Chemistry Department
Faculty of Science
Benha University

Organic spectroscopy
317Chem
3rd year students

2014-2015
Time: 2 hrs

Answer the following question: (24 Marks)

1. How many sets of equivalent protons are there for $CH_2Cl\text{-}CH_2\text{-}CH_2Cl$?
   a. 1 **b. 2** c. 3 d. 6

2. Which of the following is the most likely fragment ion formed at 57?
   a. $CH_3\ CH_2CH_2CH_2^+$ b. $CH_3\ CH_2^+$ c. $CH_3\ CH_2CH_2^+$ d. $CH_2{=}CH^+$

3. Which compound would be expected to show intense IR absorption at 2250 cm-1?
   a. $(CH_3)_2CHCN$ b. $CH_3CH_2CO_2H$ c. CH_3CONH_2 d. $(CH_3)_2CHOH$

4. What kind of compound has a sharp IR absorption band in the region of 1710 cm-1 and a broad band at 3300 cm^{-1}?
   a. Ethanol **b. Acetic Acid** c. Acetone d. Diethyl ether

5. What is the structure for a compound, $C_4H_8Br_2$, which has the following proton NMR spectrum? Doublet δ 1.7 (6 H) and Quartet δ 4.4 (2 H)
   a. 1,1-dibromobutane b. 1,2-dibromobutane
   c. 1,3-dibromobutane **d. 2,3-dibromobutane**

6. How many different type of hydrogens in 2-chloropropane
   a. 2 b. 3 c. 1 d. 4

7. Which compound gives M and M^{+2} peaks in the mass spectrum ؟
   a. $C_6H_{11}Br$ b. $C_4H_{11}N$ c. C_4H_{10} d. C_3H_7O

8. How many IR absorptions bands do an amino group, $-NH_2$, give between 3000 cm^{-1} and 3500 cm^{-1}?
   a.4 b. 3 c. 1 **d. 2**

9. How many signals would you expect to find in the ^1H NMR spectrum of $CH_3OCH_2CH_2OCH_3$?
   a. 2 b. 3 c. 1 d. 4

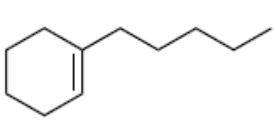
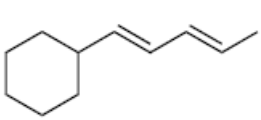
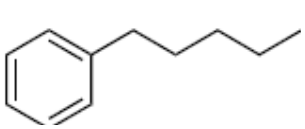
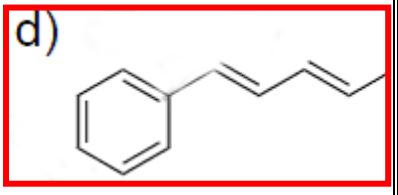
10. Rank the indicated protons in the following molecule in order of increasingly downfield chemical shift?

$$CH_3COCH_2CH_3$$
$$H_a \quad H_b \quad H_c$$

   a. $H_c < H_b < H_a$ **b. $H_c < H_a < H_b$** c. $H_a < H_b < H_c$ d. $H_b < H_a < H_c$

11. When a high energy electron impacts molecule M in the ionization chamber, what type of species is initially produced?
   a. cation b. radical **c. radical cation** d. radical anion

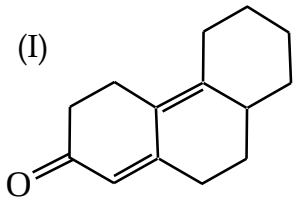
12. Which one of the following compounds is expected to have the longest wavelength absorbance (λmax)?

a) 
b) 
c) 
d) 

Answer two questions only: (**12** Marks)

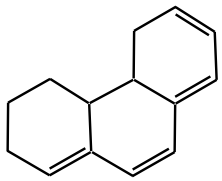
2- ***a)*** Calculate the λ max for each of the following:

(I)



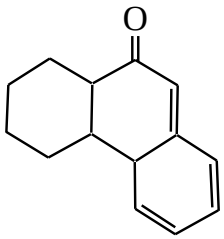
α,β-unsaturate ketones	215
β-Substituent	12
γ-Substitutent	18
δ- Substitutent	2 x 18
Exocyclic double bond	3 x 5
Extending double bond	30
λmax (calc.)	309

(II)



Homo annular diene	253 nm
Ring residue	4 x 5 nm
Exocyclic double bond	2 x 5 nm
Extending double bond	2 x 30 nm
	343 nm

(III)



α,β-unsaturate ketones	215 nm
β-Substituent	12 nm
δ –Substitutent or higher	18 nm
Exocyclic double bond	5 nm
Extending double bond	2 x 30 nm
homo anuular	39 nm
λmax (calc.)	349 nm

b) How can you calculate the stretching vibrational frequency by? Illustrate the effect of its parameters on vibration frequency**.**

Hook's low:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3 \times 10\sqrt{\frac{k}{\mu}}$$

Where: **υ\ = wavenumber of the abs. peak (cm-1)**
c = speed of light (3 x 10^{10} cm/s)
***k* = force constant**
***m* =reduced mass of the atoms($m_1 \times m_2$) / (m_1+m_2)**

The frequency is affected by:

- **The strength of the bond**

ν' will increase with increasing bond strength (bond order)

- **The masses of the atoms in the bond.**

ν' will increase with decreasing mass

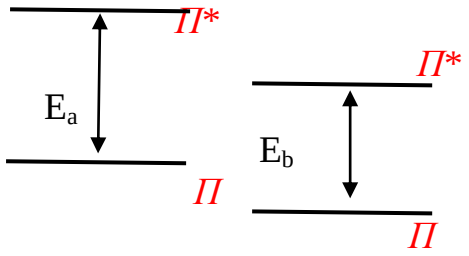
3–a) How can you distinguish between the following pairs of compounds (using spectroscopic methods)? (**8** Marks)

1. Benzamide & acetanilide.
   By using IR spectra it will show υ' at 3050 cm^{-1} for =CH in benzamide or by using ^{1}HNMR it will show singlet signal at δ=1 for CH3 in actamide or at δ=7 multiplet band for benzene ring in benzamide.

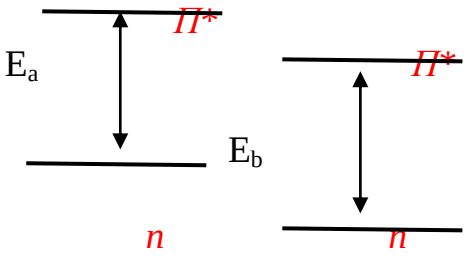
2. Anisol & methy-benzyl ether.
   By using ^{1}HNMR it will show 2 sets of protons for anisol and three sets of protons for methy-benzyl ether.

3. Ethyl acetate and methyl ethyl ketone.
   By using IR spectra it will show υ' at 1730cm^{-1} for C=O in ester and υ' at 1050 cm^{-1} for C-O for (ethyl acetate).

b) Explain the effect of polar solvents on *n* → *Π** and *Π* → *Π** transition. (**4** Marks)



In polar solvent

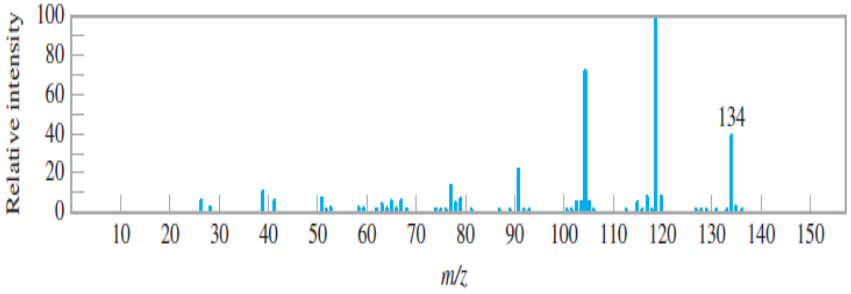


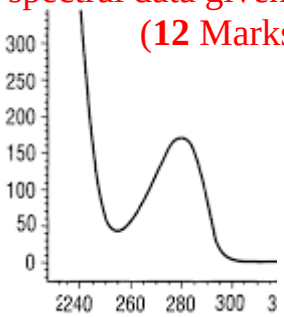
In polar solvent

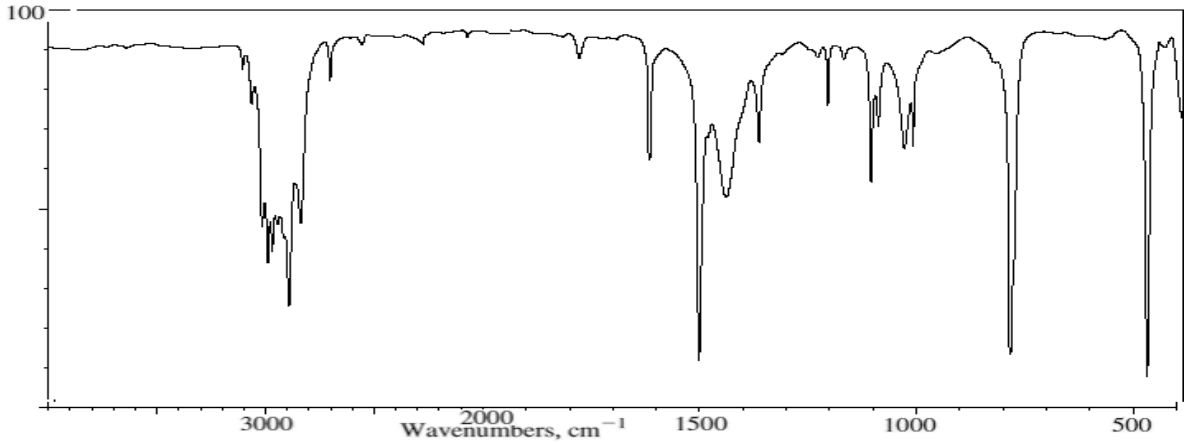
The *Π** orbitals are more stabilized by polar solvents by forming hydrogen bond so the bond shifted to longer wave length ($E_a > E_b$) Bathochromic shift.

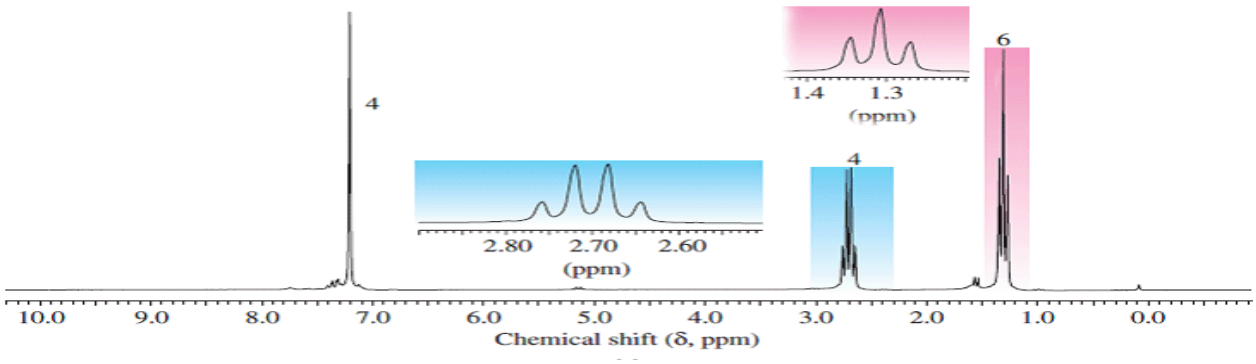
The *n* orbitals for unshared electrons are more stabilized by polar solvents the bond shifted to shorter wave length ($E_b > E_a$) Hypsochromic shift.

4- Suggest a structure of $C_{10}H_{14}$, which is consistent with all the spectral data given below: (**12** Marks)









Form UV spectra it show there are conjugated system.

H.I = 2 X 10 + 2 – 14 /2 = 4 it means there are benzene ring.

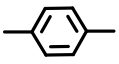
From IR spectra it shows that:

υ' at 3010 cm^{-1} for =CH

υ' at 2950 cm^{-1} for -CH

υ' at 1600cm^{-1} for C=C

From ^{1}HNMR spectra it shows that:

Type	a	b	c
δ	1.1	2.8	7.1
Multiplicity	t	q	s
Ratio	6	4	4
No. of protons	6	4	4
	2-CH_3	2-CH_2	

The structure is: