Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 10

Structure Problem solving using 1H and 13C NMR spectral dataTutorial session

Hello, welcome to the module 10 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. We will take this as a tutorial session; we will try to solves some structural registration problems using proton NMR and carbon 13 NMR spectral data. We will also have a look at how the data is presented when it is presented in the numerical form and also when it is presented in the spectral form.

Before we start the session, I suggest that you take a printout of the chemical shift values and coupling constant value tables for the proton NMR and chemical shift value charts for the carbon 13 NMR as a handy reference in front of you so that you can refer to it when the problem solving session is going on. This is how you are familiarize yourself with the various chemical shift values or different protons and carbons and the various coupling constant values of a proton NMR spectrum.

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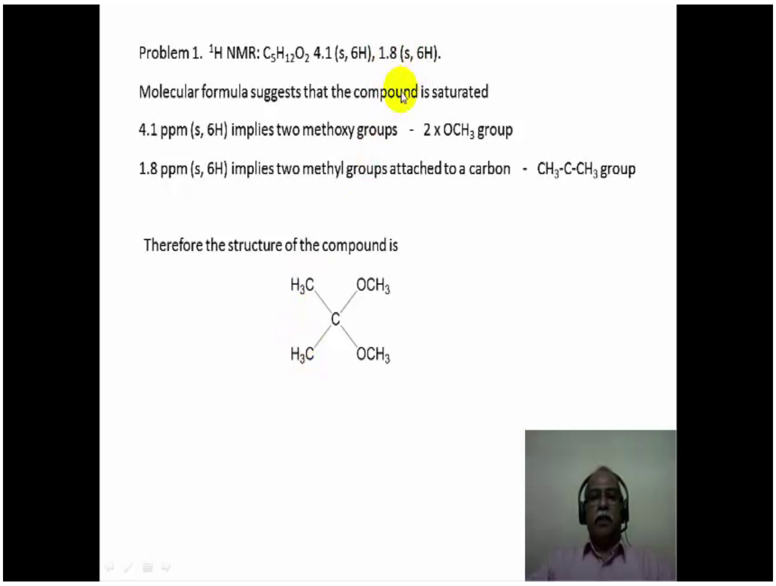

Problem 1. ^{1}H NMR: $C_5H_{12}O_2$ 4.1 (s, 6H), 1.8 (s, 6H).

Molecular formula suggests that the compound is saturated

4.1 ppm (s, 6H) implies two methoxy groups - 2 x OCH_3 group

1.8 ppm (s, 6H) implies two methyl groups attached to a carbon - CH_3-C-CH_3 group

Therefore the structure of the compound is

Let us start with the first problem - the NMR proton and NMR data is given for a very simple molecule with the molecular formula C 5 H 12 O 2 molecular formula gives very important information regarding the degree of unsaturation or the number of double bond that are being present in the molecule. Now, this particular molecular formula suggests that it is saturated compound with the double bond equivalence of one sorry double bound equivalence of zero. The proton NMR data is given; the 4.1 delta ppm as singlet of 6 hydrogen can only mean that this carbon this particular proton is attached to a carbon containing a heteroatom like oxygen. Since oxygen is present in the molecular formula, we can come to the conclusion that the 4.1 ppm signal of 6 hydrogen intensity implies that there are two methoxy groups. So, we consider 2 methoxy functional group as part of the structural resonance solution.

Then comes the next chemical shift value of 1.8; this is much smaller chemical shift value and it consists of 6 hydrogens of singlet. This can only imply that there are two methyl groups attached to the same carbon; in other words, the gem dimethyl group bearing carbon attach to a carbon is the group that is responsible for this particular resonance at 1.8 ppm of 6 hydrogen intensity. Now if you add up these numbers of carbons and hydrogen and to the oxygen that is present in the fragments that we have illustrated, it corresponds to the molecular formulas. So, the problem is essentially solved the structure of the simple organic molecule is that it is a dimethyl acetyl of acetone. So, once you have the structure ready, you can confirm that there is no unsaturation in this particular molecule, and two methoxy groups corresponds to the 4.1 that delta ppm singlet of six hydrogen and this two methyl which are gem dimethyl groups for example, corresponds to the 1.8 ppm of singlet of 6 hydrogen intensity.

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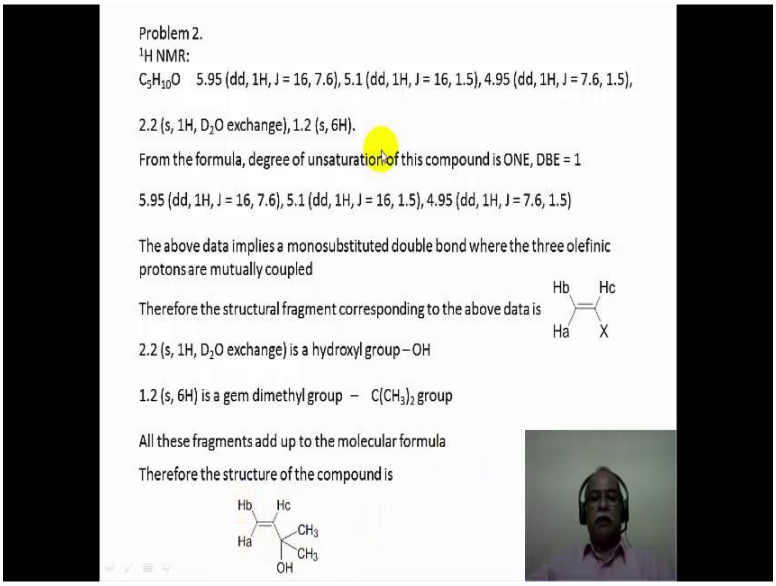

Problem 2.

^{1}H NMR:

$C_5H_{10}O$ 5.95 (dd, 1H, J = 16, 7.6), 5.1 (dd, 1H, J = 16, 1.5), 4.95 (dd, 1H, J = 7.6, 1.5),

2.2 (s, 1H, D_2O exchange), 1.2 (s, 6H).

From the formula, degree of unsaturation of this compound is ONE, DBE = 1

5.95 (dd, 1H, J = 16, 7.6), 5.1 (dd, 1H, J = 16, 1.5), 4.95 (dd, 1H, J = 7.6, 1.5)

The above data implies a monosubstituted double bond where the three olefinic protons are mutually coupled

Therefore the structural fragment corresponding to the above data is

2.2 (s, 1H, D_2O exchange) is a hydroxyl group – OH

1.2 (s, 6H) is a gem dimethyl group – $C(CH_3)_2$ group

All these fragments add up to the molecular formula

Therefore the structure of the compound is

Let us move on to the next problem. Now here the proton NMR data is given; from the molecular formula, which is C 5 H 10 O we come to the conclusion there is one double bond this molecule because C 5 H 12 should have been the saturated molecular formula, but it is C 5 H 10 2 hydrogen are deficient. Therefore, the double bond equivalence is one here. Now if you are carefully look at the proton NMR data 5.95, 5.1 and 4.95, they seem to be mutually coupled hydrogens of the type olefinic hydrogens because the chemical shift values is seem to indicate that they are olefinic hydrogen and the pattern namely the doublet of a doublet, doublet of a doublet, doublet of a doublet seem to indicate that they are mutually coupled to each other. In addition to that if you look at the J values which are coupling constant value. J value of 16 actually is a fairly large value for the coupling constant this would only mean that there is a trans kind of a double bond present in this molecule and 7.6 coupling would correspond to roughly a two hydrogen begin six to each other in a double bonded system.

So, from the data of 5.95, 5.1 and 4.95 taken together, it implies only a mono substituted olefinic derivative like this, where you will have a trans coupling, a cis coupling and the germinal coupling corresponding to the 16 hertz, 7.6 hertz, and the 1.5 hertz. The 1.5 hertz small coupling corresponds to the s p 2 germinal hydrogen coupling which is the smallest among the three coupling constants that you have in this particular fragment.

Then let us go and identify what is this 2.2 singlet 1 hydrogen of D 2 O exchange. The D 2 O exchangeable hydrogen are special hydrogens in the NMR data, and they would imply that the hydrogen is attached to a highly electronegative atom directly and these are exchangeable hydrogen that is why the D 2 O addition actually exchange a particular hydrogen and the signal vanishes in the NMR spectrum.

So, from the molecular formula we know that this molecule contains one oxygen. So, most likely the oxygen is attached to the hydrogen on one-side and the OH group is what is responsible for this particular signal at 2.2 which is an exchangeable hydrogen. So, once again this 1.2 ppm signal of singlet of 6 hydrogen would only mean the gem dimethyl group connected to a carbon. So, if you put all these fragments together we come to the conclusion that this compound can only be this particular dimethyl alkyl alcohol is the structure of the compound which is consistent with the data that is given. Once you arrive at the structure, you can always go back and see whether the structure that has been arrived at matches or satisfies these spectroscopic data that is given.

In this particular problem, you have three hydrogen of olefinic type and you have three signal in the olefinic region starting from 4.95 to 5.95. And you also have the trans couplings, cis coupling and the germinal coupling corresponding to be large J value of 16, the medium J value of 7.6 and a small J value of 1.5. So, this particular resonance which contain both the trans coupling as well cis coupling would only respond to this particular hydrogen HC which as a trans coupling and the cis coupling. So, the Hc comes at 5.9 ppm. The second signal at 5.1 consist of a trans coupling and germinal coupling and the trans coupling and the germinal coupling only would mean the Ha hydrogen which has a trans coupling and a germinal coupling.

Finally, Hb comes at 4.95 with the cis coupling and the germinal coupling. So, Hb is cis with respect to Hc, and it is germinal with respect to H a. So, this data is satisfying this particular structural fragment. D 2 O exchangeable OHis there and the gem dimethyl group is also there at 1.2, which corresponds this fragments. So, most likely this particular structure is a correct structure that satisfies the data that is given.

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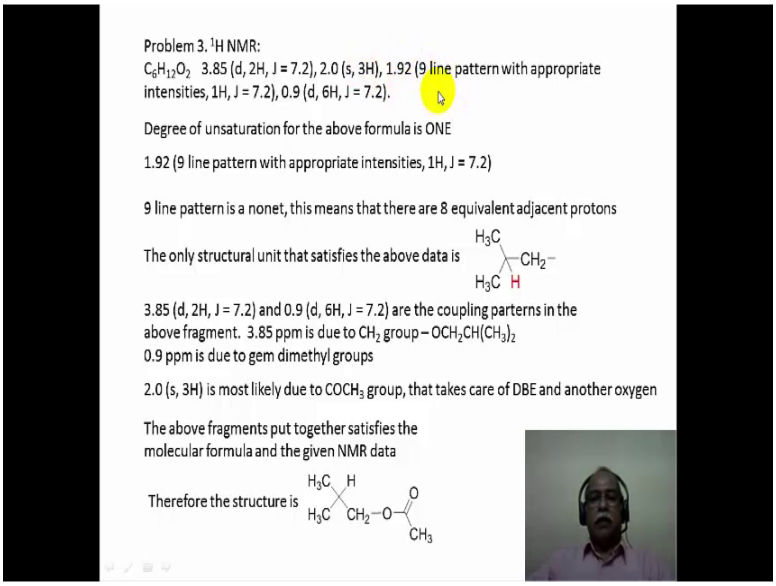

Problem 3. ^{1}H NMR:

$C_6H_{12}O_2$ 3.85 (d, 2H, J = 7.2), 2.0 (s, 3H), 1.92 (9 line pattern with appropriate intensities, 1H, J = 7.2), 0.9 (d, 6H, J = 7.2).

Degree of unsaturation for the above formula is ONE

1.92 (9 line pattern with appropriate intensities, 1H, J = 7.2)

9 line pattern is a nonet, this means that there are 8 equivalent adjacent protons

The only structural unit that satisfies the above data is

3.85 (d, 2H, J = 7.2) and 0.9 (d, 6H, J = 7.2) are the coupling parterns in the above fragment. 3.85 ppm is due to CH_2 group – $OCH_2CH(CH_3)_2$
0.9 ppm is due to gem dimethyl groups

2.0 (s, 3H) is most likely due to $COCH_3$ group, that takes care of DBE and another oxygen

The above fragments put together satisfies the molecular formula and the given NMR data

Therefore the structure is

In problem number 3, the molecular formula corresponds to C 6 H 12 O 2, and the degree of unsaturation is 1 in this particular molecule. Now if you look at this particular information namely 1.92 ppm here, 9 line intensity pattern with appropriate intensity and J value of 7.2 implies that there are 8 adjacent hydrogen adjacent to this group CH group this is a one hydrogen intensity. So, it should be a CH group and there are 8 adjacent hydrogens to the CH group which are vicinal to the CH group that we have. The only possible structures unit that would satisfy this particular data is this particular structural fragment namely the isobutyl group and the red hydrogen is the one that corresponds to the signal at 1.92, and it is surrounded by two methyl group and methylene group, total are 8 hydrogens which are vicinal hydrogen. And these 8 hydrogens essentially split this red hydrogen into a 9 line pattern of appropriate intensity with the J value corresponding to an average value of about 7.2 hertz as the J value for this hydrogens couple to the red hydrogen here. So, this is the structural unit that is consistent with this.

Once you have the structural unit, you can also extrapolate that this CH 2 should be this particular signal at 3.85 of 2 hydrogen intensity, because it has a same coupling constant as 7.2, so they are coupling partners. 3.85 suggest that the CH 2 should be attached to an oxygen, because oxygen is present in the molecular formula such a large chemical shift value of 3.85 would only mean that this is a either and ester or in either kind of CH 2.

And then if you look at this two methyl groups which are gem dimethyl group that should appear as a doublet because of that adjacent red hydrogen, we do have a doublet which is 0.9 ppm of six hydrogen intensity again with the same coupling constant.

So, putting all this information together, we come to the conclusion that this particular fragment namely OCH 2, CH CH 3 twice is the group that is responsible for the data that is given. There is one data still left out which is 2.0 of 3 hydrogen intensity that is still 1 oxygen and 2 carbons and 3 hydrogens are left in the molecular formula. In other words, if you subtract this particular fragment from the molecular formula, you come up with the group which is an acetyl group 2 ppm to 2.5 ppm singlet three hydrogen most of the time implies there you have a acetyl group or the aromatic c h three kind of a group is present. This is the characteristic region for the aromatic CH 3 or a COCH 3 kind of a group that is present in this compound. This molecular is not an aromatic molecule, you can see from the NMR that there are no aromatic hydrogen. So, most likely the 2 ppm signal with a 3 hydrogen intensity only correspond to a acetyl group and it also takes care of the double bond equal and send another oxygen in the molecular formula.

So putting all these fragments together the structure of likely is that it is an isobutyl acetate as the structure of the component that we have illustrated that is the fairly simple structure. The idea is to illustrate the point that when you have a 9 line pattern intensity that pattern recognition is extremely important. Once you recognize the pattern you should be able to translate this into a structural information which this particular fragment that is the isobutyl group is responsible for this kind of a pattern that is present in the NMR spectrum.

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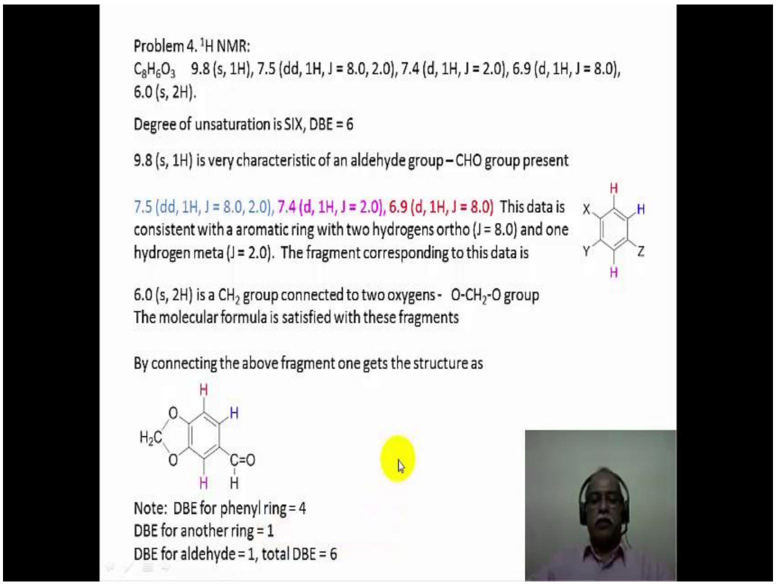

Problem 4. ^{1}H NMR:

$C_8H_6O_3$ 9.8 (s, 1H), 7.5 (dd, 1H, J = 8.0, 2.0), 7.4 (d, 1H, J = 2.0), 6.9 (d, 1H, J = 8.0), 6.0 (s, 2H).

Degree of unsaturation is SIX, DBE = 6

9.8 (s, 1H) is very characteristic of an aldehyde group – CHO group present

7.5 (dd, 1H, J = 8.0, 2.0), 7.4 (d, 1H, J = 2.0), 6.9 (d, 1H, J = 8.0) This data is consistent with a aromatic ring with two hydrogens ortho (J = 8.0) and one hydrogen meta (J = 2.0). The fragment corresponding to this data is

6.0 (s, 2H) is a CH_2 group connected to two oxygens - O-CH_2-O group

The molecular formula is satisfied with these fragments

By connecting the above fragment one gets the structure as

Note: DBE for phenyl ring = 4

DBE for another ring = 1

DBE for aldehyde = 1, total DBE = 6

Let us move on to the next problem. Again, a proton NMR spectral data is given the molecular formula is C 8 H 6 O and a double bond equivalence here corresponds to 6 double bound equivalence; in other words there are six double bounds are equivalent to six unsaturation is present in this particular molecule. If you look at 9.8 singlet as one hydrogen signal this will only be a aldehyde functional group because between 9 and a 10.5 or so, it is a very characteristic region for the aldehyde groups to come. So, there is an aldehyde group present in this particular molecule.

Then if you look at 7.5 ppm doublet of a doublet with 8 and a two hertz couplings that are present and 7.4 a doublet of J is equal 2; 6.9 a doublet of J is equal to 8, all of them or all of them are one hydrogen intensity. This would only mean that you have an aromatics skeleton with three hydrogens because of the integration one, one and one for these three signals, it is a tri substituted aromatic compound. One can also figure out the substitution pattern from the coupling constant. This is an ortho coupling that must be an ortho hydro two hydrogens are adjacent to each other in this aromatic skeleton that corresponds to the ortho coupling and two corresponds to a meta coupling. So, there should be two hydrogens which are ortho to each other and one hydrogen meta to the other two hydrogen. So, this structural unit essentially satisfies the spectral data in aromatic region.

If you look at the red hydrogen, it has a ortho coupling partner of about 8 hertz of coupling constant. And this has a blue hydrogen also has the 8-hertz coupling partner as well as a 2-hertz coupling partner which is a meta coupling partner. So, the 7.5 delta value corresponds to the blue and the 6.9 corresponds to the red and finally, the 7.4 corresponds to the magenta colored hydrogen in this particular molecule.

Now, the 6.02 hydrogen intensity of singular to only be di substituted methylene group. Since there are oxygen present in this molecule it can only be a di-oxygen substituted and other words a methylene dioxy groups is what is present in this molecule. The molucluer formula is via satisfied with all these fragments; you take the aldehyde and the O CH 2 O group as well as this C 6 H 3 fragment if you take it, there are three substituent which are supposed to be present. You can presume one of the substituent is a all the head substituent and there are two oxygen which have still one valency left and that would satisfy x and y for example.

So, using all this fragment information one arrives at the structure of this compound as a methylene dioxin derivative of benzolyhide. Now the degree of unsaturation is accounted like this. The aromatic ring will have one unsaturation for the ring structure and there are three double bonds. So, totally an aromatic ring of phenyl type constitutes a unsaturation of four then you have an aldehyde functional group which constitutes and unsaturation of one the metalian dioxy unit this ring system for example, the dioxgen ring system that constitutes another unsaturation. So, there is double bond equivalence six is also satisfied in this manner.

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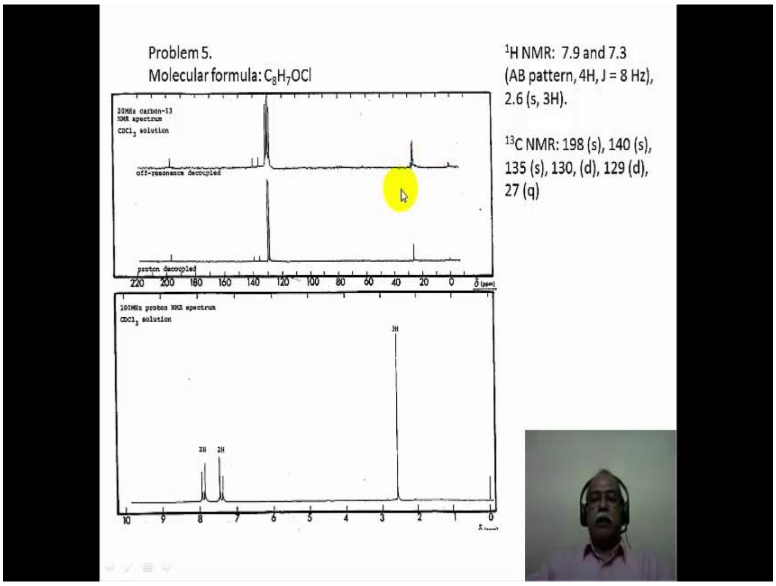

Problem 5.

Molecular formula: C_8H_7OCl

^1H NMR: 7.9 and 7.3 (AB pattern, 4H, J = 8 Hz), 2.6 (s, 3H).

^{13}C NMR: 198 (s), 140 (s), 135 (s), 130, (d), 129 (d), 27 (q)

Now, this is another way of looking at the spectrum. Whenever doing the research he is not going to get the spectral data as it is percentage in the numerical fashion like this. What is going to get of courses is a spectrum from the NMR spectrometer and one needs extract the information of coupling constants and the J chemical shift values from the spectral data to be able to present this in this particular format. So, if you take this spectrum, have a look at this spectrum in this region, this is the typical aromatic region between 7 and 8 ppm in the proton enamel spectrum. You can tell here there this is a 100 megahertz proton NMR spectrum recorded in chloroform solution which is the dutrate chloroform solution. Now the dutrated solvent is used for recording the NMR.

Now this pattern is a very characteristic pattern for a, a prime, b, b prime pattern kind of such system. So, one can assume that this is either an AB type of a pattern or an a a prime, b b prime kind of a pattern of four hydrogen intensity. So, it is most likely a para disubstitute at aromatic (Refer Time: 15:39). This pattern recognition and relating to a para disubstituted derivative is extremely crucial for solving the structure this particular compound. Then you come to the aliphatic region around 2.5 ppm, there is a singlet of three-hydrogen intensity, this three-hydrogen intensity corresponds a methyl group. The methyl group is either directly attached to the aromatic ring or it is attached to a carbonyl group then attached to the aromatic ring. Now, this is the disubstituted derivative. So, from the molecular formula, one can assume that the chlorine is one of the substituents that is present in aromatic ring of this structure.

Now let us look at the proton NMR data which is extracted out of the spectrum that is shown here 7.9 and 7.3 are approximate chemical shift values of this AB pattern. I have mentioned it as AB pattern, because it looks like AB pattern with four big lines that I have seen here; however, this is actually an a a prime b b prime kind of a pattern, so with the chemical shift values of 7.9 and 7.3. And a coupling constant which is J A B is roughly 8 hertz also in this particular case and 2.6 corresponds to a singlet of three hydrogen intensity.

Luckily in this particular spectrum, the intensity are the various signals are given in terms of the number of protons that present these signals this corresponds to two hydrogen, this corresponds two hydrogen, this corresponds to three hydrogen totally there are seven hydrogens in the moleculer formula all the 7 hydrogens are taken into account by disintegration.

Coming to the carbon-13 spectrum, if you look at the left-hand side of the spectrum around 200 ppm, there is a signal a very small signal which is the singlet which is of the top trace is operation spectrum and the bottom trace is normal broadband decoupled spectrum. So, there is no coupling information in the bottom spectrum, whereas there is coupling information of a kind that directly attached hydrogen coupling is represented in this particular spectrum. So, this essentially indicates that this carbonyl functional group is not an aldehyde, because if it were to be an aldehyde it would be have an doublet signal here the CH would have split the carbon signal into doublet since this is remaining as a singlet in the off resonance spectrum also this is likely to be a keton. Since we concluded this could be a COCH 3 that is sort of confirmed by this presence of this particular signal being a singlet signal corresponding to a ketonic kind of a signal.

The para disubstituted derivative which we concluded based on the a a prime, b b prime pattern should have four types of carbons in the aromatic unit. It is unsymmetrical paradise substituted, so there should be four types of carbon. Two of the carbon are quaternary carbons. You can see here the two small signal which, remain us singlet in the off resonance also corresponds to the ipso carbons where the substituents are presence. Then two other signals there that it is not very well resolved in this spectrum. The almost over lapping signal is what is seen and that appears to be each of them appears to be a doublet in the off resonance spectrum. So, there are 2 CH carbons and two quaternary carbons in the aromatic ring corresponding to a paradise substitute skeleton. Finally, this methyl groups is appearing in the carbon-13 spectrum the carbon is appearing around 27 ppm or so, as a singlet in the off resonance spectrum it is a quartered it is not a beautiful quartet they could normally see it is sort a distorted quartet. Usually in the off resonance spectrum of the signals can be a highly distorted, this is one such example of a distorted quartet is what you seen here.

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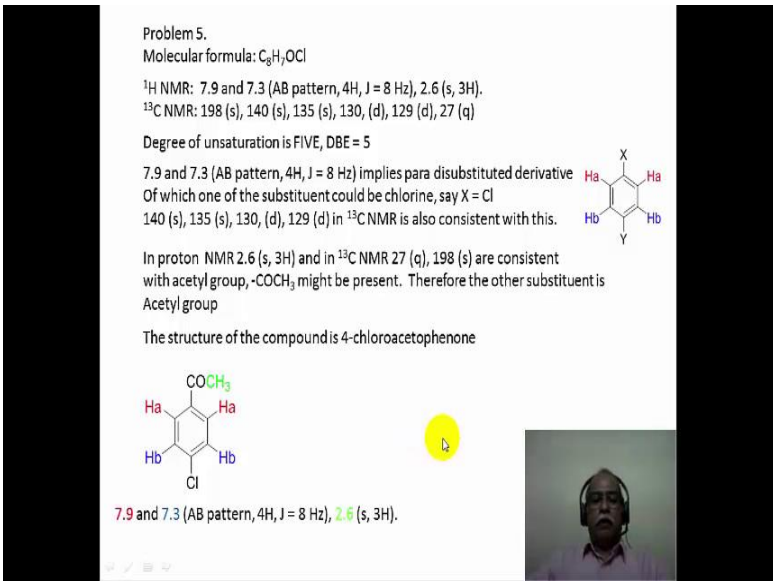

Problem 5.
Molecular formula: C_8H_7OCl

^{1}H NMR: 7.9 and 7.3 (AB pattern, 4H, J = 8 Hz), 2.6 (s, 3H).
^{13}C NMR: 198 (s), 140 (s), 135 (s), 130, (d), 129 (d), 27 (q)

Degree of unsaturation is FIVE, DBE = 5

7.9 and 7.3 (AB pattern, 4H, J = 8 Hz) implies para disubstituted derivative
Of which one of the substituent could be chlorine, say X = Cl
140 (s), 135 (s), 130, (d), 129 (d) in ^{13}C NMR is also consistent with this.

In proton NMR 2.6 (s, 3H) and in ^{13}C NMR 27 (q), 198 (s) are consistent with acetyl group, -$COCH_3$ might be present. Therefore the other substituent is Acetyl group

The structure of the compound is 4-chloroacetophenone

7.9 and 7.3 (AB pattern, 4H, J = 8 Hz), 2.6 (s, 3H).

So, let us now this data is not written in this particular fashion. From this we are going to solve the structure of this molecule. Degree of unsaturation is 5, chlorine present there. So, you need to add one hydrogen instead of the chlorine, so that would be C 8 H 8 for a saturated molecular formula it should have been C 8 H 18 and that the deficiency of 10 hydrogen corresponds to a double bound equivalence of 5. Now this we already discussed 7.9, 7.3 or as well as the carbons signal seem to indicate this kind of a para disubstituted derivative one of the substituent is chlorine you can confirm that for example. And the other substitution if you subtract this C 6 H 4 and the Cl from the molecular formula, the other substituent is an acetyl substituent. Acetyl substituent has the signature of in terms of the NMR signal at 2.6 and also these two signals in the carbon-13 spectrum namely for the CO 198 ppm signal, and the CH 3 27 ppm of quartet is essentially confirming the presence of an acetyl group. So, putting all these information together, we arrive at the structure of para chloroacetophenone for this particular spectral data. Once you arrive at the structure, it is always better go back and check whether the structure is consistent with the data that is being presented just to conform and cross check once again whether this data satisfies the spectral data the structure satisfies the spectral data.

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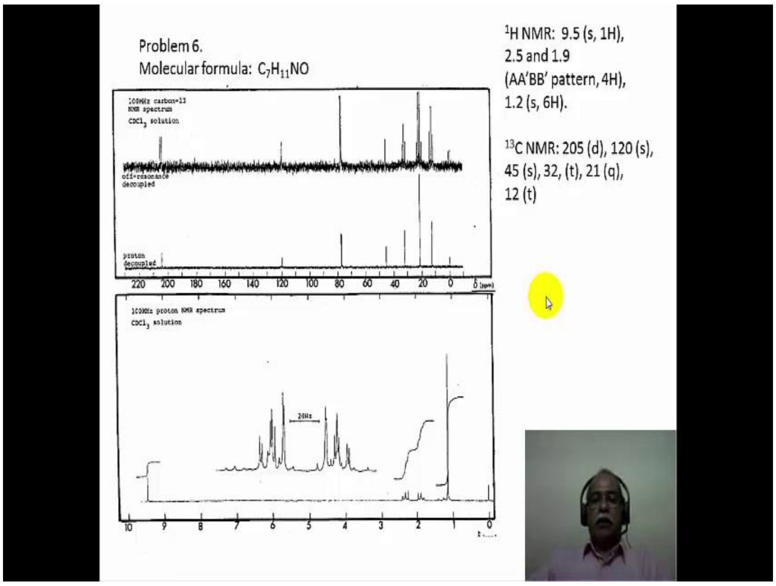

Problem 6.
Molecular formula: $C_7H_{11}NO$

^{1}H NMR: 9.5 (s, 1H),
2.5 and 1.9
(AA'BB' pattern, 4H),
1.2 (s, 6H).

^{13}C NMR: 205 (d), 120 (s),
45 (s), 32, (t), 21 (q),
12 (t)

Now, this is compound with the molecular formula of C 7 H 11 NO. Now what is important in this spectrum, this is a proton NMR spectrum this particular pattern one should be able to recognize with some practices. Now the signals that is shown here around 2 to 3 ppm. This small signal is expanded and zoomed it to show that there is a symmetrical pattern with respect to the center of the spectrum here. In other words, such a symmetrical pattern can only be due to an a a prime, b b prime kind of a spin system four spin system is what is being present in this case.

Let us also confirmed that the integration corresponds to four; let us start at the left end of the spectrum of the proton NMR somewhere around 9.5 ppm, there is a singlet and then carbon-13 also there a speak around 205 ppm or so and this signal is split into a doublet in the off-resonance spectrum that would mean that this particular signal corresponds to an aldehyde signal only an aldehyde signal can appear as a doublet in the carbon-13 spectrum in the off-resonance spectrum. So, the proton NMR data around 9.5 as singlet and this doublet here in off-resonance spectrum essentially confirms that presence of aldehyde functional group.

So, before we go into that let us say that this particular data corresponds to the 2.5 ppm and 1.9 ppm approximate chemical shifts which are the centers of the multiples that we seen these about a, a prime, b, b prime pattern of four hydrogen density. This is 4 hydrogen intensity, because this would corresponds to 1 hydrogen intensity because it is an aldehyde. So, this is two hydrogen intensity from here to here, and another 2 hydrogen intensity from here to here. So, this part of the multiplets corresponds two hydrogen intensity b, b primes side of the a a prime, b b prime pattern. On the right hand side, you have the a a prime patterned which corresponding to two hydrogen intensity.

So, totally four hydrogen intensity essentially satisfies fact that this x b and four spin system. In the aliphatic regions, such a 4 spin system can come only if it there is the CH 2-CH 2 doubly substituted ethyl groups is present; in other words, X-CH 2- CH 2-Y kind of a fragment is responsible for the structural feature in the molecular. Now there is a singlet around 1.1 ppm or so, 1.2 ppm and this is six hydrogen intensity; if this is four hydrogen intensity then you can easily figure out that this is corresponding to a six hydrogen intensity. And this could probably a gem dimethyl kind of a group. We will what is the structural feature of this particular molecule.

Now, in the carbon-13, you have a CHO group which is a doublet which is around 295 five ppm. Around 120 there is a singlet, so this is a very unique signal this could be either due to aromatic, but there are no aromatic hydrogens in the proton NMR. So, it unlikely to be aromatic this can also be olefinic, but then there are no olefinic protons in the NMR spectrum proton NMR spectrum. So, it is unlikely to be a olefinic carbon. The only other kind of carbon that can in this region is a cyano kind of a carbon. So, this molecule may be containing a cyano functional group. The presence of nitrogen also seems to suggest that such a functional group is not unlikely in this particular molecule. Now this multiplets that is seen here this is essentially because as a solvent Cd Cl 3, it is appearing as a three equally interns lines which is the triplet kind of a system is what we have corresponding to the deuterium splitting of the carbon of the Cd Cl 3.

Now since we mention there are two methylene groups in the off resonance spectrum if you look at there should be two triplets there are. In fact, two triplet in the off resonance spectrum and this gem dimethyl group should have a quartet, in fact, there is a quartet that is present. If is this is a gem dimethyl group which is that extra substituted quaternary carbon that quaternary carbon also appears around 45 ppm or so, in the carbon-13 spectra. So, we have this spectral information extracted out of the spectral picture in this case.

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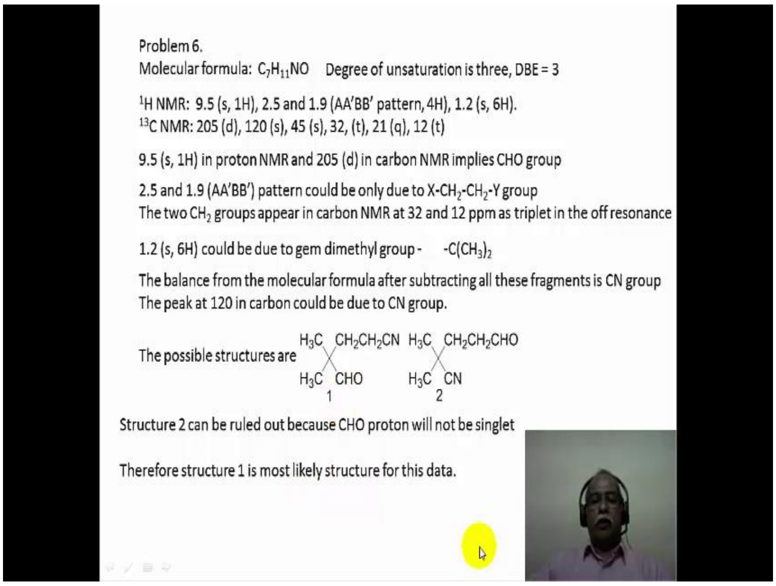

Problem 6.

Molecular formula: $C_7H_{11}NO$ Degree of unsaturation is three, DBE = 3

^1H NMR: 9.5 (s, 1H), 2.5 and 1.9 (AA'BB' pattern, 4H), 1.2 (s, 6H).

^{13}C NMR: 205 (d), 120 (s), 45 (s), 32, (t), 21 (q), 12 (t)

9.5 (s, 1H) in proton NMR and 205 (d) in carbon NMR implies CHO group

2.5 and 1.9 (AA'BB') pattern could be only due to X-CH_2-CH_2-Y group

The two CH_2 groups appear in carbon NMR at 32 and 12 ppm as triplet in the off resonance

1.2 (s, 6H) could be due to gem dimethyl group - -$C(CH_3)_2$

The balance from the molecular formula after subtracting all these fragments is CN group

The peak at 120 in carbon could be due to CN group.

The possible structures are

Structure 2 can be ruled out because CHO proton will not be singlet

Therefore structure 1 is most likely structure for this data.

So, let us try to now solve the structure, degree of unsaturation based on the molecular formula is 3, nitrogen is present it is a trivalent element. So, one has to add on hydrogen to the molecular formula that would make it a C 7 H 12 for the saturated compound it should be C 7 H 18. So, in there are six hydrogens definition in the molecule the degree of unsaturation is 3. So, the 9.5 corresponds to an aldehyde functional group we already discussed this around 205 ppm in the NMR carbon-13 NMR. The 2.5 and 1.9 pattern a, a prime pattern b prime pattern can only be a CH 2-CH 2 group of this type and that is is also confirmed by two triplets that are appearing around 32 and 12 ppm in the off resonance spectrum there is a gem dimethyl group.

So, if you put all these fragments together and subtracte it from the molecular formula what is left with is the cyano functional group. In fact, the molecular structure can be either structure one or structure two; structure two can be easily ruled out as a possibility because the aldehyde is attached to a CH 2, so the hydrogen of the aldehyde would have been split into a triplet by the CH 2 hydrogens, which is not the case the proton NMR 9.5 is actually singlet and this structure essentially would give a singlet aldehyde functional group and this would be the most likely structure.

Therefore, the structure two is inconsistent with this data of this singlet 9.5 signal if it had been a triplet 9.5 signal you would have supported this particular structure. So, one can rule out alternative structures based on the structural based on the spectroscopy data that is given that for the structure is most likely to be one for this particular compound.

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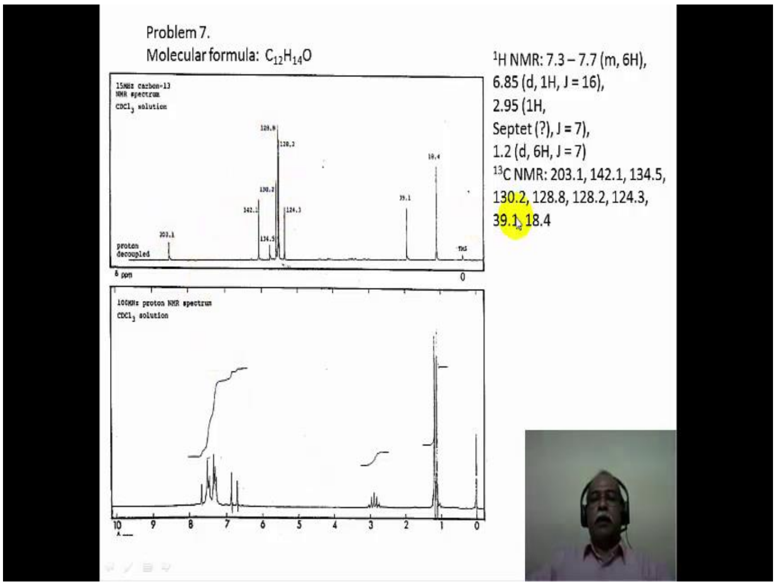

Problem 7.

Molecular formula: $C_{12}H_{14}O$

^1H NMR: 7.3 – 7.7 (m, 6H),
6.85 (d, 1H, J = 16),
2.95 (1H,
Septet (?), J = 7),
1.2 (d, 6H, J = 7)
^{13}C NMR: 203.1, 142.1, 134.5,
130.2, 128.8, 128.2, 124.3,
39.1, 18.4

I hope we had a exposure of how to solve the structures based on different types of pattern that we see in the NMR spectrum. Let us look at this particular spectra, this is a proton NMR and this is a carbon-13 NMR spectrum; molecular formula is given here C 12 H 4 and O, this is the molecular formula. Now what is important in this particular spectrum is the recognition of this particular signal here, which appears like a 5 line signal. Normally this would be mistaken for a quintet, but then for a one hydrogen intensity and the doublet of six hydrogen intensity, this is if this is one hydrogen intensity this would correspond to six hydrogen intensity. And these two signals are mutually coupled you can tell from the spacing of the lines, this coupling constant is essentially say must the coupling constant here, so these are mutually coupled. The doublet of six hydrogen intensity can only be an isopropyl group.

So, if this an isopropyl group this would have been actually a 7 line pattern; unfortunately the first line and the last which are very less interns line or not seen in the spectrum that is why the spectrum looks like a quintet. So, one can easily misunderstand spectrum by considering this to be a quintet, but then that will not match with the integration of one hydrogen and six hydrogen. If it have to be one hydrogen, six hydrogen, the six hydrogen will split this into a seven line pattern, and this one hydrogen will split the dental group into a doublet which is the two line pattern here.

So, let us go to the aromatic region; in the aromatic region looks like there is a part of an a b quartet to which is chopped off from the rest of the spectrum. This is a roof effect kind of thing you can see unequal intensity distribution is what you have, and this integration here suggest that this per part of the integration is essentially say must this part of integration.

If this is for one hydrogen, this also should have been for one hydrogen. So, where is the coupling partner of this particular doublet it is sort of merged into the aromatic multiplets here; we can see here one line of the doublet the other line is merged with aromatic multiplets. If you take the integration over all integration from this point to this point here, this would correspond to essentially seven hydrogen intensity and this is six hydrogen intensity here. If you subtract this one hydrogen intensity, the rest would be a six hydrogen intensity of the six hydrogen; you cannot have a six hydrogen intensity in the aromatic region if it is a mono substituted aromatic compound, so that also seem to indicate that coupling partner of this particular doublet is merged along with aromatic hydrogens, and that is why the aromatic integration appears to be six hydrogen integration.

So, one can simply say that this is a multiplets between 7.3 and 7, we do not analyze this multiplets, it is a fairly complex multiplets. Expect recognize there are six hydrogen intensity corresponding to the merging of a one of the signals under this particular multiplets. Then a doublet is present with sixteen hertz again a larger coupling constant for the trans kind of a coupling.

So, there is a double bond in this molecule which corresponds to a trans double bond then you have isopropyl group. Now if you look at the septet of the isopropyl group, this should have been connected to a carbonyl or directly to an aromatic functional group, because the chemical shift value of about 2.9 or so, seem to suggest that this corresponds a COCH or aromatic CH kind of a substitution pattern is what is being present. Let us look at the carbon-13, carbon-13 the values are conveniently printed. So, I just took the values and sorted out the numbers on the right-hand side.

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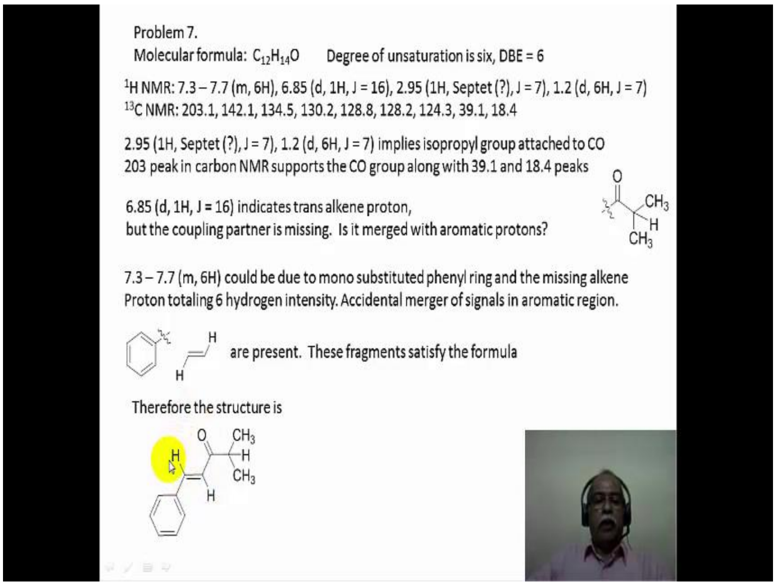

Problem 7.

Molecular formula: $C_{12}H_{14}O$ Degree of unsaturation is six, DBE = 6

^{1}H NMR: 7.3 – 7.7 (m, 6H), 6.85 (d, 1H, J = 16), 2.95 (1H, Septet (?), J = 7), 1.2 (d, 6H, J = 7)

^{13}C NMR: 203.1, 142.1, 134.5, 130.2, 128.8, 128.2, 124.3, 39.1, 18.4

2.95 (1H, Septet (?), J = 7), 1.2 (d, 6H, J = 7) implies isopropyl group attached to CO

203 peak in carbon NMR supports the CO group along with 39.1 and 18.4 peaks

6.85 (d, 1H, J = 16) indicates trans alkene proton,

but the coupling partner is missing. Is it merged with aromatic protons?

7.3 – 7.7 (m, 6H) could be due to mono substituted phenyl ring and the missing alkene Proton totaling 6 hydrogen intensity. Accidental merger of signals in aromatic region.

are present. These fragments satisfy the formula

Therefore the structure is

So, this is the data we extract from the spectrum. The degree of unsaturation for this molecule is six. And based on the isopropyl, based on the subset and the doublet we conclude that there is an isopropyl group. The chemicals shift value of 2.9 seems to indicate there is a carbon and functional group and that is collaborated with the carbon-13 spectrum a peak are appearing around 203 ppm, 203 ppm suggest that there is a carbonyl functional group. And the two gem dimethyl groups appear at 18.4 and this methylene hydrogen CH hydrogen carbon appears around 39.1 in the carbon-13 NMR spectrum. So, this data is consistent with and isopropyl ketone. Now 6.85 of 16 hertz coupling, it indicative of a trans alkene. So, 7.3 to 7.5 could only be a mono substituted aromatic ring with the missing alkene which is the coupling partner for this signal that is being present there is an accidental merger of the signals in the aromatic region.

So, these two fragments for identified from the data that is presented here. A trans disubstituted double bound which corresponds to this part of the double hydrogen is shown here. The other hydrogen is merged with aromatic system here. So, putting all these fragments together, you can arrive at play at the at this particular structure. This is a isopropyl phenyl ethenyl ketone is the structure of the compound. Now you can see the trans double bond corresponding to this particular double bound being a trans geometry, you have a 16-hertz coupling which satisfies. And this hydrogen at 6.85 to corresponds the alpha hydrogen not the beta hydrogen. The beta hydrogen will have a higher at chemical shift value and that is why it is merging with the aromatic signal. If you look at carefully in this NMR spectrum, this correspond to the alpha hydrogen of the alpha beta and unsaturated ketone this correspond to the beta hydrogen the part of the spectrum is seen here as doublet merging with aromatic signal here.

So, we solve the structure of this molecule also is a fairly simple molecule. The NMR patterned essentially implies this particular structured to be the structure correct structure for the data. So, what we have done in this particular tutorial session is looked at a very simple organic molecules, looked at the carbon-13 and proton data; try to interpret the data to the structural fragments which are a familiar in terms of the pattern recognition, in terms of the chemical shift value recognition and the coupling constant value recognition. Hope you understand the concept of logically deducing the structure from the given data fragment by fragment, and putting the fragments together at the end. Once the fragments are put together in the form of a molecule, you go back and check whether the spectral data is matching with the structure that we elucidate.

Thank you very much for your attention.