

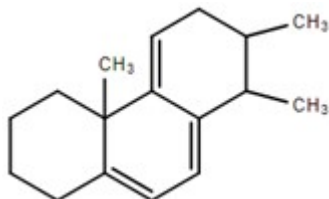
MSc DEGREE END SEMESTER EXAMINATION - OCT/NOV 2020: JAN 2021**SEMESTER 3 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY****COURSE : 16P3CHET12/16P3CPHT12 : SPECTROSCOPIC METHODS IN CHEMISTRY***(For Regular - 2019 Admission and Supplementary - 2016/2017/2018 Admissions)*

Time : Three Hours

Max. Marks: 75

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

1. Explain Multiple Cotton effect curves in the ORD spectrum of a molecule.
2. Compare the $\pi \rightarrow \pi^*$ transitions of aniline and aniline in HCl.
3. Use the Woodward rule to calculate λ_{\max} for the compound



4. Explain the consequence of Field effect in IR spectroscopy citing a suitable example.
5. How can you differentiate between acetone and acetophenone using IR spectroscopy?
6. Predict the carbon-13 NMR spectrum of N,N-dimethylacetamide
7. Deduce the structure of the amine with molar mass 101 whose ^1H NMR taken in CDCl_3 showed two peaks – d = 1.03 (t), d = 2.53 (q).
8. Deduce the structure of the organic compound with molecular formula $\text{C}_4\text{H}_8\text{O}_2$ which shows only a singlet at 3.71 ppm in its ^1H NMR spectrum taken in CDCl_3 .
9. Explain rule of thirteen in mass spectrometry.
10. For a halogen compound, the M^+ and $[\text{M}+2]^+$ ions are of equal intensity. What are your inferences?
11. An aromatic compound with molecular formula $\text{C}_{14}\text{H}_{14}$ 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. The proton NMR spectrum of a compound ($\text{C}_4\text{H}_7\text{N}$) shows signals at δ 1.1 (d) and 2.9 (m), and IR spectrum showed a strong band at 2250 cm^{-1} . Identify the structure.
13. An organic compound shows only two signals in both ^1H and ^{13}C NMR spectrum, one of the signals give a positive signal in DEPT-135. The chemical shift values in the proton NMR are 2.2 and 11.5. The EI mass spectrum shows ion of m/z 60. Identify the compound.

(2 x 10 = 20)**PART 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. List the following compounds in the order from highest wave number to the lowest for the C=O stretch absorption. Rationalize your answer.
Cyclohexanone, cyclopropanone, cyclobutanone and cyclopentanone.
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. An organic compound having molecular formula $C_4H_7O_2Br$, showed the following NMR data: Proton δ 2.9, 3.55 and 3.7(s). Carbon-13 δ 26, 38, 52, 171. Identify the molecule and sketch the hetero cosy spectrum.
19. Under electron impact ionization, loss of small molecules is sometimes observed. Draw the fragmentation modes leading to loss of: a) ethylene from 2-pentanone. b) water from 1-pentanol.
20. Propose a suitable structure of a molecule having a molecular ion peak at m/z 116 and another at 45 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.
21. 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.

(5 x 5 = 25)

PART C

Answer any 2 (15 marks each)

22. An organic compound (C_4H_8O) showed the following NMR data: Proton: δ 2.3(disappears on adding D_2O), 2.4, 3.6, 5.1, 5.8. Carbon: δ 37, 62, 117, 135. The DEPT-135 experiment showed one positive and three negative signals. Identify the molecule, explain the data, and sketch the possible Homo and hetero cosy spectra.
23. Discuss in detail on Mc Lafferty Rearrangements citing atleast five different systems.
24. An organic compound with molecular formula $C_{10}H_{12}O_3$ 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. 1H - 1H 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^{-1} . Identify the structure and assign the data.
25. An organic compound ($C_6H_{10}O_2$) showed the following spectral data. Proton NMR δ 1.3, 1.9, 4.2, 5.85, 6.95. ^{13}C NMR δ 17, 19, 60, 121, 142, 166. H-H cosy showed the following correlations (1.3-4.2), (1.9-5.85), (5.85-6.95), (1.9-6.95). H-C cosy showed the following correlations (1.3-17), (1.9-19), (4.2-60), (5.85-121), (6.95-142). The signal at δ 6.95 is a doublet of quartet, the $J=15.3$, $J=7.1$. DEPT-135 showed one negative signal and four positive signals. DEPT-90 shows two signals. The IR spectrum shows a strong bands at 2945 and 1705 cm^{-1} . The EI mass spectrum shows ions of m/z 114.0681, 69(100). Predict the structure and assign the data.

(15 x 2 = 30)