One and Two Dimensional NMR Spectroscopy for Chemists

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Lecture – 16
Factors Contributing to Chemical Shifts

Welcome back, we have been discussing about chemical shifts, one of the most important internal interaction parameters in NMR. And in the last 1 or 2 classes, we discussed about the origin of chemical shift, the reference used and how the chemical shift gets affected and how to convert chemical shift from ppm to frequency, frequency to ppm, and what happens to the chemical shift when expressed in ppm as a function of magnetic field.

What happened to chemical shift when expressed in frequency as a function of magnetic field and how to convert, everything we have discussed in that, and we can continue with the class. From today we will discuss more about the factors that affects chemicals shifts.

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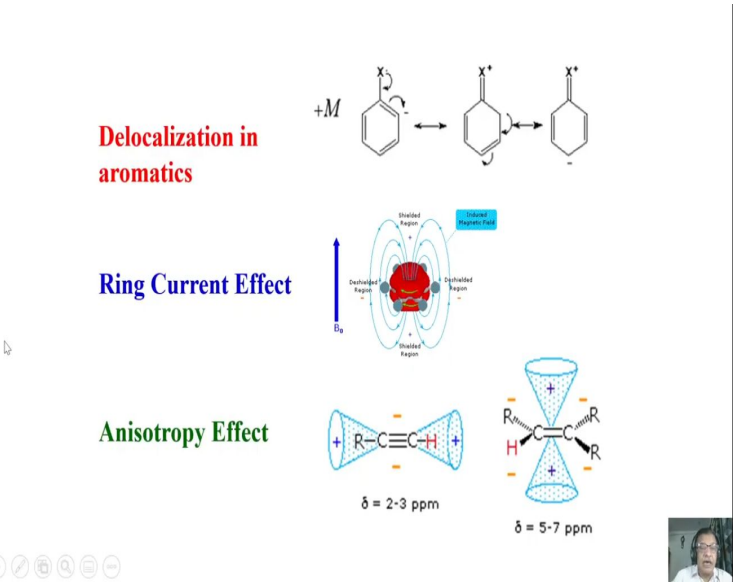

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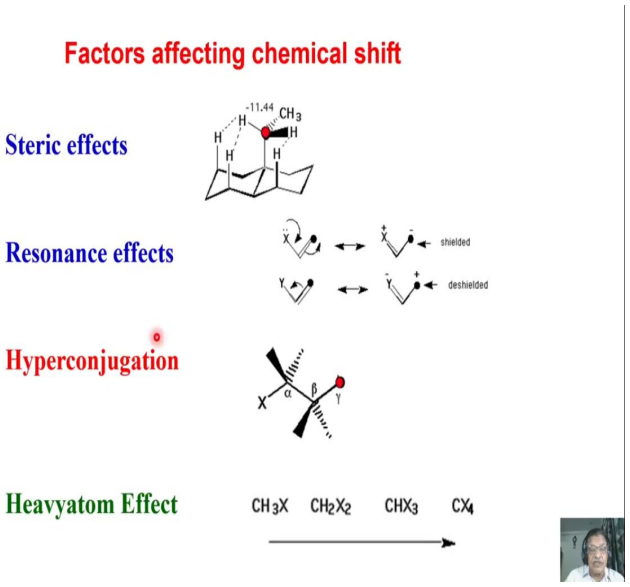

In the last class, I did say some of the factors which affect chemical shift, for example steric effect, delocalization of aromatics and ring current effect and we discussed about the anisotropy effect and resonance effect, heavy atom substitution, various factors are there which are responsible for chemical shifts. We try to understand today, with some example how these chemicals shifts get shielded, particular protons get shielded, deshielded and give rise to different chemical shifts.

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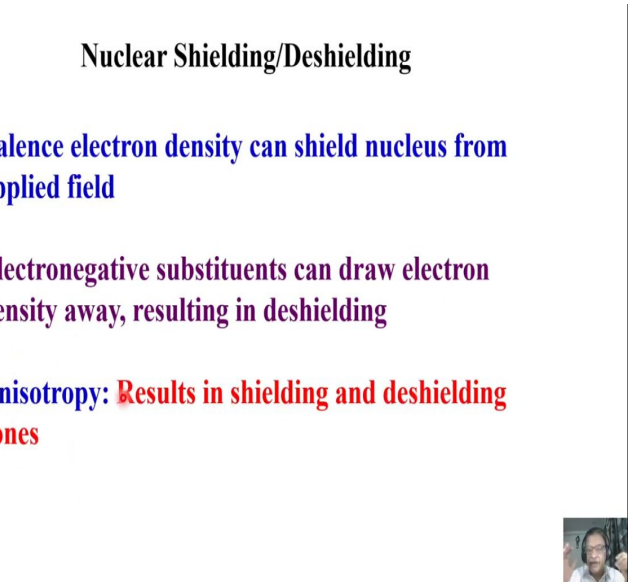

For example, if there is a valence electron density, that can shield nucleus from applied field, causes shielding. If there are electronegative substituents which can withdraw electrons away from the particular proton for which it is attached, or for the neighbouring proton causing deshielding. There is also a anisotropy effect which results in both shielding and deshielding, the anisotropy comes because of the anisotropy of the chemical bond.

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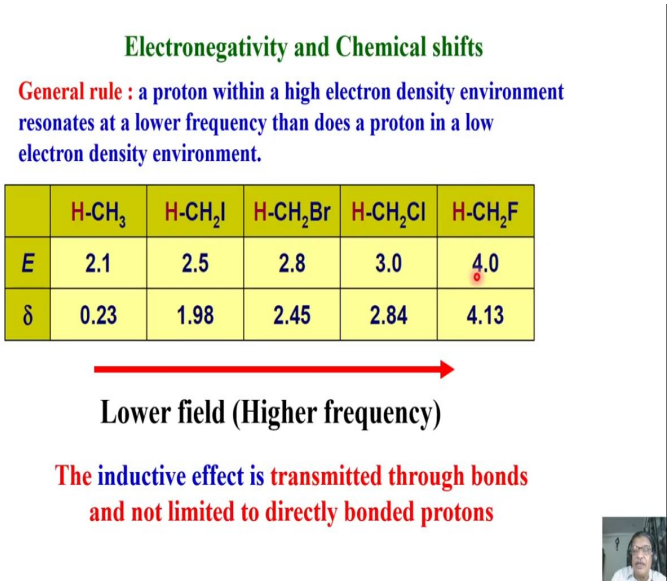

We take couple of examples today and see what are these factors? Starting with first electronegativity, how does it affect chemical shifts? Of course, you all know first and foremost thing, if there is an electronegativity group attached. What it does? It causes change in the electron density around the particular proton, because it withdraws electrons. As a consequence, if higher the electronegativity, more electron is withdrawn, peak shifts more to the down field. Remember this point. It resonates at lower field because it withdraws electrons, causes deshielding. This is one of the important effects with the different electron density substitution for hydrogen atoms. Let us see, for example, I took the example of methane, methane E is of course, in the scale of electronegativity in Millikan scale, of course, fluorine is the highest, we referred to the hydrogen atom, here refers to the fluorine. Methane, it is in the gaseous phase. We can get the chemical shift of this, no problem. Let us say, I get the chemical shift of methane, all 4 protons are equivalent, there is only one chemical shift that is 0.23 ppm. Now, what I am going to do is, knock off one of these protons here, and put there Iodine. It will become CH3I, ethyl iodine. Now, the electronegativity of Iodine is different, it is 2.5. The chemical shift of this proton, you look at it, instead of 0.23 it is shifted to 1.98 ppm. It is in delta scale.

Delta scale is in ppm scale. So that means it moved to the down field because of the attachment of the electronegative atom. Change iodine to bromine which is much more electronegative compared to iodine. It shifts further down field. Of course, you know, in the column of the periodic table we have fluorine, chlorine, bromine, iodine. Now after bromine move to chlorine. Remove bromine and put chlorine see now the electronegativity keeps on increasing for the substituent atom, iodine, bromine, now chlorine the chemical shift has

moved to 2.84 ppm, further down field compared to bromine substitute. Now, last you can take fluorine which is most electronegative, remove chlorine and put fluorine now make it this CH3F. Look at the chemical shift, it moved to 4.13 ppm. Starting with totally substituent of electronegative atom, methane chemical shift is 0.23 ppm. Now, as a function of substitution of different electronegative atoms iodine, bromine, chlorine and fluorine, there is a steady change in chemical shift which is moving towards down field. Remember it started moving towards down field and finally ended at 4.13 ppm for CH3F. Another thing I want to tell you is, the inductive effect is transmitted through bonds, and is not only restricted to directly bonded protons. In this case carbon and fluorine are directly bonded, there is CH4 you know that CH4 out of which, one proton is replaced with fluorine.

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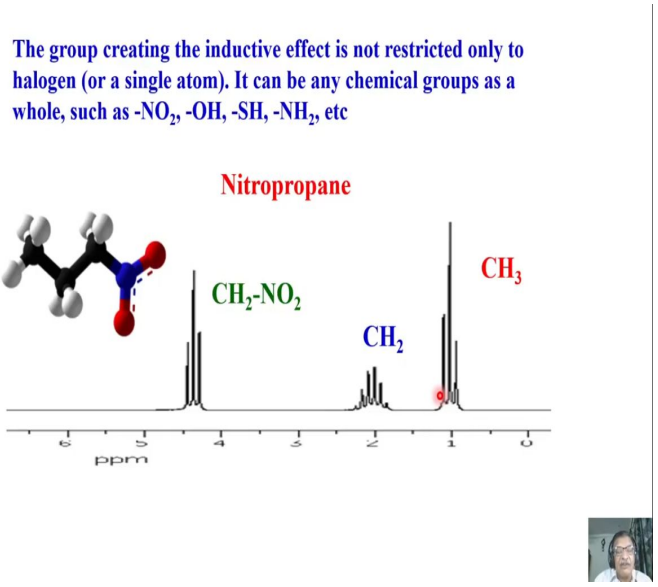

No let us look at a molecule called nitropropane. What is nitropropane, its structure is; it is CH3CH2CH2NO2, that is the structure of nitropropane. Now, if you take only propane, we have CH3 twice CH2, there is only CH3 group and CH2 group. There is a perfect symmetry at the center. CH3 CH2 CH3, if you write, there is chemically equivalence, you know that, I will come to splitting pattern everything later. But remember there is a perfect symmetry.

Now I will knock off one of the protons of CH3 group and put NO2 group. Now, it is withdrawing electrons and the symmetry is distorted now. It is no more symmetric. There are 3 different functional groups. One is CH3, other is CH2 and CH2NO2 and there are 3 groups now. What happened to the CH3? In this structure, we have NO2CH2, CH2 and CH3. CH3 is far away from NO2 group, its inductive effect is much less as far as CH3 is concerned.

So CH3 comes at high field, then comes CH2, middle CH2, attached CH3 in between NO2CH2, and CH3. This comes here and the CH2 which is attached to NO2 comes close to 4.5 ppm, around 4.5. Look at it, it has moved enormously down field because NO2 is directly attached to this CH2. So, electronegativity substitution; how when it withdraws electrons, shifts the chemical shift. This is very clear from this.

Now, your question could be why NO2? What happened to different functional groups? There are many electron withdrawing groups or donating groups. Then also it can affect instead of NO2, you can have OH, you can have SH, you can have NH2 varieties of groups. Some may donate electron, some may withdraw electrons. If the electron withdrawing groups are there, the protons moves to downfield, if electron donating group is there, it moves to high field. Simple logic. So, the electronegative substituent has inductive effect and has a great influence on the chemical shift of protons.

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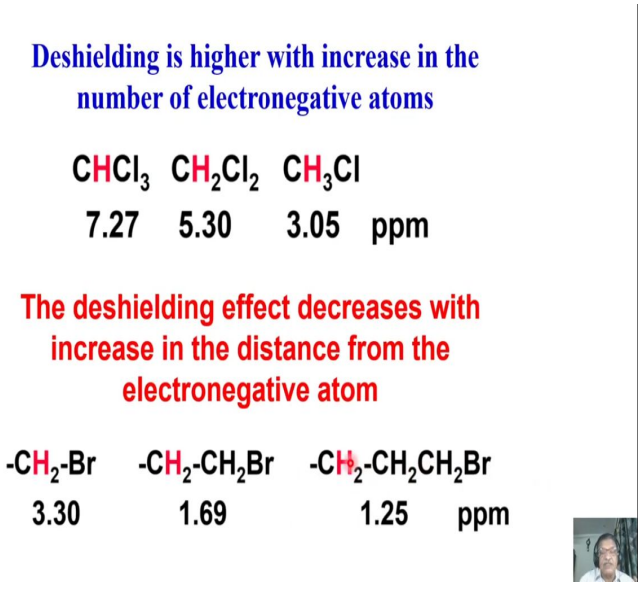

Next, take the same methane which was coming around 0.23 or 0.24 ppm, whatever that. I can lengthen this molecule. See in this knocked off one of the protons, and add a CH3 group. Now it becomes HCH2CH3. Now we will concentrate on this CH2, this proton. What is going to happen? Look at this chemical shift; it moved from 0.24 ppm to 0.8 ppm. In this molecule there is no electronegativity substituent, and there is no electronegative substituent attached. But lengthening of the carbon chain also causes deshielding. As a consequence, this proton moved down field. Now we can lengthen it further, add one more CH2 in between. Now look at this proton this move further down field. So the lengthening of the carbon chain also has an effect on decreasing of the shielding.

Now, consider a simple molecule chloroform, CHCl3. We have one single proton in this molecule. There are 3 chlorine substituents. The number of negative atoms substituted in this is 3. I take the proton spectrum of this molecule, I get only one peak at 7.27 ppm. Now, instead of 3 chlorines, I put 2 chlorine atoms and make this molecule CH2Cl2. Now what happened? You reduced one of the chlorine, the electronegative atom, instead of Cl3 we made it Cl2. So, as a consequence of reduction of one of the electronegative atom, the deshielding effect reduced. So, the proton which was coming at 7.27 moved to 5.3 ppm. Again it gives a single peak because both these protons are equivalent, it gives rise to a single peak at 5.3 ppm. Now I will do one more thing, I will remove another chlorine atom here and make it CH3Cl. Now, we have removed 2 chlorine atoms from this molecule and the electronegative substituent is much less here. As a consequence, the shielding is also much less compared to this. Now, these 3 equivalent protons resonate at 3.05 ppm.

Look at the effect of substitution of electronegative atoms. The number of electronegative atoms substituted also matters a lot, more the electronegative atoms here, there were 3, it shifted downfield, with 2 slightly high field. There is only one chlorine atom shifted high field. So the effect of substituent, the number of electronegativity substituents is very clear.

Please remember, if more electronegative substitution, greater the chances of moving into down field. The deshielding effect decreases with increasing the distance of the electronegative atom, it is another important thing. The inductive effect will not go through so many bonds. For example, take, say a fraction of a molecule, a fragment of a molecule, which is CH2Br something is here, we do not care.

Now this CH2 is attached to bromine. This gives rise to a peak at 3.3 ppm. Uderstand, This gives rise a peak at 3.3 ppm. Now, what I am going to do is, I will add another CH2 in between the CH2 and Br. Now, what is happening? The distance between this bromine atom and this hydrogen atom is increased. Because the distance is increased, the influence of this bromine atom on the CH2 is much less compared to this molecule.

So, there is not much of inductive effect. The electronegative effect is much less here. Instead of 3.3 ppm, this proton now comes at high field, 1.69 ppm. Add one more CH2, lengthen it more. Increase the length. Now, this CH2 is far away from this bromine. So the inductive

effect, effect of this electronegative atom on the CH2 is even less. As a consequence, again it moves to further high field. It moves to 1.25 ppm. See the difference.

Just by lengthening the substitution the effect of the electronegative atom keeps reducing as you go far and far away from the proton you are observing. That is an important point you must remember.

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Dependence of Chemical Shift of CH_3X, on the electronegativity of X

Molecule	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
Element	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical Shift (δ)	4.26	3.34	3.05	2.68	2.16	0.23	0

Now, the dependence of chemical shift of CH3 group; CH3X on the electronegativity. I tell you, how beautifully the effect of electronegativity is seen, in other example. Of course, we saw CH3F. We saw that in the methane. We change the substitution from iodine, bromine, chlorine and fluorine, and we saw the effect of it for this methane group.

Now, what we can do is compare with similar molecules, now instead of CH3F, I will take CH3OH.

Now the electronegative atom substitution is O, what is happening to electronegativity of the substitution? This I call it as X atom X. X here is fluorine, which has the electronegativity of 4 in the Millikan scale, we all know that. Now instead of F if I put O, this changes it from 4 to 3.5. Similarly, chlorine, bromine, iodine, if we keep on decreasing the electronegativity and methane, and finally we take tetramethylsilane, whose electronegativity because of silicon is only 1.8.

Look at the chemical shift, what is happening now? This starts with 4.26. We saw 3.34 these 3 examples we saw in one of the previous slides, and when it comes to tetramethylsilane we took as a reference is 0. See as a substitution effect electronegativity, on a group like this, depending upon fluorine, oxygen, chlorine, bromine, iodine, these changes drastically, as a consequence the chemical shift correspondingly, keeps on shifting to high field. If you go in the order of decreasing electronegativity it goes to low field, you should go from right to left in the order of increasing the electronegativity.

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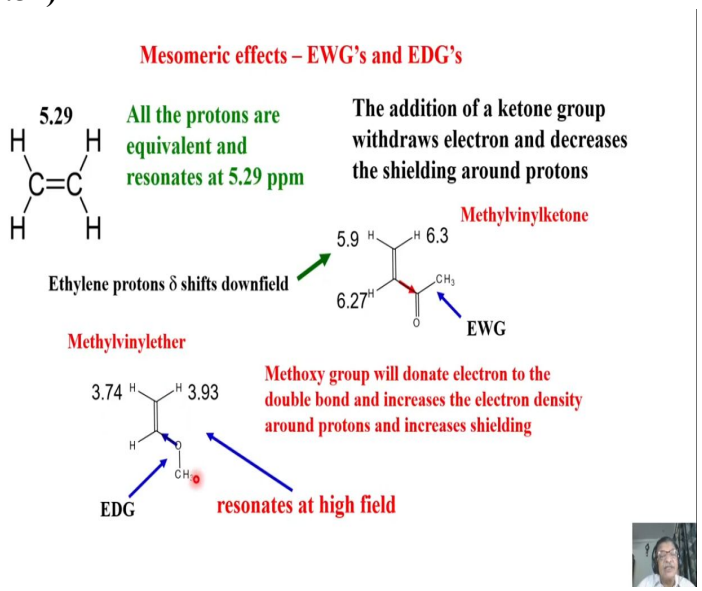

Now, another important factor is mesomeric effect. You all know what is the mesomeric effects in basic chemistry. I do not have to explain that. Now consider the example of one molecule, where we have an electron withdrawing group and also another molecule, where we have electron donating group. This start with the simple molecule. What is this? C2H4. C2H4 is ethylene, I think it is molecule of ethylene formula.

Now all the 4 protons of this molecule are equivalent. Look at it. There is symmetry for this molecule. There is symmetry along this axis, there is symmetry along this axis. So because of this axis, these 2 protons are same, these 2 protons are same. If you go along this axis, this is equivalent to this, this is equivalent to this. All 4 protons are chemically equivalent. As a consequence, how many peaks we should get? We will get only one peak, which comes at 5.29 ppm. Remember, it comes at 5.29 ppm.

Now, we add one ketone group. What is the ketone group? It is C double bond OCH3, we add. Knock out this proton, any of them you can take. I took an example. knock off this proton and put a ketone group. Now this molecule is methylvinylketone.

Is there is a symmetry for this molecule? Now compared to this ethylene, look at this molecule, the symmetry is broken because of the addition of this group and this is electron withdrawing group. What happens when it withdraws the electrons, it causes deshielding. So, peaks start moving down field, you understand peaks start moving down field, that is at higher chemical shift value. So instead of 5.29 now, they come at 3 different values because the non-equivalent, you see, none of them are around 5.29.

They change drastically. This proton because this is goes to this goes at 6.27, this is 6.3, this at 5.9. None of these protons have remained at 5.29 ppm. All have move to downfield, because we have an electron withdrawing group.

We will do one more these thing trick now; instead of electron withdrawing group let us put the electron donating group. What happens? You put OCH3. What is OCH3?Methoxy group. It will donate electron to this double bond and increases the electron density around the protons. Look at this one. Moment you put it you have broken the symmetry by substitution of OCH3 group. Look at this. When you put an electron donating group, the shielding became more. It is, instead of unlike in this molecule, instead of moving down field, in this molecule the protons started moving high field. Remember, instead of 5.29 ppm of ethylene, these protons started moving at 3.74 and 3.93 much higher than 5.29.

Of course there is a value for this also, I did not write down because all the 3 are non-equivalent we have 3 different protons, we have the chemical shift for this also I have not mentioned. Don't get confused. There are 3 peaks, this is also non-equivalent. So, all 3 have moved to high field now. This is because of mesomeric effect. So, when an electron withdrawing group is there, it causes deshielding. When electron donating group is there, it causes shielding.

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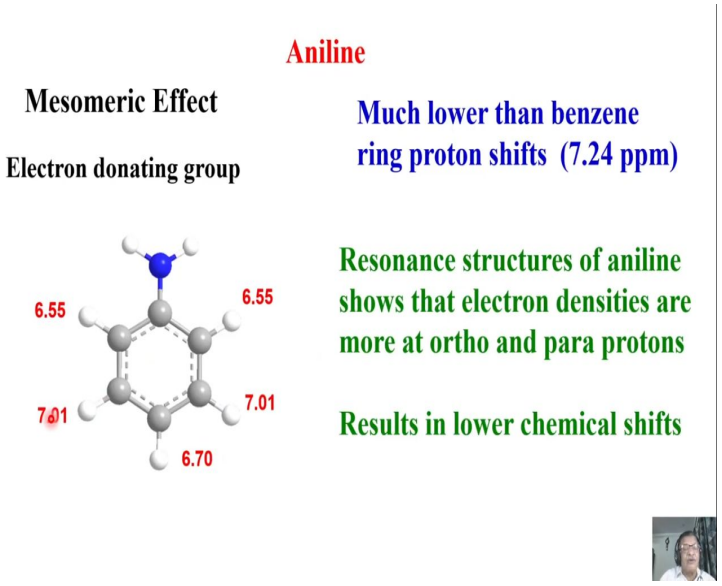

This is the important point. You must remember. The same mesomeric effect let us see in the ring system. Let us take aniline. Aniline you know the structure C6H5NH2. Now what is the resonance structure of aniline. It tells me, if you go through the resonance structure, the electron densities are more at ortho positions and at para position, and it is less at meta position. This you all know from mesomeric effect how the charged electrons start moving.

Here in this ring if you look at the resonance structure, for these ortho protons, of course, there is chemical equivalence because of NH2. This proton and this proton are equivalent, this proton and this proton are chemically equivalent and this one different. So, there are 3 different types of protons, because of the charge density situated more at ortho and the para positions, these protons come at high field, they move to high field.

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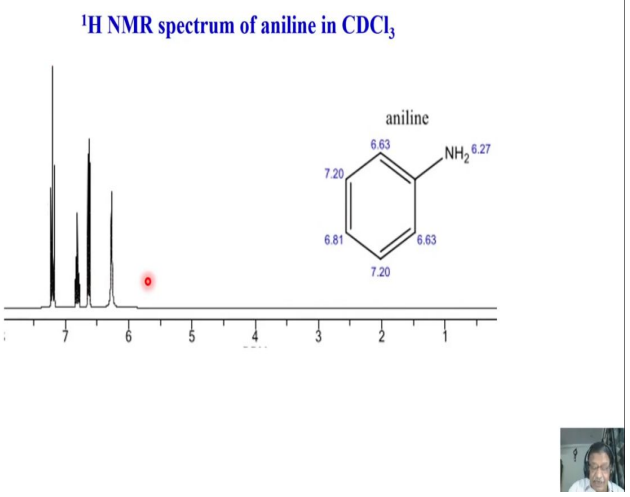

Whereas, the meta protons shift to down filed, You understand. This is the mesomeric effect of a electron donating group in a ring system. This is clearly the molecule structure, what is the peak? One of them is chloroform. 3 different groups are there, you can identify 3 different groups. The analysis part, when you come to that later, we will discuss, but remember there are 3 different groups. As I said, 2 of them are high field corresponding to this, and this one is the next one. And these 2 come to the down field. From the intensity pattern also we can understand, I will discuss that later.

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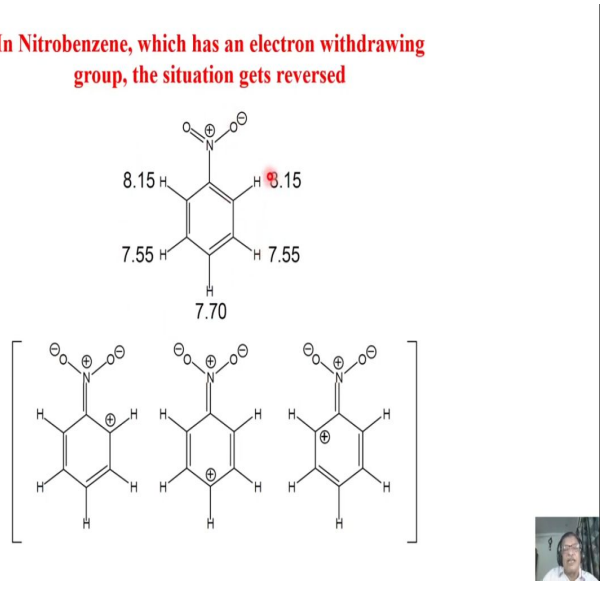

So, instead of that, aniline go to nitrobenzene. What is the difference between these 2? In the case of aniline NH2 is the donating group. Now, in the case of nitrobenzene, NO2 is a electron withdrawing group. What do you expect now? The phenomena will be reversed. So, the charge density will be less at ortho and para positions and more at meta position. As a consequence, these 2 protons move down field, and these two moves down field and these 2

moves relatively high field compared to these. Again it is symmetric for this molecule, these 2 are equivalent and these 2 are equivalent and this is different. There are 3 different types of protons, same. The phenomenon as far as where the electron charges are residing, in this molecule, it is opposite of aniline.

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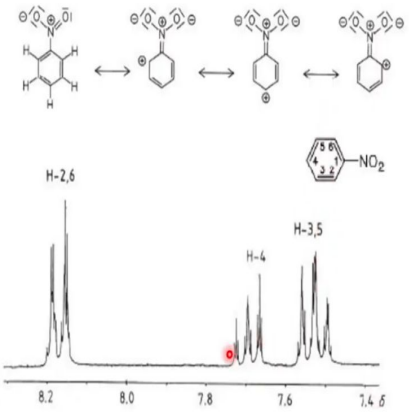

So the peak pattern will be different here. Look at this one, this is meta comes here, ortho and para comes here. Unlike the other case.

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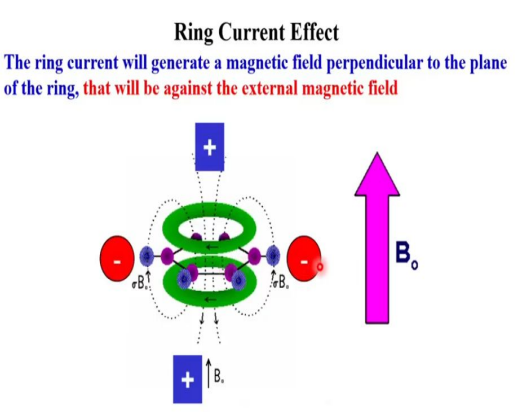

So, another thing is about ring current effort. There are important phenomena called ring current in aromatic rings. You all know in the benzene and other things if you take there is a ring current, that is because there is electron that are moving the round in the ring generates a magnetic field. How does it generate magnetic field? We all discussed under chemical shift, the moving electron produces magnetic field. Right?

So, that magnetic field will be against the external field, this also we discussed. Remember, When we discussed the chemical shift, we discussed this point, this magnetic field that is generated by moving electrons is opposite in the direction of the external magnetic field. As a consequence, what is going to happen is, there will be shielding and deshielding areas. Remember, you can trace the lines of force of the magnetic field emanating from the center of the ring, go back and it can come like this, and go back or it can come like this.

So, and when such a thing is going to happen, take a plane of the benzene ring like this. For example, it starts like this, come back like this, and start like this. So, when they started with the midle of the plane of the benzene ring, the lines of force starts emanating like this, and come back. So you can now understand more about the benzene ring current, which I do not want to go in details.

As you understand there are deshielding and shielding zones, just above and below the plane of the ring, it is going to be shielded zone, it is written plus, plus means shielded. Just in the plane of the ring protons are deshielded. Look at this one. Protons above and below the ring are always shielded, protons in the plane of the ring gets deshielded. So if I take a ring system of a molecule, if somehow the proton because of a substitution or attachment of another group commences above the ring, it moves to high field, because it is shielded. If I have a proton just situated in the plane of the ring, then what happens? It moves downfield.

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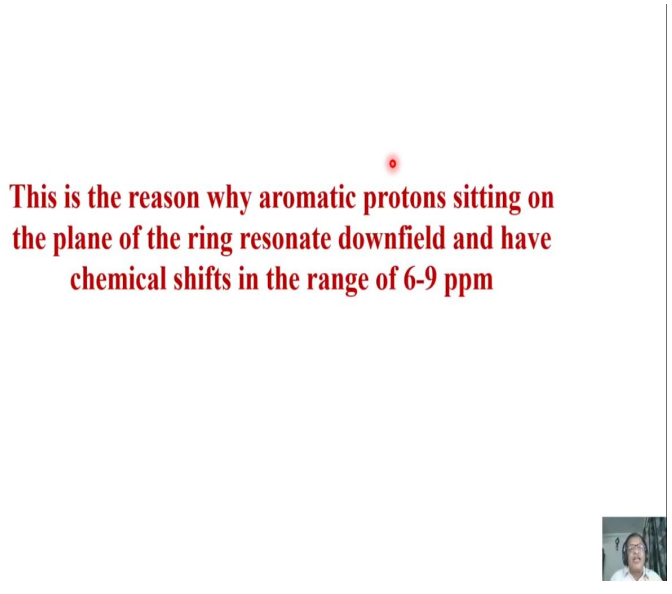

This is exactly what happens, the reason why if I take the aromatics, the protons in the plane like this, all the protons that are situated in the plane of the ring, generally, the aromatic proton comes between 6 to 9 ppm. Please remember. The chemical shift of protons of the aromatic ring just situated in the plane of the ring, always resonates between 6 to 9 ppm, important point.

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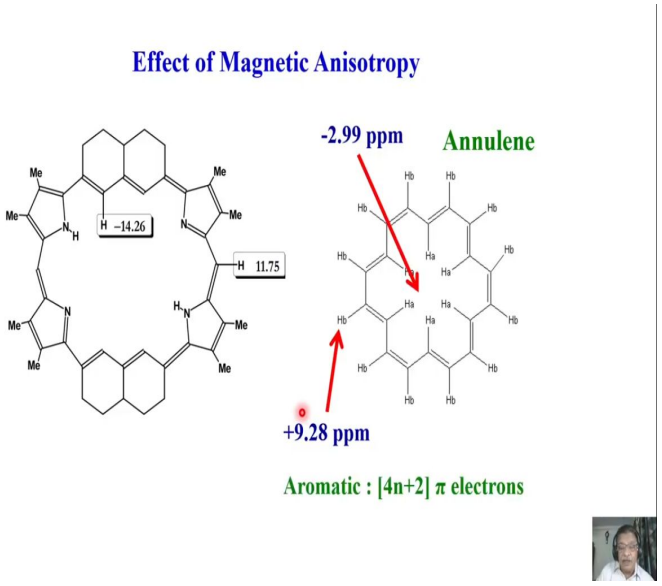

Next I want to quickly introduce about what is called magnetic anisotropy. Effect of magnetic anisotropy, you all know because of the magnetic anisotropy sometimes it is for happened, how the charge is situated you can find out. Of course this comes with the ring current effect also. You can look at the molecule like annulene, look at a bigger molecule like this. Now, we have protons which are projecting inside, this cavity like thing, here are also there are protons that are projecting inside. There are also peripheral protons here. This is an annulene molecule. Look at this one. The protons which are projecting outside this one, comes at very much down field nearly 11.75 ppm, much, much lower. Look at this proton which is inside this. Here it is more shielded, shielding effect is much more here. As a consequence, this proton comes at - 14 ppm, remember much, much higher than the TMS. TMS is at 0 and much higher field than TMS. It is much lower field. Chemical shift difference between the internal protons and peripheral protons if we take, it is nearly 25 ppm difference. Not a small value, it is just because how the charge is distributed inside and outside. Same in the case of annulene, internal protons come at - 2.99 ppm and peripheral protons comes at 9.28 ppm, remember, the internal protons goes nearly 3 ppm beyond TMS. That is the important point you must remember. OK.

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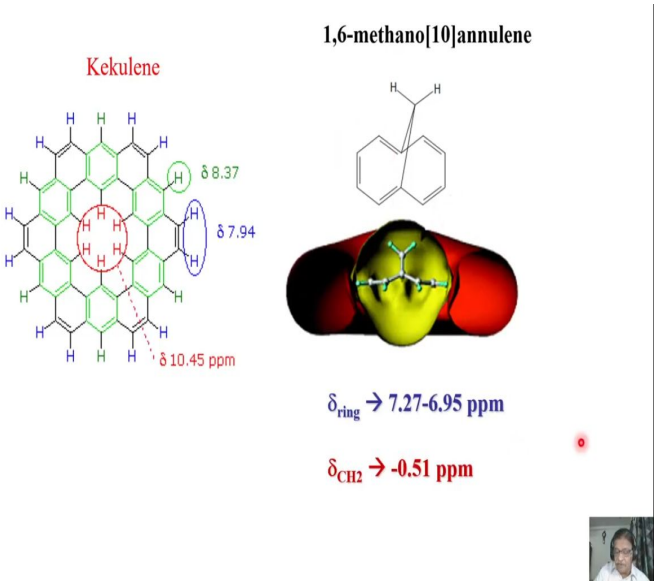

Similarly, you have a kekulene structure, if you look at the protons internal which comes at 10.45 ppm, and protons at the outside peripheral is at 7.94. Not so much drastic change like the previous 2 molecules, but still the difference of interior protons and peripheral protons chemical shifts are obvious here. Consider the molecules like this, something like these protons. The structure wise they are sitting above this ring, that is what we said, shielding and deshielding we discussed, when the protons are sitting above the plane of the benzene get deshielded, that is what I said or in the plane of the ring gets ddeshielded. That is what I said. These 2 protons are sitting above this plane of the ring. Consequence, it comes at 7.27 ppm, whereas, I am sorry, that this proton comes at – 0.51 ppm, whereas these ring protons comes at 7.27 ppm. See the difference? These 2 CH2 protons sitting above the plane of the ring gets shielded so much, they goes beyond TMS, and these ring protons comes at 7.27 ppm.

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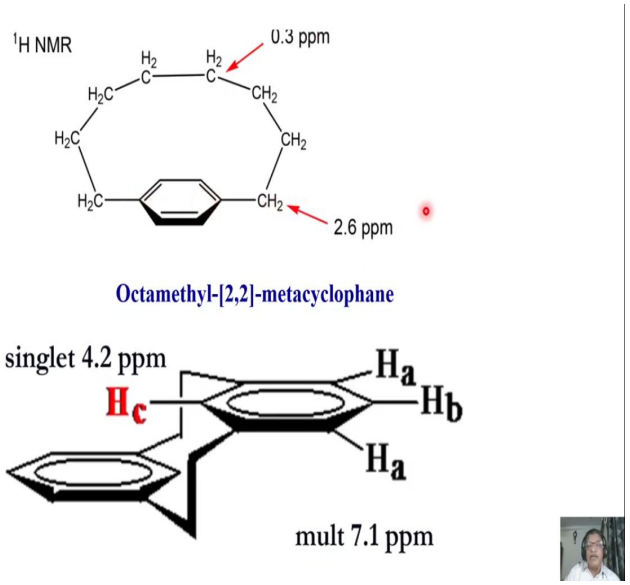

Of course, similarly another example you can see, what happened to the protons which are in the ring and above the ring. These 2 to come above the ring and comes at 0.3 ppm. These 2 protons as far as this ring is concerned, it is in the plane and it comes at 2.6 ppm.

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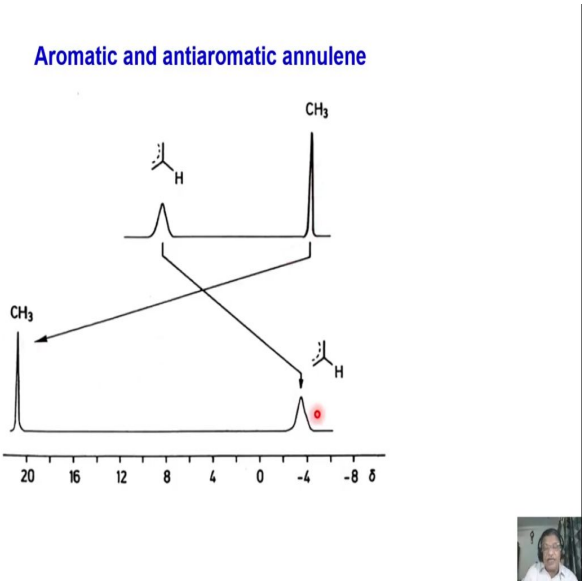

So, a very good for comparison is, aromatic and antiaromatic annulene you take. In one case, see for example, CH3 comes here, and aromatic proton comes here. If you take antiaromatic CH3 comes downfield, whereas aromatic protons comes high field, just gets completely reversed. Remember, aromatic and antiaromatic protons, their appearance of the chemical should get completely reversed like this. That is an important point you must remember. In the case of aromatic protons, the aromatic protons always come down field and CH3 and others that are substituted will come high field, whereas in the antiaromatic the situation gets completely interchanged.

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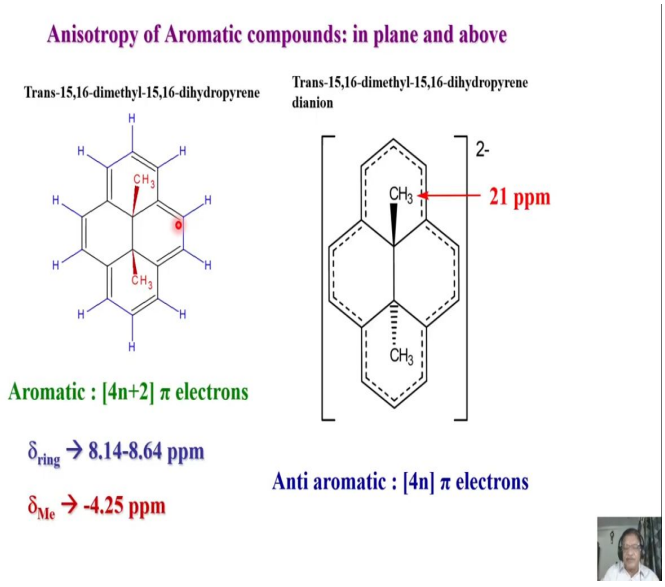

Same way you look at this molecule. This is the name of the molecule, and look at these 2 protons. CH3 groups, just shifting above the ring, it is heavily shielded, comes at - 4.25 ppm, beyond TMS. Whereas these ring protons come at 8.14. This is true of all anisotropic aromatic compounds, because the ring current effect is there, charge density is there, it is not uniform, charge density , it is more at the above and below the plane and less on the side. So, it gets shielded above and below and deshielded in the plane. These are all concepts.

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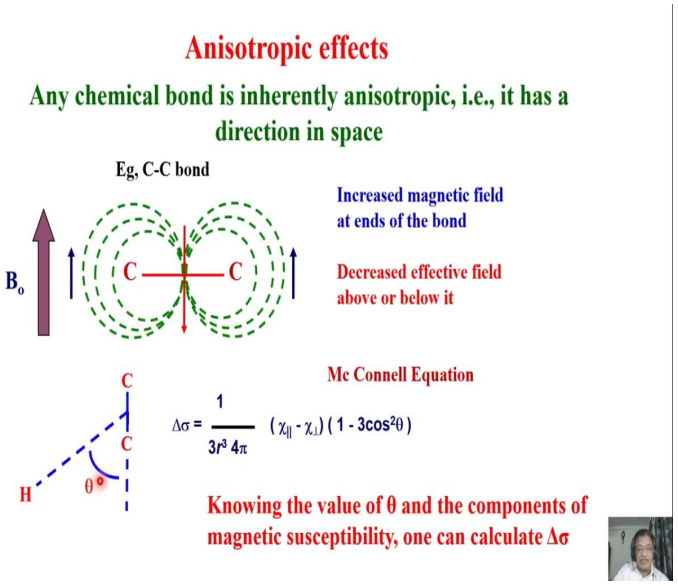

So, in the anisotropic effect you can learn about what happened to anisotropic effect of a chemical bond. Remember, any chemical bond is inherently anisotropic. It has a direction in space. Look at the chemical bond here, what is happening if you take the chemical bond, there is increase in the magnetic fields at the ends of the bond, than at the center above and below this bond. This is well known concept of anisotropy of chemical bond, all of you know that. But then you can find out the anisotropy if you know this one you can find out the contribution to sigma.

If I know magnetic susceptibility anisotropy, that by using a simple equation called Mc Connell equation. It is a very basic equation, available in all the books, read the book by Pople, Bernstein and Schneider, and many other good book on NMR. Basic book will explain about the Mc Connell equation, how to do derive it and everythin,g and that is not the important point for us. Just to tell you, the anisotropy of this bond can be there. And depending upon where you are seeing this bond sitting, whether here, here or here, it varies with the function of angle theta.

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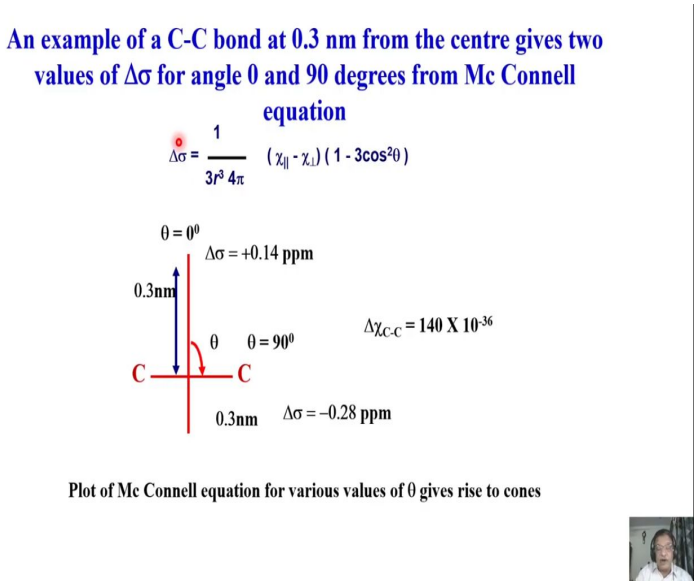

And now, simple example for a C-C bond, if you are sitting, let us say, just exactly about this C-C bond, at the center 0.3 nanometre away, theta equal to 0 degree. Then delta sigma turns out to be 0.14 ppm. Whereas, if you go along the C-C bond, theta is equal to 90 degree, for the same 0.3 nanometer distance, the delta sigma becomes -0.28. Remember, of course, we know the value of susceptibility anisotropy of C-C bond. This is well known and available in the literature.

So, now what you can do is these 3 extreme values, theta equal to 0 or 90 we knew. We can calculate knowing the parameters, because r is known 4 is known, pi is known, delta, this difference is known, where is the angle theta and calculate what is delta sigma, very simple.

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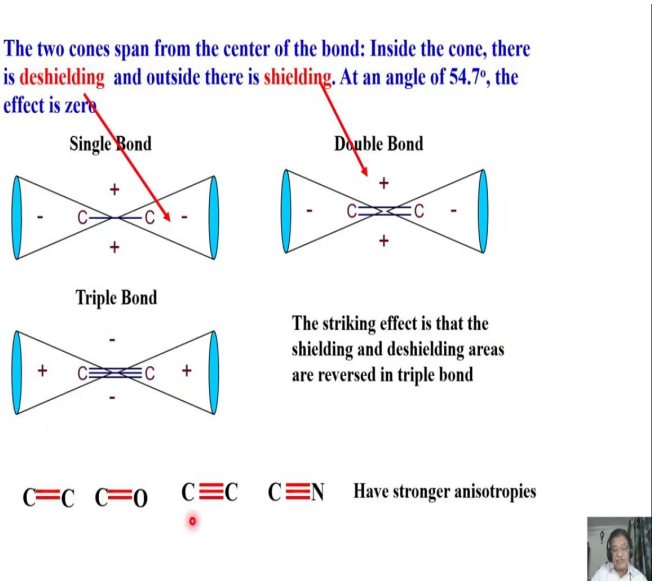

Now, as a function of theta you can plot it, what happens for a single bond, C-C bond, what happened C double bond C, double bond and what happens if you take a triple bond?

Interesting things, you now what happens, in each of these case, as a function of theta if you use Mc Connell equation and plot the charge densities, you will see that in single bond, double bond, just above and below that bond, the protons in this region gets shielded, just in the plane of this or in the axis of CC double bond or CC single bond, the axis of this bond, this charge is that, it gets deshielded. Please remember this, when I am talking about single bond and double bond, triple bond of this type of molecule, in the single bond and double bond just see above and below the bond, proton if it is situated it gets shielded but in the axis of the bond, they get deshielded. But in the case of the triple bond, interesting thing happens. It gets reversed.

Just above and below the triple bond, the protons get deshielded and in the axis of this, Axis of bond it get shielded. A very, very striking difference you see, for a triple bond compared to a single bond and double bond. As a consequence, we can see a lot of stronger anisotropic effects in this type of molecule.

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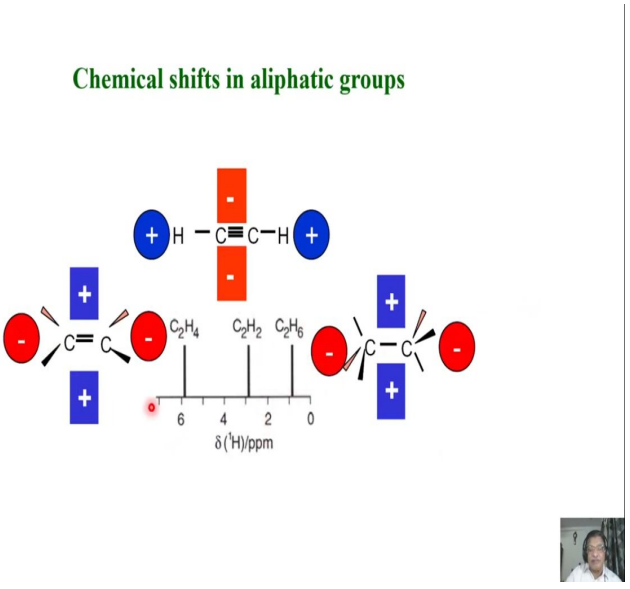

Similarly, so, in a simple logic I tell you what is going to happen if I take the aliphatic group like this if I have a triple bond structure like acetylene like this, C2H2. In this triple bond above and below, the protons get deshielded and acetylene comes much downfield. Whereas, in C2H4 and C2H6, ethane and whatever that alkanes if you take, in this bond axis the protons get deshielded, above and below the bond get shielded. As a consequence, C2H4 ethylene, deshielded more. It comes around this ppm, 2 point or close to 3 ppm, whereas C2H4 and C2H6 because if you are going into the axis of the bond, they have different chemical shifts.

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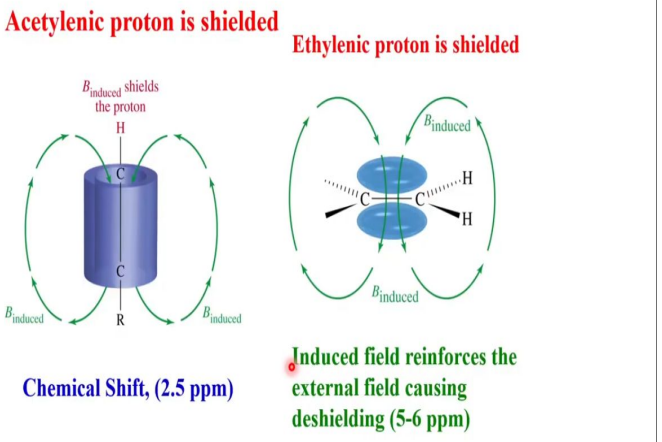

So this is what I just wanted to share. This is how acetylene proton shielding and deshielding can be explained. So, we will stop here. We will come back and continue later.