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Total Pages : 8

**1785/M**

**M-35/2051**

**APPLICATIONS OF ORGANIC MOLECULAR  
SPECTROSCOPY**

Paper-421

Semester-IV

Time allowed : 3 Hours] [Maximum Marks : 55

**Note:** The candidates are required to attempt two questions each from Section A carrying 8 marks and Section B carrying 8½ marks each and the entire Section C consisting of 11 questions carrying 2 marks each.

**SECTION-A**

1. (a) What are auxochromes and chromophores? Explain how an auxochrome exerts a bathochromic shift on a chromophore such as C=C. 4

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- (b) Explain why the UV spectra of homoannular dienes show an absorption maxima at longer wavelength with lower extinction coefficient as compared to heteroannular dienes which show absorption maximum at lower wavelength but with higher extinction coefficient. 4

2. (a) The dehydration of 1,2-dimethylcyclohexanol (*cis*- or *trans*) can give three alkenes. Give the structure of these alkenes and explain how IR can differentiate among these. 4

- (b) With proper reasoning distinguish between the following pairs of compounds by IR spectroscopy.

(i) *o*- and *p*-hydroxyacetophenone. 2

(ii) C<sub>6</sub>H<sub>5</sub>COOCH<sub>3</sub> and CH<sub>3</sub>COOC<sub>6</sub>H<sub>5</sub>. 2

3. (a) An unknown substance has a molecular ion peak at  $m/z = 107$ , with a relative intensity of 100. The relative intensity of the M+1

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2

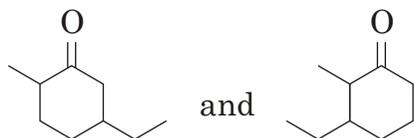
peak is 8.00 and relative intensity of M+2 peak is 0.30. What is the molecular formula of the unknown compound? 6

(b) Explain McLafferty rearrangement and its use in structure determination. 3

(c) Comment upon the salient features in the mass spectra of compounds containing two chlorine atoms. 2

4. (a) What are metastable ions? Explain their usefulness in confirming a proposed fragmentation pattern. The mass spectrum of 1-propanol shows a metastable peak at  $m/z$  29.4. What does it convey about the fragmentation mode? 4

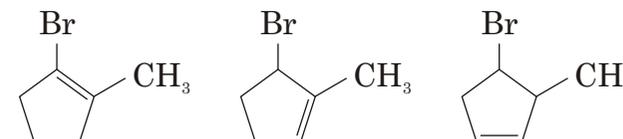
(b) How could be the following pairs of isomers be differentiated by their respective mass spectra? 4



## SECTION-B

5. (a) What do you mean by anisotropy? How does it effect the chemical shift of protons in different molecules? Explain why acetylene protons absorb at high field while benzene protons absorb at a low field? 4

(b) Discuss how  $^1\text{H-NMR}$  spectra could be used to distinguish between the following isomers. 4½



6. (a) With one example in each case, explain the use of the following in simplifying  $\text{H}^1\text{-NMR}$  spectra :

(i) Double resonance and 2

(ii) Chemical shift reagents. 2

(b) Discuss briefly the factors governing geminal and vicinal coupling constants.

Also comment upon virtual and long range coupling. 4½

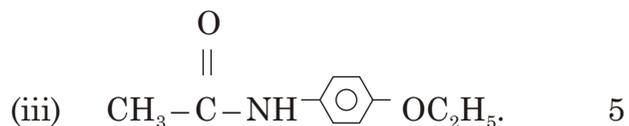
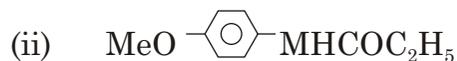
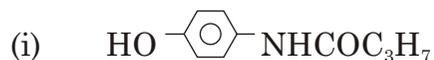
7. (a) Use  $^{13}\text{C}$ -NMR to distinguish between the two diastereoisomers of 1,3,5-trimethylcyclohexane. 3½

(b) How COSY and HETCOR spectra have been useful at ascertaining the structure of geraniol? 5

8. (a) The off resonance  $^{13}\text{C}$ -NMR spectrum of a compound gave the following data :

15(*q*), 24(*q*), 64(*t*), 115(*d*), 123(*d*), 132(*s*), 157(*s*) and 171(*s*).

Examine which of the following compounds shall stand for the above data :



(b) The peak at 171(*s*) is of very small intensity. Why? ½

(c) Product the  $^1\text{H}$ -NMR spectrum of the above compound in terms of number and types of different protons their approximate chemical shifts and multiplicities. 3

### SECTION-C

9. (i) Explain the following variation in  $\nu_{\text{max}}$  (in nm):

MeCl(173), MeBr(204), MeI(258).

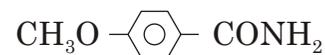
(ii) In  $^1\text{H}$ -NMR, spectrum of 2-cyclohexenone,  $\text{C}_3\text{-H}$  appears at a lower field than  $\text{C}_2\text{-H}$  whereas in dihydropyran, it is  $\text{C}_2\text{-H}$  which appears at a lower field than  $\text{C}_3\text{-H}$ . Explain why?

(iii) What differences are expected in the  $^1\text{H}$ -NMR spectrum of cyclohexane recorded

at ambient temperature and at 173K?  
Explain giving plausible reasons.

(iv) Explain why *cis* stilbene shows  $\lambda_{\max}$  at 278nm with  $E_{\max}$  of 9350 while its *trans* isomer shows  $\lambda_{\max}$  at 294nm with  $E_{\max}$  of 24,000.

(v) State giving reasons how will you distinguish the following pair of compounds by IR spectroscopy?



(vi) Taking a suitable example, explain the significance of DEPT-135 spectrum.

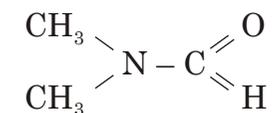
(vii) Chloroform proton absorbs at 87.27 but in benzene, this absorption shifts upfield to 86.27. Explain why?

(viii) Highlight the importance of 'Nitrogen Rule' in mass spectrometry.

(ix) The mass spectrum of nitrobenzene shows fragment ions at  $m/z$  93, 77, 65 and 51. Write structure for these fragment ion.

(x) Using  $^{13}\text{C}$ -NMR spectroscopy how will you distinguish between carbonyl isomer of  $\text{C}_4\text{H}_8\text{O}$ ?

(xi) Discuss briefly the principle of the technique used to determine which methyl group in the following compound is *syn* to the aldehyde hydrogen.



11×2 = 22