

LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FOURTH SEMESTER – APRIL 2010

CH 4809 - APPLICATIONS OF SPECTROSCOPY

Date & Time: 17/04/2010 / 9:00 - 12:00 Dept. No.

Max. : 100 Marks

PART A

Answer all the questions

10 x 2 = 20

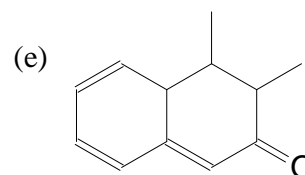
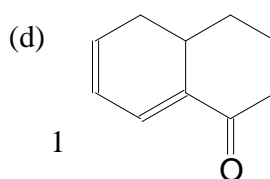
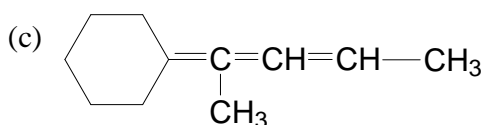
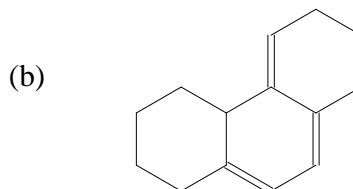
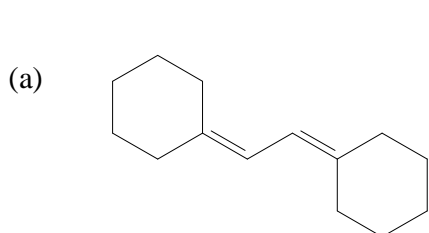
1. What is the origin of CT bands?
2. Give an example of Retro Diels Alder reaction.
3. Why Catechol shows two –OH stretching frequencies at 3600 and 3570 cm^{-1} ?
4. Why p-amino acetophenone shows IR value at 1677 cm^{-1} whereas p-methoxy acetophenone shows at 1684 cm^{-1} ?
5. What is the reason for the variation in λ_{max} of the following compounds?
 $\text{CH}_3\text{Cl} = 173 \text{ nm}$, $\text{CH}_3\text{Br} = 204 \text{ nm}$ and $\text{CH}_3\text{I} = 258 \text{ nm}$.
6. What is isochronous? Give an example.
7. Which of the following has the higher geminal coupling? Cyclopentane or cyclohexane.
Account for your choice.
8. What is pure NQR?
9. Calculate the g value for Zn^{2+} complex.
10. How will you obtain Mossbauer spectrum of a liquid sample?

PART B

Answer any eight questions

8 x 5 = 40

11. Calculate λ_{max} for the following



12. a) Why there is a variation in λ_{\max} of the following compounds
acetone (1715cm^{-1}), chloroacetone (1725cm^{-1}) and dichloroacetone (1740cm^{-1})
b) An organic compound answering Libermann's test shows the following IR spectra pattern
3330, 3040, 2000-1650, 1580, 1360, 1200 and 800cm^{-1} . Determine the compound and explain.
- 13 Identify the compound with molecular mass 120 which absorbs in UV spectrum at 268 nm. In IR spectrum medium absorption bands are formed at 3067 – 2907, 1608 and 1473 cm^{-1} . The NMR spectrum shows absorption at 3.21 τ singlet and 7.74 τ singlet.
14. Assign a structure to the compound $\text{C}_{10}\text{H}_{12}\text{O}$ whose mass spectrum shows m/e values of 15, 43, 51, 91, 105 and 148. It answers iodoform test and burns with sooty flame. Which other spectral technique will confirm the structure.
15. Distinguish primary, secondary and tertiary alcohols by mass spectroscopy.
16. Explain the mass spectral pattern of 3-heptanone.
17. Discuss the spin-spin splitting of 3-hydroxy glutaric acid.
18. Distinguish between A_2 and AA^1 types of protons with examples.
19. How will you account for the g values obtained in free radicals and ionic crystals?
20. Why are EPR spectra not presented as an absorption curve?
21. How will you compare the NQR of K_2PtCl_6 with that of K_2PtI_6 ?
22. What is quadrupole splitting? Mention its significance.

PART C

Answer any four questions

4 x 10 = 40

23. An organic compound with the molecular weight 108 is not acidic in nature but can be easily oxidized to a crystalline compound. It shows the following spectral data
UV : λ_{\max} 255 m μ ϵ_{\max} 202
IR: 3402 (s, b), 3065 (w), 2288 (m), 1499 (w), 1455 (m)
NMR: 2.74 τ (singlet), 5.4 τ (singlet), 6.10 τ (singlet)
Mass: m/e values at 108, 106, 77, 51 and 39. Deduce the structure of the compound.
24. An organic compound with the molecular weight 130 gave a negative iodoform test. It absorbs at 292 m μ (ϵ_{\max} 10) in the UV spectrum. It shows IR values at 3042 (m), 2941 (w), 2862 (w), 1722 (s), 1575 (m) and 1462 cm^{-1} and exhibited NMR signals at singlet 2.73 τ , doublet 7.2 τ and triplet 0.22 τ . Determine the structure of the compound.

25. a) An organic compound showing positive test to Lucas test shows the following spectral pattern

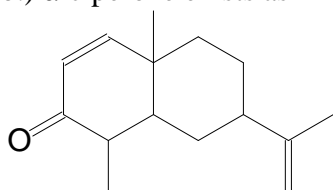
NMR: singlet 7.7 τ , triplet 6.4 τ

IR: 3500, 2960 and 2870 cm^{-1}

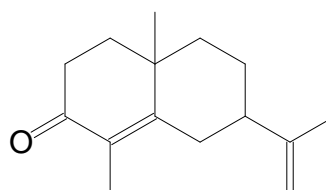
Mass: m/e values at 60, 43, 31 and 29. Identify the compound and explain.

b.) α -ciperone exists as

(i)



(ii)



Using Woodward's rules, decide whether structure (i) or (ii) is consistent with the observed value of 252 nm. (6+4)

26. a) How are correlations carried out in COSY and HECTOR?

b) Mention the importance of learning phenomenon (7+3)

27. a) Distinguish between enantiotopic and diastereotopic protons with examples.

b) Explain the origin of quadrupole moment and electric field gradient (5+5)

28. a) Explain the EPR of triplet state naphthalene biradical.

b) What is isomer shift? Mention the factors which give rise to isomer shift.

(4+6)
