

Interpretative Spectroscopy

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Lecture 07

N+1 Rule and Pascal's Triangle

Coupling constants for different types of molecules

Hello everyone, once again I welcome you all to MSB lecture series on Interpretative Spectroscopy. In my last lecture I started discussion on spin-spin splitting and also the term I introduced is coupling constant. Let us continue from where I had stopped in my last lecture. So, coupling constant, I had mentioned it is very vital in understanding and elucidating the structures using NMR, and what one should remember is equivalent protons do not split each other. Usually, protons present on the same carbon atom we are considering as equivalent and they do not split each other and especially in methyl groups (CH_3) and it is likely that in some cases where we have methylene (CH_2) and if they are substituted with differently on adjacent side then there is a possibility of splitting each other that arises when we have a second order situation. So, as far as first order spectra are concerned equivalent protons do not split each other.

Protons bonded to the same carbon atom will split each other if they are not equivalent due to unsymmetrical nature of the molecule. As I had mentioned the unsymmetry comes into the picture, when they are differently substituted on both sides. Protons on adjacent carbon atoms normally will couple most of the time unless they are separated by atoms such as oxygen or sulfur or chlorine (O, S or Cl), something like that, then they may not couple but on other side in general, protons and adjacent carbon atoms normally do couple. And protons separated by four or more bonds will not couple or show very weak coupling.

So, as long as they are fewer bonds apart, that means one two three or to an extent four, they can show coupling, but if they are beyond that, they may or may not show any

coupling. Even if they show coupling, five bond, six bond or something that is very very weak. So, now let us consider one example of ethyl benzene (C_8H_{10}) and look into the splitting pattern. While elucidating, understanding and interpreting the spectra the symmetry comes very handy. For example. if you just look into the molecule, if you want to focus your attention on aromatic protons, you can rotate this way. When you can rotate this way through C_2 axis, this one and this one are equivalent and these two are equivalent and this one is there that means it should show three signals in its aromatic region in a ratio of one is to two is to two (1:2:2). On the other hand, this one would be very similar to what we come across in case of ethyl alcohol or chloroethane. We see here, this one is appearing as a triplet (t) and this one as a quartet (q) and this is overall a multiplet (m). So, something like this, it can show here and then to make you familiar with splitting pattern let me write again here how CH_2 is getting quartet (q) here. So, for example here, now we have three protons and these three protons I am representing in this format something like this, and then let us consider the situation one, where all of them are aligned with the magnetic field, this is one situation, and the next situation is, one down and two are up, and then one up and two down and lastly all are down.

So, the middle one is down and the third case is this one is down and these two up. So, these are the possibilities when we have two aligned and one opposing and next when we look into it we can have one like this and two down and then here I can write here. So, two down like this and one here or I can like one here one here and one here. So, these are the three possibilities and then the third case is all of them are opposing the applied magnetic field. So, here it is shielded and here it is deshielded that is in the same order, the peaks will appear as four peaks. We are seeing here, you can see, this is one two three are there three one two three are there and one and one.

So, we will see here one three three one (1 3 3 1). So, this is how it comes and same analogy holds good for identifying here. One is to two is to one (1:2:1). How that happens? Now CH_2 as I mentioned, here both of them can be something like this or one up one down or one down one up and then both of them are down. So, here one is to two is to one you will see, one is to two is to one (1:2:1). So, this is how we can calculate and

look into relative intensities simply by doing this one of course, we cannot do for all of them, that is reason we use Pascal triangle to identify the intensity of each line in a multiplet. Here I have shown the chemical shifts also all of them are here. Multiplet with very low coupling between them and you can see here this is two point seven two and this is one point one eight here.

So, now let us look into the splitting pattern for isopropyl groups ($i\text{Pr}$) here, and here we can anticipate three types of signals here. This one is not coupled this may show a singlet and this would be showing a septet (s) seven one is there and of course, I do not want to write here. Seven you can calculate the intensity or look into the intensity by simply looking into the Pascal triangle and the spectrum would look something like this you can see here. So, this one if you see. This one is a singlet (s), it is appearing here and then this one is split by these two n plus one ($n+1 = 7$), this is seven lines and seven lines are there. Here one two three four five six seven will be there and then these two are split by this one and appear as a doublet (d). If you just look into it carefully, this spacing is same as this spacing this we call it as J and then if you calculate here one two three three J_{HH} coupling is what we are observing between these species. I have shown the expansion here. This is the expanded one. How nicely one two three four five six seven lines are here. So, now distance between the peaks of multiplet measured in hertz (Hz), we as coupling constant. This is always measured in hertz (Hz) and then they are independent of strength of the external field. Again, when we measure the coupling constant in hertz (Hz) they are independent of strength of the external field, B-naught (B_0). Similarly, chemical shifts when they are presented in ppm, they are independent of strength of the external field. So, multiplet with the same coupling constants may come from adjacent groups of protons that split each other, I repeat again: multiplet with the same coupling constants may come from adjacent groups of protons that split each other.

So, now let us look into coupling constant values for different types of molecules. You can see here: one two three bond coupling is there and then this is around seven hertz (7 Hz) and then here one two three bond coupling is there and between we have a double bond. So, it is ten hertz (10 Hz) for cis and when we have trans, the magnitude of trans

coupling is more than the magnitude of cis coupling. You can see here, cis coupling is ten hertz (10 Hz), whereas trans coupling is fifteen hertz (15 Hz) and the geminal, if there is any non-equivalence due to the substituents, in that case what happens you can observe very small coupling between the hydrogen atoms present on the same carbon. This we call it as geminal coupling. This geminal coupling is very low and then in case of aromatic groups, this ortho proton coupling will be in the order of eight hertz (8 Hz) and then meta will be one, two, three, four bonds here one two three bonds this is three J and then here one two three four bond four J it is two hertz (${}^4J = 2$ Hz) and then in case of allylic what we have is one two three this is around six hertz (6 Hz). So, some of these things, one should remember. While interpreting the spectra of organic molecules you will be knowing exactly where the coupling constant value would come what is the magnitude of the coupling constant. In the absence of free rotation, due to steric hindrance by a ring or bulky groups, splitting and coupling constant values may vary again. You cannot really set this as a standard value. It can also vary due to free rotations or due to steric hindrance by ring or bulky groups because coupling constants are often conformation sensitive. So, now let us look into complex splitting. Let us consider styrene (C_8H_8) molecule: If you look into styrene molecule, these three protons (3 H) are there. They are designated as H_A , H_B and H_C . If you look into molecule this is unsymmetrically substituted because H_A is cis to H_C whereas trans to H_B as a result what happens these two appear to be chemically equivalent. No doubt, but they are not magnetically equivalent.

So, that means when two nuclei or two hydrogen atoms on same carbon atom are chemically equivalent but they are not magnetically equivalent then we come across complex splitting. But let us consider assuming this is a first order spectrum. In this case, what happens, you can see signals may be split by adjacent protons different from each other with different coupling constants example H_A of styrene is split by adjacent H_B trans to it because first it should be split by trans, because trans coupling is larger you know that. It is 17 Hertz ($J = 17$ Hz) and it is 11 Hertz ($J = 17$ Hz) then it will be further split by a trans H_C proton. How that can be shown? You can see here: the spectrum is given here and then values are also given here. This comes around 5.25 and this comes

around 5.76 this comes around 6.72 and all aromatic protons are coming around 7.3 to 7.4 ppm and then interestingly, if you see here, although it appears like a doublet (d) it is actually a doublet of doublet (dd). Same thing is true in case of this one. This also a doublet of doublet and this you can clearly see it is also a doublet of doublet. That means four lines are there and here also four lines are here also four lines, but spacings are little smaller. So how that is happening you can clearly see here. First consider H_A , we have the chemical shift of 6.60. First H_A is split by H_B because the magnitude of trans coupling is more. It first splits that into a doublet with the separation of 17 Hertz ($J_{ab} = 17$ Hz). Then each line in the doublet is further split into doublets because of cis coupling that is in the magnitude of 11 Hertz ($J_{ac} = 11$ Hz). Now at the end what we are getting is doublet of this is called as doublet of doublets the H_A multiplet is called as doublet of doublets and similarly when we look into H_B , H_B again, first it is split by H_A because it is a trans coupling. Magnitude is more and now H_B is further split by H_C present on the same carbon atom. Because they are no longer equivalent, so there is some non-equivalence, they split each other. As I mentioned, this is called geminal coupling and geminal coupling values are of the order of two or less so here. What we are getting is BC coupling about 1.4 Hertz ($J_{bc} = 1.4$ Hz) that is the reason you can see in the spectrum you see the spacing between the two lines is very narrow. So now let us consider H_C and in H_C consider the larger coupling which is cis coupling $H_A H_C$ that is 11 Hertz ($J_{ac} = 11$ Hz) first fits into a doublet (d), and each line in H_C in this one will be further split into doublet (d) and the magnitude of this BC same what we came across here so this is 1.4 Hertz ($J_{bc} = 1.4$ Hz) that means this is also a doublet of doublets this also a doublet of doublets this also doublet of doublets and so as a result what we see is in this portion styrene the olefinic region what we are seeing is four signals each one is having four lines that four lines can be designated as a doublet of doublets doublet of doublets and doublet of doublets so this is what we saw in the spectrum here you can see here so this is all doublet of doublets here now let's look into another example here in this one chemical shift values are given here this is 1.63 a doublet, because this is coupled with this one. These two are coupled and next 3.52. Here it is coupled with this one and then 3.78 again 3.78 here and then what we have is 4.10. Now you can see the number of lines you should be able to tell what are the couplings involved in those things. Okay try to work

out if it is not possible we will solve that once again. Now let's look into another aspect while determining the coupling constant, is stereochemical non-equivalence. So, what is this stereochemical non-equivalence? In general two protons on the same carbon atom are equivalent and do not split each other, so it means I gave emphasis about that no geminal coupling as long as the protons or hydrogen atoms on the same carbon atoms are equivalent, but that is not the case for styrene, because in styrene, if you just look into it, I showed you H_A is coupled having a trans relationship with one H_B , whereas it has cis relationship with H_C . As a result, what happens, the entire molecule is not symmetrical, you observe geminal coupling. So, if the replacement of each of the protons of a CH_2 group with an imaginary Z gives stereoisomers, then the geminal protons becomes non-equivalent and will split each other that's what exactly happened in case of styrene molecule. So molecules having non-equivalent geminal protons I am showing you here few examples in this one you can see H^a and H^b are on the same carbon atoms but they're non-equivalent and you can anticipate coupling between H^a and H^b they are geminal protons and same thing is to in case of styrene also so H^b and H^c are geminal and they are non-equivalent and you can anticipate coupling between them, but however the magnitude of this coupling is very small. Same thing is true in case of this one also. You can see here D and C. So geminal coupling is observed here. So, now the time dependence, what is the time dependence? Molecules are tumbling relative to the magnetic field. So, NMR is an average spectrum of all orientations. If you recall, when we placed H_2 and F_2 molecules perpendicular to the magnetic field and parallel to the magnetic field. These are the orientations considered taking average of all possible orientations, that means the molecules will be tumbling relative to the magnetic field. So, NMR is an average spectrum of all the orientations. That's the reason we do not see splitting, Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal at room temperature. If you record NMR spectrum for cyclohexane they interconvert axial and equatorial although, we can differentiate them but the exchange or interconversion of axial to equatorial is much faster than NMR timescale of 10^{-9} seconds (10^{-9} s). As a result, what happens, we get a single signal, so proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule. The exchange happens when we have groups

such as OH and NH in a molecule and they exchange so rapid, basically what happens? We do not see any splitting due to the presence of OH or NH on adjacent protons. Now let us look into hydroxyl proton (OH) here. I have considered ethyl alcohol here, and if you consider ultrapure samples of ethanol, it shows splitting ultrapure sample of ethanol. If you record quickly NMR, it can show splitting of methylene (CH_2) due to OH as well. For example, you can clearly see here, this is a triplet (t) for methyl because of split by two methylene protons here, and then this will be split into quartet (q) and each line in the quartet is further split into a doublet (d), because of HO and HO again split by this one into a triplet. This is a very interesting, not often you come across very clearly you can see here, so basically, first it splits into quartet (q). This is 1 is to 3 is to 3 is to 1 (1:3:3:1) and each one is split into doublet (d) then it would appear something like this. So, this is what we are seeing in case of CH_2 here, and of course here in this case, what happens, this will split into a triplet. Here ethanol with a small amount of acidic or basic impurities will not show this splitting due to OH vanishes with a small amount of acidic or basic impurities. So, now if you see here, in this one, it is not pure as a result, splitting we saw is disappearing here. OH will show only one signal here and CH_2 shows as usual quartet (q) and CH_3 shows a triplet (t). How about NH protons? Moderate rate of exchange is observed when we have NH protons, peak may be broad, you can see here. This compound, we have CH_3 here and CH_2 is a quartet and then this NH_2 is showing a very small broad peak. So, this is how most of the time we observe for OH and NH or NH_2 peaks in the NMR spectrum. So, identifying the OH or NH peaks, how to do that? Chemical shifts will depend on concentration and solvent. To verify that a particular peak is due to OH or NH, shake the sample with D_2O , for example, because of difference in concentration, we may not see signals due to OH and NH or in the beginning we see it and then to confirm that one, what one should do is the keep the solution in D_2O for 24 hours (24 h) and then record NMR. If the peaks due to OH or NH disappears that confirms that OH or NH is there. Deuterium will be exchanged with OH or NH protons and in the second NMR spectrum, the peak will be absent or it is less intense.

Let me stop here and continue more discussion on coupling constant and type of spectra we come across in my next lecture until then have an excellent time thank you.