

**MSc DEGREE EXAMINATION - OCTOBER 2015**

SEMESTER: 3, SUBJECT: CHEMISTRY / PHARMACEUTICAL CHEMISTRY

COURSE: P3CHET12 / P3CPHT12 - SPECTROSCOPIC METHODS IN CHEMISTRY

Time: Three Hours

Max. Marks: 75

**SECTION A***(Answer any 10 questions. Each question carries 2 marks)*

- Identify the spin system present in difluoromethane (CH<sub>2</sub>F<sub>2</sub>).
- William C. Agosta has closely examined the nature of excited states of pyrimidines. Both  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  transitions are possible for these compounds. He showed that in aqueous medium, the lowest energy transition for pyrimidines is the  $\pi\text{-}\pi^*$  transition while in nonpolar solvents, lowest energy transition is the  $n\text{-}\pi^*$  transition. Based on your knowledge on solvent effects on *K* and *R* bands, account for this observation.

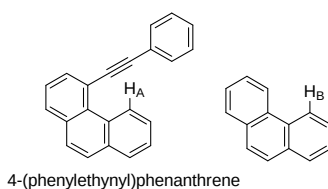


pyrimidine

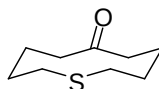
- Give number of signals observed in the DEPT-135 and DEPT-90 spectra of the following compounds.

Compound	Number of signals	
	DEPT-135	DEPT-90
CDCl <sub>3</sub>		
2,2-dimethylpropane		
pyrimidine		

- On the basis of  $^1\text{H}$  NMR spectral data, how will you differentiate between *ortho*-, *meta*- and *para*-dinitrobenzenes?
- Give the main advantage of ORD over CD.
- In the IR spectrum of aromatic acid halides, the carbonyl stretching appears as two distinct bands. Why?
- Consider the following molecules. Protons marked  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  appears at very different chemical shift positions. Which among these will appear more downfield shifted? Why?



- In the context of mass spectrometry, explain the relevance of metastable peaks.
- Explain why  $\text{CDCl}_3$  is preferred over  $\text{CHCl}_3$  as solvent for recording noise-decoupled  $^{13}\text{C}$  NMR spectra.
- In the UV-Visible absorption spectrum of the following compound, a peak of moderate intensity ( $\epsilon$  5000) is observed at 235 nm. Account for this observation.



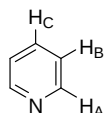
thiecan-6-one

- Magic acid, a 1:1 mixture of fluorosulfonic acid and antimony pentafluoride ( $\text{FSO}_3\text{H-SbF}_5$ ), is  $10^{15}$  stronger than sulfuric acid. It is so powerful that it can convert hydrocarbons to carbocations and hence the name magic acid! George A. Olah and co-workers used this acid to study the nature and stability of carbocations. They observed that the  $^1\text{H}$  NMR

spectrum of paraffin wax (mostly  $C_{31}H_{64}$ ) in magic acid exhibited only one signal (needless to mention, a singlet!). Account for this observation.

12. To ascertain  $^{13}C$ - $^1H$  correlations, HETCOR experiments are now replaced by HSQC and HMQC experiments. Why?

13. For pyridine,  $J_{AB}$  is smaller than  $J_{BC}$ . Account for this observation.



(10 × 2 = 20)

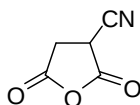
### SECTION B

(Answer any 5 questions. Each question carries 5 marks)

14. Explain structural factors affecting carbonyl stretching frequencies.

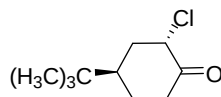
15. Explain factors affecting chemical shift position of protons attached to carbon.

16. Draw the HSQC ( $^{13}C$ - $^1H$  correlated) spectrum of 2,5-dioxotetrahydrofuran-3-carbonitrile (approximate only, estimation of exact chemical shift positions is not expected).

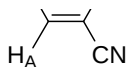


2,5-dioxotetrahydrofuran-3-carbonitrile

17. The following cyclohexanone derivative absorbs at 289 nm. Predict the approximate  $\epsilon$  value for this absorption. Draw the UV spectrum (200-400 nm region), CD spectrum (200-400 nm region) and ORD spectrum (200-400 nm region) for the enantiomer exhibiting positive Cotton effect.



18. In the  $^1\text{H}$  NMR spectrum of acrylonitrile, three signals are observed:  $\delta$  6.20 (dd,  $J_{\text{AM}} = 17.9$  Hz,  $J_{\text{AX}} = 0.9$  Hz, 1H), 6.07 (dd,  $J_{\text{MX}} = 11.8$  Hz,  $J_{\text{AX}} = 0.9$  Hz, 1H), 5.70 ( $J_{\text{AM}} = 17.9$  Hz,  $J_{\text{MX}} = 11.8$  Hz). Assign the signals to the three individual protons present in acrylonitrile. Justify your answer



19. Draw the pulse sequences for recording: a) normal pulsed FT  $^1\text{H}$  NMR spectrum, b) noise decoupled  $^{13}\text{C}$  NMR spectrum. Justify your answer.
20. In the mass spectrum of hexan-1-ol, molecular ion peak is absent. However, prominent peaks appear at  $m/z$  (relative intensity): 84 (10), 56 (100), 31 (45), 28 (25). Draw fragmentation patterns leading to these characteristic fragments.
21. Predict approximate values for specified spectral characteristics of the following isomers:

Structure	$\lambda_{\text{max}}$ (for <i>E</i> band, nm)	$\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ )	$\delta$ $\text{CH}_3$ (ppm)		Base peak ( $m/z$ )
			$^1\text{H}$	$^{13}\text{C}$	

(5 × 5 = 25)

### SECTION C

(Answer any 2 questions. Each question carries 15 marks)

22. Draw the splitting pattern for an AMX spin system exhibiting the following characteristics:  $\delta_A = 1$ ,  $\delta_M = 3$ ,  $\delta_X = 5$  ppm downfield of TMS,  $J_{AM} = 10$  Hz,  $J_{AX} = 8$  Hz,  $J_{MX} = 6$  Hz. Predict the position and relative intensity of individual lines (in Hz) when the spectrum is recorded on an instrument operating at a) 2.34 T, b) predict the pattern obtained and position and intensity of lines for proton A when the spectrum is recorded on an instrument operating at 9.36 T. Take integrated intensity for one proton = 4. On a 1 T magnetic field, protons resonate at 42.6 MHz.

23. Compare and contrast the UV-Vis, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectra of cis and trans isomers of 1,2-diphenylethene (stilbene).

24. Identify structure of compound **A** based on spectral data provided hereunder:

For compound **A**: UV (methanol) transparent above 210 nm; IR ( $\text{CCl}_4$ ) 2970, 1743, 1465, 1238  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz in  $\text{CDCl}_3$ ) four signals at  $\delta$  4.02 (t,  $J = 6$  Hz, 2H), 2.15 (s, 3H), 1.65 (sextet,  $J = 6$  Hz, 2H), 0.95 (t,  $J = 6$  Hz, 3H),  $^{13}\text{C}$  NMR (75 MHz in  $\text{CDCl}_3$ ) five signals at  $\delta$  171.1 (disappears in DEPT-135), 66.1 (negative in DEPT-135), 22.1 (negative in DEPT-135), 20.9 (positive in DEPT-135, disappears in DEPT-90), 10.4 (positive in DEPT-135, disappears in DEPT-90); EIMS  $m/z$  (relative intensity) 102 ( $M^+$ , absent), 73 (14), 61 (27), 43 (100), 42 (48), and other peaks. Formula mass: 102.0681 corresponding to  $\text{C}_5\text{H}_{10}\text{O}_2$ . Fragmentation mode leading to base peak should be clearly identified.

25. Identify structure of compound **B** based on spectral data provided hereunder:

For compound **B**: UV (methanol)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 369 (300), 322 (125) nm; IR ( $\text{CCl}_4$ ) 3083, 2959, 1596, 1345, 849  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz in  $\text{CDCl}_3$ ) three signals at  $\delta$  8.10 (d,  $J = 7.5$  Hz, 2H), 7.31 (d,  $J = 7.5$  Hz, 2H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz in  $\text{CDCl}_3$ ) five signals at  $\delta$  146.3 (disappears in DEPT-135), 146.0 (disappears in DEPT-135), 129.9 (positive in DEPT-135), 123.4

(positive in DEPT-135), 21.6 (positive in DEPT-135, disappears in DEPT-90); EIMS  $m/z$  (relative intensity) 137 ( $M^+$ , 75), 121 (2), 107 (30), 91 (100), 65 (58) and other peaks (meta stable peaks are observed at  $m/z$  83.57 and 46.43).

(2 × 15 = 30)

\*\*\*\*\*