

Interpretative Spectroscopy
Prof. Maravanji S. Balakrishna
Department of Chemistry
Indian Institute of Technology Bombay
Lecture 53
Problems and Solutions-3

Hello everyone, once again I welcome you all to MSB lecture series on interpretative spectroscopy. Since my last lecture, I started really looking into problems and giving the right kind of solutions, real interpretation. I started considering problems although I was discussing many problems in between while discussing many of the spectroscopic methods, I thought of focusing your attention entirely to only on problems and different ways of finding solutions when some data is given from any of the spectroscopic methods. So, let us begin today with another problem.

17. Solve the structure using the following spectral data. Molecular formula is given here.

So, I am going to show you ^1H NMR spectrum in a minute or so. First you look into the formula and try to make familiar yourself, how many different types of elements are there in it.

In this one carbon is there, hydrogen is there, bromine is there and oxygen is there. So, molecular formula is given, but structural formula is not given.

It is more important to know whether the compound is saturated or unsaturated; whether double bond, triple bond is there by looking into hydrogen deficiency index.

Formula, I am sure you are familiar. Let me write again $C + 1 - \frac{H}{2} - \frac{X}{2}$ (X is halogens) + half N ($C + 1 - \frac{H}{2} - \frac{X}{2}$). One should remember; this is the formula we use to identify hydrogen deficiency index. From this one we can get information about possibility of a presence of a ring, double bond, and triple bond.

Here $8 + 1 - 3.5 - 0.5 = 5$

That means here the deficiency is 5. Five means certainly there is a ring and 4 double bonds. Now, we know that ring is there, that means probably aromatic group a benzene ring is there and then that will take care of 3 double bonds and the ring. Now we have to account for one more double bond. So, that means we have O possibility of a ketonic carbonyl group or O methoxy group or something else.

With this information let us look into the ^1H NMR spectrum. You can see here: In NMR spectrum, first identify number of groups of identical protons present. That you can just see by simply counting the number of multiplets. We have here 1, 2, 3, 4, 5, 6, 6 groups are there. That means you can clearly tell six different types of hydrogen atoms are there. When you look into a doublet which is around 3.7, then we have 2 triplets closely spaced that means they have very similar chemical shifts and similarly we have 2 more doublets again they have very similar chemical shifts and then we have a triplet far away much deshielded. That means probably this could be due to an aldehydic or acidic hydrogen and it does not show any coupling.

So, it must be aldehydic hydrogen. By looking into this, probably it looks like they are from aromatic group. Now, let us try to write down the structure. First, I will write a benzene ring, then bromo group is here. Let me put one bromo group here and then by just looking into this probably there is a something like this I can write. Now, we look into how many different types of proton signals can be expected for this one.

Certainly 1, 2, 3, 4 only 4. So, if you just see here because you can do free rotation with respect to C_2 axis. As a result, what happens these 2 will be identical that means 1, 2, 3, 4. So, here you can anticipate 4 different type of proton signals, but we have 1, 2, 3, 4, 5, 6 are there. So, this is ruled out this is not.

So, next let us consider another one. Now, let me put it here if I put here now what happens 1, 2, 3, 4, 5, 6 all are different here and then once after identifying now we have to check whether we get triplet pattern or not. For example, if I consider this hydrogen here this is equally coupled to these 2 hydrogens as a result this can show a triplet and similarly

this hydrogen can also show a triplet and this can also show a triplet and then this one is coupled only to this one show a doublet and similarly this can show a doublet and now this one would show a doublet here this one and this will show a triplet this triplet is here this is.

So, now, we have identified the compound with correct structure. So, let us see what information we have from ^{13}C NMR. In ^{13}C NMR, we can see 1, 2, 3, 4, 5, 6, 7, 8 are there, that means all 8 carbon atoms are nonequivalent. That means here if I just look into it, in this ortho-bromo 1, 2, 3, 4, 5, 6, 7, 8 all are different.

Now without any hesitation one can assign this spectrum and write the structure for this. one should be like this is the compound hydrogen deficiency 5. So, now, yes this is the compound here now we can identify signals yes 7.33 7.33 here and these two are showing triplets and then this is higher and this is slightly higher than this one this is a doublet again and further high because next to bromo this is 1 and then 3.66 it should be a doublet here it is for this one and then this hydrogen here this one it is showing a triplet because of coupling with this two.

18. Now, let us look into another problem here: An organic molecule shows two absorption peaks at 870 and 975 Hz in a magnetic field of 3 T. What are the corresponding chemical shifts in ppm.

First, it is given in Hz. We have to convert into ppm. Before we convert this into ppm we should know this is ^{13}C . We should know first the frequency corresponding to 3T to solve this problem. We should find out the frequency corresponding to ^{13}C nucleus with respect to magnetic field strength of 3T.

For that, we should use this equation: ν equal to $\frac{\gamma h}{2\pi B_0}$. We know now ν equal to $\frac{\gamma}{2\pi B_0}$. Simply if we use the formula, we get is 32.1 or approximately 32 Hz.

That means the frequency corresponding to ^{13}C in a magnetic field strength of 3 T is 32 Hz. So, now we know now we have to convert the given peaks in Hz to ppm first let us

consider the 87. So, to convert delta in hertz to ppm. Divide 870 by 32 (870/32) and 975 by 32 (975/32). This will give you 27.1 ppm and 30.4 ppm.

19. Now let us go to another problem here very similar problem. In a magnetic field of strength 2.349 T, the resonance frequency of ^{15}N nuclei is 10.13 MHz. what is the resonance frequency of ^{15}N in a magnet of 11.745 T.

Again, use the same equation ν equal to gamma over $2\pi B_0$ ($\nu = \frac{\gamma}{2\pi B_0}$). So, h we can remove

After calculation, this will give 50.65 MHz.

20. Let us see one more problem. In NMR spectrometer commonly used in medicine, the resonance frequency for the protons in water is 60 MHz. If such an instrument was to be used to observe ^{31}P , what frequency of radio radiation would be required.

This is again a simple question. For water, it is 60 MHz and then we have to find out what would be the frequency for phosphorus at 60 MHz. If the frequency corresponding to hydrogen is 60 MHz and then if such an instrument was to be used to observe ^{31}P , what frequency of radio frequency would be required.

$$\nu_{\text{H}}/\nu_{\text{P}} = \gamma_{\text{H}}/\gamma_{\text{P}}, \text{ Therefore } \nu_{\text{P}} = \gamma_{\text{P}}/\gamma_{\text{H}}/\nu_{\text{H}} = 24.31 \text{ MHz.}$$

21. Another problem here. I have also given the solution here.

The magnetogyric ratio of the deuterium (^2H) is approximately 6.5 times smaller than that of the proton. In a magnet, where ^1H spectrum can be observed at about 400 MHz, what is the approximate radio frequency radiation you would need to observe the ^2H NMR spectrum.

The question asks for a comparison between the frequencies required for the observation of protons (^1H) and deuterium (^2H) in the same magnet. The magnetogyric ratio of ^1H is 6.5 times that of ^2H , so the frequency required to observe ^2H will be 1/6.5 that required to observe ^1H .

$$^2\text{H frequency} = ^1\text{H frequency} / 6.5$$

$$= (400 / 6.5) \text{ MHz} = 61.54 \text{ MHz.}$$

22. The structure of $(t\text{BuLi})_4$ is similar to that of $(\text{MeLi})_4$, but with each H atoms replaced by a methyl group. The 75 MHz ^{13}C NMR spectrum of a sample of $(t\text{BuLi})_4$, prepared from ^6Li metal, consists of two signals, one for the methyl carbons and one for the quaternary carbon atoms. The signal for the quaternary carbon is shown below: (a) at 185 K and (b) at 299 K. Explain how these signals arise. For ^6Li , $I=1$.

The structure of tertiarybutyllithium is similar to that of methyl lithium and you should know the fact that both exist as tetrameric compounds, but with each H atom replaced by a methyl group. So, ^{13}C NMR spectrum of a sample of $(t\text{BuLi})_4$ prepared from ^6Li , consists of two signals, one for methyl carbons and one for the quaternary carbon atoms.

Two different temperatures, one is taken at 185K and the other one at 299 K. That means there is a dramatic difference in the multiplet pattern at recorded at 185K and 299K. How these signals arise

For ^6Li , I equal to 1. Now we are looking into ^{13}C spectrum. The geometry of tertiary butyl lithium, I have shown here.

The red ones are lithium and these are all tertiarybutyl carbon. Now, you can see lithium and tertbutyl carbon are occupying alternate corners of cubane. This one like a lithium tetrahedra similar to white phosphorous and now each triangular faces of 3 lithiums one t butyl carbon is interacting and then this leads to 4 centered 2 electron bond. Go back now at 185 k we are seeing 1 2 3 4 5 6 7 we are seeing and then at 299K we are seeing 1 2 3 4 5 6 7 8 9. This we need to explain. At this temperature the structure is static and carbon is confined to these three. When it is confined to these three, if you use $2nI + 1$ rule here, which show seven lines.

At 299K because of flexibility what happens this carbon will be moving to another and then this one this one as a result each carbon will look interact with 4 equivalent lithium atoms. So, in that case, $2nI + 1$ rule depicts 9 lines and that is the reason we see 9 lines.

With this let me stop here and continue to solve more problems in my next lecture. Until then have an excellent time. Thank you.