Introductory Organic Chemistry - II
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Lecture 03
Essentials of NMR Spectroscopy - Part 2

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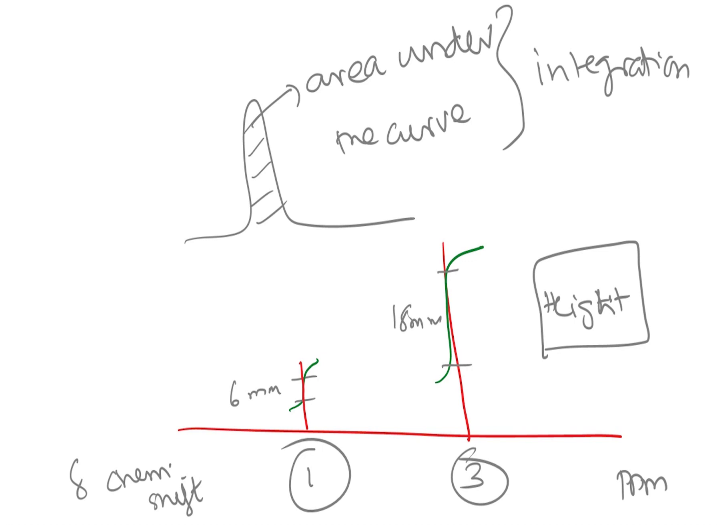

So, now, the next concept that you need to understand is actually Integration. So, normally when you look at a curve. So, let us take any curve of the shape. If you look at mathematics, what happens is that the area under the curve is very important, that is the area under the curve is very important and the area under the curve can be determined by integration.

So, again I will not go into too many details, but this area under the curve is useful in terms of when you want to quantify. So, in NMR spectroscopy, what we normally see are extremely quite sharp peaks. So, what we normally see are very sharp peaks and so, therefore, what is useful to know is that when you integrate it, integration is represented like this and when you integrate it the height of these peaks, so, the height of these peaks become important.

So again, we can look through this in more detail in our later course. But let us say, this height is 6 mm and this is 18 mm. So now, what we can say is that the ratio of the peak is 1:3. So again, remember this is a chemical shift, which is also represented as delta and the unit is ppm. So, this ratio is 3 to 1.

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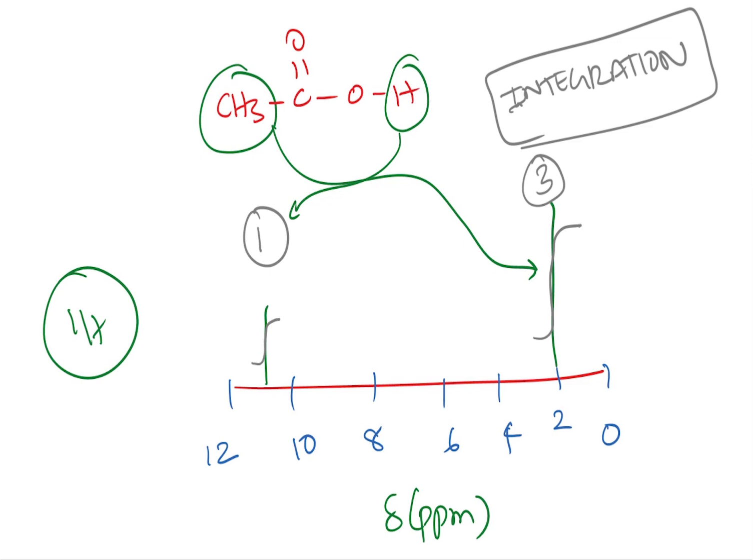

So, for example when you look at a molecule such as $CH_3C{=}OOH$. So,when I record the NMR spectrum of this, do not worry too much about the position of these peaks as yet, we will get to that very soon. So let us say this is 0. And now I have to slightly extend the scale a little bit because of the OH. So, 2, 4, 6, 8, 10 and 12, so this is the delta (ppm).

So, let us say we record the NMR spectrum of Acetic Acid, now, you see a nice peak at 2 chemical shift, and then you will see another peak at around somewhere between 10 and 11 ppm. Now, when we integrate these peaks, so as I mentioned to you, integration is done, is a mathematical sort of analysis that is done on the peak, and it gives you a value and here, what we are going to look at is the height of the peak.

So, when you integrate this peak, we find that it is in the ratio of 1:3. So, from this, one can deduce that the OH must be this peak, and the methyl must be this peak. So therefore, Proton NMR is a very, very powerful technique, wherein not only can you understand about the chemical environment, but also you can understand, you can figure out how many Hydrogens are there actually, at that particular position. So, we will get to the example of Acetic acid again, or some similar examples later. But now, let us spend a little bit of time and try to understand what the various regions of the Proton NMR spectrum looks like.

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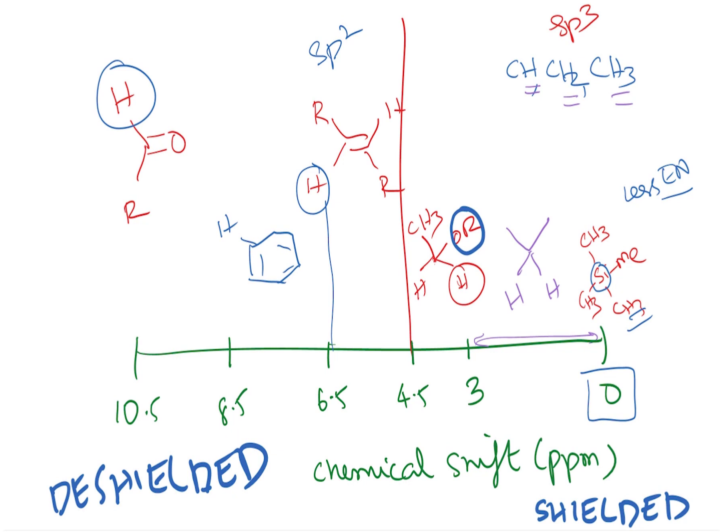

So, the major, the important thing for us to understand is that when I draw a scale like this, so 0 to 10. Again, this is chemical shift, and the value, and it is denoted by ppm. So typically, what happens is that we can divide this into three or four regions, and they are not evenly divided, so I am not going to divide it evenly.

So, let us look at the region between 0 and 3. Then we look between 0 and 4.5, and then 6.5 8.5 and 10.5. So, I am going to call this as 10.5. So, this is 8.5, 6.5 or 6 and 4.5, 3 and so on. Now, let us look carefully at these regions. So, as we already know, this is where Tetramethylsilane comes, so it is $Si(CH_3)_4$.

And we already discussed that Silicon is less electronegative. So, less electronegative and therefore it shows up at around, at 0. And keep in mind, we are looking at these hydrogens over here. Now, when compared with Silicon, Carbon is obviously more electronegative. So, if we look at CH, CH_2, and CH_3, these are the Hydrogens, which are sp^3 hybridised.

So, when I look at these Hydrogens, that is CH, CH_2, and CH_3. And if they are connected only to Carbon, then since Carbon is more electronegative, compared to Silicon, we can expect it to be in this region, that is between 0 and 3. And you know, so I am just going to draw it over here. So, this is, the CH_2 can be expected to be here, we will look at it in more detail very soon.

Now, when you add an electronegative atom, for example, let us say you add an OR that is an ether, that because the more electronegative atom, so these Hydrogens are going to, we are talking about these Hydrogens, because this is going to be more electronegative, that is, this

OR is more electronegative, so it becomes more de-shielded. So, keep in mind that we discussed already that this is the shielded and this is the de-shielded.

So, therefore being electronegative, Oxygen being electronegative, it pulls electrons from this Carbon-Hydrogen bond and this as a consequence, this Hydrogen starts sort of resonating at a higher chemical shift or it is called as more de-shielded. Now, moving along, we go to the next region, which is between 4.5 and approximately 6.5. So, this is the region where typically olefins show up, so where you have RCH=CHR.

So, these Hydrogens which are attached to a sp^2 Carbon typically show up between 4.5 and 6.5. So again, you can understand that sp^2 Carbons are more electronegative. And so, they want to pull electrons from the Hydrogen and make it more de-shielded. The next important region which we are going to use quite extensively is that of an aromatic ring, which is a Benzene ring. So again, we will get into more details later about the origin of this effect. But aromatic rings typically show up between 6.5 and 8.5.

And lastly, you have the combination of being next to a sp^2 Carbon as well as an electronegative atom, which is in the case of aldehydes. So, these Hydrogens of aldehydes actually show up between 8 and 10. So, this cartoon looks a little cluttered now. But I would urge you to go back and look at any good textbook, Clayden is a good book to look at and in the edition that we are looking at, this shows up in chapter three, where it talks about determining organic structures.

And there is also a separate chapter, chapter 13 on NMR, I would urge all of you to go back and look at it. But the bottom line is that you need to understand that NMR spectroscopy allows us to develop a framework where we can understand the local environment around Hydrogen.

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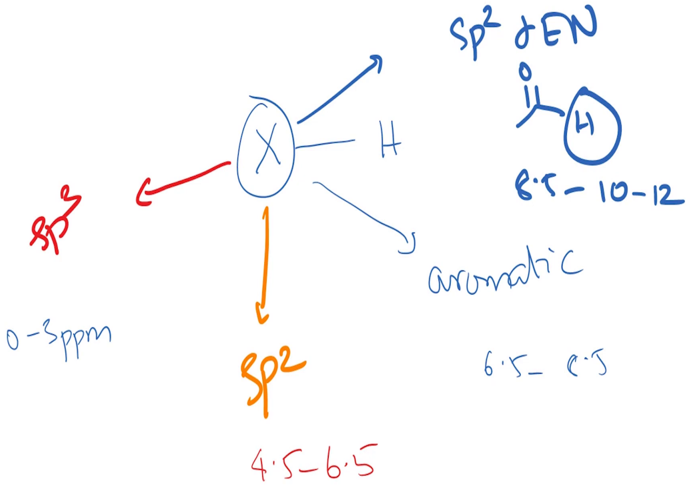

So, if the Hydrogen is connected to a group X, and if this X is sp^3, I mean this Carbon, I am talking about a Carbon, but if this Carbon is sp^3 hybridised, then you have a fairly reasonable idea that it will show up between 0 and 3 ppm. Now, if the X is sp^2 hybridised, such as an olefin, then you have a good idea that it is going to be, I am talking about a Carbon-Carbon bond, it is going to be around 4.5 to 6.5.

And now, if it is aromatic, that is, it is attached to a Benzene ring, then it shows up between 6.5 and 8.5. And lastly, if the X is attached to an aldehyde, I mean to a sp^2 and electronegative atom, such as an aldehyde, it can also be a carboxylic acid. If you remember Acetic Acid, one of the peaks showed up at around 10, between 10 and 11. So these Hydrogens actually show up between 8.5 and 10, or sometimes to 12.

So, this is a very useful guide for us in understanding where your various functional groups show up. Now we have a good idea about where the Proton NMR spectrum shows up. But a similar trend can also be seen in the Carbon NMR. So, I am just going to draw out the Carbon NMR scale. So, we know that it is somewhere between 0 and 200.

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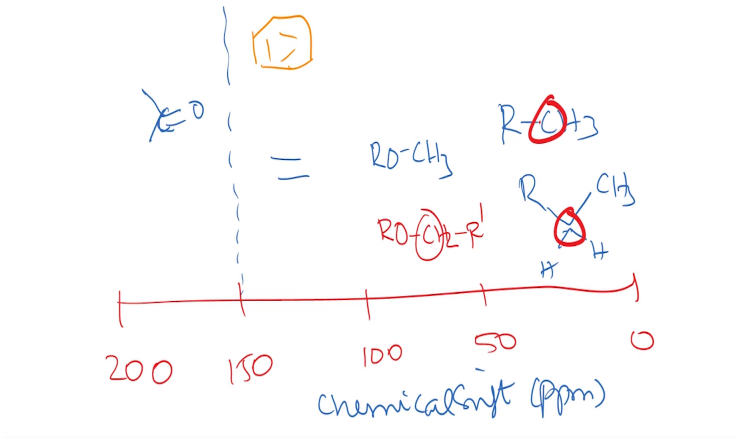

And here, let us just divide it into 50, 100, 150. And as we discussed this is chemical shift (ppm). And so, what we normally see is that this region between 0 and 50 is for saturated Carbons, so, RCH_3, RCH_2CH_3. So, these types of carbons show up between 0 and 50. And much like the Proton NMR the region between 50 and 100, as we saw in Proton NMR, it was between 3 and 4.5 is when you have an electronegative atom such as an ether $ROCH_2R'$. So, this Carbon again shows up between 50 and 100.

In the Carbon NMR interestingly, both olefins and aromatic compounds which we will look at in detail later, show up at around the same range between 100 and 150. So, this is the region where the aromatic Carbons show up. And lastly, as you would have correctly guessed, the Carbon attached to a carbonyl typically shows up, you know, is in between 150 and 200.

So, together these, if you record the Proton NMR, as well as the Carbon NMR, you get a very, very good idea about what kind of functional groups, what is the local environment, etcetera, etcetera. So therefore, together, this is going to be very useful in determining the structures of molecules.

Now, what we will do is, we will just take a couple of examples and try to understand whether we can, you know see, whether we can understand the NMR spectrum after looking at the spectrum. The first example that we are going to look at is, let us look at the various groups that are attached to Carbon or to Hydrogen in our Proton NMR spectrum.

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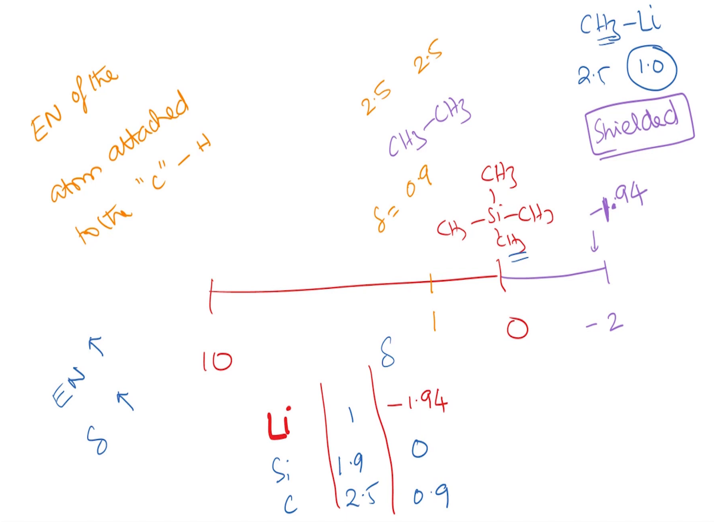

So, let us say we take 0 to 10. So, as we discussed, this is a Si $(CH_3)_4$, Tetramethylsilane. And now, if you actually record, if you prepare a molecule such as Methyl Lithium, the electronegativity of Lithium is 1.0 and the electronegativity of Carbon is 2.5 as we discussed earlier.

So, what you would expect is that the Carbon which is next to Lithium is going to be quite shielded. Because this is going to increase, being an electropositive group or a less electronegative group, it is not going to pull electrons as much and so it is going to be more shielded. So, if we record the NMR spectrum of Methyl Lithium, it shows up somewhere around, -1.94, so the Methyl Lithium, as we would have expected, shows up in a more shielded region when compared to Tetramethylsilane.

Now, let us take the example of just ethane with a CH_3CH_3 and here, the electronegativity of Carbon is 2.5, this Carbon is 2.5 and so this is around 0.9. So, the chemical shift for this is around 0.9, the Hydrogen. So, therefore, in this example, what we see is that there is an almost excellent correlation between electronegativity of the atom attached to the Carbon, which is next to the Hydrogen.

So again, I will just quickly repeat here. So, Lithium, the electronegativity is 1, Silicon is 1.9 and Carbon is 2.5 and the chemical shift here, delta value is -1.94. Just draw a line here, so that it is easy for us to see it. For Silicon is 0, that is TMS and here is 0.9, so this is an excellent correlation. So, as the electronegativity increases, the chemical shift increases; electronegativity increases, delta value goes up.

And we can understand this purely by invoking the concept of shielding and de-shielding. So, the more shielded the atom is or the more shielded the group is, the lower the chemical shift. So, when we saw in the previous example, we saw that the electronegativity of the group is very important in determining the chemical shift.

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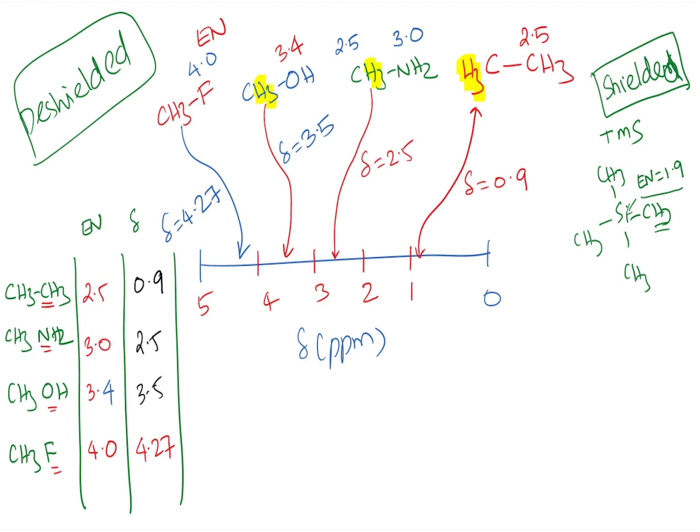

	EN	δ
CH_3-CH_3	2.5	0.9
CH_3 NH_2	3.0	2.5
CH_3 OH	3.4	3.5
CH_3 F	4.0	4.27

Now, let us expand the scope of the investigation and let us take the region again, between 0 and let us say we take 6, delta (ppm). So, what we looked at was for Carbon, CH_3CH_3, the electronegativity of Carbon was 2.5. And when we look at these Hydrogens, which are next to this Carbon, then it shows up the delta value is around, so I am just going to 1, 2, 3, 4 and let me call this as 5, we may not need 6, but so this Hydrogen shows up around, delta equals 0.9.

Now, the next group that I am going to take is Methylamine. So, the electronegativity of Nitrogen is 3.0, so Nitrogen is more electronegative than Carbon, and this electronegativity continues to be 2.5 and so what we are looking at is again these Hydrogens and these show up at around 2.5.

So, is this a surprising result, let us analyse that. So, if you see here, what we discussed earlier was Tetramethylsilane, which is basically Silicon next to four CH_3's. The Hydrogens show up at 0 and the electronegativity of Silicon is 1.9. So, what we figured out was that the more shielded, that is the more electronegative the group is, the Hydrogen next to it is going to be more shielded, whereas, the one which has an electronegative group on it, is going to be more de-shielded.

So, having an electronegativity of 1.9, the Silicon has a tremendous influence on this Hydrogen which is next to the Carbon. So similarly, Methylamine, CH_3NH_2, the Nitrogen being more electronegative pulls electrons more efficiently and makes it more de-shielded or less shielded.

Now, does this translate to Methanol? So, let us draw out the structure of Methanol, CH_3OH, again, the Hydrogens that we are looking at is this and here, the electronegativity of Oxygen is 3.4. So, it is more electronegative than Nitrogen and so this, the chemical shift for this Hydrogen is 3.5 i.e., delta equals 3.5.

And lastly, let us look at Fluoro methane, which is CH_3F, and electronegativity of Fluorine is 4.0 and the chemical shift is, of this Hydrogen is, 4.27. So, what this tells me is that if I have to draw a plot, or table, CH_3CH_3, let me make two columns here. The first column would be electronegativity of the atom, and the second one would be chemical shift. So, CH_3NH_2, CH_3OH and CH_3F.

So, let us just write down the electronegativities of these atoms over here. So, this is 4.0, this is 3.4, this is 3.0 and this is 2.5 and the chemical shift is in the order of the electronegativity 0.9, 2.5, 3.5, for Fluorine, it is 4.27. So, therefore, if you see here, it perfectly correlates with the electronegativity of the atom. So, if you expand this discussion from Lithium to Silicon, to Carbon to Nitrogen to Oxygen to Fluorine, you will find that it really beautifully correlates with electronegativity.