Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna

Department of Chemistry

Indian Institute of Technology Bombay

Lecture 56

Rule of Thirteen and Nitrogen Rule

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. I am sure you are all enjoying some of those interesting problems. Let me discuss more problems today. Once again let me begin with inorganic problem related to phosphorus NMR. Just look into the problem here.

36.   Consider all possible isomers that could be obtained for the 8-membered ring compound $P_4N_4Cl_4Ph_4$ and indicate the ideal ^{31}P NMR spectrum expected for each. I have already given the spectra here, but let me explain. So, this is cyclotetraphosphazene because we have alternate double bonds, this is cyclotetraphosphazene usually the parent compound has 8 chlorine atoms, 2 chlorine atoms on each phosphorus and then 4 chlorine atoms have been replaced by phenyl groups.

One can start writing all possible isomers. Only 5 isomers are possible here and then by using different arrangement of 4 chlorine atoms and 4 phenyl groups here and the first one is here like this. If you just look into it, the equivalent phosphorus atoms I have given the same color here. So, 2 blue are there in the first one and then 2 red are there, they are chemically and magnetically equivalent and the second one also same thing, but their positions are little different. They are close to each other and they are opposite to each other and one bond apart, whereas here these 2 red phosphorus are identical. These 2 phosphorus are identical and then in the third one we have 1 phosphorus has 2 phenyl groups and one has 2 chlorine and other remaining have 1 each of chlorine as well as phenyl and in this fashion if you just see these 2 are identical and then P red and P blue are again unique and then if you look into this one all of the phosphorus atoms have 1 each of chlorine as well as phenyl. This one is very symmetrical molecule and the chemical and magnetically equivalence of all phosphorus atoms is same. As a result, it is expected to show a single

resonance. Now the last isomer possible, we have something like this we have a diphenyl phosphorus here and opposite to that one we have phenyl, chlorine and then here of course, 8 membered ring you should remember it is not planar it is little bit puckered. Only 6 membered rings, cyclotriphosphzenes are planar and in this case, we have all 4 phosphorus atoms are unique; all are chemically and magnetically very different. First let us look into the first one: These two are identical they couple equally with red ones to show a triplet and then the blue ones will also show a triplet. First one has two triplets and the second one if you look into it here this one and this one looks identical, but they are different because one is here P1 is here and these two couple with these 2 to show a triplet and then these 2 would also couple with this one should to show a triplet here.

And then if you look into 3 here these 2 are identical, but these 2 are different first this one would couple to form a triplet and then each triplet will be split into doublet. So, we will see this here 2 doublets, doublet of triplets here and then this will form a doublet and then another doublet. So, this if you look into here is doublet here and again it is a doublet here. So, these 3 signals are here this the ratio if you look into it 1 is to 1 is to 2 integration and then all are different and the long-range coupling is ruled out. So, 2 bond coupling is possible here first it couples with this one a doublet and then it couples with this one doublet of doublet.

Similarly red one will couple with this one doublet and then this is doublet red one and pink one here this couples with first blue and then the green one doublet of doublet and similarly green would couple with first with this one and then this one it gives. So, it gives 4 sets of doublet of doublets; first one will give a 2 sets of triplets and this one would give again 2 sets of triplets very similar to 1. Whereas, this one will show triplet and then this one will show a triplet whereas, middle ones will show doublet of doublet here pink one and then this is all are equivalent it shows a singlet and then we get. So, this is how you can draw the splitting pattern for all 5 isomers and understand for example, when we take this octa chloro compound $P_4N_4Cl_8$ and if add phenyl lithium 4 equivalents we do not know what kind of isomer we are going to get and probably we may get a mixture of isomers and if you look into the mixture by simply looking into the coupling constants and the

splitting pattern we should be able to identify how many isomers are formed and also we can also do quantification in what ratio they have formed.

37. Another problem is there this is with respect to cyclotriphosphazine $N_3P_3Cl_6$. Two chlorine atoms have been replaced by 2 fluorine atoms, as a result we have $N_3P_3Cl_4F_2$. Then again one can draw ^{31}P NMR. For this compound, after writing all possible isomers here, only 2 isomers are possible one is both the fluorine atoms are geminal on the same phosphorus atom or they can be on two different phosphorus atoms.

In this one this would be coupled with these two. So, that means, we should know the fact that the PF coupling is larger and also it is one bond it first splits into a doublet here and then each doublet will be split into a triplet because of this one. So, we should get triplet of triplets here for P_A. For B these two will be coupling first with phosphorus to a doublet and then each line will be further split into three bond PF coupling to give a doublet of triplets.

Here again this will be coupled with these two first form a triplet and then with fluorine atoms it will split into a triplet here. So, we get triplet of triplets. The second P (PFCl) will first couple into fluorine to give a doublet and then each line will be split into doublet. So, doublet of doublet. We can interpret the data in this fashion for two isomers of $N_3P_3Cl_4F_2$.

38. Now, let us look into another example: This is about some reaction that is carried out we have to identify the product. All the details are given here. An air sensitive tungsten complex, $W(CO)_3(NCCH_3)_3$ (prepared in situ) was treated with two equivalents of a diphosphine (P∩P) to give a crystalline complex **A**. The IR spectrum of **A** showed three $v(CO)$ at 2040, 2000 and 1950 cm^{-1}. The ^{31}P NMR spectrum shown below shows relative intensities of 1:2:1. Deduce the structure of **A**. The free ligand shows a single resonance around 62 ppm in its ^{31}P NMR spectrum.

Tungsten complex $W(CO)_3(NCCH_3)_3$ can be prepared by taking WCO_6 and refluxing in acetonitrile for 24 hours in absence of air under argon. The maximum number of carbon

monoxide we can get rid of using nitrogen donor centers is only three. So, we cannot get anything else other than this one, but if we stop the reaction in the beginning or for two hours we may get two substituted, mono substituted, but if we drive the reaction for completion for more than 24 hours we can knock off 3 carbon monoxide to have a composition, something like this $W(CO)_3(NCCH_3)_3$. So, this can be prepared in-situ and then it was treated with 2 equivalents of bisphosphine. Let us not worry what is the bridging group here. Two bisphosphines are there then we are getting a compound A. The IR spectrum of A showed 3 ν_{CO} at 2040, 2000 and 1950 cm-1. All of them are terminal. There is no bridging that indicates we have three terminal carbon monoxides. Then ^{31}P NMR spectrum shown below with relative intensities is 1:2:1.

One doublet, another doublet and one is triplet of doublets. How to arrive at this? Now we have to deduce the structure and then interpret the data given here. It retains octahedral geometry. It is a bidentate ligand it has a tendency to form chelation thermodynamically favored one and another phosphorous is also bound. So, here unless the coordination is expanded to 7, it cannot bind let us assume it is not expanded to coordination number 7. So, in that case what happens one should be uncoordinated this is coordinated this is coordinated this is coordinated.

 Now, if we just look into this compound, here this one would only couple with this one to show a doublet and also this uncoordinated show a chemical shift very close to the that of the free ligand and free ligand value is also given 62 ppm. So, possibly this one for uncoordinated P. This chelated would represent now we have to see this one. This one is coordinated it can couple with this one as well as this one because both are two bonds apart. So, in this case first it couples with this one a triplet and then it shows a doublet.

 So, that means, it should be something like this. So, now, other option is it can show first a doublet and it can show a triplet here then it should be. We have to compare which pattern corresponds to this one. This is correct. First it couples with this coordinated ones (chelated ones) and then these two chelated ones are chemical and magnetically equivalent

they couple only with this one shows a doublet here with intensity 2. This is this one this is one. So, now, it is done.

Let us look into what is this rule of 13. Very important to arrive at the molecular formula for a given mass identified from mass spectrometry. What we have to do is once when we get M^+ or M divided by 13 (M/13), it may or may not be completely divided, we get the quotient and also the reminder. In that case, we divide by n and then n plus r (n+r) we should put here. n is the quotient here and n is quotient plus whatever the reminder. This would make the first basic formula and from that one we can check here. For example, let us say 78 is there to begin with. Before we add some hetero atoms, let us divide 78 by 13 we get 6 that means it is completely divided. If you see this is equal to n. So, C6 has 6 this is 72 plus 6 = 78.

We can say without anything this is the benzene molecule. Now let us look into 92. 92 by 13 will give 3 quotient and remainder one. It is should C_7H_7 plus 1 equal to C_7H_8. We have C_7H_8 here cycloheptatriene.

Now we have 162. Divide it by 13. We get quotient 12 and remainder 5. We get this $C_{12}H_{17}$. This is the formula for a molecule. Now we have to work out again using another formula, that is hydrogen deficiency index. Now the question is, is it aliphatic or aromatic hydrocarbon. If you have hetero atoms, first derive formula as above. First, we have to find out this one. C_nH_{n+r}. n plus r (n + r) can be 0 or any number. Once after identifying that, we have to see whether any other hetero atoms are there. If oxygen is there oxygen, atom equates to $CH_4 = 16$.

So, you eliminate one CH_4. To add 1 oxygen atom eliminate 16. that is CH_4. So, next if you have nitrogen eliminate CH_2. If you have ^{19}F, take away CH_7 to replace ^{19}F. For ^{28}Si take out C_2H_4. To add ^{31}P, take out C_2H_7 and then for sulfur take out 32, i.e. C2H8.

We have to take out from the actual formula. How do we know those things? By simply looking into the parent ion fragmentation. For example, whether it is m, m plus 2 (m + 2),

m plus 4 (m + 4), that can tell you about the presence of halides. This already we discussed while dealing with mass spectrometry. So, remember from there and you use this simple formula and then after arriving at the molecular formula, what we should do is we can go for identifying whether it is saturated or unsaturated. How many rings are there, how many double bonds are there and then whether in the CO group is there, that information comes from either IR spectroscopy. So, we should proceed like that.

So, again I am telling you, so for example, consider 108 divide by 13. So, 4 will be left. So C_8H_{12}. So, this is it. So, that means possible candidates with heteroatoms. So, here take this, remove one CH_4 for oxygen, it can be C_7H_8O or take out $2CH_4$ and add O_2, it can be $C_6H_4O_2$, something like this. So, we can work out all possible ways to arrive at the right kind of structural formula by taking help from the data we have obtained from various spectroscopic means for an unknown sample. Nitrogen rule is also there. A molecule with even numbered molecular weight must contain either no nitrogen or even number of nitrogen atoms.

This information also quite helpful in for example, when you go for proteins and other amino acids and other things where possibility of more are there we can use this rule. So, molecular weight is even only even number of nitrogen atoms will be there or there will be no nitrogen atoms when odd number is there there has to be odd number of nitrogen atoms. So, with this again showing you consolidating here divide the molecular weight by 13 and remainder less than 13 has to be there is termed as remainder r and the quotient is n. So, the molecular formula is CnHn+r here and then elements of unsaturation may found out from the molecular formula. If O is there, add O and subtract CH_4 if n is there add n and subtract CH_2 again remember this odd and even molecular weight and if Cl is there add Cl and subtract C_2H_{11} or subtract C_3H minus 1.

That means, add one more H and take out 3 carbon atoms after obtaining correct molecular formula, find out hydrogen deficiency index using this formula here C+1 minus half into all H plus half X $(C+1-1/2H+1/2X)$, X is halogen and plus half n with this one we can

arrive at molecular formula and also about is saturation or unsaturation and the presence of a aromatic group or so. I think I would not say aromatic group there can be aliphatic ring can also be there. So, now let us look into problem here a compound composite of carbon, hydrogen and oxygen has a molecular weight molecular ion at m by z (m/z) equals to 112 in its mass spectrum the base peak is at m/z equals to 28 atomic mass units the infrared spectrum shows strong absorption in the region 2850 to 2980 very strong absorption at 1717 centimeter minus 1(cm^{-1}). The ^{1}H NMR spectrum shows a single sharp signal at 2.7 ppm and ^{13}C NMR also has 2 signals at 37 and 208 ppm. So, this one we should take here first. 112 divided by 13 is equal to what we get is 104, another 8 will be left. It becomes C_8H_{16}, it says 1717, there is strong absorption probably one or more CO groups can be there. Let us try both the options first, let us add one oxygen, for adding we have to remove CH_4. So, for this, what we get is $C_7H_{12}O$ and now we can try to remove one more because it is strong, it may be $C_6H_8O_2$. Now with this one, let us assume this is the correct molecular formula. Now let us look into hydrogen index deficiencies.

So, 6 are there 6 plus 1 minus 4. So, 3 are there. Three means basically ring plus, two double bonds, one ring and two double bonds are there. This indicates the ring may not have inside double bonds. So, in this case, we are seeing around 2.7. 2.7 does not fit into aromatic hydrogen in ^{1}H NMR signal.

That means, possibly it is not an aromatic ring, 6 are there let us try to write something like this CH_2CH_2 let us assume because if we write something like this. C_8 are there 8 is satisfied and 6 are there and then O2 then possibly this one. Now, this is symmetric and they show only one sharp signal at 2.7. Any other possibility is there something like this. So, then also it is symmetric, but what happens here 1 is there and this 2 on this. So, there are different 1 2 3 signals, we get it in ^{1}H NMR and another possibility is and possibility is 3.7. So, this is the same. Also, if you do like this one and this one are identical and we get two types of signals here. That means, these two are not possible. This is possible here and probably the structure is something like this. Now, I have taken for this one here you can see we are seeing only one signal here at 2.73 are very close. This compound is confirmed from ^{1}H NMR. Let us look into now ^{13}C. 13C shows only 2 signals. One is this one, one is this, one

is here 208 and 36.5. The molecule what we predicted is correct by using 13 rule, number 13 and also hydrogen deficiency index with these two and also giving some vital information from IR spectroscopy and also NMR. Now without any problem we can identify the right product. So, this is how we can combine all information and also by using empirical information given by people who have worked thoroughly with this kind of spectroscopic methods and arrive at the structures easily. Let me come back with more problems in my next lecture until then have an excellent time. Thank you.