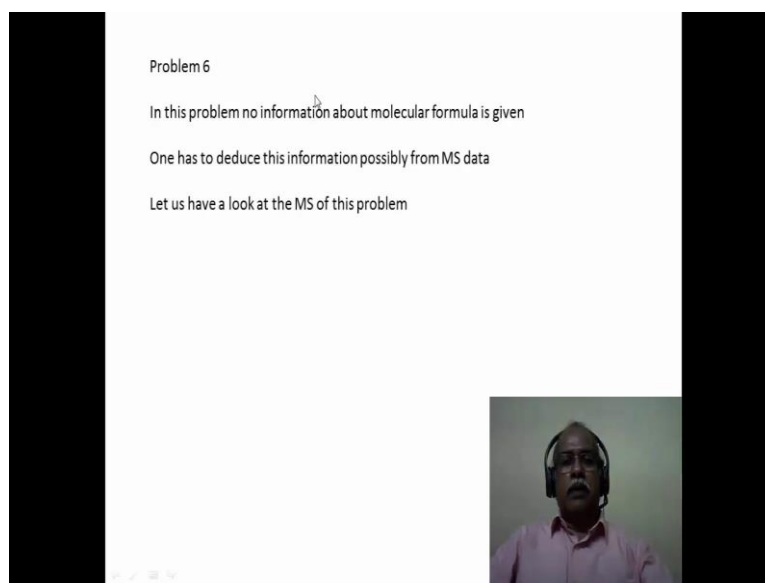


**Application of Spectroscopic Methods
in Molecular Structure Determination**
Prof. S. Sankararaman
Department of Chemistry
Indian Institute of Technology, Madras

Lecture - 31
**Structure Solving based on IR, MS, ^1H
and ^{13}C NMR Spectroscopic Data**
Problem solving session III

Hello, we will move on to problem solving session 3. This will be module 31 of the course on Application of Spectroscopy Methods in Molecular Structure Determination. We will continue use the data from infrared spectroscopy, mass spectrometry, proton and carbon-13 NMR spectroscopy for solving simple organic structures.

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Problem 6

In this problem no information about molecular formula is given

One has to deduce this information possibly from MS data

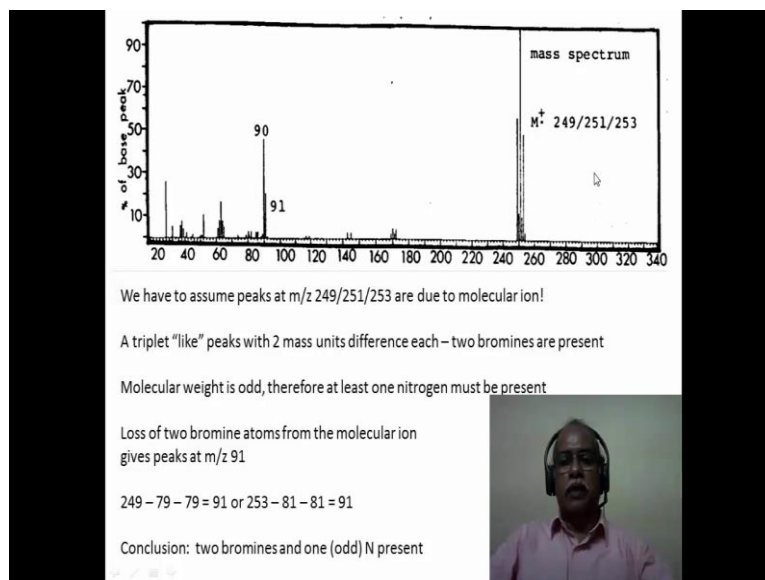
Let us have a look at the MS of this problem

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This is problem number 6. The first 5 problems were in module 29 and 30. So, we start with problem number 6 in this particular module. Surprisingly, the molecular formula information is not given in this problem. In other words, we have to deduce this information possibly from the mass spectroscopy data. So, this is an example of a simple problem where the molecule is the fairly simple molecule. Molecular formula is not known, we are going to deduce even the molecular formula from the spectroscopic data

that we have. So, instead of starting with the IR spectrum which we normally do for problem solving, let us start with the mass spectrum in this particular problem.

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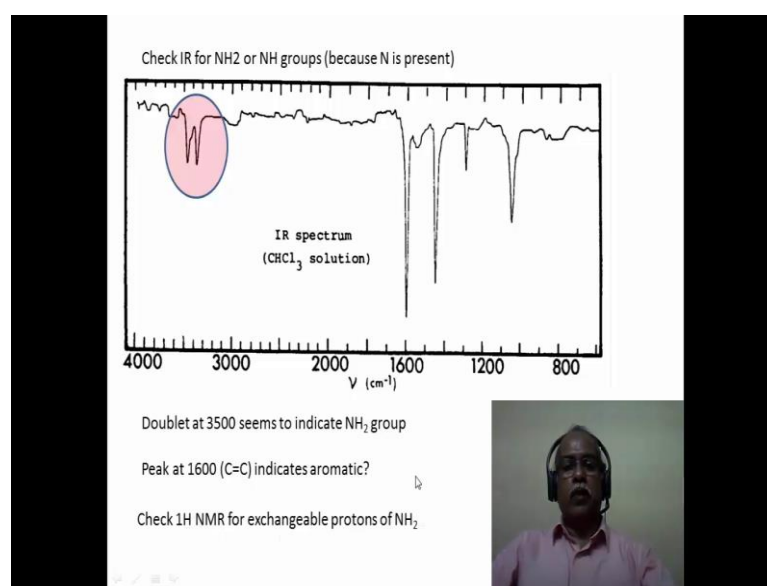
This is a mass spectrum of this compound. The one that you need to immediately identify this particular pattern, which is the triplet pattern with the two mass unit differences of 249 to 51 and 253 and this should immediately tell you that there are two bromine atoms present in this molecule. Only presence of two bromine atoms will give you 1 is to 2 is to 1 triplet of this type in the molecular ion region.

First of all, we have to assume that this is a molecular ion of this compound because that information is also not given although, it says M^+ here, we cannot be very sure and less the M^+ is mentioned here we cannot be sure the highest ion weight peak is the molecular ion peak. Triplet like peak with 2 mass unit difference definitely confirms the presence of two bromines. In addition to that, if you look at the molecular weight they are odd mass 249, 251 and 253. So, the odd molecular weight seems to tell that odd number of nitrogen must be present in this compound, and in addition to that you also look at the molecular fragmentation.

The molecule fragments by losing two bromines to give one, sequentially one after the

other it loses two bromines to give 91 as the molecular fragment peak here. In other words 249 minus 79 minus 79 which is a loss of two bromine units correspond to 91. In other words 253 also can be taken, if we take 253, it will be loss of 81 isotope bromine another 81 isotope bromine corresponding to 91. So, the 91 peak seems to be indicating that the fragmentation is by loss of the bromine. So, we conclude from the mass spectrum that there are two bromine atoms and one or odd number of nitrogen atom present in this particular system.

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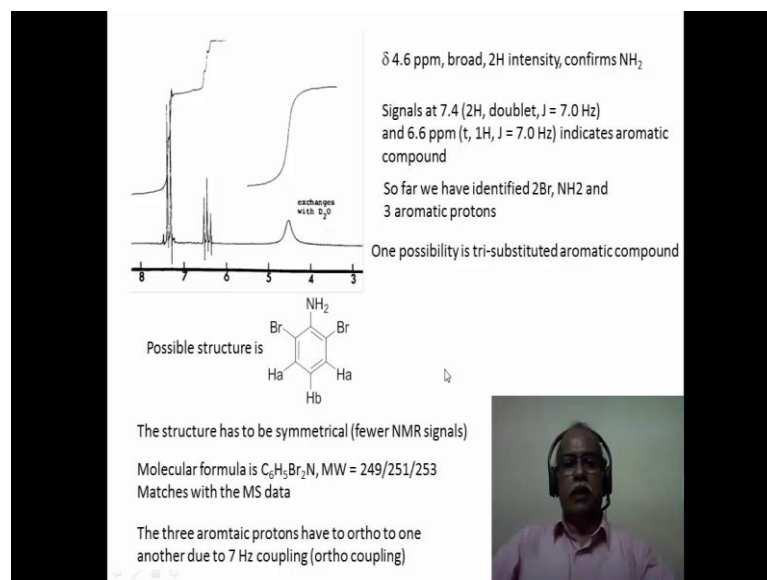


Now, having start about the presence of nitrogen from the mass spectrum, one has to look at the infrared spectrum carefully to rule out or confirm the presence of the NH stretching frequency to check for primary or secondary amines that may be present in this particular system. Straight away you see the NH stretching frequency; there is a nice doublet that is seen here which confirms the presence of an NH₂ functional group in this particular case. Also, there is a fairly intense peak around 1600 inverse centimeter which correspond to the carbon carbon unsaturation stretching frequency, carbon double bond carbon stretching frequency, possibly, because of the aromatic C double bond C; one can have this kind of a stretching frequency in this particular spectrum.

So, now you have to check for the presence of NH₂ in the proton NMR. The proton

NMR characteristic peak corresponding to NH₂ will be a D₂O exchangeable peak.

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This is a proton NMR spectrum of this compound. The region between 3 and 8 alone is shown because all the signals are seen only in this particular region. We can straight away see a broad signal around 4.6 or so and it says very clearly that it is a D₂O exchangeable proton. So, this 2 hydrogen intensity integration would correspond to an NH₂ kind of a group. So, the NH₂ is confirmed by the presence of this broad peak which is the D₂O exchangeable group in the proton NMR spectrum or so. The signal at 7.4 is looking like a doublet and that is a same integration as this integration NH₂ integration, so this would correspond to 2 hydrogen intensity. So, the number of hydrogens that we have 2 hydrogen here, 2 hydrogens here; 4 hydrogen and then 1 hydrogen in this particular region which will be half of this integration, so there are 5 hydrogens present in this molecule, of which 3 of them are aromatic hydrogens and 2 of them of NH₂ hydrogens.

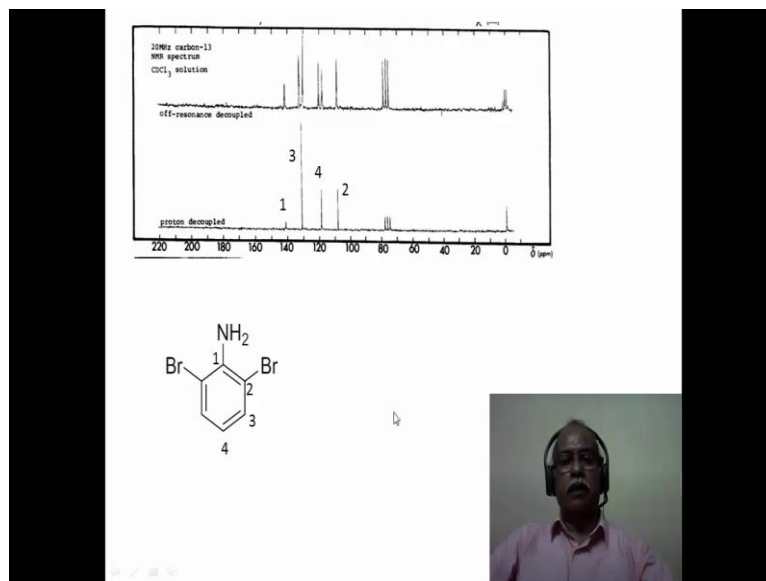
So far we have identified 2 bromines, NH₂ hydrogen and 3 aromatic hydrogens. So, totally 3 aromatic hydrogens means this is probably a tri-substituted derivative. We already have 3 substituents, 2 bromines and the amino group would be at a substituent on the aromatic ring, so the possible structure is the 2,6-Dibromoaniline is the structure. Why did we decide on 2,6-Dibromoaniline? Because of the 7 hertz coupling constant,

the molecule has to be first of all symmetrical because there are only fewer number of signals in the aromatic region, only a triplet and a doublet is seen. And, the coupling constant, if you want to measure in this triplet and you would take the gap between any adjacent line, this is a 100 megahertz NMR spectrum, so between 6 and 7 this is 100 megahertz. So, this should be roughly about 7 or 8 hertz is the gap between these lines that are here. So, an ortho coupling is what is responsible for the signals that is seen here. So, the molecule should have ortho hydrogen, the molecular formula then it will be $C_6H_5Br_2N$, the molecular weight 249, 251 and 253 matches with the mass spectral data that we have already seen.

So, this is a molecular structure of this particular compound. Essentially, deduced from the mass spectrometry first, identify the NH_2 group and the presence of bromine and the NH_2 is confirmed in the infrared spectrum and finally, it is also confirmed in the NMR spectrum by the exchangeable hydrogen that is seen here. What gave the clue that it is a tri-substituted derivative is, because of the presence of 3 hydrogen's in the aromatic regions. So, 3 other positions must be occupied by for substituents. We had already identified 2 bromines and 1 amino group and these are the most likely substituent in the molecule and we place them in the adjacent position leaving the other 3 positions for the hydrogen, so that the H_a can be split into a doublet by H_b so this is a H_a 2 hydrogen intensity and the H_b is split by the H_a into a triplet so one can see H_b at signal in the lower delta region. This is para to the amino functional group, so it is at lower delta value and meta 2 amino group will come at higher delta value and this, NMR spectrum of this particular compound.

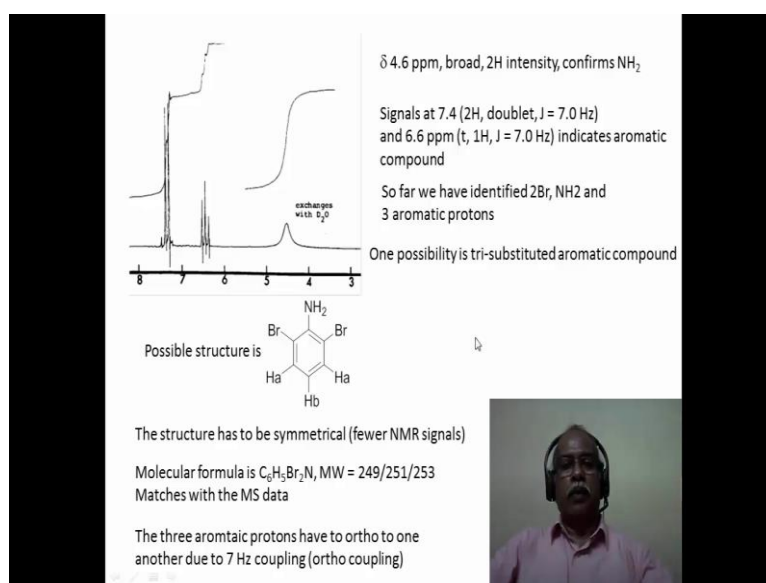
The 3 aromatic protons are to be ortho with respect to each other because of the 7 hertz coupling which is seen, which is a major coupling that is seen in this spectrum let us see here.

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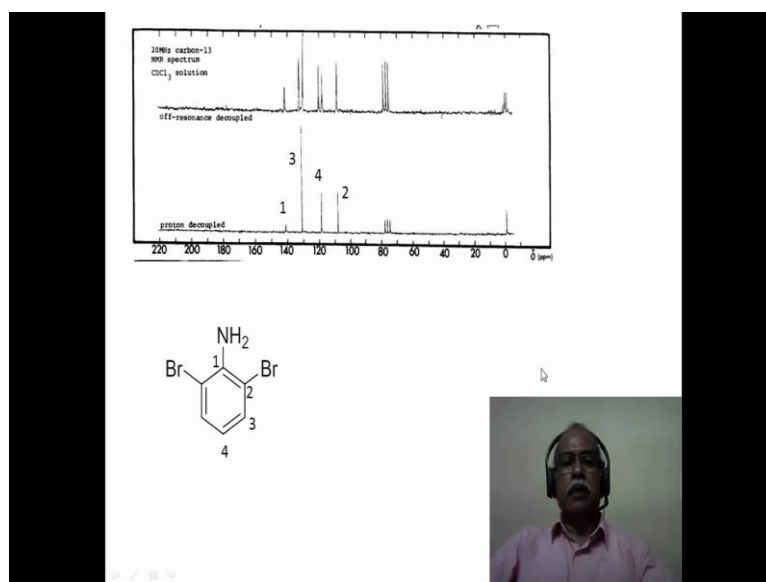
So, symmetry considerations is important in the structural elucidation problem. This is an illustration of how a molecular structure has been decided, based on the cemetery pattern or the substitution pattern that is deduced from the proton NMR spectrum of this particular compound.

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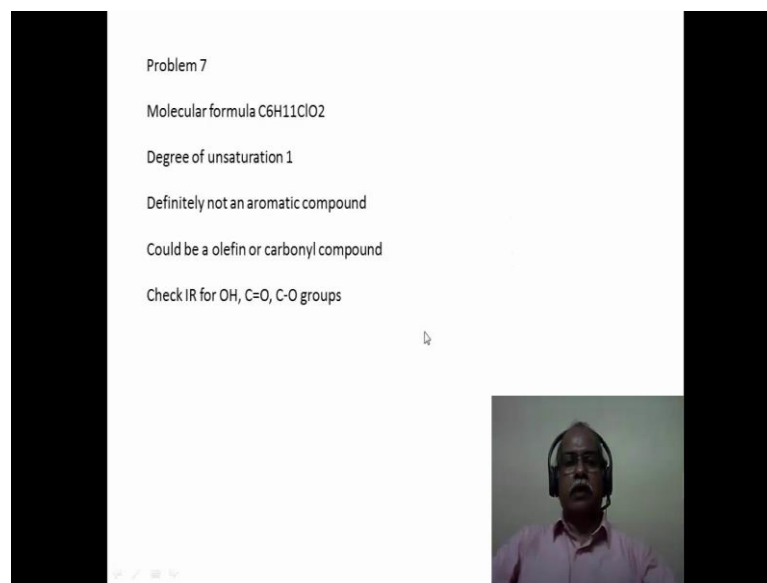
The fact that you have a doublet and triplet seem to indicate, that you should have 3 adjacent hydrogen's ortho to one another in a symmetrical environment such that, H_b would be a triplet and H_a will be a doublet as in seen in the NMR spectrum.

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This is a carbon-13 NMR spectrum of this compound. There are 4 aromatic carbons in this distinctly different aromatic carbon in this molecule. The ipso carbon which has the electron withdrawing NH₂ group, comes as a very low intense peak around 141 ppm or so. And, the ortho carbons which is ortho to the amino functional group it should be the most electron deficient that should, sorry, the most electron rich in this particular case because of the nitrogen lone pair which can be delocalized on to the ring, so that comes to around 110 ppm, 109 ppm or so. And the other 2 carbons, carbon number 3 for example, is the CH carbon which is coming around 130 years or so, and the para carbon comes close to the ortho carbon which is around 120 or so, in this particular case. This peak again is due to the presence of the chloroform CDCl₃ peak and this is due to the TMS peak at 0 ppm in this case.

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Problem 7

Molecular formula $C_6H_{11}ClO_2$

Degree of unsaturation 1

Definitely not an aromatic compound

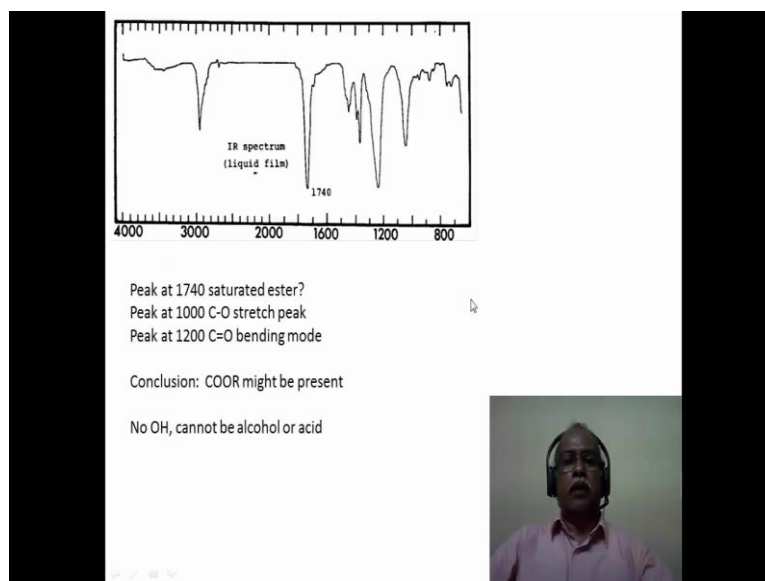
Could be a olefin or carbonyl compound

Check IR for OH, C=O, C-O groups

The screenshot shows a presentation slide with a white background and black text. The text is centered and lists the following information: 'Problem 7', 'Molecular formula $C_6H_{11}ClO_2$ ', 'Degree of unsaturation 1', 'Definitely not an aromatic compound', 'Could be a olefin or carbonyl compound', and 'Check IR for OH, C=O, C-O groups'. A mouse cursor is visible near the bottom right of the text. In the bottom right corner of the slide, there is a small video inset showing a man with glasses and a headset, wearing a pink shirt, speaking.

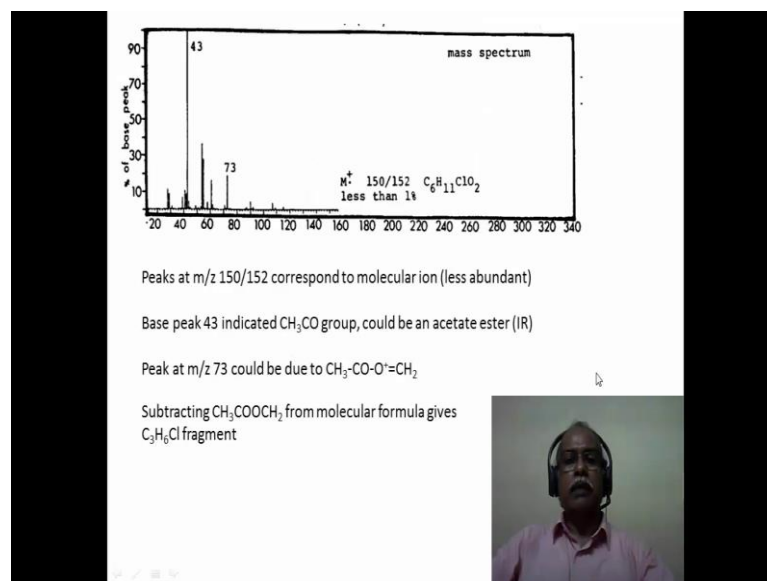
Let us move on to the next problem. The next problem, the molecular formula is given as $C_6H_{11}ClO_2$. The degree of unsaturation is 1, so you can immediately conclude that this is definitely not an aromatic compound because aromatic compound will be highly unsaturated in nature. A degree of unsaturation of 1 is probably due to a C double bond C or a carbonyl functional group alone can be accounted and not an aromatic compound. So, because of the presence of oxygen we will give the routine check of the presence of or absence of OH carbonyl functional group and because there are 2 oxygen present here, one can check whether there is a carbon oxygen double bond as well a carbon oxygen single bond stretching frequency in the infrared spectrum of this particular compound.

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Now, the infra spectrum is shown here. 1740 is a saturated ester peak, carbonyl stretching frequency of an ester is what you seen around 1740 or so. Around 1000 there is a peak, which is intense, fairly intense peak which could be because of a C single bond O stretching frequency and the broad intense peak around 1200 1250 or so, might be because of carbonyl bending mode of this particular compound. The conclusion is, that an ester group may be present mainly because of the fact that you have a 1740 signal and there are no OH signal which is very important; no OH so, it cannot be alcohol or an acid for sure. So, it could be probably an ester kind of a functional group in this particular system.

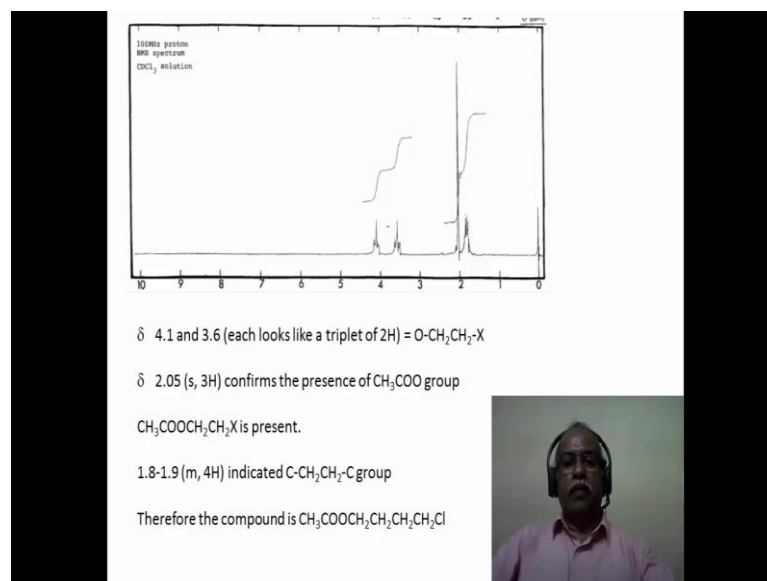
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This is the mass spectrum of the compound. The molecular ion is not seen very clearly it is very less abundant, less than 1 percent which is not seen in this spectrum. So, this is molecular ion 150-152, because of the presence of chlorine you have 150 and 152 peak. What is important is the base peak which is 43; it could be acetyl group, so the molecule could be actually an acetate ester, fragmenting to give the acetyl group at 43 or so.

The peak at 73 could be due to the presence of $COOCH_2$, CH_3COOCH_2 . In other words, this is an acetate ester containing a CH_2 group in the alpha position of the oxygen of the ester. So, the remaining molecular formula if we subtract the CH_3COOCH_2 from the molecular formula, the fragment gives you C_3H_6Cl . So, we need to find out what is this C_3H_6Cl ; perhaps we can make use of the proton NMR spectroscopy data for the elucidation of the complete structure.

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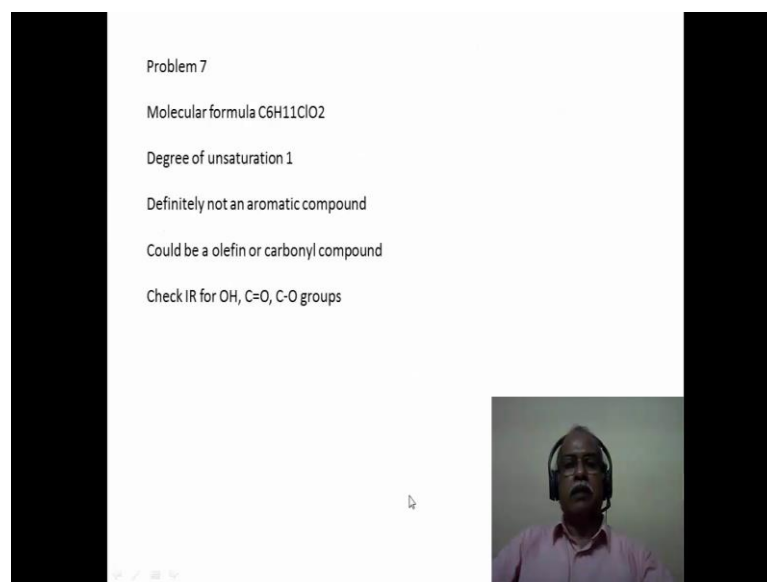


The signal at 4.1 and 3.6 each of them look like a triplet and it could be because of the presence of a O-CH₂ CH₂ -X kind of a functional group that is present here. In other words this CH₂ will be a triplet because of the adjacent CH₂ and vice versa, they are mutually coupled to each other so they sort of give you a triplet and triplet kind of a functional group in this case. The acetate group which we identified in the NMR spectra, sorry, in the mass spectrum as well as in the infrared spectrum is confirmed here. The singlet of 3 hydrogen intensity corresponding to this particular peak which is a sharp singlet corresponding to 3 hydrogen intensity could be a CH₃COO group, so the presence of a CH₃COOCH₂CH₂X is confirmed by the NMR spectrum.

If you see the peak around 1.8 or 1.9 this multiplet here, this is an unresolved multiplet. It corresponds to 4 hydrogen intensity. So, if you start looking at this CH₂ here which is a 2 hydrogen intensity and 2 hydrogen intensity, this would correspond to a 4 hydrogen intensity. In other words, the low chemical shift value tells us that this two CH₂s are connected to 2 carbons at the either end and this CH₂ is connected definitely to a oxygen because of the 4.1 delta value and this CH₂ is connected to some electronegative group, maybe chlorine, maybe an electronegative group; so, O-CH₂ CH₂ CH₂ CH₂Cl is the group that we have identified from the NMR spectrum. This corresponds to O-CH₂ and this one corresponds to CH₂Cl and in between two you have 2 CH₂s which is a second

order kind of multiplet is what is seen in the region of 1.9 ppm. So, CH₂ CH₂ CH₂ CH₂ CL is a fragment, which is very clearly seen in the proton NMR spectrum of this compound and the acetate group of course, is very visible in the proton NMR spectrum.

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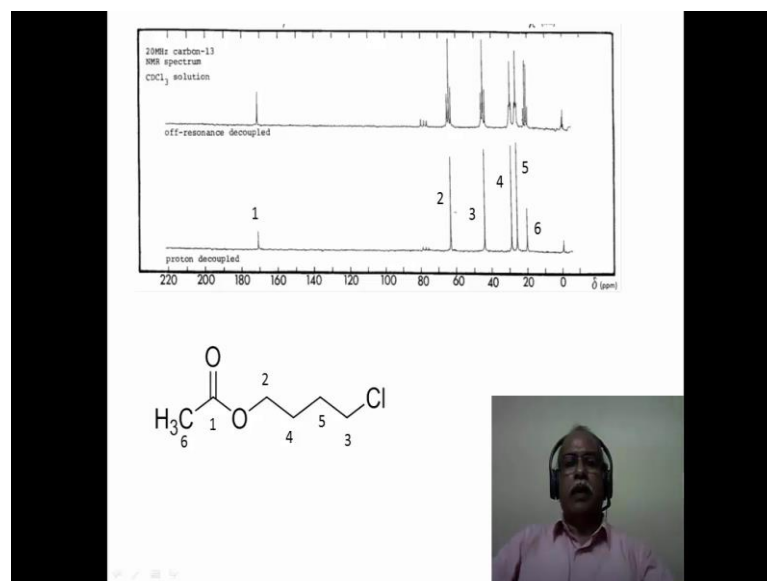
Problem 7

- Molecular formula C₆H₁₁ClO₂
- Degree of unsaturation 1
- Definitely not an aromatic compound
- Could be a olefin or carbonyl compound
- Check IR for OH, C=O, C-O groups

The slide is part of a video recording, as evidenced by the small inset of a man wearing a headset in the bottom right corner. The slide content is centered on a white background with black text.

So, this corresponds to the molecular formula which is given here as C₆H₁₁ClO₂, this is C₆; C 1 2 3 4 5 6, there are 6 carbon, C₆. And, this is H₁₁O₂CL it fits the molecular formula this particular structure and let us see if the carbon-13 spectrum also confirmed this particular data.

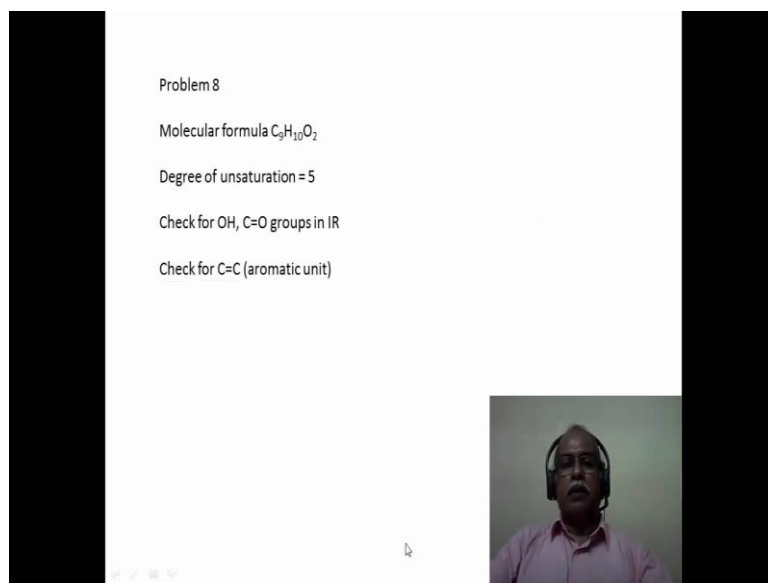
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This is a carbon-13 spectrum the (Refer Time: 13:32) spectrum is given on the top trace and the broadband decoupled spectrum is given in the bottom trace and the carbonyl peak is very clearly seen around 172 or 173, which is labeled as 1. Then, the next carbon would be the carbon that is directly attached to the oxygen which is coming around 63 or 64 ppm, which is a triplet, so it has to be a CH₂ kind of carbon is very clearly seen. Then comes this one that is attached to the chlorine directly, that comes around 45 ppm or so, which is also a triplet. So, number 2 and number 3 are taken care of in the spectrum corresponding to a O-CH₂ and CH₂ Cl in this particular case.

Number 4 and 5 carbons come at a lower delta value because they are attached to only a carbon, not to an electronegative element. So, they come in the region between 25 to 30 in this particular region. Finally, carbon number 6, which is a terminal CH₃ comes around 20 ppm which is a quartet. This triplets are not very well resolved triplets, never the less, they corresponds to carbon number 4 and 5. This quartet is very clearly seen for the CH₃ in the (Refer Time: 14:39) spectrum. So, labeled 6 is the carbon which correspond to the CH₃ of this particular functional group.

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Problem 8

Molecular formula $C_9H_{10}O_2$

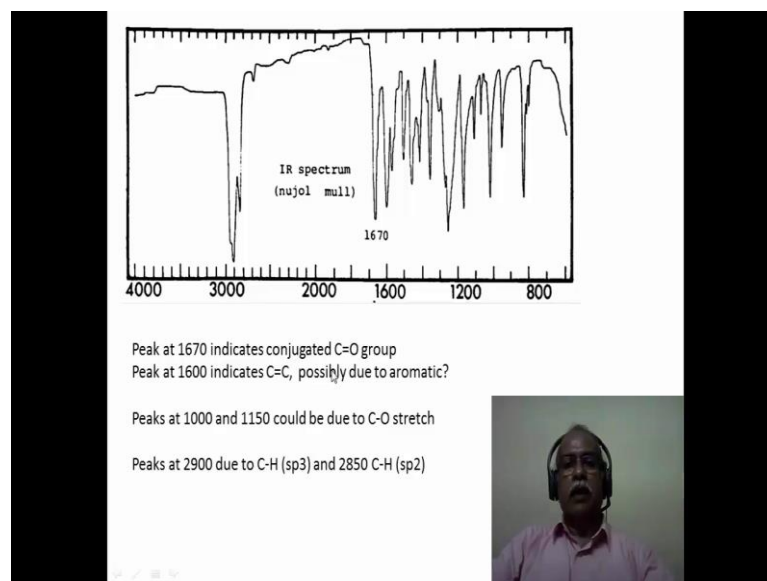
Degree of unsaturation = 5

Check for OH, C=O groups in IR

Check for C=C (aromatic unit)

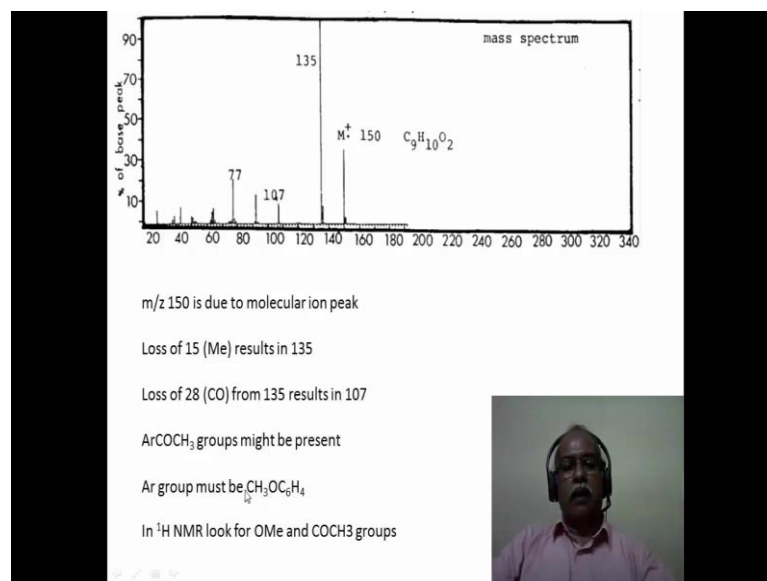
Let us move on to the next problem. The problem, the molecular formula is given here as $C_9H_{10}O_2$. The degree of unsaturation from this molecular formula is 6, it is possibly an aromatic compound because of a large degree of unsaturation that is present here. Because of the presence of oxygen, let us again, once again check the presence or absence of the OH and the carbonyl functional group in the infrared spectrum of this particular compound.

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This is an infrared spectrum of this compound. The carbonyl peak is very clearly seen at 1670. 1670 is corresponding to an alpha beta unsaturated or a conjugated carbonyl functional group and 1600 peak, which is this particular peak here, corresponds to C double bond C possibly because of an aromatic unit that may be present here. Now, the peak at 1000 and 1150 could be corresponding to a C-O single bond stretching frequency. The molecule has 2 oxygen units, so it could be 1 carbonyl and another oxygen maybe present as a C single bond O in this particular case. And, the peak at 2900 to 2850 corresponds to the sp³ and sp² type of C-H stretching frequency which is fairly intense in this region of 2800 or so.

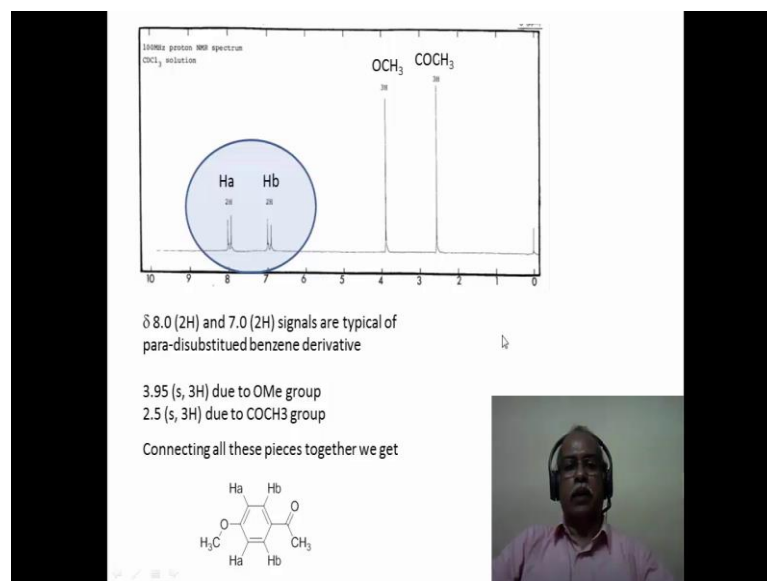
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So, the mass spectrum of the compound is seen here. The molecular ion and peak comes at m by z value 150 and a 15 mass unit which is a loss of a methyl group corresponding to 135 is seen here very clearly and from 135 if you lose a carbon monoxide molecule 28 mass unit you get 107 and from 107 you get the fragmentation peak which corresponds to 77 in this particular case. So, because of the loss of a methyl followed by a carbonyl, one can conclude that the molecule maybe containing an acetyl kind of a group in this particular instance, in this particular case. An aryl COCH₃ might be present in this case. So, first loss of methyl group will give an acyl cation and followed by loss of a carbon monoxide will give you the peak at 107.

So, we have to look for in the NMR spectrum; peaks corresponding to methoxy, how did we decide there is a methoxy peak here? This is because of the presence of 107, 107 corresponds to a methoxy substituted phenyle derivative and this is essentially 76 plus 15 plus 16 is corresponding to 107 for example. So, one has to look for a methoxy group and an acetyl group in this particular NMR spectrum.

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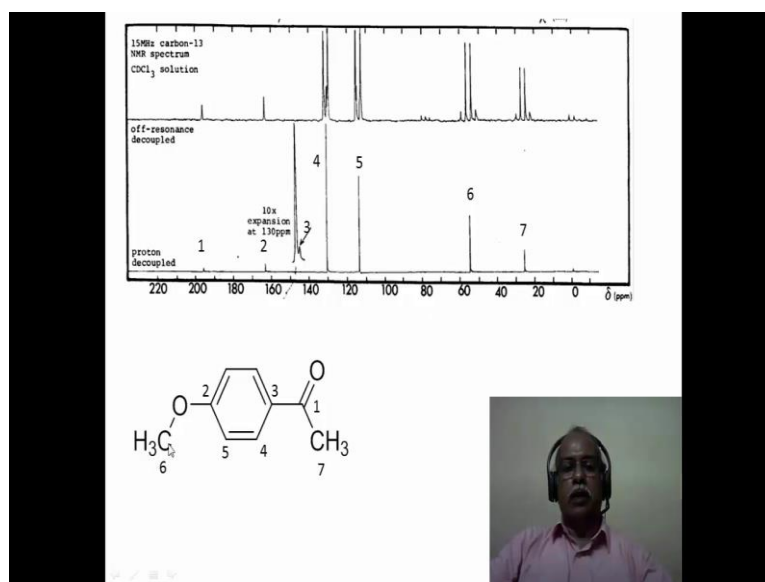


NMR spectrum is fairly simple. This peak which is a doublet of a doublet or an a b quartet as you want to call it, is because of very characteristic feature of the para substituted aromatic derivative. So, peak around 8.0 and 7.2, each one of them has 2 hydrogen intensity. It is already the integration is given in the digitized format as 2 hydrogen and 2 hydrogen is clearly seen here. So, this is definitely a para substituted derivative. Then 3.95 could be because of methoxy functional group and 2.5 could be because of the acetyl functional group in this molecule. So, the molecular formulas; the structure is solved very clearly.

A para substituted derivative bearing a methoxy group and an acetyl group, in other words it is a para methoxy acetophenone is a compound. The para methoxy acetophenone, the 2 chemical shift values of aromatic units aromatic hydrogen Ha and Hb are very wide because one is adjacent to an electron withdrawing functional group namely the acetyl functional group, that would correspond to, I am sorry; the Hb should be this particular one and the Ha should be this particular one. This wrongly labeled, I am sorry about it. This is Hb and this is Ha, the Hb is adjacent to the electron withdrawing acetyl group and the Ha is adjacent to the methoxy functional group which should be at a lower delta value here.

The methoxy signal itself comes in the region of 3.95 or so and the acetyl signal comes around 2.5 ppm or so in this particular NMR spectrum.

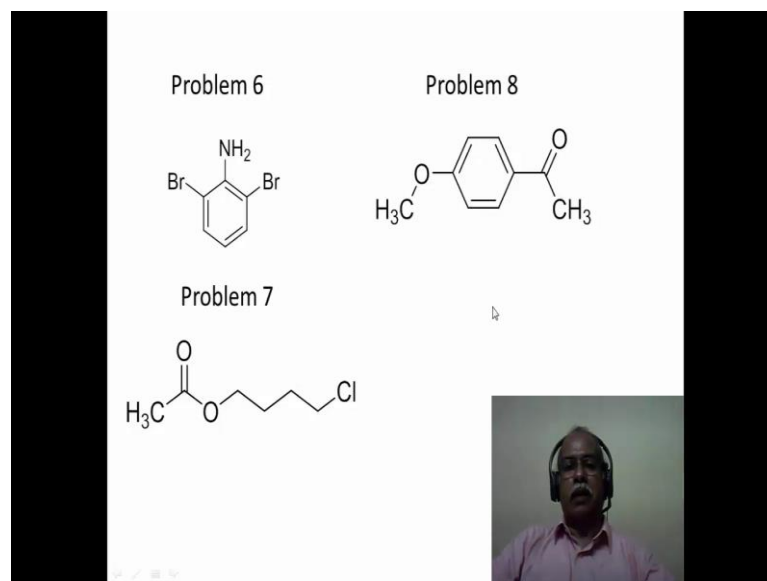
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Carbon-13 spectrum should give 4 lines for the aromatic carbons. The 2 ipso carbon should come at a very low intensity; this is one ipso carbon which has a the low intensity, the other ipso carbon is merged here, in other words it is seen here as carbon number 3 is merging here. The one that has methoxy functional group which is an electron withdrawing oxygen substituted carbon, comes around 162 or so, and the other ipso carbon which is only connected to a carbonyl functional group comes around 130 or so in this particular case. And, the 2 types of carbons which are CH aromatic carbons 4 and 5 come as intense peak which doublet in the (Refer Time: 19:28) spectrum very clearly it tells us it is corresponding to. Here again, the ortho to methoxy will be electron rich in nature, so, that comes at a lower delta value. A one that is adjacent to the electron withdrawing functional group should come at higher delta value in this particular case.

Finally, the methoxy comes at 55 ppm or so, and the methyl group of the acetyl comes around 25 ppm or so in this particular spectrum. And, both of them are quartet in nature because of the CH₃ CH₃ groups that are present in the methoxy and the acetyl functional group.

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So, in this module we have seen an interesting molecule which is a Dibromoaniline, without even having the molecular formula we were able to solve the structure of this particular compound purely based on primarily mass spec, IR and proton NMR spectrum. Then we have an aliphatic ester, chloro ester, chloro alkyl ester is what is seen here. Here the important point is, that these two CH₂s are appearing as nice triplets whereas, this CH₂s appear as a second order multiplet in the region of 1.9 ppm or so. And that was figured out from the proton spectrum of this particular compound.

Finally, an aromatic compound which is a para disubstituted derivative with a nice paradise substitution pattern which is this particular pattern is seen, and the 3 compounds have been elucidated, structures have been elucidated form the spectroscopic data that is provided.

Thank you very much for your attention.