

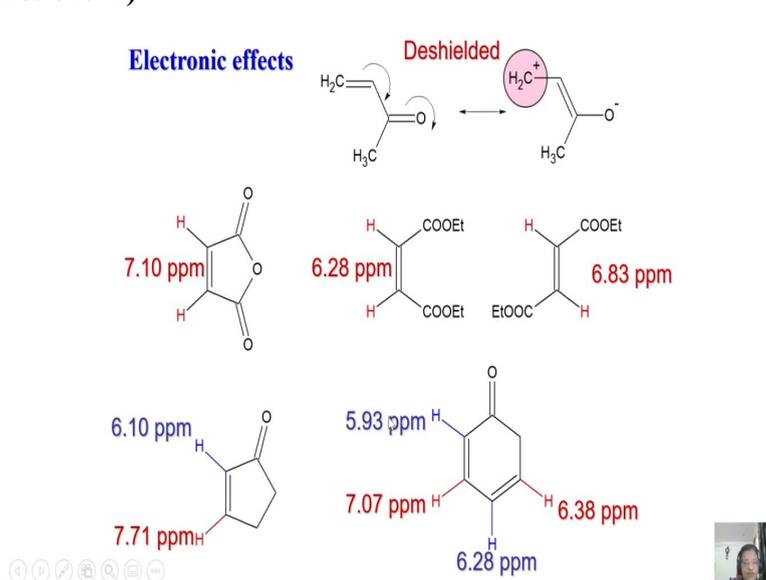
One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture – 17
Factors Contributing to Chemical Shifts - 2

Welcomes back all of you. Since last 3 or 4 classes, we have been discussing about internal interaction parameters, one of the internal interaction parameters, that is chemical shift. We understood quite a bit about chemical shifts and the causes of this chemical shift, various reasons for that, and for example, the effects which give rise to shift in the peaks. like ring current effect, anisotropic effect, substitution of electronegative atom, various concepts we discussed.

So I think we have taken a lot of time discussing this. Instead of dragging too much, I think this is time that we need to put an end to this, because in chemical shift, we can discuss lots and lots and lots of things. I just wanted to give you the flavour of what is chemical shift, and how to utilise and what is that which governs the shift in the peaks, and what are the effects on the molecule, the stereo effect and the substitution effects various things we discussed. Little bit of thing I will say today, and then we will switch over to another parameter as soon as possible.

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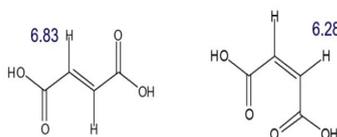
You see there is another important effect, for example, electronic effect, which causes shift in the peak positions. For example in the molecule like this substitution of C double bond O in the 5 membered ring, made these 2 peaks, of course there is a chemical equivalence, to move

to down field. This gets deshielded, this is because of this. And of course we have come across molecules substituted ethylenes, and you see this is cis- substitution of COOEt. In this molecule, these 2 peaks, of course, again chemical equivalence is there, shifted at 6.28 ppm down field, whereas instead of cis make it trans, you see the peak is already moved to another close to .6 ppm down, so close to 6.8 ppm. So, this is all because of electronic effect, if you study this why it is happening, there will be additional deshielding here, because of that.

So, as you can see the effect of all those things, about different electronic effects. In a benzene ring like this, you put a C double bond O here. Now, of course, what is here, it is a difference, not a fully aromatic system. There is no double bond here, but look at this; these 4 protons are completely non-equivalent, and because of that, you can see just by substitution of C double bond O group in this and all the 4 protons are different. This sees little bit high field, whereas this one, especially these 2 that are marked, which are meta for this is more downfield compared to this.

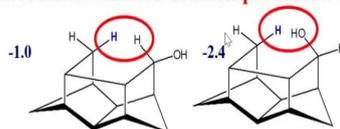
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In cis-malonates the deshielding is not as strong because the two cis groups bend the molecule out of the plane, resonates at high field



Van der Waals effect

The effects of close contacts on chemical shifts. In these molecules, the close H...H or H...O contacts produces a low field shift



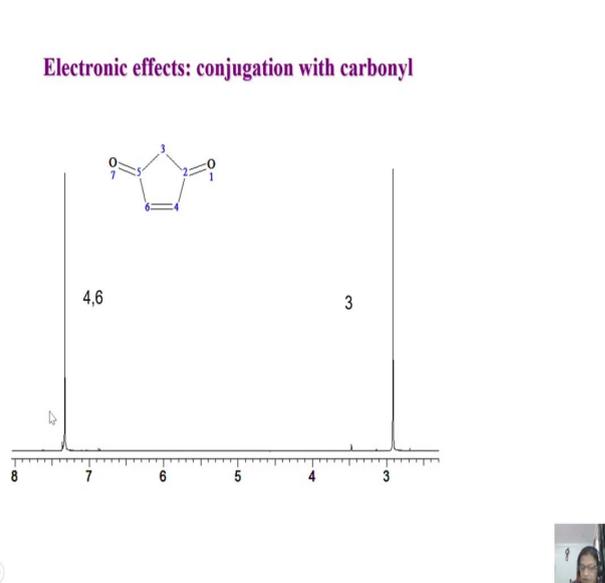
So, these are the electronic effects. And this is a classic example in cis-malonates. What is happening is, deshielding is not very strong because 2 cis groups bend the molecule out of plane in this type of molecules, and resonates at high field. As a consequence, you see in this case, this proton comes at 6.83 ppm, whereas, this proton comes at 6.28 ppm. So, these are some of the examples.

Of course, this is not the end, we need to look particularly for your molecule of interest, when you are looking for your system, various other effects would be there? You have to consider

various things. Of course there is one more important factor which can affect chemical shift, is van der Waals effect. See, this is the effect of close contacts on chemical shifts in these 2 molecules, which are shown here.

For example, this proton and this proton come in close spacial proximity. Similarly, this proton and this O comes, in spatial proximity, because of this van der walls effect, this gets more shielded, see this goes up to -1 ppm, this goes up to - 2.4 ppm.

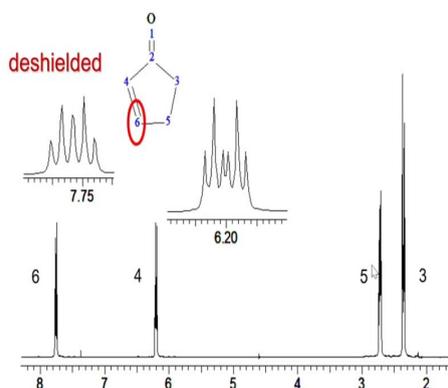
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So, these are all some effects, which happen because of substitution. It is the electronic effect, as I said in the conjugation of this C double bond O in this case, this proton you see, coming at high field, close to 2.9 ppm, whereas these 2 protons, 4 and 6 coming very close to this. See the effect of this on this molecule, it is simple molecule, symmetry here, these 2 protons are equivalent and just by substitution of C double bond O, in this position made this proton come to high field, whereas 4 and 6 protons come down field.

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Electronic effects: conjugation with carbonyl

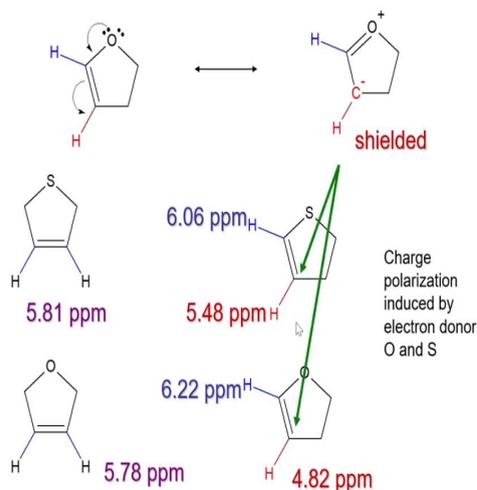


And the electronic effect can be seen with a carbonyl group if a carbonyl is attached here like this, you see what is going to happen, how the protons, this proton is more deshielded. Of course, there is a double bond here, you can see that. Of course, this proton on the other hand moves to 2.8 ppm. See the difference? How this electronic effect can drastically change the chemical shifts, especially when you are conjugated with the carbonyl group, this proton comes down field, whereas this proton come high field.

On the other end, same way this is proton goes along with this proton 6. This also comes down field. Similarly, along with 5 this proton 3 also comes down field. It is a beautiful effect you can see when a conjugate with the carbonyl group, these 2 with these 2 carbon double bond 4 and 6 come down field and 3 and 5 come to high field.

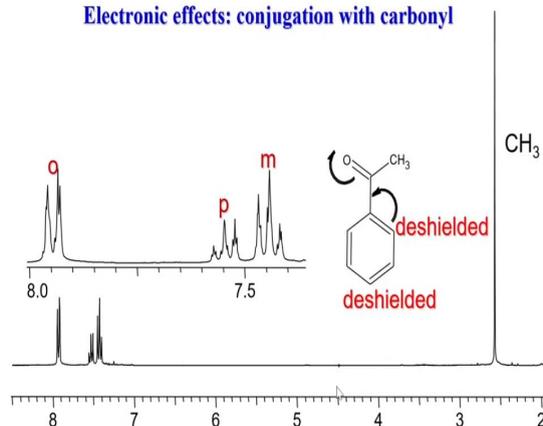
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Electronic effects: conjugation with heteroatom



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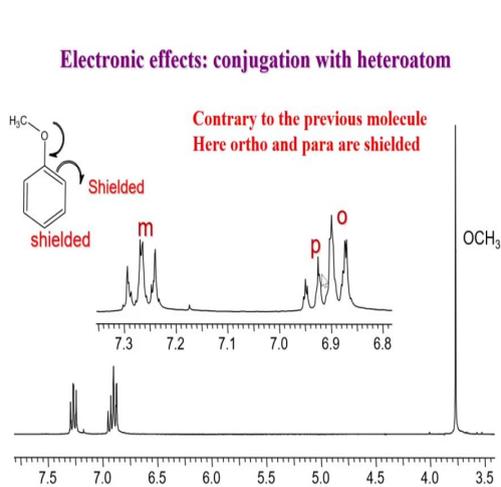
Electronic effects: conjugation with carbonyl



So, you can keep continuing like this. There are lot more things one can discuss and depending upon conjugation within the heteroatom like oxygen, which is put. Again how the electrons are moving here you can find out. It is in this case you can see that, this proton gets more shielded here. Whereas, if you have a sulphur here, see this comes at 5.81 ppm, whereas, in this case this proton is more deshielded than this proton.

So, like this, you can talk lot of things. And of course, I said especially in a benzene group, we discuss some of the things in the mesomeric effect with the nitrobenzene and annulene when we discussed, how the charge density when it is located more in the ortho and para positions, how those fields get shifted. Similarly, C double bond OCH₃ when it is added to the benzene ring, of course, these protons which are in the ortho position to this functional group and to the para position, these two get deshielded. Whereas, the protons which are in the meta position gets shielded. As you can see meta protons come high field whereas ortho and para protons come down field. Of course, ortho is more down field shifted because it is in close spatial proximity with this functional group as you can see this.

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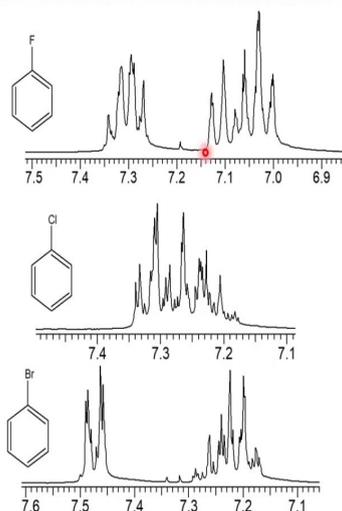
The same thing, of course, if you put a OCH₃ group this also we saw when we understood the mesomeric effect with ethylene, one of the examples I took. The same thing where we had the symmetry, which was broken which I showed you how electron donating group and electron withdrawing group affects the chemical shift during the mesomeric effect. That is what we saw. Similar example here, for the benzene ring also. We discussed about the mesomeric effect aniline as an example.

But in this case, take the aromatic protons here, when the addition of OCH₃ in this position makes the protons in the ortho and the para position shielded, whereas meta protons are deshielded, exactly what you see. The meta protons come down field, but ortho and para protons come high field. So, these are some of the examples we are giving. Same thing when we conjugate with an heteroatom like this NH and CH₃ group.

Same way another example similar to a mesomeric effect, if you see how the charges, electrons are moving, you can see that the charge density is more at this place, and this place that is ortho and para yet again, compared to meta. As you can see meta protons move to the down field, whereas para and ortho protons come high field.

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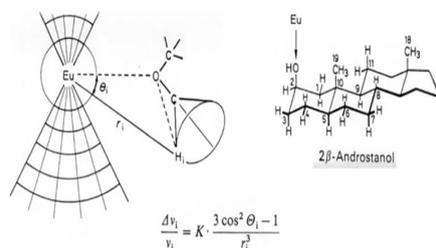
Aromatic: inductive effect and resonance effect



Of course aromatic inductive effect with fluorine, chlorine and bromine different electronegativity of the substitution, the spectrum drastically changes. You can see the change in the spectrum because how ortho, meta and para protons move. In same way we can work out, this is an inductive effect on the aromatic systems.

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Use Shift reagent to disentangle complex multiplet



Distinguishes between protons based on their proximity to the functional group coordinated to the lanthanide

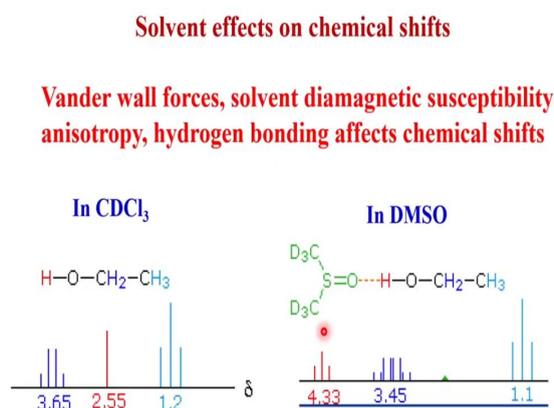
The angle dependency can produce shifts in either direction.



Of course, one example I want to tell you, we do not discuss this now, we will discuss later. We will come back again later. When you use shift reagents, as an example, sometimes like a europium salt or praseodymium. These are some salts, which we can use when the spectrum gets completely entangled. Very, very, over-crowded spectrum with there, which you may find it difficult to analyse, for example, in a molecule like this. Then if you put this type of complex, which is called europium salt, of course, we have a praseodymium, varieties of salts, which are called shift reagents. Then what happens? It goes and attacks at this place.

And it distinguishes the protons based on the proximity with the functional group, when it coordinates with the shift reagents, when it coordinates with a lanthanide complex.

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So all of these effects, you can utilize when you start analyzing the spectrum, depending on the judicious choice of what you want to see, you can make use of some of these tricks. To disentangle the complexity you can use shift regions. More about shift reagents, when we will come back in one of the classes later. But at the moment, I just wanted to tell you because you need to understand many things.

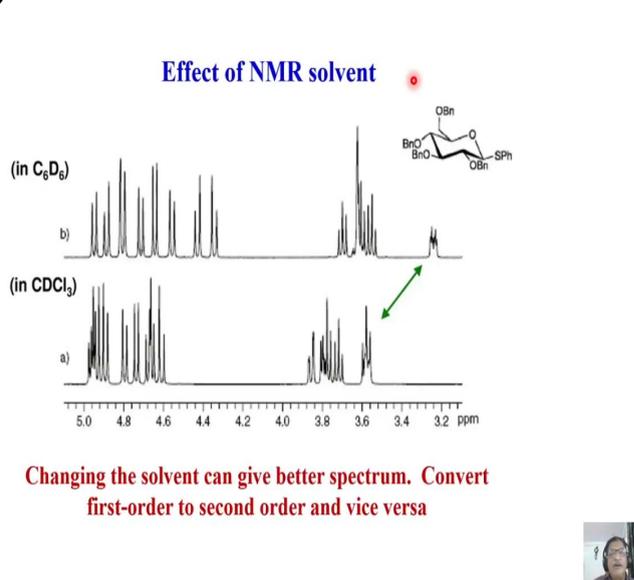
Sometimes it so happens you synthesize the molecule and you will see that you record a spectrum in chloroform, we will get one type, you record the spectrum in the different solvent like dimethyl sulfoxide, DMSO, you will get a different spectrum. Sometimes it may appear different. You may be wondering why? what is happening, these solvents sometimes influence your molecule, the solvent effect is there on the chemical shift. What happened looks at in this molecule CH₃CH₂OH, which is famous ethanol molecule.

Now, if I take this thing in chloroform, very clearly I am going to get a peak for CH₃ group. Peak for CH₂ group and a peak for OH group. No doubt about it. Very clear. What happens if you take the same molecule in a different solvent? That is DMSO. See what is happening? This SO group of DMSO starts forming a hydrogen bond with OH group. It is intermolecular between 2 different molecules. SO group of DMSO and OH of these starts forming a sort of hydrogen bond.

And as a consequence, you will see different type of thing. What is happening here. Remember, for this and this spectrum is same, but you will see additional effect. You must understand what we are seeing. This CH₃ group remain the same, small change in the chemical shift because of the solvent. Let us not worry about it. Look at the CH₂ group. CH₂ group was a quartet here, 4 lines pattern. Why it is a quartet comes, in the next topic of our discussion, when we come to scalar couplings, and OH was a singlet.

Now, you look at it. The CH₂ from downfield move to high field, and OH group which was around 2.5 come to 4.33 ppm moved to down field. In addition to that, this OH which was singlet appears like a triplet here, whereas this was quartet, now you see 2 sets of quartets here. What does it mean? Means because of that, this hydrogen, this proton can interact with this CH₂, make this quartet into 2 sets of quartets, that we understand in the next class about coupling interaction. Similarly, this will interact with this, instead of one peak, it will make this as a triplet. This is the effect of hydrogen bond, sometimes affect the chemical shifts and you will see all this information.

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Now for understanding another step of effect of NMR solvent, look at this molecule. This was taken in CDCl₃. What is the difference between these spectra? Same molecule, it was taken in benzene solvent. What is the meaning of that? Here what is happening in the chloroform, the spectrum gets crowded and sometimes chemical shift becomes so small, I will tell you later what is second order. It was a first order and becomes more like a second order spectrum, the second order spectrum is easy to analyse.

Moment you change the solvent, there is a change in the chemical shifts, spectrum gets better dispersed, look at this region. Look at this region, better dispersed. Similarly, look at this portion. This has completely moved about nearly 0.4 ppm away to the high field, and with such things what happens? it will aid you in the analysis of this spectrum because the complexity gets reduced now. I will tell you this in the analysis,

Understand the problem; sometimes you do not do anything. Simply change the solvent. When you change the solvent, sometimes, because of that, you can see this spectrum gets better and better, in some way. But not always, do not think that you keep on changing the solvent to take the NMR spectrum to get a better quality spectrum, like that. No. In some examples I am giving you, it can sometimes happen. But by and last, it do not change so drastically. But in some examples of the molecules like this, or where we saw in the previous example where OH was there, which was performing hydrogen bond with the SO group of the DMSO. So there was a change in the spectrum, only when there is an intermolecular interaction between the solvent molecule and that of your molecule of interest, sometimes your see different spectrum. The quality of the spectrum will be different, you get better dispersion and better resolution, that not always, but just remember this point.

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Chemical shifts through hydrogen bonding

There is no distinctive scale for the exchangeable protons, OH and NH

Resonance positions of these protons are strongly dependent on the medium and temperature.

The formation of hydrogen bond leads to significant down field shifts

Intra and intermolecular hydrogen bonding can easily be distinguished



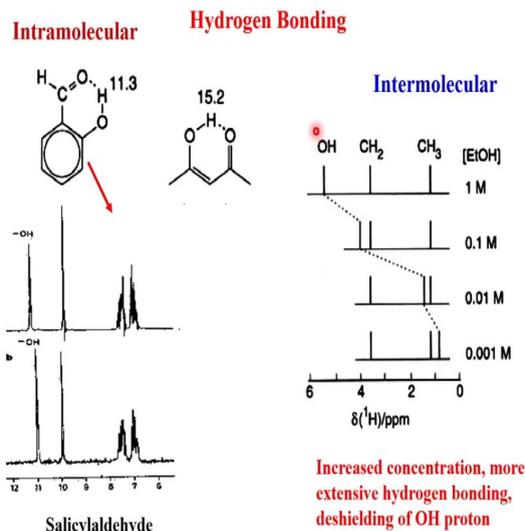
Of course, deshielding how it happens in the electronic effect we saw this and there is no point in going further, but I want to tell you one thing, in a given molecule if you come across OH and NHs present. There was a scale which I gave you, different regions where you can see different functional groups. I showed you one table where chemical shifts, regions of interaction, where each group chemical shift come from.

For example, where CH₃ comes, where benzene ring comes in proton. Everything has been more or less tabulated by many, many people, pioneers who did work in this area. They have done a lot of work and tabulated. To start with, we have an idea where to look for your peak. If you have a particular group in your molecule. But, if OH and NH is present in your molecule, there is no distinctive scale like that. I can say in the proton spectrum CH₃ peak comes between 1 to 2 ppm or 0.5 to 2 ppm. But if you ask me, where does OH peak comes in my molecule or I have an NH proton in my molecule, where does that NH peak come. I cannot tell you that off hand. There is no distinctive scale for these. They are called exchangeable protons. For these type of exchangeable protons there is no preferred region of observation. It can move anywhere in the spectrum depending upon the type of interaction.

This is very important and we should remember that, it also depends upon the physical condition of the experiment like temperature, solvent medium, solute concentration, various things, depending on the hydrogen bond. So but one thing is, you can also notice if your molecule is forming a hydrogen bond, this lead to significant down field shifts, you can understand if OH is there NH is there, it is forming a hydrogen bond. That particular proton can move to down field. Remember in the example of ethyl alcohol when they form a hydrogen bond with the dimethyl sulfoxide what happened to OH peak? which was somewhere around 2.5 or 3 ppm move to 4.3 ppm, remember, that is the thing. So when there is a hydrogen bonding, peak moves downfield. Now you ask me a question how do I know what type of hydrogen bond it is?

If your interest is to study hydrogen bond, weak molecule interactions within the molecule and if you want to know if the hydrogen bond is intermolecular or intramolecular. Both are possible, can we identify by NMR? Of course we can do, there is a way for it. But we will not go into that details when we will come to the application if there is timem, we will discuss. Otherwise, simply remember, If there is hydrogen bond in your molecule weak molecule interactions are there, you can study by NMR. The hydrogen bonded proton moves to downfield, the significant downfield shift will be there.

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So, this is a simple example, when a molecule like this is there, when it forms hydrogen bond with OH, intramolecular hydrogen bond is there, then, how the peak is moving, OH peak. Of course, slight shifting is there, whereas if we take ethyl alcohol, then what happens it can form an intramolecular hydrogen bond with itself or with EtOHm then what happens? As you keep on increase the concentration of ethyl alcohol from low concentration to high, you see OH peak it was somewhere here, it come, comes, comes here.

In fact OH peak was going beyond CH₃. That is what I said, exchangeable protons OH and NH, there is no distinctive chemical shift range, at very low concentration of EtOH, it was beyond CH₃, that is very high field. As we keep on increasing the concentration of EtOH see it moves so much downfield, drastic shift is there. So, these things help you in understanding hydrogen bonding and other things.

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Empirical Prediction of Chemical Shifts

Shoolery Rules



So, I have given you some basic idea about various things about chemical shifts, how it arises, how do we express in ppm, frequency, what happened as a function of magnetic field to the peaks, and what are the things which contributes to the shift in the peaks of that chemical shift, why it comes? And what happens if there are different functional groups present? How do we use some idea to interpret with electronegativity substitution there, if ring current effect is there, If they are the anisotropy of the bond is there, all those things, some basic ideas I gave. Of course, these are only some physical pictures clearly that I am giving you idea to start interpretation, but no in doubt if you want to understand the NMR, it is huge ocean, a lot more things you can discuss. So this should be more than sufficient to make you to begin the analysis, already.

And rest of things you have to capture yourself, you can go and read lots of fundamental books, how to interpret many of these things. There are many more ways to interpret, I have taken only a few examples, a lot more examples we can take, and then you will become a master some day. With this now I ask you one question. We know where the chemical shift comes, everything. We had some idea based on the tables, which was given by the workers in the field over the years, that is a starting point for analysis.

But you can ask me a question, Is there any way empirical I can calculate and say, I can predict where should be this chemical shift of a particular peak in my molecule. Suppose I have small some small molecule, can I predict where should it be, where I should look for this peak, in which region of the NMR spectrum. So, empirically is there a way to predict chemical shifts. Not for all big molecules. Remember, it is just some idea.

There are examples in small molecules in both aliphatic and aromatic, both for proton chemical shifts and carbon chemical shifts also, which I tell you later when you come for heteronuclear analysis. There is a way, where empirically we can predict the chemical shifts. They are called Shoolery rules. Remember, they are called Shoolery rules. So what I am going to tell you is, so, these things if I start discussing it will take, or drag lot of time, another half an hour I require to explain to you, with examples.

But this is another interesting topic, please remember, I will not cover this topic to empirically predict the chemical shifts by using Jim Shoolery rules. I will try to come back if there is a time. So, that we can discuss with how some examples, what is the experimentally determined chemical shifts or what is the theoretically calculated or empirically predicted chemical shifts. So, one thing you know, I have the choice, I can go to the discussion of the second interaction parameter called coupling interaction, scalar coupling.

Or I do not know how much time I am left with. What I will do is instead of changing the topic and coming back to the Shoolery rules again, I will give 1 or 2 example quickly, because these things are not practiced too much nowadays, nobody uses these things. This is only an idea which was given in the early days of NMR by Jim Shoolery. But actually, just to give you a feel, I will give you one simple example in about 10 minutes instead of coming back again. So, that from the next class we can start afresh with scalar couplings.

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Can we estimate the chemical shifts?

Yes !!! Shoolery rules

Chemical shifts arise due to electronegativity, electronic effects, hydrogen bonding, ring current effects, etc...

Most of the effects are *additive*

If we can know the contribution from the different groups and bonds the chemical shift of ^1H can be estimated by adding all these contributions

There are several empirical rules, derived by Shoolery



So, now, the question I asked you, how do you derive out the chemical shifts using Shoolery rules. Remember I was telling you the chemical shifts arise because of various reasons, electronegativity, electronic effects, hydrogen bonding, ring current, several effects are there and in any given molecule, this is not one effect, there are multiple such effects could be there. You can simultaneously have electronegativity effect may be there, there will be a hydrogen bond going on, there will be a ring current effect.

Many things may be possible it is not that exclusively only one interaction is present; one type of effect is seen. But interestingly what Jim Shoolery rule says is if you know these things, there is a way we can find out effects of all those things. Because, all these effects are additive. You can add all these things, different effects, and finally get what is the chemical shift for a particular proton.

Then where you add it. You must have something. And there is a base chemical shift is given for a particular group, by Jim Shoolery, base chemical shift. With base chemical shift, now we look at the other groups which are present and find out their contributions, which there is an empirical way, which is already predicted, add or we keep on adding this value and get finally total value of this thing.

Then you will know what is a total chemical shift, because of addition of all these effects, if they are present to the base value, and do the experiment and find out the chemical shift experimentally, and in most of the cases, by and large they are comparable. Understand, this is the way we can predict these chemical shifts. But of course, nowadays with the most advanced things are available, nowadays nobody is interested in doing this type of predictions.

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Identify the type of proton we have, such as aliphatic CH₃, CH₂, CH, olefinic CH₂ or CH, aromatic, α or β to a ketone or alcohol, belonging to an α,β-unsaturated system, etc.

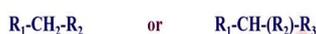
They will have a base value

Then add up the contributions from different groups in the surrounding

$$\delta_H = \delta_{H_{base}} + \sum \text{contributions}$$

Example : For Aliphatic compounds

Just use two 'skeletons' with two base values,



and add the effects from the R₁, R₂, or R₃ groups



And there are lots of ways to get the chemical shift by using Gaussian and other things. But an idea is very important to understand. What I said is, for example, if you want to identify the type of protons you have, like aliphatic could be like this. Olefinic, ketone, aromatic, ketone, alcohol, many things could be there. So, this type of proton if it is there, what Jim Shoolery said is, there is a base value of chemical shift for all those things, take a base value.

How do you get the base value? It is already there, many people have worked out and we know what is base value to start with. The value is given to you. Do not need to worry about it. Then, start summing up the various contributions one by one, keep on adding everything and find out what is the total chemical shift you get. You get the point. Now, that should be your predicted chemical shift, after adding all the contribution to the base value.

Now, for example, we take this group CH₂ which has R₁ substitution and R₂ on higher side. Or you can have a CH, which is R₁, R₂, R₃ are the substitutions. And then CH₂ can have an additive effect, because of R₁ and R₂, it can be additive, it can be subtractive also. Additive means all these factors are taken together, but this contribution could be negative also. Similarly, take a CH proton here, this has R₁, R₂ and R₃.

Again for this proton all these additive groups are close to it. And if you have something which is 25 bonds do not worry. Because as bond increases its effect reduces. We saw inductive effect. If you go 3 to 4 bonds away, the effect is less. That is what we observed in several examples of chemical shifts. And we are trying to understand what happened if we

lengthen the chain like that. So, at least one or 2 substitution next to each other. If you consider you can get the chemical shift.

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$$\frac{R_1-CH_2-R_2}{\delta = 1.25 + R_1 + R_2}$$

Substituent	δ
Alkyl	0.0
-C=C-	0.8
-C≡C-	0.9
-C ₆ H ₅	1.3
-CO-R	1.3
-OH	1.7
-O-R	1.5
-O-CO-R	2.7
-NH ₂	1.0
-Br	1.9
-Cl	2.0

For CH₂Br₂

$\delta = 1.25 + 1.9 + 1.9 = 5.05$ ppm,

Experimental value of 4.94 ppm

$$\frac{R_1-CH-(R_2)-R_3}{\delta = 1.50 + R_1 + R_2 + R_3}$$



This is a simple example I will give, 1 or 2 examples, so that we do not have to go deep into these things Jim Shoolery rules, but you should have the idea. I am considering the example of a CH₂ protons, CH₂ proton, there are 2 protons here, and R 1 and R 2 are the substituents on either side. If you see the type of molecule you have, if I am looking for CH₂ group with a substitution on either side, then according to Shoolery rule, base value for this is 1.25 ppm, and for this base value, the effect of R1, R2 have to be added up. Then you know what is the total chemical shift for CH₂ protons. Did you get my point? Do not get confused. We take the simple example of this group. For that we will take CH₂BR₂. Di-bromo ethane, what is going to happen? He says, for this type of thing 1.25 is the base value. Take 1.25. Now, what is the effect of the substitution here?

How much you have to add up. Here has a table given. Remember for different substituents, table of contribution for chemical shift is already made. This is a lot of work, we should really appreciate the quality of the work they did, or how much they have contributed for our understanding. So much of work has been done and they have made a list. If there is a bromine substitution, go into this table, is there is a bromine attached for CH₂.

You have to add 1.9. If instead of bromine, if let us say OH is attached, then you have to add 1.5. Now take the example of CH₂BR₂. There are 2 bromines attached. Take the base value of 1.25. Now, what is it for each bromine, it is 1.9. For 2 bromines R1 and R2 on either side.

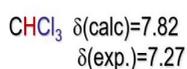
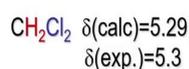
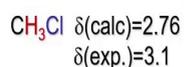
1.25 + 1.9 + 1.9; you add up you get 5.05 ppm. This is the predicted value. In experiment, when we really did the experiment, they found the value to be 4.94.

But 0.1 ppm difference is there. But look at this nearness value of the predicted value. So, this gives an idea that by and large to some extent, you can predict the value. Do not say that I do not have to do NMR experiment now onwards. I know this value I will predict it. No, it is not always true. Now this is only accurate, no, not accurate only approximate. But you want to really get the chemical shifts, you have to really do the experiment, analyze, do not go back tomorrow and say I have this table. I know what to do, and I got the idea. I save the experimental type. I don't have to do any NMR work? No, do not do that, that is not right. This is the important point. Now what happens if I consider a CH proton? If there is a 3 type of substitutions like these, R1, R2, R3. Same way, depending on what is the R1, you can do that.

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Calculating Shifts for simple aliphatic compounds
using methane as the base value

$$\delta = 0.23 + \sum S_i(\delta)$$



Substituent	$S(\delta)$ (ppm)
Cl	2.53
Br	2.33
I	1.82
NRR'	1.57
OR	2.36
SR	1.64
CR-O	1.70
CR=CR'R'	1.32
C≡CH	1.44
C≡N	1.70
CH ₃	0.47
Phenyl	1.85
OH	2.56
OCOR	3.13
COOR	1.55
CF ₃	1.14



Very simple way. Now, I will take the example for aliphatic carbon CH_3Cl . For base value for that is 0.23, that is for the chemical shift of the methane. Remember, I told you the chemical shift of methane. Now you have to add the total value for the other substitution. Now if there is chlorine, it is 2.53, base value is 0.23 + 2.53, if you add, it turns out to be 2.76. But what is experimentally observed is 3.1 ppm.

Now, extend this logic we also did that what happens if we change the substitution of number of electronegativity atoms, how the chemical shifts, shifts, we saw that, you know, shifting of the chemical shift. And we knew more the electronegativity atoms, more the number and it

shifts more to the down field. We observed that in one of the previous classes. I hope you are with me, do not forget. We discuss this point.

What is the chemical shift for CH₃Cl, CH₂Cl₂ and CHCl₃, all the 3 we got it. And this is the calculated and this is experimental. Now do the same thing for this molecule CH₂Cl₂. Base value you take it and Cl₂ is 2.53 times into 2, if you add it up, it turns out to be 5.29. And experimentally, what is observed is 5.3 almost matching. Right! Now for CHCl₃ calculated value, the 3 times you take it and add it up to this base value, it comes to 7.82, but experimentally 7.27.

So all this values of prediction with a chemical shift, using Jim Shoolery rules gives you an idea about the contribution from the different substituents. You should know the contribution from each of these substituents, if you have a table, if you know the base value, you can arrive at the approximate value of the chemical shifts, you can predict.

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Calculating Shifts for aliphatic compounds

$\delta = 0.933 + \sum S_i(\delta)$

e.g. $\overset{1}{\text{CH}_3}-\overset{2}{\text{CO}}-\overset{3}{\text{CO}}-\text{CH}_3$

Subst. Effect value	
-C ² -C ³	+0.244
=O (at C ²)	+1.021
=O (at C ³)	+0.004
-CR ₃ (at C ³)	-0.038
$\Sigma S_i(\delta)$	+1.231
$\delta = 0.933 + 1.231 = 2.164$	
Experimental = 2.16	

Structure	S _i (ppm)
-C ²	0.248
-C ² -C ³	0.244
-C ² -C ³	0.147
-C ² -C ³	0.006

Substituent	Position	S _i (ppm)
-CR ₃	3	-0.038
Double bond	1	3.802
	2	0.583
	3	0.203
Triple bond	1	1.032
	2	0.694
=O	2	1.021
	3	0.004
-OCH ₃	2	-0.374
-OCH ₂ CR ₃	2	-0.237
	3	0.210
-OH	1	2.467
	2	0.048
	3	0.235
-O-CO-CR ₃	1	2.931
	2	0.041
	3	-0.086
-F	2	0.089
	3	0.131
-Cl	1	2.170
	2	0.254
	3	0.177
-Br	1	1.995
	2	0.363
	3	0.023
-I	1	1.946
	2	0.388
-NH ₂	2	0.094

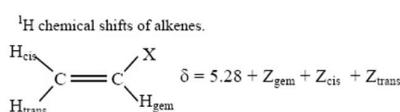
So with this last example, I am going to stop here because there is no point in going too much about these things. Basically the idea is, with the base value you have to add the value of substituents. Now, for aliphatic compounds, again, this is taken from one of the books, where you can see for different substitutions, and substitution in which position that is also important.

For example, the substitution may be in the position 1, 2 and 3 and if the substitution is different position what is the contribution, and keep on adding for that. For example, in case in some case it is negative, see minus here. So it is minus here. In some cases, as I say it is

not always additive, it is only the contribution factor which we have to take into account as a sum while working out the approximate value of the chemical shift, predicted chemical shift.

Now for this molecule example for this one substituent effect for C2C3 is 0.244. For oxygen at C2 is 1.021. You can see oxygen 2 at position 2, 1.021. Oxygen in position 3, 0.004; take that value. CR3 at CH 3 group, but position 3, you see that - 0.038; add up all these values. And this is a base value for this type of molecule and total if you add up everything you get the chemical shift of 2 ppm, approximately for this proton. You understand, So, experimentally, the given value is something which is 2.2, it comes around 2.2.

(Refer Slide Time: 36:41)



Substituent	Z _{gem}	Z _{cis}	Z _{trans}
H	0.0	0.0	0.0
Alkyl	0.44	-0.26	-0.29
CH ₃ O, CH ₂ I	0.67	-0.02	-0.07
CH ₂ S	0.53	-0.15	-0.15
CH ₂ Cl, CH ₂ Br	0.72	0.12	0.07
CH ₂ N	0.66	-0.05	-0.23
C=C	0.50	0.35	0.10
C≡N	0.23	0.78	0.58
C=C (isolated)	0.98	-0.04	-0.21
C=C (conjugated)	1.26	0.08	-0.01
C=O (isolated)	1.10	1.13	0.81
C=O (conjugated)	1.06	1.01	0.95
CO ₂ H (isolated)	1.00	1.35	0.74
CO ₂ R (isolated)	0.84	1.15	0.56
CHO	1.03	0.97	1.21
OR (R aliphatic)	1.18	-1.06	-1.28
OCCOR	2.09	-0.40	-0.67
Aromatic	1.35	0.37	-0.10
Cl	1.00	0.19	0.03
Br	1.04	0.40	0.55
NR ₂ (R aliphatic)	0.69	-1.19	-1.31
SR	1.00	-0.24	-0.04

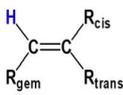


So, like that you can find out chemical shift of the alkenes for trans, cis, and geminal protons, if present. What happens if there is an H cis position, geminal position, trans position and for this case, alkenes base value is 5.28. We have to take what happened to different substituents whether it is, Cis to this proton, geminal to proton, trans, if is there a geminal group let us say, is proton.

What is germinal proton then value for this is 0. If it is CH₂N take 0.66 geminal. And trans if it is let us say, bromine trans 0.55. Like that you add up and you will know what should be the chemical shift for this proton. Like that you can easily do it. This is the basic idea I want to tell you about Jim Shoolery rule to predict the chemical shifts. of course, if I have to discuss this, this time is not enough. I need at least another half an hour to an hour, to give more examples, and slowly to calculate and show what we can do, and everything.

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Olefines : For alkenes the table for the base value is different, also the stereochemistry of the substituent (*cis*, *trans*, or *gem*) is to be considered



$$\delta = 5.25 + R_{gem} + R_{trans} + R_{cis}$$

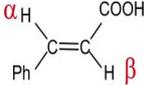
Eg. cinnamic acid
(*trans* Ph-CH α =CH β -COOH)

$$\delta H_{\alpha} = 5.25 + 1.38 + 0 + 0.98 = 7.61$$

$$\delta H_{\beta} = 5.25 + 0.80 + 0 + 0.36 = 6.41$$

reported values are 7.82 and 6.47 ppm

Substituent	δ_{gem}	δ_{cis}	δ_{trans}
H-	0.0	0.0	0.0
Alkyl-	0.45	-0.22	-0.28
-OR	1.21	-0.60	-1.00
-COOH	0.80	0.98	0.32
-Ar	1.38	0.36	-0.07
-C=C-	1.24	0.02	-0.05
-OH	1.22	-1.07	-1.21
-Cl	1.08	-0.40	-1.02



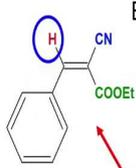


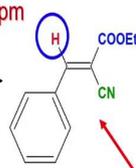
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Use of empirical values to decide the isomer)

Experimental: 8.22 ppm

Which one ??





Z isomer	effect
Base	5.23
Ph (gem)	1.43
CN (cis)	0.78
COOR ^{conj} (trans)	0.33
Total	7.77

E isomer	effect
Base	5.23
Ph (gem)	1.43
CN (trans)	0.58
COOR ^{conj} (cis)	1.02
Total	8.26



And ofcourse right now, I have lots of example to discuss. And one of the important application I tell you with Jim Shoolery rule. in a molecule like this I told you an ethylene molecule depending upon the substitution you can calibrate the chemical shift. this is what I showed just now in the example here. You can find out what is the substitution and calculate, and why you know one of the examples like this, the question was whether this is the molecule or this is the molecule. So whether COOEt is cis to this, or trans to this proton.

Because experimental value is 8.22. Now, what they did is, they started making the calculations by taking this base value 5.23 adding all these substituent effect and if this was the case, if it is COOEt or CN group cis to this, you will get this the chemical shift approximately predicted, whereas in this case it is 8.26 and it is very close to it. So these are one of the few applications of Jim Shoolery rule which used to be there in olden days.

Now, enough for the day. I will stop it. I have given you basically a vast information about chemical shifts, their prediction various effects of chemical shift as how to know what happens on different substituents and everything and about 3 to 4 classes we have discussed about it even more. So, that shows the voluminous nature of this information available about chemical shifts. So rest of things I leave it to you. This is only the initial point.

Rest you have to build up on your own, start reading more and more. will tomorrow I will come back. I will discuss more about another interaction parameter called scalar coupling, in direct coupling. That is a very, very important parameter with which you can start analyzing more complex molecules.