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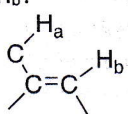
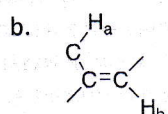
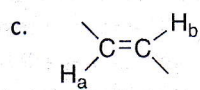
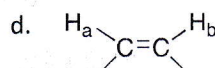
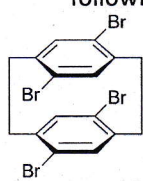
School: School of Science
Program/s: MSc Chemistry (Organic)
Year: 2nd **Semester:** 3rd
Examination: End Semester Examination
Examination year: December - 2021

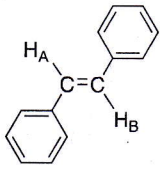
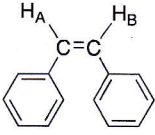
Course Code: CH221 **Course Name:** Organic Spectroscopy
Date: 01/12/2021
Time: 08:30 am to 10:30 am

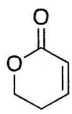
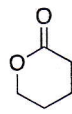
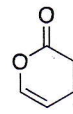
Total Marks: 40
Total Pages: 4

Instructions:

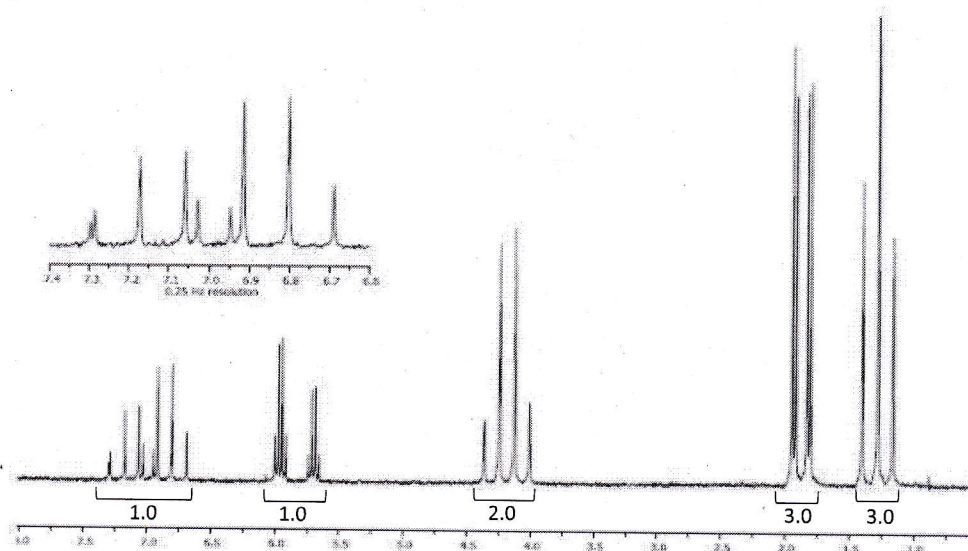
- Write each answer on a new page.
- Use of a calculator is permitted/~~not permitted~~.
- * COs=Course Outcome mapping. # BTL=Bloom's Taxonomy Level mapping

Q. No.	Details	Marks	COs*	BTL#
Q.1	<p>Choose the correct answer (s) from the followings.</p> <p>1. Which one of the following statements is false for IR spectroscopy</p> <ol style="list-style-type: none"> Conjugation decreases the carbonyl group frequency Higher the frequency if more strained the acyclic ring containing C=O Electron releasing substituent's decreases the frequency of C=O band Electron withdrawing substituent's decreases the frequency of C=O band <p>2. $^3J_{HH}$ coupling constants may have a value of</p> <ol style="list-style-type: none"> 140 Hz 35 Hz 8 Hz 70 Hz <p>3. Which of the following molecules has the largest $^3J_{HH}$ coupling constant between H_a and H_b?</p> <p>a.  b.  c.  d. </p> <p>4. Number of signals present in the proton decoupled ^{13}C NMR spectrum of the following compound is</p>  <ol style="list-style-type: none"> Four Six Eight Ten 	8	CO1 CO2 CO3 CO4 CO5 CO6	BT1 BT2 BT3 BT4

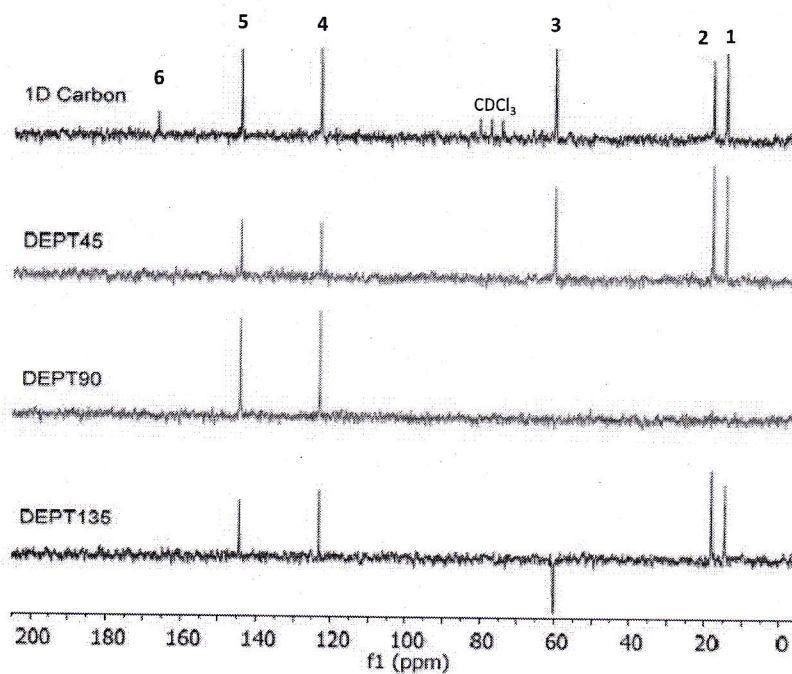
	<p>5. Which of the following statements is wrong?</p> <ol style="list-style-type: none"> UV absorption is attributable to electronic transitions. UV spectra provide information about valence electrons. IR absorption is attributable to transitions between rotational energy levels of whole molecules. NMR spectrometers use radiofrequency electromagnetic radiation. <p>6. Which of the following quantities is not changed at a different magnetic field strength?</p> <ol style="list-style-type: none"> Chemical shift (in hertz) Nuclear spin population in an energy state J coupling constant Energy difference between two energy states of nuclei with non-zero spin quantum number <p>7. Which of the following statements regarding electron-impact mass spectrometry is true?</p> <ol style="list-style-type: none"> Samples need isotopic labels. The base peak is formed by loss of one electron from each vaporized molecule by an electron beam. Compounds must have a functional group to show a mass spectrum. A meaningful mass spectrum can sometimes be obtained on a very small sample of an impure compound. <p>8. When the λ_{\max} of a compound shift to a shorter wavelength on certain treatment, the compound is said to have undergone</p> <ol style="list-style-type: none"> Hypochromic effect Hypsochromic effect (Blue shift) Bathochromic Shift (Red shift) Hyperchromic Shift 			
Q.2	<p>Answer the following questions. (Any Four)</p> <ol style="list-style-type: none"> Electrospray mass spectrum of heptan-2-one (mass 114) shows molecular ion peak at 137. Why? Mass spectrum of methyl bromide shows pair of peaks at $m/z=79$ and $m/z=81$. Show the fragment ion corresponds to $m/z=79$ and $m/z=81$. Mass spectrum of 2-methylpentane shows fragment ions at $m/z=71$, 57 and 43. Show the fragmentation of 2-methylpentane corresponds to fragment ions at $m/z=71$, 57 and 43. Draw the structural formula that are consistent with the following observations. A ketone $C_8H_{14}O$ shows a UV maximum at 248 nm. Identify the geometric isomers of stilbene from their λ_{\max} values of 294 and 274 nm. Justify your answer. <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 20px;"> <div style="text-align: center;">  <p><i>cis</i>-Stilbene</p> </div> <div style="text-align: center;">  <p><i>trans</i>-Stilbene</p> </div> </div>	6	C01 C02 C03 C04 C05	BT1 BT2 BT3 BT4

<p>Q.3</p>	<p>Do as directed. (Any Four)</p> <p>(i) The mass spectrum of cyclopentanone shows peak at m/z 84, 55, 41 and 28. Show the mass fragmentation of cyclopentanone corresponds to above mentioned m/z values.</p> <p>(ii) The carbonyl stretching absorptions for the following lactones are 1760 cm^{-1}, 1745 cm^{-1} and 1720 cm^{-1}. Match the absorptions with the appropriate structure and justify your choice.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>(I)</p> </div> <div style="text-align: center;">  <p>(II)</p> </div> <div style="text-align: center;">  <p>(III)</p> </div> </div> <p>(iii) The mass spectrum of Anisole (methyl phenyl ether) shows peaks at m/z 93, 65, 78 and 77. Show the mass fragmentation of Anisole corresponds to above mentioned m/z values.</p> <p>(iv) With respect to absorption frequency of internal double bond (C=C stretching vibration) in cyclic compounds, the absorption frequency decreases as the internal angle decreases, until it reaches a minimum 90° in cyclobutene. The frequency increases again for cyclopropane when the angle drops to 60°. Justify.</p> <p>(v) The mass spectrum of <i>n</i>-butylbenzene shows peaks at m/z 92, 91, and 65. Show the mass fragmentation of <i>n</i>-butylbenzene corresponds to above mentioned m/z values.</p>	<p>10</p>	<p>C01 C02 C03 C04 C05 C06</p>	<p>BT1 BT2 BT3 BT4 BT5</p>																		
<p>Q.4</p>	<p>Do as directed. (Any Four)</p> <p>Note: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, dd = doublet of doublet</p> <p>(i) An organic compound, $\text{C}_6\text{H}_8\text{O}$ shows the following spectral data:</p> <ol style="list-style-type: none"> UV: λ_{max} 225 nm ($\epsilon = 10,000$), 318 nm ($\epsilon = 40$) MS: Molecular ion at $m/z = 96$, base peak at $m/z = 68$. IR: A strong band at 1690 cm^{-1} $^1\text{H NMR}$ (δ ppm): 1.54 (m, 2H), 1.94 (q, 2H), 3.16 (t, 2H) 5.9 (d, 1H), 7.0 (m, 1H) <p>Propose the structure for this compound with explanation (explanation necessary).</p> <p>(ii) Following are the NMR data of three isomeric compound with the formula $\text{C}_7\text{H}_{14}\text{O}_2$. Provide structure for each.</p> <p>Compound A: $^1\text{H NMR}$ (δ ppm): 0.9 (d, 6H), 1.15 (t, 3H), 1.95 (m, 1H), 2.35 (q, 2H), 3.85 (d, 2H)</p> <p>Compound B: $^1\text{H NMR}$ (δ ppm): 1.1 (t, 3H), 1.45 (s, 9H), 2.2 (q, 2H)</p> <p>Compound C: $^1\text{H NMR}$ (δ ppm): 0.9 (t, 3H), 1.15 (t, 3H), 1.3-1.5 (m, 2H), 1.55-1.75 (m, 2H), 2.3 (q, 2H), 4.05 (t, 2H)</p> <p>(iii) The proton NMR data for a compound with formula $\text{C}_9\text{H}_8\text{O}$ is given below. The infrared spectrum has a strong band at 1746 cm^{-1}. The DEPT-135 and DEPT-90 spectral results are tabulated. Draw the structure of this compound and justify.</p> <p>$^1\text{H NMR}$ (δ ppm): 3.5 (s, 4H), 7.25 (bs, 4H)</p> <table style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Normal Carbon (ppm)</th> <th>DEPT-135</th> <th>DEPT-90</th> </tr> </thead> <tbody> <tr> <td>44</td> <td>Negative</td> <td>No peak</td> </tr> <tr> <td>125</td> <td>Positive</td> <td>Positive</td> </tr> <tr> <td>127</td> <td>Positive</td> <td>Positive</td> </tr> <tr> <td>138</td> <td>No peak</td> <td>No peak</td> </tr> <tr> <td>215</td> <td>No peak</td> <td>No peak</td> </tr> </tbody> </table>	Normal Carbon (ppm)	DEPT-135	DEPT-90	44	Negative	No peak	125	Positive	Positive	127	Positive	Positive	138	No peak	No peak	215	No peak	No peak	<p>16</p>	<p>C01 C02 C03 C04 C05 C06</p>	<p>BT1 BT2 BT3 BT4 BT5</p>
Normal Carbon (ppm)	DEPT-135	DEPT-90																				
44	Negative	No peak																				
125	Positive	Positive																				
127	Positive	Positive																				
138	No peak	No peak																				
215	No peak	No peak																				

- (iv) The proton NMR spectrum and ^{13}C NMR spectrum for a compound with formula $\text{C}_6\text{H}_{10}\text{O}_2$ is given below. Draw the structure of this compound and justify.
proton NMR



^{13}C NMR data



- (v) Typical bond dissociation energies in organic molecules are around 400 kJ mol^{-1} . Calculate (a) the frequency and (b) the wavelength of the electromagnetic radiation which corresponds to this dissociation energy. In which part of the spectrum does this radiation lie?

*****End of Question Paper*****