Introductory Organics Chemistry - II
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Lecture 4
Essentials of NMR Spectroscopy - Part 3

So, in the previous lecture, we spent quite a bit of time trying to understand the various trends of Proton and Carbon NMR. So, now what we will do is we will spend some time and try to understand the effects of or the NMR pattern of Benzene. So, we will be spending quite a bit of time on aromatic compounds in this course, and therefore, it is quite useful.

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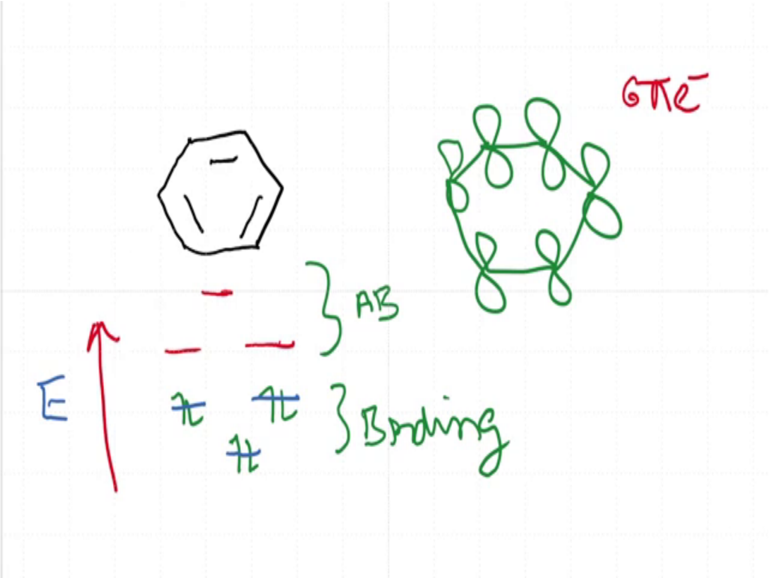

So, just to recap, Benzene basically is three pi bonds in a hexane ring, and so, the orbital picture is going to look something like this. So, you have basically bonding orbitals, which have 6 pi electrons. So, now, you know to understand this picture, let us now look at the energy levels of Benzene.

So, we have already seen that the molecular orbital picture is going to look something like this. So, here are the bonding orbitals and here are the anti-bonding orbitals. And now, if you fill in electrons, you have 2, 4 and 6 electrons, and so, these are the anti-bonding orbitals and these are the bonding orbitals. Now, you have 6 pi electrons in the system, and they are delocalized.

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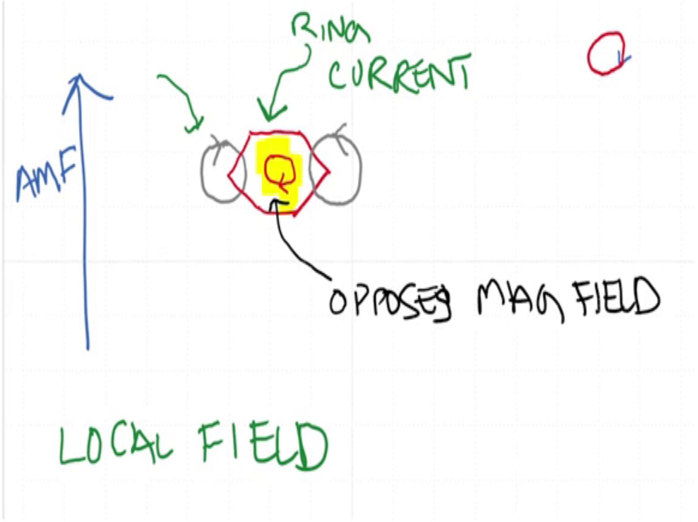

So, from an NMR standpoint, what we want to understand is that when there is a magnetic field that is applied, so there is an applied magnetic field. So, when this magnetic field is applied, magnetic fields are nothing but, magnetic fields are produced by circulating electrons.

So, if you remember, we had looked at the example of Hydrogen atom, and we found that there are electrons that are going to be circulating and therefore, there is going to be a magnetic field that is produced by the electrons which contributes to the shielding and de-shielding for example. So, the greater the shielding, the nucleus experiences less of the magnetic field.

So, now in the case of Benzene, it is very interesting, because Benzene has 6 pi electrons as we discussed. So, what happens is that these are the electrons that are going to be shown here. So, when the magnetic field is applied in these delocalized electrons, what happens is that it produces a local field, so a local magnetic field is established. And this local field does two things.

So, it does the following thing, so basically, I am not drawing out the Hydrogens here, but it is obvious that there is Hydrogen and this local field basically is, this is called as the ring current, as the name suggests, it is a current that is produced in the aromatic ring. And so, this ring current leads to a very peculiar situation where you have a local field that is going to be produced.

So, now in this local field what it does is that, it does two important things. One thing is that it produces an additional layer for Benzene. And so, what it does is that inside the Benzene ring, the induced field opposes the magnetic field. And outside the Benzene ring, the field reinforces the applied field.

So, I will repeat it, so it does two things, one is that it, inside the Benzene ring that is here, inside the Benzene ring, opposes the magnetic field, so this is what it does. Whereas outside the Benzene ring, what it does is, it reinforces the applied field. So, in other words, what happens is that you have a situation where the electrons are going to have two different effects on, depending on where the Hydrogen is placed.

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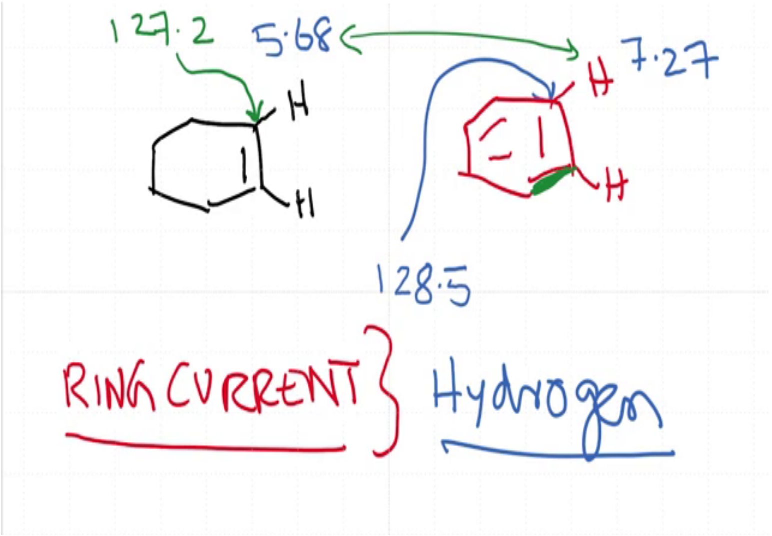

So, you may recall that when you compare the chemical shift value for an olefin, so this Hydrogens versus these Hydrogens, or any of those Hydrogens, the chemical shift value here is about 5.68 and whereas here it is 7.27. So, this is a very significant difference, that is between these two numbers is really significant, it is huge.

So, therefore, this difference in aromatic ring is attributed to the ring current effect that is prevalent only in aromatic rings. But what happens is that it is a very peculiar effect in that it only affects the Hydrogens. So, the Carbon for example, if I look at the chemical shift of this Carbon, it is 127.2. And whereas, this Carbon here, the chemical shift value is 128.5. So, if you see here, there is not really a whole lot of difference between 127 and 128. So, the effect, the ring current effect or the aromaticity effect in the Benzene ring is localised or is primarily it affects the Hydrogen atoms.

So, that is very important to understand because the Carbon-13 on the other hand, is not affected. So, I will repeat this. So, when the Benzene ring is placed in a magnetic field, there is an induced magnetic field that is present that leads to what is known as a ring current.

And this ring current produces a local field and the local field, it has an uneven effect. The Hydrogens that are inside or the groups that are inside the Benzene ring, lead to opposition of the magnetic field, whereas the ones that are outside lead to a reinforcement. So, therefore, the outside values are more de-shielded, and they lead to a larger delta value.

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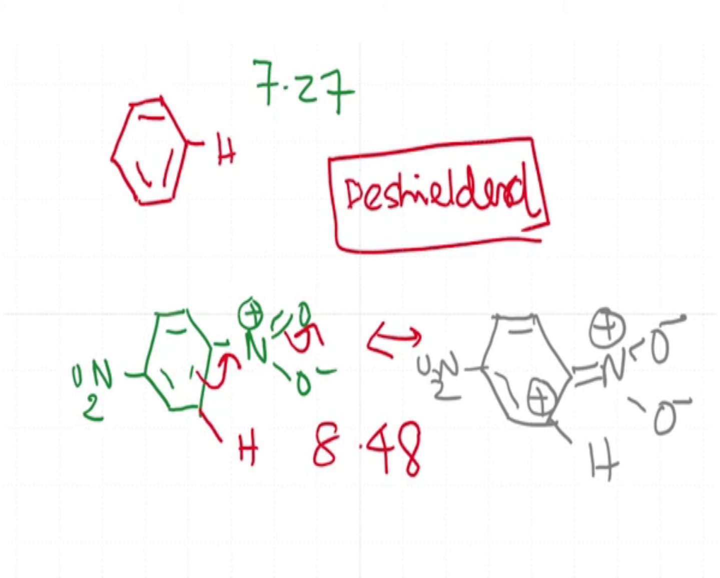

Let us look at some examples of various Benzene ring containing compounds, which are basically substituted Benzene rings. So, as we saw, just for regular normal Benzene itself, the chemical shift value is around 7.27. Now, what we are going to do is we are going to put in two nitro groups. So, these are, and we will understand why we are doing this substitution a little bit later.

But these Hydrogens for example, when you look at the chemical shift value of this, this shows up at around 8.48. So, how do we understand this, the way we understand this is that if you draw out the nitro group, such as shown here, so, if we draw out the nitro group band, if you pull these electrons over here, this is going to form, give rise to a resonance form where you have double bond NO minus, O minus, with a positive charge on N and this Hydrogen here is going to be next to an electropositive NO_2.

So, what happens is that, because it is an electron-withdrawing effect, the electron withdrawing group makes it more de-shielded. So, as you remember from the previous examples, anything that removes electrons from the nucleus is going to lead to more de-shielded. So, therefore Nitrobenzene is more de-shielded when compared with Benzene. Now, as we do a few more examples, these concepts will become much clearer.

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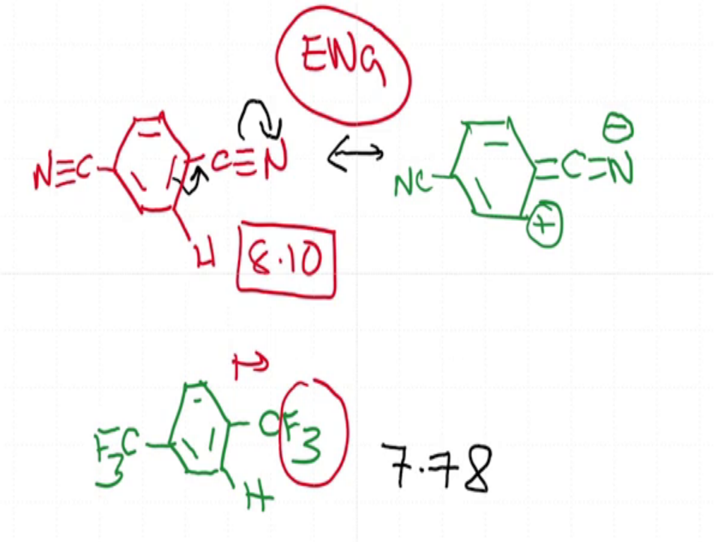

So, now the next example we are going to take is a Cyano Benzene. So, Cyano Benzene or Benzonitrile, as it is called. So, as you can see here, this triple bond is very nicely placed to pull electrons and so you can draw out a resonance form over here, so you have double bond C double bond N and then you have a negative charge here and it leaves a full positive charge here, and the remaining molecule is the same.

So, what it does is again, this is an electron withdrawing group, and therefore, the electron withdrawing group is going to make it more de-shielded. I am sorry, I forgot to tell you the chemical shift value, so the chemical shift value is 8.10. So clearly the nitro has a stronger electron withdrawing ability when compared to cyano and so cyano has a slightly lower value in comparison with the nitro group.

And the last example we are going to look at is this compound which has CF_3. So CF_3, as you may know, the Fluorine is highly electronegative, there is no possibility of resonance-based effects. So, this is going to be completely an inductive effect. And the chemical shift value of this Hydrogen here is 7.78. So, this value again is much greater when compared to Benzene. So, the CF_3 definitely has a significant effect.

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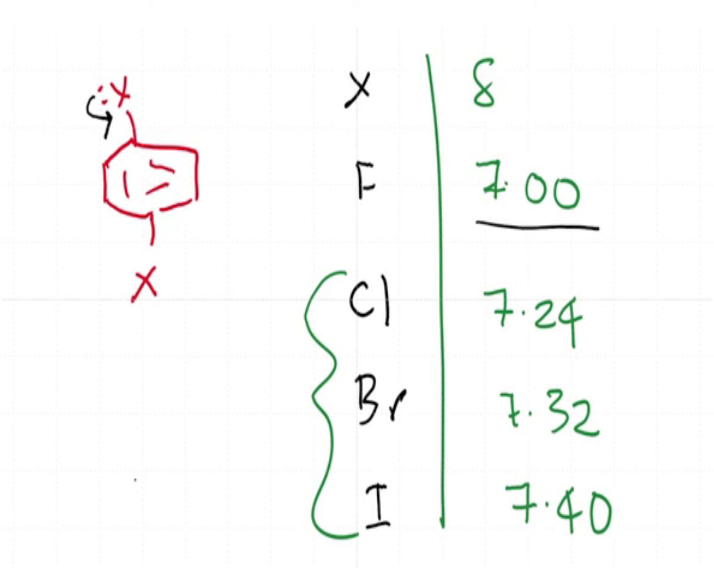

X	δ
F	7.00
Cl	7.24
Br	7.32
I	7.40

Now, let us move on to a couple of more examples in the Halogen series. So, let us look at, I am just going to draw out the compounds as X and X. So, when X is Fluorine, then you can look at Chlorine, Bromine, and Iodine. And what we are going to do is we are going to list out the chemical shift value. So, the value for Fluorine is 7.00 and that for Chlorine is 7.24, Bromine is 7.32 and Iodine is 7.40.

So, if I look at these three substituents, it seems like these values are either, for Chlorine is comparable with that of Benzene, but Bromine and Iodine are definitely more de-shielded. Now, when it comes to Fluorine, Fluorine is very interesting because Fluorine is the most electronegative atom but having lone pairs, having 3 lone pairs Fluorine can also donate electrons by resonance.

So, it makes it a weakly electron donating group by resonance but a strongly electron withdrawing group by induction. So therefore, this balance leads to this kind of shift here, where Fluorobenzene is actually going to have a lower chemical shift when compared with Benzene. We will also look at this later when we are looking at selectivity in substitution reactions.

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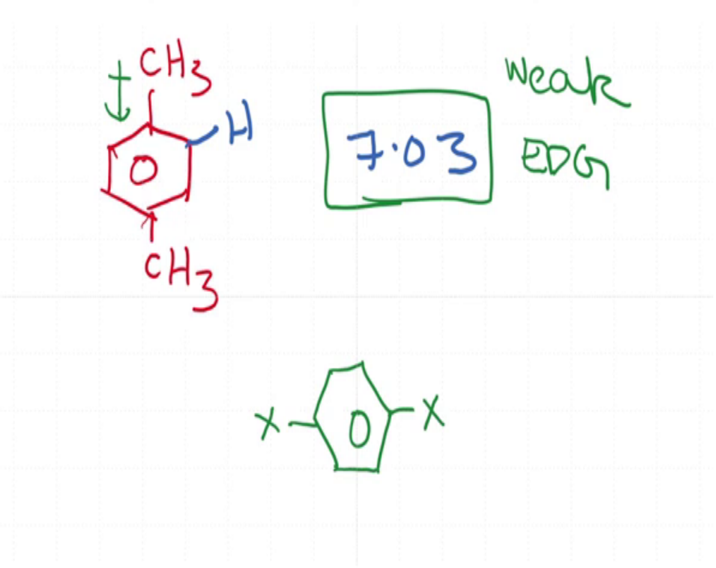

So next, let us move on to a few other substituents. So, the next substituent, we are going to look at is Toluene or CH_3 , CH_3 in para positions, so here the value is 7.03. Then I am going to just draw out a general structure and then we will look at the trend. So, this 7.03 is again can be rationalised because this methyl group is weakly electron donating, weak EDG, so that is going to lead it to a more shielded situation, and therefore the Hydrogen is going to be coming at lower chemical shift values.

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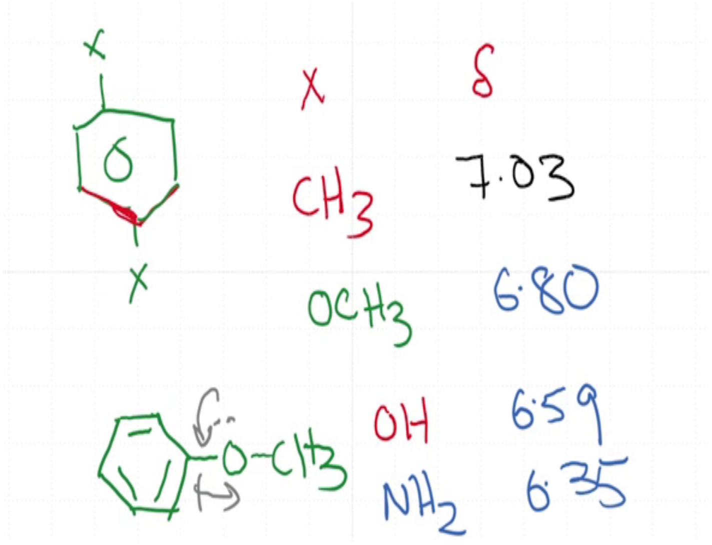

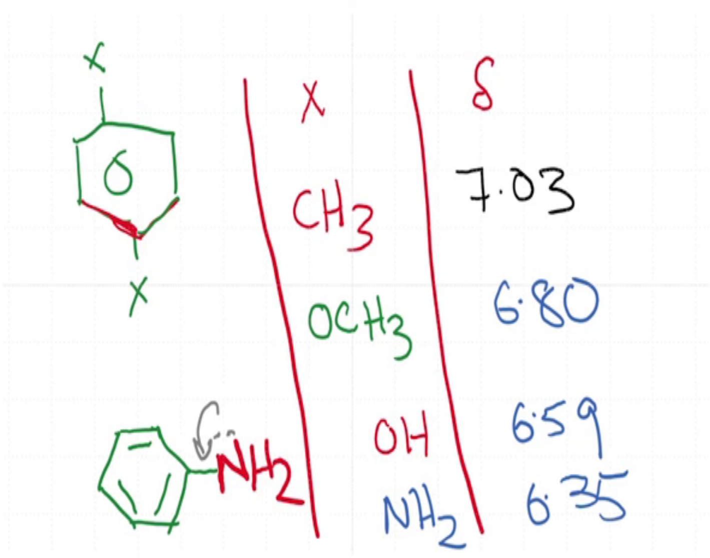

So, now let us look at a few more examples and we will then sort of wrap up this lecture. So, the next compounds that we are going to look at are basically, again, 1,4 substituted. Just for simplicity, so, I am just going to call this as X and X. So, the first example that we will look at is X is and we are going to look at chemical shift; X is methyl group.

So, if there are two methyl groups in the 1 and 4 positions of the Benzene ring, the delta value is 7.03. So, this value is again lower than that of Benzene and one can understand this by the weakly electron donating effect of methyl group.

The next example is OMe, which is OCH_3. So OCH_3 group, the methyl group itself is electron donating but there is an electronegative atom right next to it. So, what we would expect is that there is going to be a little bit of, you know, the Oxygen is going to dominate, but Oxygen itself is very interesting because, if you see the sort of situation with respect to Oxygen is that you have a lone pair.

So, you have OCH_3, so, the electronegative atom is going to be pulling electrons whereas, the Oxygen being electronegative can also donate electrons. So, there is going to be again just like fluro there is going to be a balance between electron withdrawing effect and electron donating effect. And here in this case, the electron donating effect dominates and therefore, this becomes more shielded, 6.80.

The next example that we are going to look at is Phenol. So, when you look at Phenol or 1,4-dihydroxy benzene as shown here, so, what we are going to look at is the, again because of the Oxygen, it can do two things, it can donate electrons and it can also pull electrons. So, when you look at OH at this position, the value is 6.59. So, as discussed, you know it, Oxygen can donate electrons through resonance, but withdraw electrons by induction.

And the last example that we are going to look at is 1,4- diamino benzene and here the value is 6.35. So, clearly the electron donating effect of the Nitrogen dominates. So, if I have to describe this, the effect of Nitrogen is mainly by electron donation. So, therefore, this becomes a very useful sort of guide for us to understand how aromatic rings are being affected by both electron donating as well as electron withdrawing groups. And the nature of the group can determine whether it is an inductive effect or a resonance effect and depending on the strength of it, the chemical shift can vary.