One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis

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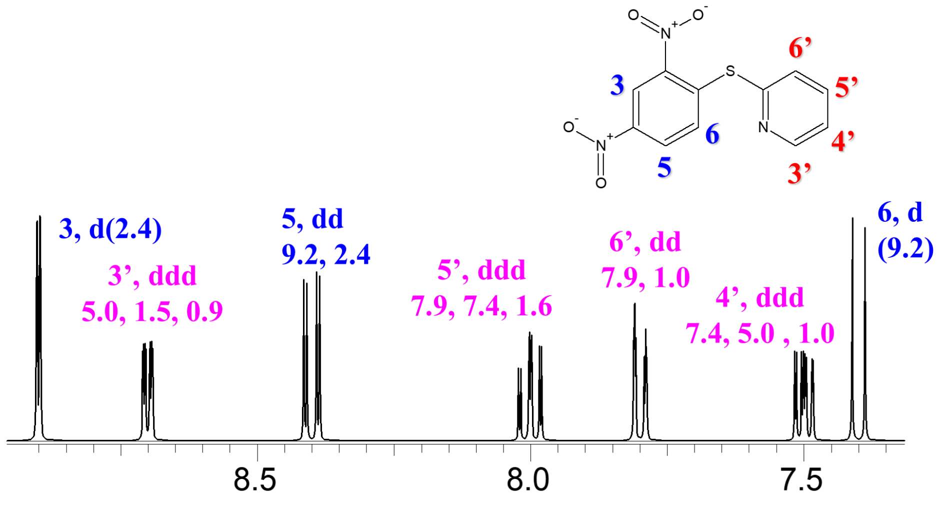
Lecture 21: Analysis of 1H NMR spectra-III

In the last class, we discussed a lot about analysis of the proton NMR spectra. We started by simulating the spectrum in a hypothetical example of CH, CH2 and CH3 coupled among themselves with the different coupling strength. Using a family tree approach, we synthesized the stick plot of the spectrum for CH group, CH2 group and CH3 also. And we saw in the given molecule depending upon which is the functional group you are looking at, the pattern can be entirely different. It could be double of triplets, quartets of doublets, varieties of things we saw that. And afterwards, we started really analyzing the spectra of molecules including simulation of a molecule called CH2D2, where we simulated the spectrum for carbon 13 proton and deuterium. All of them are coupled among themselves. carbon 13 in its natural abundance, and carbon 13 and proton are spin half nuclei, deuterium is spin 1 nuclei. We just saw when we simulated the spectrum how in a small molecule like this, depending upon the nuclei of your interest, the type of spectra we are going to get, the appearance of the spectrum can be entirely different. That is what we observed. Then, we took realistic example of a small molecule right from small molecule, we started analyzing proton spectra. Based on the chemical environment assuming we know or we have some knowledge about shielding and deshielding. We always started with the CH3 group which is coming at the very high field. And then, looking at the splitting pattern when the CH3 is coupled to CH2, what is the possible splitting patterns. Using that idea and also using the intensity pattern and with the idea of the chemical shifts, ranges of the chemical shift which appears because of shielding and deshielding, we did the analysis of large number of molecules. From fairly q simple molecule we went to complex molecule, not too complex, simple organic molecule to some extent is complex. Molecules may not be big, but spectra are complex. Then, I wanted to introduce to you how we can analyze the spectra of molecules containing phenyl groups. We took the example of a mono substituted benzene where we saw ortho protons. Ortho protons will experience one ortho to the substituent. That will experience one ortho coupling and also one meta coupling. And as a consequence, I said it can be doublet of doublets. If you look at the meta protons, meta protons depending upon whether the ortho couplings are identical or not, again it is going to be triplet, or it is going to be doublet of triplets. That is what we saw. And then, we also went into the example of benzene in which we took the example of molecule like asymmetrically ortho disubstituted benzene like this.

We took the example of asymmetrically ortho disubstituted benzene; and I said if I look at the proton A, there is a possibility it can experience ortho coupling, meta coupling and para coupling, all are of different strengths. As a consequence, it is going to be doublet of doublet of doublet. It is going to give you 8 line pattern. That is what we saw. It is going to be like this, we get 8 lines. Whereas, if you look at proton B, I said proton B again has two ortho couplings which are different. As a consequence, you may get 8 line pattern, because it has two ortho couplings and meta coupling. Whereas, if you go to this, this is the splitting pattern you are going to get. One ortho split into a doublet, other ortho splits each of these into doublet of doublet, then para will make it 8 line pattern. Assuming a situation, the two ortho couplings are identical, not different in which case you are going to get the triplet of doublets. Large triplet comes because of two ortho couplings are equal and then each of the triplet split into a doublet because of another para coupling. This is how it is. It is a triplet of doublet. And of course, what happens to the HC and HB? There HC can be doublet of triplet, if two ortho couplings are equal because HC can experience two ortho couplings and one meta coupling. Similarly, HB experience two ortho couplings and one meta coupling. The pattern for both of them could be ddd doublet of doublet of doublet. Or if the two ortho couplings are equal, again you are going to get triplet of doublets. That is what we are going to get. Only thing is the appearance pattern will be different because of the coupling strengths are different. That is what it is. So, we got the pattern similarly for, of course, HD 8 line pattern we should get. With this now we want to continue further today.

We will look at asymmetrically meta-disubstituted benzene. What will happen if they are asymmetrically disubstituted like this? In which case all the protons are chemically inequivalent. HA if I look at it, it experiences two meta couplings and one para coupling. Both the meta couplings can be different, because the substituents are different. In which case you are going to get 8 line pattern for proton HA. If accidentally meta coupling both are equal as I said it is going to be a triplet of doublets. If these two meta couplings will split this into a triplet they are equal and then it will para coupling will make it triplet of doublets. What happen to proton HA? if is like this. It is going to be 8 lines or like this. We go to the proton HB. How does proton HB comes? Very simple. You should see, look at it. Now we are looking at proton HB. This has one ortho coupling and two meta couplings. Obviously ortho coupling is going to be a large doublet and each of these doublet peak splits into doublets of doublet because of two meta couplings. If the meta couplings are equal it is going to be large doublet, and then it is going to be triplet. Each of them would be triplet. Otherwise it is going to be 8 line pattern. Similar thing happens if you look at proton HC. This experiences two ortho couplings and one para coupling. Again if the ortho couplings are accidentally equal it is going to be a triplet and then para coupling makes it triplet of doublets. So these are the things which you should know how when a phenyl group is present in a molecule depending upon what is the type of substitution you can have different patterns. For example if you look at HB again it is all are chemically equivalent. HB is experiencing one ortho coupling and two meta couplings. Again it has to be a large doublet because of ortho and each line is going to be 4 line pattern depending upon if the two meta couplings are equal or not. Otherwise it is going to be doublet and it is going to be doublet of doublets like this. That is the pattern you are going to get. So this is the idea just I wanted to tell you, if you have phenyl group present in your molecule how you go ahead and analyze this thing.

We will go to the example of asymmetrically disubstituted benzene group, asymmetrically para disubstituted. Remember this para disubstituted, in principle at a low frequency spectrometer, is going to be strongly coupled spin system. I already explained to you what is a strongly coupled. These two protons are chemically equivalent, but the coupling of this, this and this could be different. There can be coupling between A and A' also. Similarly, these two B and B' are chemically equivalent; there can be coupling between B and B' and also B' to A. And these couplings are all different; they could be different. As a consequence this forms a strongly coupled AA'BB'spin system and generally AA'BB' spin system if you analyze you should get 24 peaks, well separated 12 lines. But if all of them are resolved, in big molecules generally they are not resolved and you are going to get a what is called two doublet like pattern. It is like two doublets in case of asymmetrically para disubstituted benzene. This is the idea as how a spectrum appear for a phenyl group.



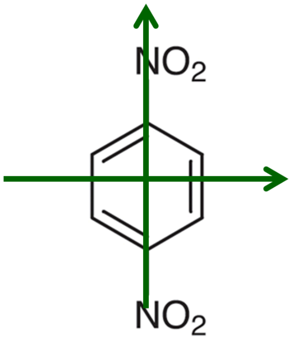
Let us analyze the spectrum of the simple molecule. This molecule is say, a little bigger molecule. We have 7 chemically inequivalent protons; 4 of them are situated in this phenyl ring and 3 are situated in this phenyl ring. If we start looking at it with the idea I already I have given you; you have to look at the phenyl ring which experience ortho coupling, meta coupling, para coupling etcetera. Start thinking. If you look at this, in this two molecule I would fairly say this proton 3 is easy to assign, because this experiences only meta coupling here, becomes a small doublet. And then if at all you resolve there can be a para coupling. It could be doublet of a doublet with the separation of 1.5 Hertz, and each of that line could be a doublet. So if it is not resolved, the long range coupling, fairly you can say this should be a doublet with a small separation. If you look at the spectrum, I would say this is a peak which is coming here. So fairly I would say that could be proton 3; And then you look at the other thing, then if you look at this one this experiences an ortho coupling and a meta coupling. This has to be a large doublet and then a large doublet because of ortho coupling of 8 hertz, around 8 hertz and then meta coupling of 1.5 Hertz. It is going to be doublet and each line of the doublet is split into a doublet. It is a doublet of doublet. Where we can think, look at it, it is one possibility, that could be, we do not know, that could be one of the ideas; that is how you have to start. If you look at this one, what is that you are going to look at? you see here if the para coupling is absent here, you say it is not visible. The only thing which it can experience is an ortho coupling. So it has to be a doublet, you find out where you are seeing the doublet. Here, of course, this is a big doublet. I would say this could be proton 6, I would say this is proton 5. This is proton 3. This is my first choice, we will see whether it is true or false. We can go ahead and then start interpreting everything slowly. Now we will start looking at it; what I said is correct. It is a proton 3, it is a doublet of 2.4 hertz coupling coming because of meta coupling. Then I said this is the sixth one, it has to be a doublet. That is also correct. My guess is correct. See idea with which we discussed about how the pattern comes for different protons, how the splitting pattern is there in the phenyl group. I could make the assignment like this. Then, of course, what I said was true. This is proton 5. This has to be doublet of doublet; large doublet is because of this thing and then ortho coupling and then it is split by meta coupling, because of this. So it is a doublet of doublet. Similarly you can extend this. Of course, if you go to this proton, this is ortho, meta, para all are there. It should be 8 line pattern; it could be doublet of doublet of doublet, very clearly you can see. One interesting thing you should know is when there is a heteroatom substituted in a phenyl ring; if there is a heteroatom ortho coupling is generally very small; not 7 or 8 hertz. As a consequence here you see ortho coupling is only of the order of 5 Hertz. So I could fairly say this is proton 3'. And then go ahead extending further if you go to this one, then proton 5'. This is very interesting because it experiences two ortho couplings and one meta coupling. I told you with the ortho coupling are nearly same then you get a triplet like pattern, and each of the triplet is going to be split into a doublet because of meta coupling. And this is what it is, this is 5'. Similarly next is 4', exactly this experiences two ortho couplings and one meta coupling. This also should be like that. Now how do you distinguish between these two? Of course, one which is at close to nitrogen, this ortho coupling is smaller; and this ortho coupling is larger. Very easily you can find out. And then with that we assign 4' also 5'. Also what is left now 6'. 6' is very easy. It has ortho coupling, one doublet and doublet of doublet because of this. This para is not resolved. It is going to be two doublet of doublet like this, similar to what is for 5; exactly that it is. So very easily you can make the assignment of the molecule containing the phenyl group, with the idea I gave you about splitting patterns for ortho and meta protons; depending upon the substituent where it is situated whether it is ortho, meta, symmetric or asymmetric substitution, we can start arriving at it.

There is also a way we can predict the aromatic proton chemical shifts, especially if you know what is the substituent. This has been worked out over the years by many many stalwarts in the area. Every information has been tabulated. If in a given molecule there is a particular substitution, how this will affect the chemical shift of the neighboring protons that has been tabulated. That is called substitution effect. And for this is for phenyl group. Of course, we can also do for aliphatic group protons. Also I am giving you an example for a phenyl group, but in which case if you want to calculate the or predict the chemical shift values of protons of the phenyl group, start with the base value of proton chemical shift, which is to be taken as 7.28 ppm. That is the base chemical shift of protons. Using that then you look into the additive effect of other substituents based on whether it is in ortho position, with respect to the substituent, whether observing proton is in ortho, para or meta position. And then what is its contribution. It is simply an additive factor you can use that, and then predict the chemical shift of all the protons of the phenyl group. It is fairly simple. And for that there is a table like this. Remember this is easily available in any of the books. Let us say I look at the NO2 group, if I am looking for a proton if the substitution is ortho to that proton, then for the base value you have to add plus 0.91. If substitution is instead of ortho, it is the meta to the proton you are looking at is having a substitution at the meta position, you have to add 0.24. If the proton you are looking at has a substituent at para position it is plus 0.37. Not only is addition you can also subtract with negative signs. So for different functional groups this has been worked out. By and large it gives you precise values, by and large. Of course, nothing can beat the experiment. You cannot say it is an experimental value, but by and large it comes close to the experimental value. Using these values of the substitution substituent and then the values which has been given in the table we can predict the chemical shift of all the protons.

Substituent	Δδ(*ortho*)	Δδ(*meta*)	Δδ(*para*)	δ(*exo*)
NO_2	+0.91	+0.24	+0.37	—
CO_2H	+0.84	+0.17	+0.34	12.09
CO_2CH_3	+0.74	+0.22	+0.34	3.89
$C(O)CH_3$	+0.66	+0.17	+0.20	2.59
$C(O)NH_2$	+0.65	+0.19	+0.25	7.46, 8.05*
$C(O)H$	+0.59	+0.23	+0.33	10.00
SO_2NH_2	+0.57	+0.30	+0.30	7.33*
CN	+0.33	+0.16	+0.27	—
C_6H_5	+0.31	+0.16	+0.07	—
Br	+0.16	−0.11	−0.07	—
F	−0.25	+0.03	−0.15	—
Cl	−0.05	−0.11	−0.17	—
$CH_2{=}CH$	−0.07	−0.02	−0.06	6.69, 5.74/5.23
SH	−0.08	−0.09	−0.19	3.40
CH_3	−0.16	−0.09	−0.18	2.34
tert-butyl	+0.02	−0.09	−0.20	1.31
$NHC(O)CH_3$	+0.21	+0.02	−0.18	7.79, 2.14
$O(CO)CH_3$	−0.31	+0.01	−0.09	2.23
OCH_3	−0.40	−0.02	−0.36	3.75
OH	−0.44	−0.04	−0.35	5.35
Et_2N	−0.61	−0.10	−0.66	3.30, 1.14
NH_2	−0.64	−0.16	−0.55	3.55

*in DMSO-d_6

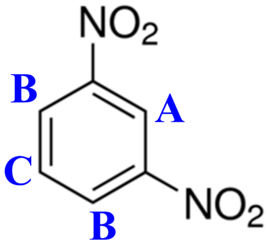
Now I will take an example like this. It is a para dinitrobenzene.



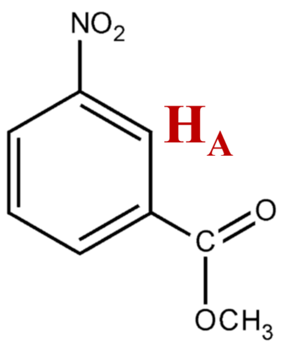
If I look at this para dinitro group, I look at this proton. this proton has one substitution in the ortho position NO2, another NO2 is in the meta position. Go back to the table here. In this table you can find out the values. If it is in the ortho position +0.91 you have to add for the base value. If it is in the meta position +0.24 you have to add to the base value. Now come back here, it has got values in such a way, if you look at any of the protons, always you can see one of them is in the ortho position, and the other in the meta position. So take the base value for which add the value of the substitution in the ortho position and value of the meta position.

$$\delta_H = 7.28 + 0.91\ (NO_2\ \text{ortho}) + 0.24\ (NO_2\ \text{meta})$$

And this is the total value. So you can predict the value of the chemical each of these protons. All are equivalent here, in a para nitro dinitrobenzene; and you see this is the predicted value, and this is the experimental value. Fairly close, very close fairly. And this is the way you can even predict the chemical shifts of many of the aromatic protons, if you know what is the substitution.



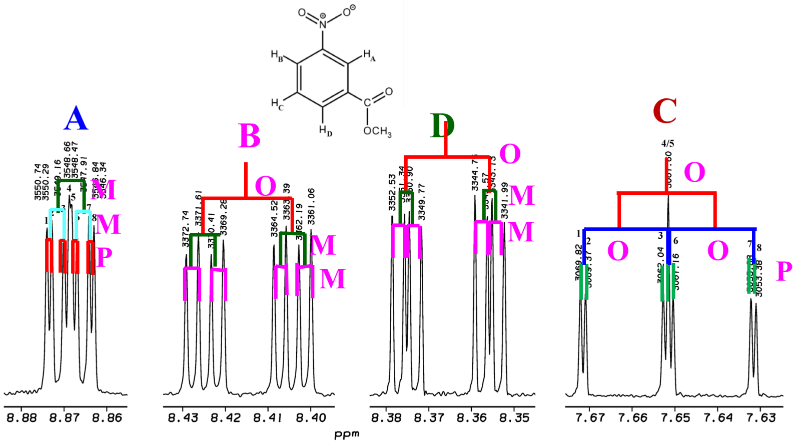
Let us take the example, earlier was the para nitro dinitro, now let us take meta dinitro. Meta-dinitrobenzene if I take, remember here all the 4 protons are chemically in equivalent. Let us start with calculation, of course, not all the 4. These 2 are same and only there are 3 possible chemical shifts, 3 are chemically equivalent. These two B are identical and though I can calculate the chemical shift, predict it for all the 3 protons, proton A, I will start with. The case of the proton A: take the base value 7.28 and for proton A. We have NO2 substitution in the ortho position, there are 2. What did we see in the table? you go back to the table, here ortho position value is 0.91. So add it 2 times. You have to add because there are 2 nitro groups in the ortho positions, then if you add it with the base value this turns out to be 9.1 ppm. And look at what is experimentally observed 9.073 ppm, very close to the predicted value. Go to proton B now, proton B, what will happen? if you any proton if you take any one, one is in the ortho position other is in the para position. This is the base value 7.28, the ortho position value is 0.91 and then of course para position is 0.37. That is the contribution for the chemical shift depending upon which and where it is. Now I will take this proton; or even if you take this proton, this is ortho and this is para. So does not matter. You can take whatever it is. Finally if you add this thing, this is the value you are going to get 8.56. And look at the experimental value 8.573. Same way for proton C. What is happening is both of them are in the meta position. The base value takes 7.28 add the meta position value 2 of them it turns out to be 7.76 and what is the experimental value 7.805. Fantastic look at this one. This is the way ; if you have an idea of the substituent and if you know which are the protons you are looking at in the phenyl group it is possible for us to predict what are the aromatic proton chemical shifts. It is possible. We will go ahead and most of the time you can use this idea to assign the peaks starting with this. You can assign based on the multiplicity pattern and also based on the predicted chemical shifts.



I will take this one. This is a real molecule we have analyze the spectrum of this. This is a methyl metanitrobenzoate molecule. I look at proton HA. Remember this has one NO2 group in the ortho position one C=O-OCH3 group in the another ortho position. So I take the base value of 7.28 and NO$_2$ I know it is already 0.91, from the previous example, we took for the ortho position. And for this CO2-CH3, if you go to the table which I showed you this is 0.74. So the contribution for proton A because of NO2 is 0.91 ppm and because of CO2-CA3 is also 0.74 ppm. Add this to the base value of 7.28. Now if you add all of them this is what is the chemical shift for proton A. You can predict it. This is a proton chemical shift. Similarly predict the predict the chemical shift of proton B, C, D everything. So I was if this is A, this could be B, C, and D. I can mark everything and then calculate everything and for proton B again you take which is ortho which is in the meta position all those things you can find out. So for B this is para position, if you take this one as B and you know the value of it; you add it up. It turns out to be 8.53 ppm. Similarly for protons C proton D values can be predicted like this. What are the experimental values 8.668 is 8.365, 8. 415 and 7.652. And the this is the what you get. Look at it each of them HA is 8.93, this is very close to this one 8.86. And of course, HB is 8.53, 8.53 is somewhere here or you can take this one and 8.35 is here; and this is 7.4 not precisely, but close by. But that is enough to make the assignment, and then further you can iterate it and then you know. Make it very precise looking at the multiplicity pattern and etcetera, this is what it is. Now, the proton A if I consider this is proton A based on my chemical shift, the proton A is the one which comes at the lowest field 8.93 ppm. Based on that I made a assignment. This is A, B, C and D. This is A and D, based on the predicted value. Let us see whether my predicted value agrees with the splitting pattern or not. Use the idea of predicting the chemical shifts of phenyl protons using the table, make the assignment. Now, let us see whether my assignment agrees with the predicted value or the splitting pattern that I already discussed. I told you how you should think of the splitting pattern for different protons of the phenyl group. The proton A you take it what is the possible splitting. So, you can think of this one meta coupling; other meta coupling and then a para coupling. This is how it is. There is one meta coupling. This is a chemical shift, always at the center, and each line of the doublet splits into another doublet. It will become doublets of doublet, because of meta coupling and this is also there, this will split due to para coupling. So, it will become 8 line pattern. Here this meta coupling and this meta coupling are not identical. As a consequence it is not triplet of doublet, it is only doublet of doublet of doublet. So, it is 8 line pattern. It agrees with the chemical shift predicted. Also agrees with the splitting pattern. Go to proton B now. The proton B experience two meta couplings. You look at this proton B, it experiences one ortho coupling and two meta couplings. So, this is how it is, the proton B, one ortho coupling and one meta coupling is like this. And other meta coupling is like this. So, it will become again doublet of doublet of doublet pattern is agreeing with our chemical shift predicted value. What is the next one? the proton C. The proton C is interestingly experiences two ortho couplings. Proton C look at this one. This proton C has one ortho coupling, another ortho coupling, and then one para coupling. One ortho coupling splits into a doublet, and another ortho coupling splits each of these lines into a doublet, and then para coupling splits each of them into doublet of doublet of doublet. So, we are going to get 8 line pattern. Actually in principle it is a triplet because two lines are overlapped, triplet of doublets you are going to get. Actually in principle it is there, there is a resolution here if you carefully see it is not overlapped.

So, it is 8 line pattern. Go to D, what pattern you expect for D? one ortho, one meta and another meta. So, one ortho coupling is a large splitting and two meta couplings are there which are split like this. So, it is going to be 8 line pattern, the meta couplings are different, fantastic. Now, we know how we can analyze the spectrum for different protons of the phenyl group based on the substitution. We predicted the values and then used the multiplicity pattern and then analyzed it very easily with this idea.

I will take one more example very simple example. This is aspirin, it is a tablet. It is also called acetyl salicylic acid. This is a structure given. See there are COO CH3 and COOH two ortho substituents are there in this molecule. And we have four protons all are chemically inequivalent because the substituents are different, there is no symmetry operation here there is no symmetry element. Of course, plane of symmetry is there, apart from that, there is no chemical equivalence that is it.



Now, we will predict the substituent effect on proton A. Start with proton A, the base value is 7.28 and it has got proton A. If you consider one in the ortho position is COOH and meta position C=OCAH3. Use the value given in the table. I put it and added up everything. It turns out to be 8.13 ppm very good. Similarly, if you go to the proton B what happens? This one is in the meta position; other in the para position. For the meta position it is 0.17; for para position is -0.9. You have to add. it is not only always additive, it is also subtractive it turns out to be 7.36 ppm. Similarly, workout for proton C, proton C if you go you will see proton C has one in the meta, one in the para; similar to B only. Exactly you work it out and then of course, remember the substituents are different. So, values are different, it need not be same. Finally, for proton D this is is what the value you get. And these are the predicted values. All the predicted values for all the 4 protons based on this using the table we could do. Now, what are the experimental values these are the experimental values? look at it 8.113 this is 8.13; 7.346 it is 7.36; 7.61 it is 7.614 and 7.14, it is 7.131. Fairly accurate. Very precisely we could do that you see. We can predict the values of the proton chemical shifts. Now, go back and assign this one. With this idea we know the chemical shift of A is the least shielded, more shielded it comes to the down field, then C, B and D. You have to assign as A, C, B and D. Why it is least shielded everything is more of chemistry you can understand. That is because of COOH substituent it is electron withdrawing group. And for the case of D and B, there is a electron donating group. Fine, this is the spectrum. COOH group is there and COOCA3 and OH, is there of course, this is CH3 group and COOH group is here. Always I told you OH group will be very very broad, when I was talking to you about selection rule and natural line width, I told you. You know what will happen because of the resident time of proton in the excited state is very small it relaxes very fast. So, OH and NH peaks are usually broad that is what, I said you remember that. So, this is COOH this is CH3 that is assigned. Then you have to assign only the remaining protons remaining 4 protons are mentioned here. What was our assumption based on the chemical shift? the proton, one of them which is down field is proton A, which is resonating down field. proton A; then proton B, C and D; that is what we predicted. Let us see whether it agrees with our splitting pattern. What we have already worked out for proton A. This is an ortho coupling, one meta coupling, and one para coupling; true there is one ortho coupling and each line is split into doublet, because of meta coupling and if you carefully see each of them is further split into doublet of doublets. So, it is a eight line pattern. Fantastic it agrees with our assumption. Ho to proton C now proton C it experiences two ortho couplings from here, one ortho coupling, another ortho coupling like this. And each one of them becomes a doublet because of meta coupling. Same with proton B; I am sorry this is proton C. That is also of course, same two ortho and meta, proton B is also like that two ortho and one meta, exactly similar pattern. If the resolution is not there this also gives 8 lines. HB also experiences two ortho and one meta couplings. What about D? this is proton D. This experiences one ortho coupling; one meta coupling and one para coupling; all are different. So, what will happen ? what is the pattern you are going to get is a large coupling, ortho coupling each of them is split into a doublet, meta coupling and each line is split into two two lines like this, you get 8 lines here. There are 8 lines here. If you carefully see each of them is a two, two line doublet doublet doublet, 8 line pattern. So, the multiplicity pattern agrees with the chemical shifts what we predicted agrees. So, very easily you can make the assignment.And this is aspirin tablet. So, acetylsilacetic acid you can make the assignment here very easily. So, that is how we can understand. Please remember proton A has one ortho meta para couplings; proton C has ortho ortho meta couplings; proton B has again ortho, ortho meta couplings, and proton D has ortho meta and para couplings. All the patterns very easily we could assign without any difficulty. So, now I fairly you got the idea how we can analyze the spectrum of the molecules. Simple molecule with lot of examples we took. Yesterday I took aliphatic group molecules and I did not take the example of the phenyl group, and based on the multiplicity patterns we made the assignment of all the protons without any difficulty; based on the shielding and deshielding, where it is resonating and looking at the multiplicity pattern in the molecule, which is the group sitting next to it will tell me what is its multiplicity pattern. And I am able to analyze these, that is easy, but only in the case of the phenyl group we have to be little bit careful because the phenyl group we have three different couplings ortho meta and para. Depending upon the substituent whether it is symmetric or asymmetric; whether it is ortho, meta or para disubstituted; depending on that we have different multiplicity patterns for different protons. That we understood how to do that. I told you how multiplicity patterns come for different substitutions, if it is a mono substituted, disubstituted, etcetera. We know ortho meta para couplings, based on whether thre is one large coupling or two couplings or three couplings, we can say one proton experiences two ortho couplings of identical strengths, and then one meta coupling or para coupling. It will be triplet of doublets. Like this we could explain everything. Sometimes there could be complications and you may not be able to assign so easily, so we can predict the values of the chemical shift of the phenyl protons, because we have the table of values where different substituents can contribute for the protons depending upon whether it is in ortho para or meta position, with respect to the substituent. And there are N number of substituents. Take a molecule look at the proton position look at it, and for that proton look at it what is the substituent in the ortho meta and para positions. Pick up that value from the table. Yake the benzene value of 7.28 that is the base value and then keep adding all the other values. Finally arrive at the values that is predicted chemical shifts. By and large they agree with the experimental ones, and use that and then use the knowledge of splitting patterns fairly you can make the assignment for all the phenyl protons. This how we can go ahead. Next we will go for another topic, the heteronuclear coupling in the proton spectrum. So, I am going to stop here. Thank you very much