J=2 Hz), 5.9 (dd, J=17 Hz, J=10Hz). Show that in a 100 MHz experiment the compound gives a non-first order spectrum and in a 400 MHz experiment the compound give a first order spectrum.
18. Predict the proton and carbon-13 NMR spectra of 2-nitropropane. Sketch the HMQC spectrum of the compound.
19. The HRMS mass of the molecular ion is 58.04185. This on dissociation gave an ion of  $m/z$ -15.02347. Propose a possible structure for the molecule and predict the important bands in the IR spectrum.
20. Give a brief note on LC-MS. What are its advantages?
21. Propose a suitable structure of a molecule having a molecular ion peak at  $m/z$  115 and another at 44 u. On MS/MS analysis, another peak at  $m/z$  15 is also observed. Suggest any two prominent bands in the IR spectrum and assign them.

(5 x 5 = 25)

### Section C

#### Answer any 2 (15 marks each)

22. What is vicinal coupling? Discuss AX, AX<sub>3</sub>, A<sub>2</sub>X<sub>2</sub>, A<sub>2</sub>X<sub>3</sub> and AMX coupling systems taking one example for each.
23. Discuss in detail on Mc Lafferty Rearrangements citing atleast five different systems.
24. An organic compound with molecular formula C<sub>10</sub>H<sub>12</sub>O<sub>3</sub> showed the following spectra data: Proton NMR δ 1.4, 3.6, 4.0, 6.8, 7.2, 12.5. Carbon NMR δ 15, 40, 63, 115, 125, 130, 158, 179. DEPT-135 show positive signals for δ 15, 115, 130 and negative signals at δ 40 and 63. DEPT-90 show only two peaks δ 115 and 130. <sup>1</sup>H-<sup>1</sup>H cosy show correlations (6.8-7.2) and (1.4-4.0). HMQC show correlations (1.4-15), (3.6-40), (4.0-63), (6.8-115), (7.2-130). EI mass spectrum showed ions of  $m/z$  180, 135(100). IR spectrum shows a strong absorption band at 1720 cm<sup>-1</sup>. Identify the structure and assign the data.
25. A organic compound, molecular formula C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>, showed the following spectra data: IR spectrum displays a strong band 1739 cm<sup>-1</sup>. Proton NMR: δ 1.4, 1.6, 2.3, 3.8. Carbon-13 NMR: 18, 31, 35, 53, 63, 170. DEPT-135 showed two positive signals and one negative signal. DEPT-90 showed no signals. The H-H cosy spectrum shows only one correlation (1.4-2.3) and The HETCOR spectrum showed the following correlations (1.4 -31), (2.3 - 31), (1.6-19), (3.8-53). The EI mass spectrum showed ions of  $m/z$  183, 147, 124. Both chlorine atoms are attached to the same carbon. Identify the molecule.

(15 x 2 = 30)