Application of Spectroscopic Methods in Molecular Structure Determination
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Lecture - 04
Nuclear Magnetic Resonance Spectroscopy
Principle and Application in Structure Elucidation

Hello. Welcome to module 4 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. In this module, we will continue with NMR spectroscopy, and we will actually see some NMR spectra of very simple organic compounds. We will try to interpret the spectrum of these compounds, spectrum of this compounds and see whether we can familiarize ourselves with the chemical shift and the coupling constant values. Molecular structure determination by NMR spectroscopy is all about pattern recognition. There are certain patterns which appear in the NMR spectrum. If one can recognize this pattern, and identify the structural element or structural feature that is responsible for the pattern then, it solves the problem of structure elucidation. Let us start with a very simple example.

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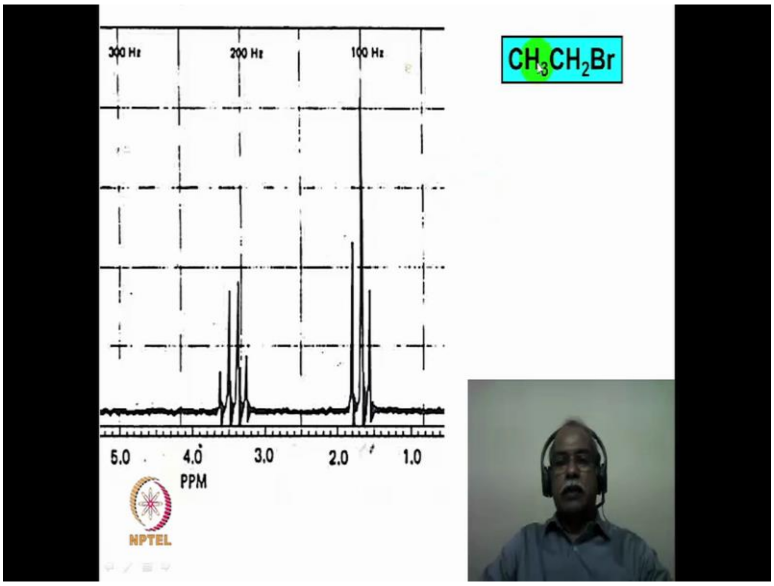

Ethyl bromide is what is shown here, the spectrum of ethyl bromide. Ethyl bromide contains a CH 3 and a CH 2 group. So, the CH 3 will be appearing as a triplet, because it will be split by the adjacent 2 hydrogens of the CH 2. So, this triplet is appearing in the region of 1.6 p p m or so; and, the CH 2 which has 3 hydrogens which are adjacent to it, will be split into a quartet. So, one observes a quartet around 3.5 p p m or so. Now, the CH 2 is directly attached to anelectro-negative bromine, and that is the reason the chemical shift value of the CH 2 is much higher than the chemical shift value of the CH 3. If one measures the intensity ratios of these 2, or the area under the peaks of these 2 multiplets, it would correspond to 2 is to 1, 2 is to 3, corresponding to the CH 2 and CH 3 groups. You also notice the pattern which is a quartet with an intensity ratio of 1 is to 3 is to 3 is to 1, and the triplet as 1 is to 2 is to 1. There are some distortions which are actually explained as a second order effect, which we will see at a much later stage.

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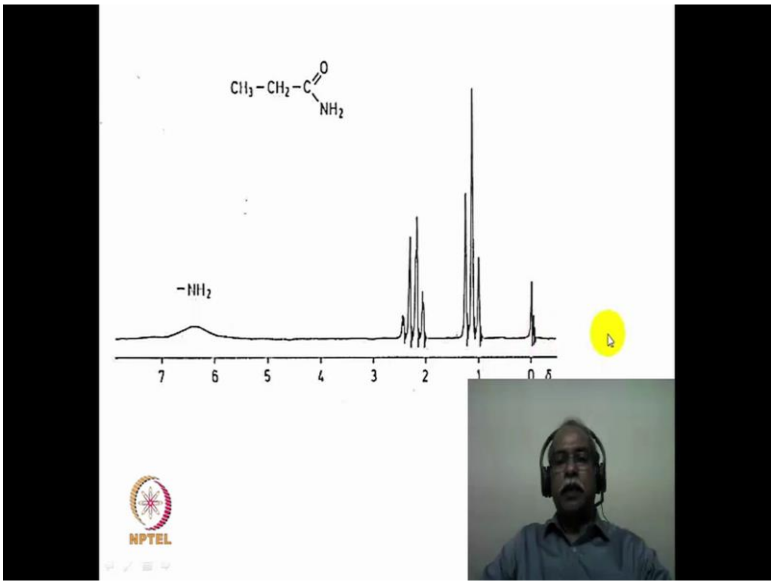

This is the spectrum of propionamide. The purpose of showing this spectrum of propionamide is to illustrate that, hydrogens which are NH 2 and OH would appear normally as broad peak in the NMR spectrum, because of their exchangeable nature. The chemical environment of the exchangeable nature of hydrogen is uncertain. So, as a result, there is some uncertainty associated with the chemical shift value of this hydrogen; that is why, they appear as broad signal here. In this particular case, the broadness may be due to another factor that, the hydrogens are attached to a nitrogen nucleus. Nitrogen is a quadrupolar nucleus. Quadrupolar nucleus also gives broadening effect in the NMR spectrum. The way to identify this to peak to be the NH 2 peak, is to do a deuterium exchange experiment.

In other words, if you take the sample, and add a drop of deuterium oxide and then, measure the NMR spectrum, the NH 2 hydrogens will be exchanged by deuterium to ND 2. As a result of that, the peak due to the NH 2 hydrogens will be completely lost after the deuterium exchange, during the experiment of deuterium D 2 O addition to the sample. Otherwise, this spectrum is fairly routine and simple. We have a ethyl group, which is recognized by this pattern of quartet and a triplet. Please notice that, the chemical shift value of the CH 2 here, which is adjacent to a carbonyl functional group, which is about 2.2 p p m. Anytime a CH 2, or CH 3 group is adjacent to a carbonyl functional group, this is the region in which the CH 2 or CH 3 adjacent to the carbonyl group would appear in the NMR spectrum.

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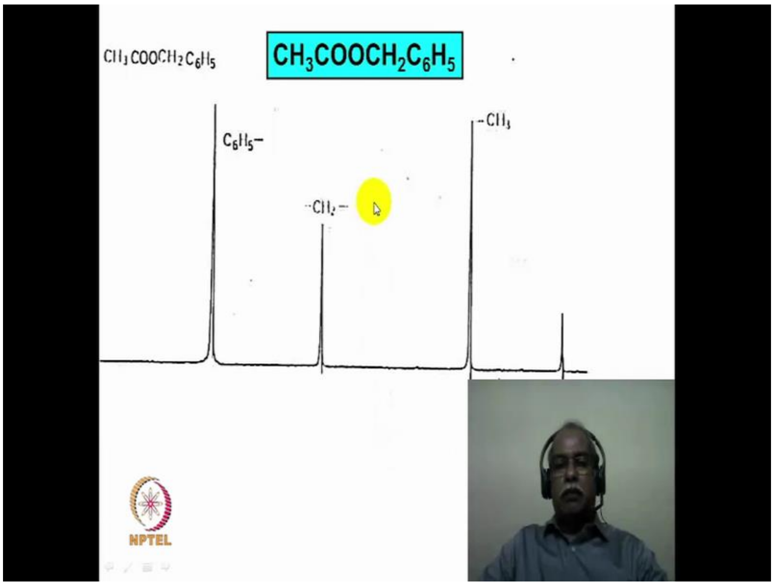

$CH_3COOCH_2C_6H_5$

This is a spectrum of benzyl acetate. It is a simple ester compound. We can see here, the phenyl hydrogens are appearing in the region of about 7.3 p p m; sorry, the chemical shift values are not given here. But, I will tell you that, this is corresponding to about 7.3 p p m and this CH 2 singlet corresponds to about 5.5 p p m or so; whereas, the CH 3 corresponds to about 2.1 p p m or so.

Now, the CH 3 does not have any partners to couple with; as a result, it appears as a singlet of 3 hydrogen intensity. Similarly, the CH 2 also does not have any partners which are adjacent hydrogens. So, it appears as a singlet around 5.5 p p m or so. The mono-substituted benzene, the phenyl derivative should have appeared as a multiplet, because the ortho, meta and para hydrogens are not chemically equivalent. They should have given 3 different chemical shift values; however, the CH 2 group is not a strongly perturbing group; it is not a strongly electron donating, or an electron withdrawing group. So, it is only a carbon based substituent; does not have much of electronic influence on the phenyl derivative. So, as a result of that, the ortho, meta and para hydrogens accidentally come in the same chemical shift region, appearing, what appears to be a singlet, for the case of the phenyl derivative.

Normally, a phenyl derivative with electron withdrawing group, or electron donating group, such as nitro group, or amino group, would appear as some multiplet in the region. Anytime, in the aromatic region of about 7 to 7.5 p p m, a multiplet is observed with 5 hydrogen intensity, the inference is that, it is a mono-substituted phenyl derivative. This is a spectrum of ethyl formate. The formyl group hydrogen, essentially, comes at a higher delta value of about 8.1 p p m in this particular case. This is because of the anisotropic effect of the carbonyl functional group, which pushes the chemical shift value all the way up to 8 p p m in this particular case. Otherwise, this spectrum is fairly simple; you can see here, this is an ethyl ester; the ethyl ester essentially appears as a quartet and a triplet.

Notice the chemical shift value of the CH 2, which is directly attached to a oxygen functional group. Whenever the CH 2 group is attached to an oxygen functional group in the form of an ether, it will be less than 4 p p m. If it is attached to an oxygen in the form an ester, it will be more than 4 p p m. In this case, it is about 4.1 p p m is the chemical shift value of the CH 2 that appears in the spectrum.

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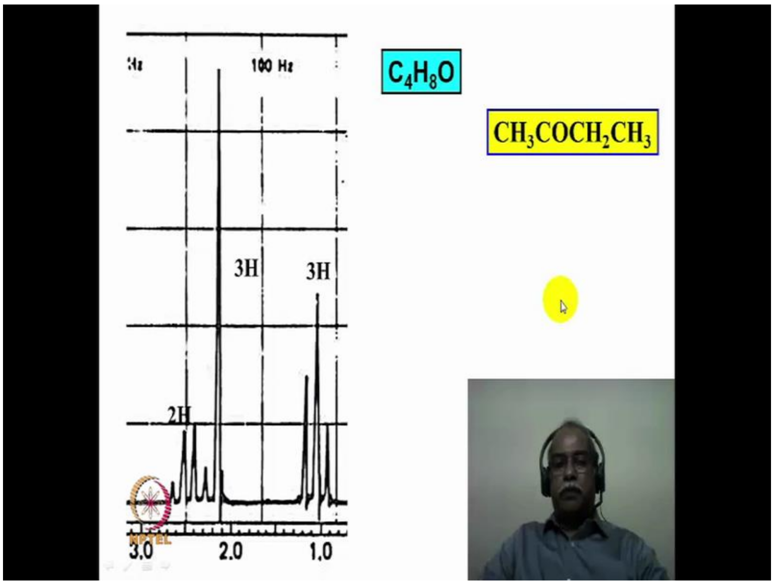

C_4H_8O

$CH_3COCH_2CH_3$

Let us try to solve a simple problem here. This is a compound with a molecular formula C 4 H 8 O. If you look at the molecular formula, it gives you an information regarding the unsaturation that is present in this compound. For a saturated molecular formula, this should have contained 10 hydrogen, but there are only 8 hydrogens in the molecular formula. So, the degree of unsaturation corresponds to 1. This is important information we will make use of, in the logical deduction of the structure of this particular compound.

Now, looking at the NMR spectrum, one obviously refers to the quartet and a triplet, and infers that, there is an ethyl group that is present here; and, looking at this singlet of 3 hydrogen intensity, one infers that, there is a methyl group present in this system. So, the compound, essentially, contains 1 methyl group and 1 ethyl group, and if one subtracts these fragments from the molecular formula, what we will be left with, is a C O functional group, which is a carbonyl functional group, and this is probably CH 3 C O CH 2 CH 3. In other words, it is ethyl methyl ketone is what we are referring to, or 2-butanone is what we are referring to.

Now, notice that, the CH 3 and the CH 2 which are adjacent to the carbonyl functional group, comes in the typical region between 2 to 2.5 p p m chemical shift value. You also notice that, there is no coupling between this CH 3 and the CH 2, because of the intervening carbonyl functional group, which acts as an insulator. So, normally, you do not see any kind of a coupling across the carbonyl functional group of the 2 hydrogens which are attached to the carbonyl functional group.

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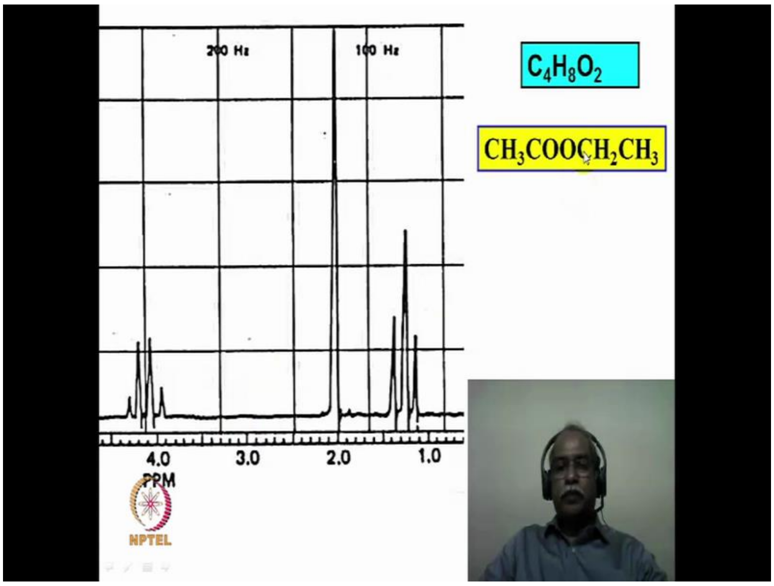

$C_4H_8O_2$

$CH_3COOCH_2CH_3$

This is, again another simple molecular formula, except this has one oxygen more than the earlier example. The earlier sample was C 4 H 8 O and this is C 4 H 8 O 2. Now, if you look at the spectral pattern, it looks similar to the spectral pattern we saw earlier, in the earlier example. The earlier example, we had a quartet, triplet and a singlet of intensity 2 is to 3 is to 3. Here also, we have a quartet, singlet and a triplet, and approximately, the intensity ratio, take it from me, it is about 2 is to 3 is to 3. So, this molecule also has an ethyl group and a methyl group, but then, it has one extra oxygen. So, most likely, instead of a ketone, this could be an ester.

How do we identify this to be an ester? Look at the chemical shift value of the CH 2 hydrogen. The CH 2 hydrogens come around 4.2 p p m. The earlier example, the CH 2 hydrogen which is adjacent to the carbonyl functional group came around 2.5 p p m. Now, because it is an ester type of a molecule, the C H 2 is attached directly to the oxygen, which in turn, is such as the carbonyl functional group. So, any time you see a quartet above 4 p p m, one can infer that, it is about ester functional group, ethyl ester functional group is what we, is being inferred from this quartet and the triplet in the NMR spectrum. So, this is, essentially, the spectrum of ethyl acetate, which is a very simple molecule.

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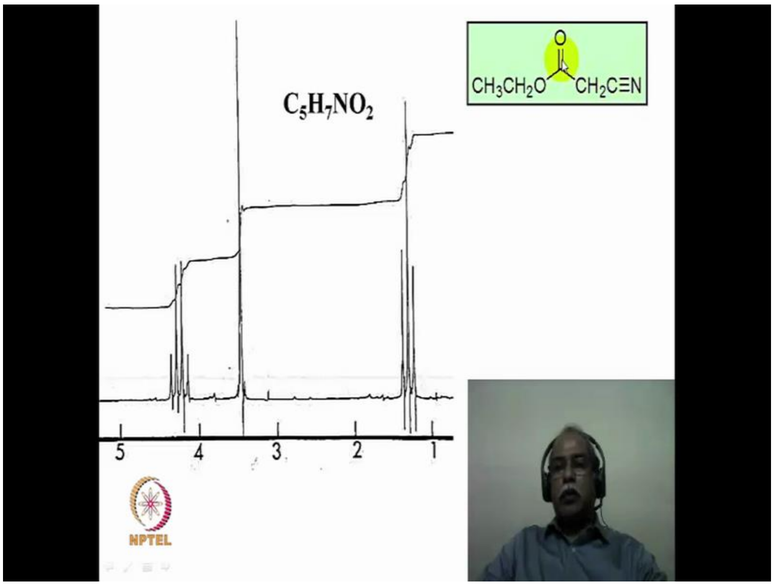

$C_5H_7NO_2$

Let us go into a little more complex problem. If you look at the molecular formula here, the molecular formula, saturated formula should have had 12 hydrogen. Now, nitrogen is trivalent. So, one has to subtract 1 hydrogen from the available hydrogen; instead of 7, it would become 6, because of the trivalent nature of a oxygen. So, instead of 12 hydrogen, this molecule has equivalence of about 6 hydrogen only; that means, the degree of unsaturation of this particular molecule is 3.

Now, look at this pattern; essentially, same as the previous pattern that you saw, except that, you have a integration difference here. Now, what is this integration? The line that is shown here, essentially, represents the area under each of this peak. This height, starting from here, this particular height, is what is referred to as the area under this peak, integration under this peak, and starting from this base, up to this point, this height is, essentially, the integration of this particular hydrogens; and this height is integration of this particular multiplets signal.

If you look at, carefully, this integration height, and this integration heights are, essentially, same. This is because of a CH 2 hydrogen, because it is a quartet. So, this is also most likely a CH 2 type of a functional group. See that, the CH 2, actually, the multiplet quartet comes above 4 p p m. So, once again, it is most likely an ester functional group. So, it is an ethyl ester. So, what we have identified as structural feature is COO C2 H5 and a CH 2 group.

Now, if you subtract the COO C2 H5 and a CH 2 group from the molecular formula, what will be left with, is the cyano functional group. So, if you look at the CH 2, this should be di-substituted; CH 2, obviously, had to be a di-substituted derivative. So, one substituent probably is a COO C2 H5; the other substituent probably is a cyano functional group. Indeed, the molecule is, actually, ethyl cyano acetate is the molecule. Now, having got the structure, one can go back and interpret this molecule. The O CH 2 CH 3 appears as a ethyl group signature, which is a quartet above 4 p p m, and a triplet around 1.5 p p m or so. And, this CH 2, it is a di-substituted CH 2; one of the substituent is a cyano functional group; the other substituent is a carbonyl functional group. So, that appears as singlet around 3.5 p p m or so.

If you look at the degree of unsaturation, which turns out to be 3 for this molecular formula, you can see there are 2 pi bonds of the cyano functional group, and 1 pi bond of the carbonyl functional group, contributes to the degree of unsaturation, which is 3 in this molecule.

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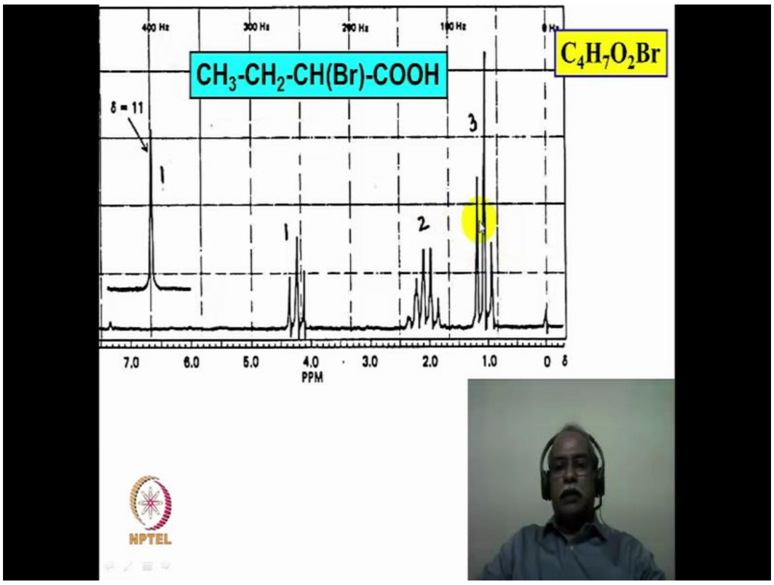

CH_3-CH_2-CH(Br)-COOH

$C_4H_7O_2Br$

This is an interesting example of a carboxylic acid. One can readily identify this as a carboxylic acid, because of this peak here. Actually, the spectrum is recorded only from zero to 7 p p m; whatever was above the 7 p p m is folded over, and recorded in the same region; but it is indicated very clearly that, the delta value of this particular hydrogen is 11. Such a very highly deshielded hydrogen could be only due to carboxylic acid. So, the carboxylic acid hydrogen of 1 integration, 1 hydrogen integration would correspond to COOH. Then, you have a CH functional group, because it is a 1 hydrogen intensity; a CH2 functional group, because of 2 hydrogen intensity, and a CH3 functional group, which is because of the 3-hydrogen intensity of this.

The multiplicity here is a triplet; the multiplicity here is a quintet, and the multiplicity here, again is a triplet. So, the compound is probably CH3 CH2 CH, which is di-substituted; one of the substituent could be bromine, from the molecular formula you can see that. The other substituent could be COOH. So, it is a fairly simple molecule, alpha bromo butyric acid is the molecule.

Now, having got the structure, we can go back and interpret the spectrum. The COOH appears as a singlet; this CH, which has adjacent 2 hydrogens, appears as a triplet, because it is di-subsituted, connected to both electro-negative bromine, as well as electron withdrawing COOH group; it comes around 4.3 p p m or so. This CH2, which has adjacent 4 hydrogen, there are 3 hydrogens on the CH3, and 1 hydrogen on this CH.

Accidentally, because of the free rotation of the carbon-carbon bonds, the J value of this hydrogen to the CH2, and these 3 hydrogens to the CH2 will be essentially identical. So, it is as if, you have 5 hydrogens, sorry, 4 hydrogens adjacent to the CH2. The molecule is, the CH2 group is split into a quintet. So, you can see here, a quintet; 1, 2, 3, 4, 5, 5 line intensity is what you see in this particular signal. Terminal CH 3 is split by the CH 2, and it appears as a triplet around 1.2 p p m or so.

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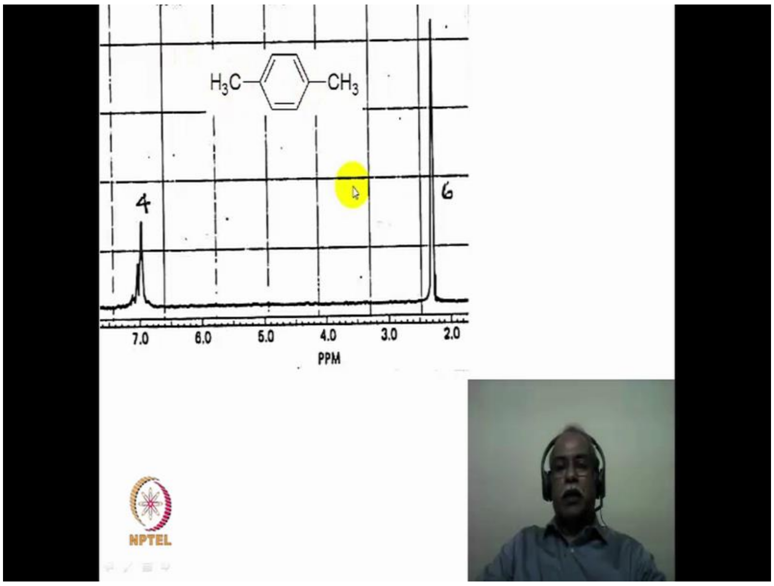

This is a spectrum of a simple hydrocarbon molecule, namely para xylene. Para xylene is highly symmetrical. It has a plane of symmetry, vertical plane of symmetry, as well as a horizontal plane of symmetry. Therefore, the 4 hydrogens of the aromatic unit are identical chemically. So, it appears as a singlet of 4 hydrogen intensity. The 2 methyl groups are also equivalent, chemically equivalent. So, a single peak of 6 hydrogen intensity is what is seen for this molecule. Fairly simple spectrum to interpret.

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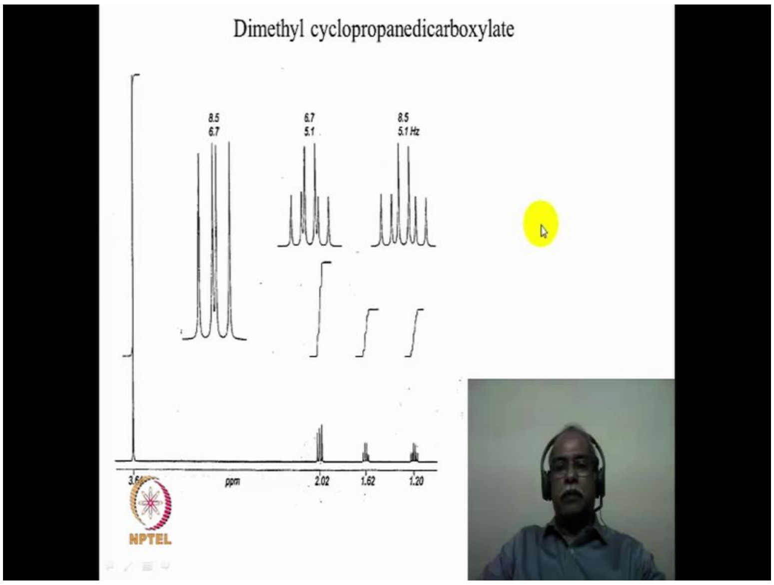
Dimethyl cyclopropanedicarboxylate

Now, let us ask ourself a question, and try to solve this problem. This is the spectrum of dimethyl cyclopropanedicarboxylate, but which isomer of dimethyl cyclopropane's dicarboxylate, is not given in the question; that is the question we would like to address in this particular thing. What is important to notice in this spectrum is that, there are 4 different, chemically different hydrogens in this molecule.

There are 4 chemical shift values associated with this spectrum; one corresponding to 3.64, which appears to be a singlet here; and another one, corresponding to 2.02, which appears to be a multiplet; then, one more signal around 1.62, which appears to be a multiplet; and, another signal at 1.2, which appears to be a multiplet. Since the multiplicities are not clearly seen in the spectrum here, the expansion is shown.

In other words, this is a multiplicity of this particular signal; and, this is a multiplicity of this signal, here; and finally, this multiplicity corresponds to the signal which is around 1.2 p p m. We will come back to the multiplicity a little later, because, it is not important to identify the multiplicity, at this point of time, to solve this problem.

What we need to identify is, see how many isomers are first of all possible for the dimethyl cyclopropane dicarboxylate; of the possible isomers, which one will have 4 different types of hydrogen, in terms of the 4-different chemical shift value, that it offers, in this particular spectrum.

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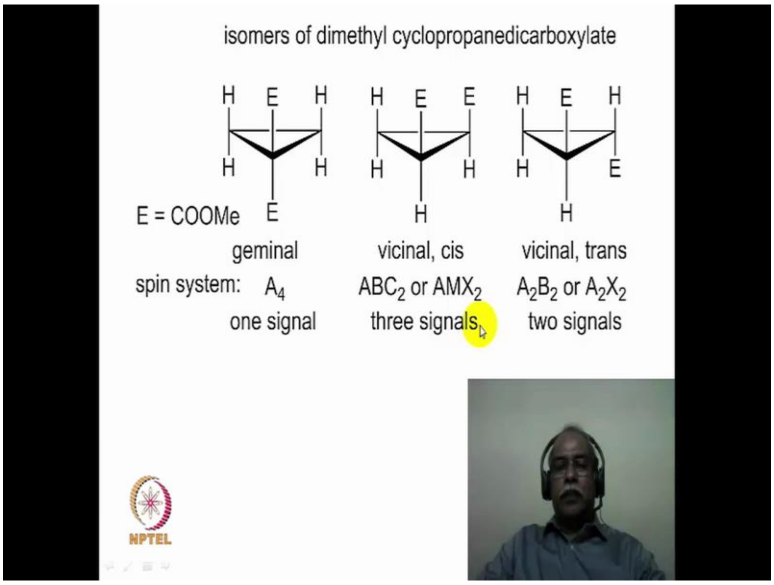
isomers of dimethyl cyclopropanedicarboxylate

E = COOMe

	geminal	vicinal, cis	vicinal, trans
spin system:	A_4	ABC_2 or AMX_2	A_2B_2 or A_2X_2
	one signal	three signals	two signals

Now, these are the possible isomers of dimethyl ester of di cyclopropane dicarboxylate. Now, the E group is, essentially, COOMe group; just for convenience sake, I have represented the COOMe as the E group here. So, this is a geminal di-ester; this is a 1, 2, cis di-ester, and this is a 1, 2, trans di-ester. These are the 3 different types of isomers that is possible for the dimethyl cyclopropanedicarboxylate.

Now, if you take the geminal di-ester, and look at the number of spins that you have, these are the 4 hydrogens in the molecule. So, we need to identify, whether all these 4 hydrogens are same, or different. From the symmetry perspective, a symmetry point of view, if you look at, the molecule has a plane of symmetry passing through this particular carbon, and bisecting this particular carbon-carbon bond, and such a plane of symmetry would put this hydrogen, and this hydrogen into mirror image relationship. So, the 4 hydrogens are essentially identical in this molecule, in their chemical environment.

From the substitution criterion also, one can find out, irrespective of whichever hydrogen is substituted by the chlorine, or a bromine, you will essentially end up with the same compound, which is a bromo derivative of the dimethyl cyclopropane. So, one can either use a symmetry criterion, or substitution criterion, to come to the conclusion that, this molecule is of the type A 4; in other words, all the 4 hydrogens are identical, chemically equivalent in nature. Therefore, this cannot be responsible for the spectrum we saw in this; this spectrum is not due to this particular compound, because, this would essentially offer a singlet, for all the 4 hydrogen, because, they are chemically identical hydrogens. Now, come to this particular example; this is a cis vicinal dimethyl cyclopropanedicarboxylate.

Now, this molecule also has a plane of symmetry, passing through this particular carbon, and bisecting the carbon-carbon bond bearing the ester functional group. So, that puts these 2 hydrogens to be identical with respect to each other; in other words, these 2 hydrogens are chemically equivalent with respect to each other.

However, if we take these 2 hydrogens, here, these 2 hydrogens are not chemically equivalent, because one of the hydrogen is cis to the ester, 2 esters; the other hydrogen is trans to the 2 esters. So, geometrical relationship between these 2 hydrogens and the ester functional group are very different. Therefore, this would correspond to either an ABC 2 type of a system; in other words, this is A; this is B; and these 2 are the same. So, it is C2. It could be either an ABC 2, or an AMX 2; ABC 2 or AMX 2, depending upon what is the difference in the chemical shift value between the various hydrogens in the molecule. If the chemical shift differences are very close, then, you would call it as a ABC system; if the chemical shift differences are very vast, then, you would call it as AMX system; giving alphabets, which are different alphabets, for example, for the vastly different alphabets compared to ABC system.

So, this would essentially give 4 signal; 1 signal because of the methyl group of the ester; 1 signal because of this CH 2, the 2 hydrogens which are the ester, connected to the ester carbon; and, this CH 2, which are the 2 hydrogens are different from each other. So, this would, essentially, give 4 signals, including the ester signal. And, if you look at this particular compound, here, there is no plane of symmetry; however, there is a C2 axis of symmetry passing through this carbon, and passing through the middle of the carbon-carbon bond, bearing the ester functional group. So, if you look at this molecule, these 2 hydrogens are C2 symmetric with respect to each other, and these 2 hydrogens are also C2 symmetric with respect to each other; that makes these 2 hydrogens equivalent in terms of the chemical equivalence; similarly, these 2 hydrogens are also chemically equivalent, in this molecule. So, at the best, one can describe this to be a A2B2 or a A2X2 system. So, it would give only 2 signals of the cyclopropyl carbons and 1 signal corresponding to the methyl signal. In all the 3 isomers, the methyl of the ester would appear only as a singlet, because ester groups are identical in all the 3 structures of this isomers.

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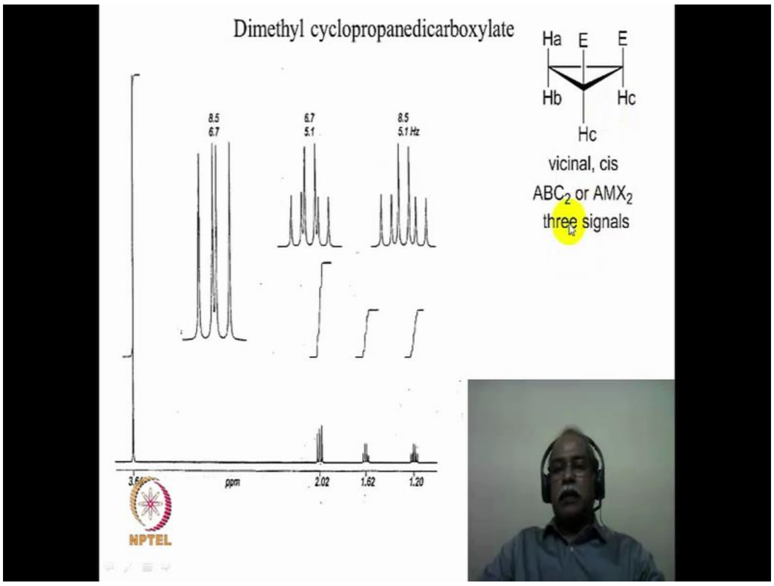
Dimethyl cyclopropanedicarboxylate

vicinal, cis

ABC_2 or AMX_2

three signals

So, the conclusion is that, it is the cis isomer which is responsible for the, the 3 signals that you are seeing as multiplets, is essentially due to this particular isomer. Now, let us try to interpret the multiplicity of this particular spectrum.

Now, let us take the example of Hc. Hc is 2 hydrogens, which are attached to a carbon bearing the ester functional group. Most likely, these are the 2 hydrogens which will come at higher delta value of around 2 p p m, or so, which is having a multiplicity of doublet of a doublet; you can see 4 line pattern here. The chemical shift, the value is 2.2. The coupling constant values are already given here; this is 8.5 and 6.7. So, this corresponds to 8.5 and this corresponds to 6.7 or so, in terms of the 2 coupling that it can have. So, what is this doublet of a doublet due to? These 2 hydrogens, in the absence of any coupling partner, would appear as a singlet, because they are chemically equivalent. Then, they can couple with the trans hydrogen, which is a Ha hydrogen. So, the Jac is 1 coupling constant, and Jbc is another coupling constant. So, Ha will split the signal of these 2 hydrogens into a doublet, and Hb will in turn split the doublet into a further doublet so, causing a appearance of a doublet of a doublet for the Hc. So, this is explained easily by Ha splitting it into a doublet, and then, Hb further splitting it into

a doublet. So, doublet of a doublet is the signal that you see for this. Now, let us take the example Ha. Ha is trans or in the other words, the dihedral angle between Ha and Hc is about 180 degree; this is anti, or trans with respect to each other. So, that is probably having a higher J value, compared to the cis coupling, which is the Hb Hc coupling, which would probably be around 6.7 p p m, or so.

Now, the multiplicities of Ha; Ha is probably the next one, having the higher delta value of about 1.62 p p m, or so, and if we look at the multiplicity of this, it would be split into a doublet by H b, and it will be split into a triplet, further into a triplet, by these 2 hydrogens, which are Hc's. So, Ha is split into a doublet by Hb, which is further split into a triplet by Hc. So, it should be a doublet of a triplet; doublet of a triplet should have A6 lines; you can actually see, 1, 2, 3, this is 1 triplet; another one is this one, this one and this one; you can see overlapping doublet of a triplet in the spectrum.

Similarly, if we look at Hb also, it will be split into a doublet by Ha, and it will be further split into a triplet by Hc. So, again, another doublet of a triplet is what should be seen. So, you can again, once again, see 2 overlapping doublet of a triplet is in this particular case. So, Ha appears as a doublet of a triplet; Hb appears as a doublet of a triplet; Hc itself appears as a doublet of a doublet; the 2 ester functional group which are COOMe, appears as a singlet around 3.64 p p m, as intensity, highly intense signal here, because of the 6 hydrogen intensity. So, the integration wise also, if you look at the Hc, which are 2 hydrogen, the integration is twice as big as the Ha and the Hb. So, this is 1 hydrogen intensity; 1 hydrogen intensity; 2 hydrogen intensity, and this is 6 hydrogen intensity, which satisfies the spectral pattern.

Therefore, out of the 3 possible isomers, it is possible to easily distinguish them based on the NMR pattern. Remember, we picked this isomer, not based on the multiplicity pattern; we simply picked this isomer because, this would alone given the 3 signals for the cyclopropyl hydrogen. The other two will not give the 3 signals; one gives a single signals the other one gives 2 signals, for example, that many number of chemically non equivalent hydrogens are there. This is the only isomer which has 3 different chemically nonequivalent hydrogens, which is corresponding to the spectrum that one sees, and hence, the assignment is a correct assignment.

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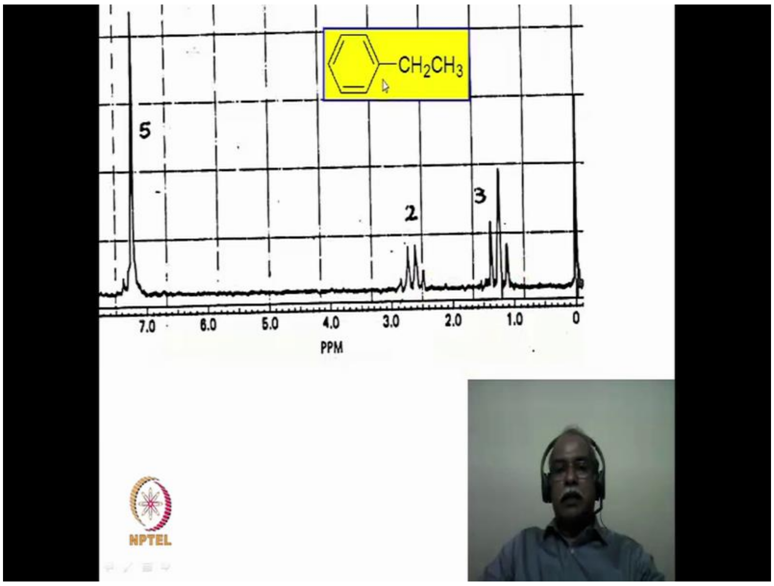

Now, let us identify this particular compound. This is a fairly simple compound. You can see here, 5 hydrogen intensity on the aromatic region of a signal that you see, would correspond to a mono-substituted phenyl derivative; then a quartet, and a triplet is seen. So, this should be ethyl groups. So, mostly likely, the compound is ethyl benzene, and that is what is seen in this particular spectrum. This is a spectrum of ethyl benzene.

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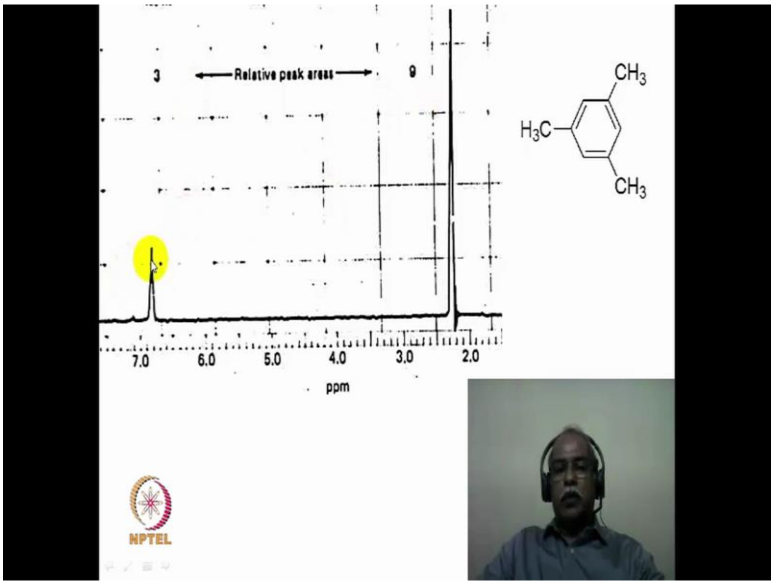

This is a spectrum of mesitylene, which is 1, 3, 5 trimethylbenzene. 1, 3, 5 trimethylbenzene is a c3 symmetric molecule. So, all the 3 methyl groups are identical. So, the 9-hydrogen intensity that you see here for the singlet, corresponds to this 3 methyl groups; and, there are 3 hydrogens in the aromatic ring, which are also chemically identical; and, that appears as a singlet of 3 hydrogen intensity. So, you have a 1 is to 3 ratio of the intensity; area under this peak is about one third of the area under this peak, corresponding to mesitylene structure.

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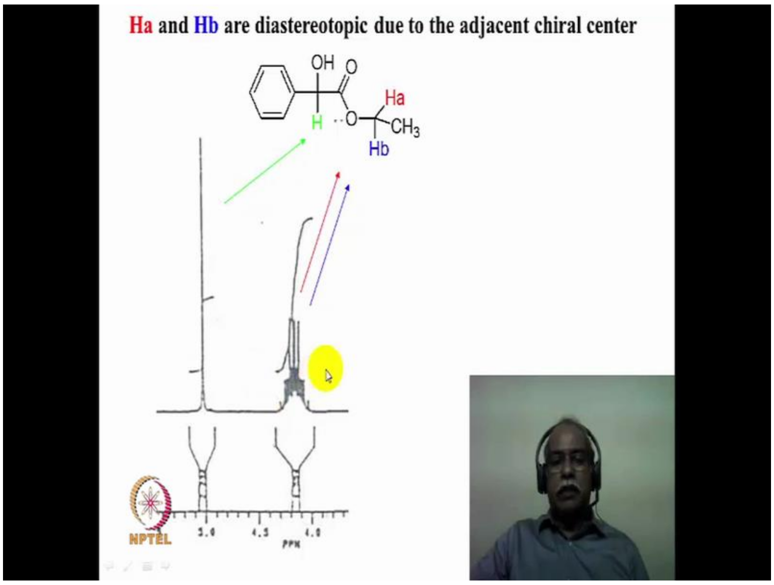

Ha and Hb are diastereotopic due to the adjacent chiral center

Now, let us consider this example, which is an illustration of diastereotopic hydrogen, adjacent to a chiral center. This is actually, ethyl mandelate is the compound; mandelic acid ethyl ester is what is shown here. This particular center is a chiral center in mandelic acid. As a result of that, this 2 hydrogens of the methylene, of the ethyl group here, the CH 2 of the ethyl group, the 2 hydrogens are diastereotopic in nature. How do we know that it is diastereotopic in nature? If it is a simple ethyl group, you would always observe a quartet and a triplet for the signals of the CH 2 and the CH 3, like we saw in the earlier examples; however, in this particular case, the CH 3 does appear as a triplet; however, the CH 2 is a fairly, a complex multiplet is what is seen here.

Now, this particular hydrogen, which is a benzylic hydrogen, and also attached to 2 electron withdrawing functional group, comes around 5 p p m or 5.1 p p m, or so, as 1 hydrogen intensity. Now, the CH 2, you can see is a fairly complex multiplicities is what is seen. In the next slide the expansion of this particular region is shown.

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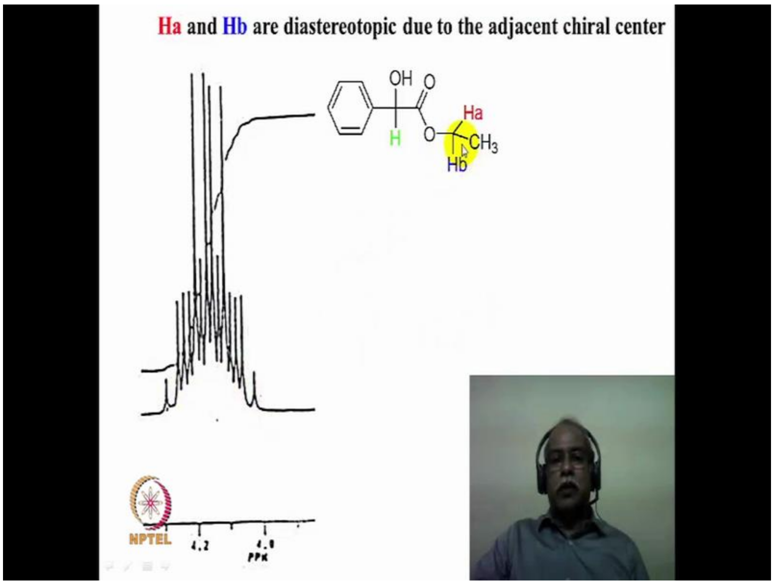

Ha and Hb are diastereotopic due to the adjacent chiral center

And, this is the expansion of the region corresponding to the Ha and Hb. Both Ha and Hb come in the same chemical shift region. If the Ha and H b are truly diastereotopic in nature, then Ha will split Hb into a doublet. Similarly, Hb will also Ha into a doublet. So, what you should see is, A4 line pattern for the Ha and the Hb. This 4 line pattern will be further split into a quartet, because of the adjacent 3 hydrogens of the methyl group. So, essentially, one should see a quartet of a doublet of a doublet, which would be 16 line pattern.

If we count here, starting from here, this is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13; there are 14 signals, that are, 14 lines are seen in this particular case; out of the 14, it should have been a 16 line pattern; out of that, 2 lines are accidentally merging with each other, resulting in the overlap of the 2 signals, reducing the number of signals seen to be 14. So, this is actually, an example of a diastereotopic hydrogen being split with each other; the geminal splitting is what is responsible for the multiplet. So, the Ha and Hb appear as a doublet of a doublet, which is further split into a CH 3 group, into a quartet. So, doublet of a doublet of a quartet is, what is actually seen for the ethyl group. So, this is an example of a diastereotopic hydrogen, splitting itself, each other.

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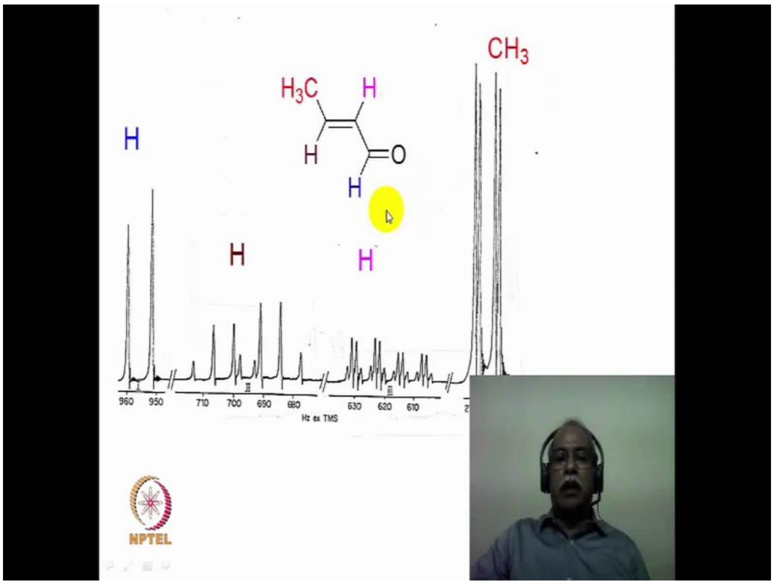

Now, let us take the example of crotonaldehyde. In this particular example, the hydrogens are color coded for convenience. If you take the aldehyde hydrogen, which is this particular hydrogen, that comes around 9.5 p p m, or so. This is a 100 mega hertz NMR spectrum. So, this is expressed in hertz. So, if we just divide it by 100, you will get the parts per million. This is about 9.55 p p m is the chemical shift value of the blue hydrogen, which is aldehyde hydrogen, which is shown here, of 1 hydrogen intensity. This has an adjacent vicinal hydrogen, which is this magenta hydrogen. So, it undergoes a spin-spin interaction with the magenta hydrogen, and as a result of that, it is about, doublet multiplicity is what is seen here.

Now, if you take the alpha hydrogen and the beta hydrogen, namely, the magenta hydrogen and the brown hydrogen, because of the electron withdrawing nature of the carbonyl functional group, and the resonance that is associated with the double bond being conjugated with the carbonyl functional group, this would be an electron deficient carbon; the beta carbon is always an electron deficient carbon in alpha-beta unsaturated system. So, electron deficient carbon bearing the hydrogen will have less electron density. So, between these two hydrogen this will have a higher delta value, compared to this particular hydrogen. So, the higher delta value, this comes around 7.7 p p m, or so, in terms of the chemical shift value.

What would be the multiplicity of this hydrogen? This has a adjacent hydrogen which is a trans hydrogen. This trans hydrogen will split this into a doublet. So, you do get a doublet, and this would, doublet is further split into a quartet.

So, what you should see, is a doublet of a quartet. So, what you should see is a 8 line pattern; start counting from here, 1, 2, 3, 4, 5, 6, 7, 8. What you are seeing is a overlap quartet; you can see 1 quartet, signal number 1, signal number 2, signal number 3 and signal number 5 corresponds to one quartet; signal number 4, signal number 6, 7 and 8 corresponds to another quartet. So, overlapping quartet of a doublet is what is seen for the multiplicity of this hydrogen, which is the brown hydrogen.

In the case of magenta hydrogen, it is little more complex, because, it has 2 coupling partners; one trans coupling partner; the other one is a vicinal coupling partner. So, this will be split into a doublet by this, and further doublet, by this blue hydrogen. So, this would be a doublet of a doublet. Further, it will split by the allylic hydrogen, which is the CH 3 hydrogen, into a quartet. So, doublet of a doublet of a quartet is, what you should see. In fact, 16 line pattern is what you should see. You can actually see 2 sets of quartet; one set of quartets here, another set of quartets here. So, the 4 quartets are essentially seen as a doublet of a doublet, which will give 4 lines, and 4 lines are further split into a quartet by a CH 3 functional group.

So, this is essentially, the spectral feature of the magenta hydrogen, in terms of the multiplicity pattern of the hydrogen. Now finally, let us come to the CH 3; CH 3 is coupled to both the geminal hydrogen, sorry, the vicinal hydrogen, which is this brown hydrogen, as well as the allylic hydrogen, which is the magenta hydrogen. So, it will be split by brown hydrogen into a doublet; further split by the magenta hydrogen into a doublet. So, it should see a doublet of a doublet; the 4 line pattern that you see for methyl group, is essentially a doublet of a doublet pattern, is what you are seeing in this particular molecular.

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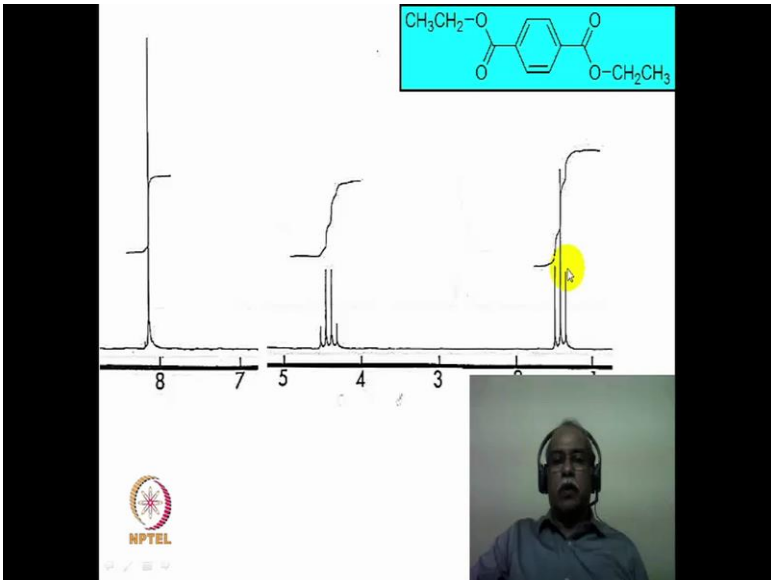

Now, this is very similar to the para xylene molecule. It is a symmetrically di-substituted derivative. The 2 ethyl groups are identical. So, it gives only 1 set of signal, 1 quartet and 1 triplet for both the ethyl groups. So, if we look at the integration intensity here, there are, you take the height of this particular integration, and the height of this integration, and height of this integration, this will be exactly 2 is to 2 is to 3, corresponding to 2 of the CH 2, 2 of the aromatic hydrogen, and 3 of the methyl group hydrogens.

So, although there is, there are 2 methylene group, it appears as a single quartet, because of the chemical identity; these 2 CH 2s are chemically identical, because of the symmetry of this molecule. So, you see only 1 quartet and 1 triplet for both the ethyl groups. Of course, the aromatic ring is a highly symmetrically substituted aromatic rings. So, all the 4 hydrogens are chemically identical, and it just gives you a singlet. So, the diethyl terephthalate molecule gives, essentially, a very simple spectrum of a quartet, triplet and a singlet, corresponding to the CH 2, CH 3, and the aromatic hydrogens of the molecule. Now, let us see what happens, if you make the ortho isomer.

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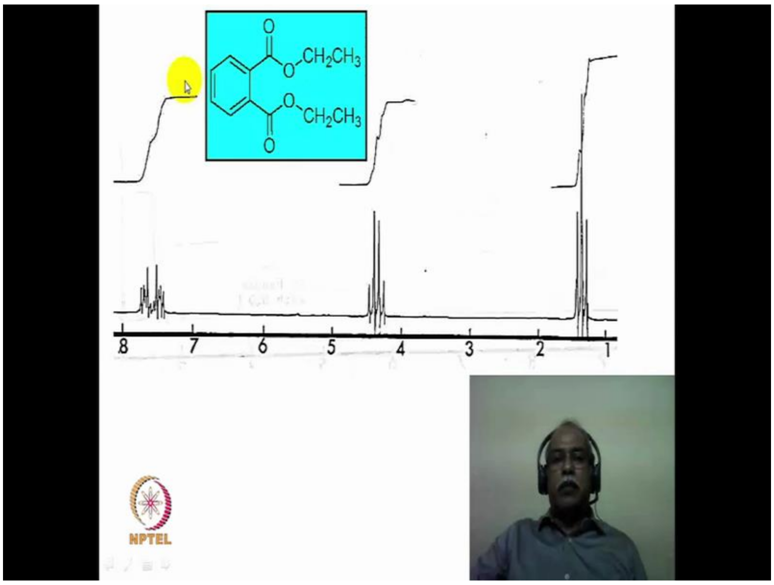

In other words, instead of terephthalate, if you just take phthalate; this molecule is less symmetrical, compared to the terephthalate. This has only 1 plane of symmetry, instead of 2 planes of symmetry. So, if you look at the aromatic hydrogen, there are 2 sets of aromatic, chemically non-equivalent hydrogen; one set corresponds to the one adjacent to the ester functional group; the other one corresponds to meta to the ester functional groups. So, these 2 hydrogens are chemically equivalent, and these 2 hydrogens are also chemically equivalent, but, they are chemically distinct from each other. So, you can see, a complex multiplet pattern is what is seen here, because the spin system is AA prime BB prime. So, this is a 2 spin, it is actually a 4 spin system; 2 chemically equivalent, but 4 magnetically non-equivalent spins is what we are having; that is why, you get a complex.

We will deal with this complex situations a little later. For the time being, let us come to the conclusion that, the more symmetrical the structure is, the NMR pattern is much simpler, compared to a less symmetrical structure will lead to more complex NMR spectrum. In this particular isomer also, the ortho isomer also, the 2 ethyl groups are identical, in terms of their chemical nature. So, it, essentially, gives 1 set of quartet and a triplet, for the 2 ethyl groups of this molecule. The integration, again, would be 2 is to 2 is to 3 is the integration, which is actually, 4 is to 4 is to 6, in terms of the number of hydrogens that you have in this molecule.

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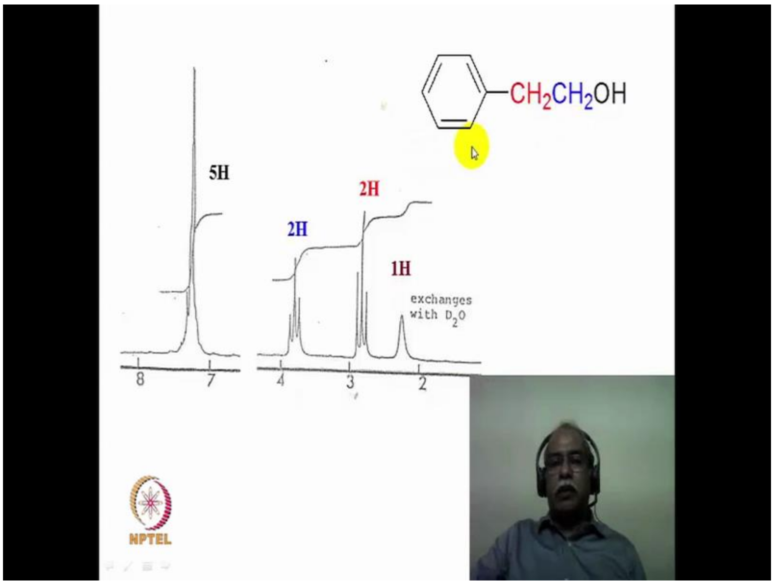

Now, if you take this simple molecule, this is a mono-substituted benzene derivative. So, in the aromatic region, you have signals between 7 to 7.5 p p m as 5 hydrogen intensity. And, the CH 2, which is a red CH 2, which is a benzylic CH 2, comes around 2.8 or 2.9 p p m; and, this CH 2, which is attached to oxygen, comes more than 3 p p m. We can see the difference between the chemical shift values of these 2 types of methylene. So, this methylene is a triplet because, of adjacent 2 hydrogen.

Similarly, this is methylene is also a triplet, because of the adjacent 2 hydrogen. So, 2 triplets are seen for this molecule. This methylene hydrogen is, the methylene carbon is also attached to an oxygen; that is why, the chemical shift value of this, is much higher than the chemical shift value of the benzylic hydrogen. Finally, the OH hydrogen is a D 2 O exchangeable hydrogen. So, it appears as a broad signal around 2.2 p p m. This can again be identified by deuterium exchange experiment, by adding a D 2 O; upon adding D 2 O, this particular signal will vanish, indicating that, this is an exchangeable hydrogen.

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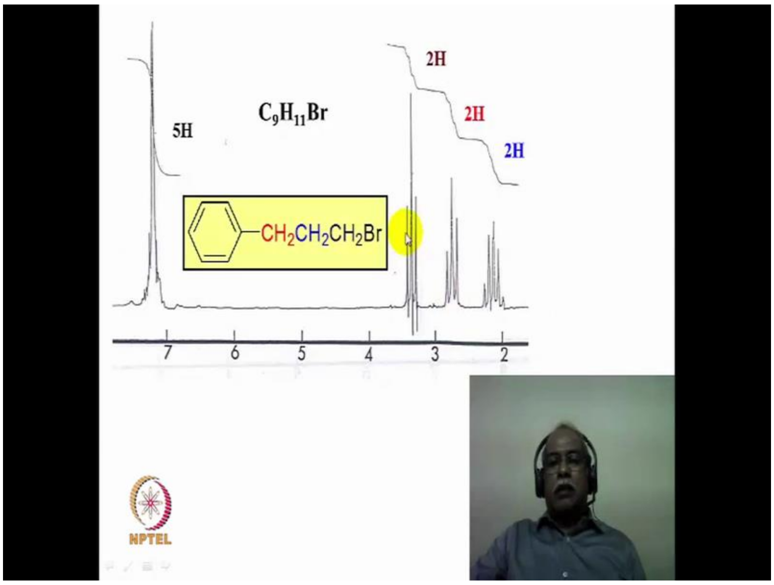

This is a molecule with CH 2 CH 2 CH 2 Br. So, that means, this CH 2, which is the blue CH 2, has 4 coupling partners. So, it should be a quintet, and you do see a quintet here; 1, 2, 3, 4, 5 line intensity is what you are seeing here. The other CH 2 simply appears as a triplet; this is a triplet because of the 2 neighboring hydrogen.

This is also a triplet because of the 2 neighboring hydrogens. The 2 triplets are seen. Chemical shift-wise, the one that is attached to the bromine has the highest chemical shift value, around 3.5 p p m; the one attached to the benzylic will be the next one, which is around 2.8, or 2.9 p p m. Finally, this one, which is flanked between the 2 CH 2s will be the least chemical shift value, around 2 p p m, r so, is what is seen. The aromatics signal, you can see 5 hydrogen intensity of multiplet is what is seen here, in this particular spectrum.

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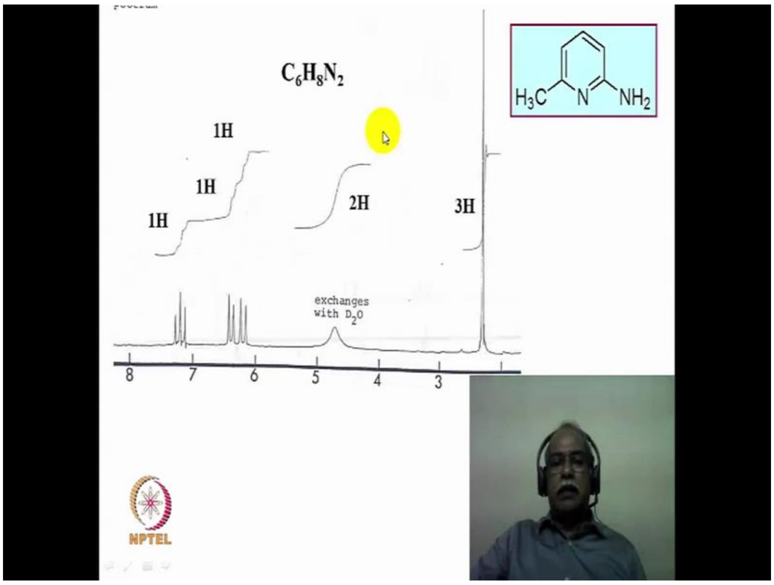

Let us take this particular example. This is a pyridine derivative. Now, the pyridine derivative, you can see here, this is a amino-substituted pyridine derivative. All the 3 hydrogens in the aromatic ring are non-equivalent in nature, chemically, they are non-equivalent in nature. So, if you take this particular hydrogen, it will be split into a doublet by this ortho hydrogen, another doublet into an ortho hydrogen, which is this particular hydrogen. So, they should actually appear as a doublet of a doublet, or a triplet, if the ortho coupling happens to be identical.

In fact, the ortho couplings are nearly identical. So, this hydrogen, which is in the fourth position essentially, appears as a triplet of 1 hydrogen intensity. And, this hydrogen and this hydrogen essentially, appear as a doublet, and a doublet. So, you see 2 doublets also for the 2 types of 3 and 5 hydrogens; 3 position and 5 position hydrogens come in this region as a doublet each. Finally, the NH 2 appears as a broad signal.

We have already seen NH 2 as a broad signal in the propionamide; it is a very similar case. It is D 2 O exchangeable, because, it is a exchangeable hydrogen. Finally, the CH 3 appears as a singlet in the spectrum, which is shown here. So, what we have seen in this module is, a number of proton NMR spectra and the interpretation of the proton NMR spectra, to make yourself familiarize with the chemical shift values and coupling constant values. We still have not seen an example where, how to calculate the chemical shift and the coupling constant value from this spectrum, which we will see in the next module.

Thank you very much.