Principles and Applications of NMR spectroscopy

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Module 2

Lecture No 8

welcome back, so we looked at in the last class we looked at how the different chemical shifts arise due to what are the different effects which factors which influence these values we looked at the inductive effect and we looked at mesomeric effect. So, let us continue with the mesomeric effect now, and see some more examples how in the aromatic systems specially.

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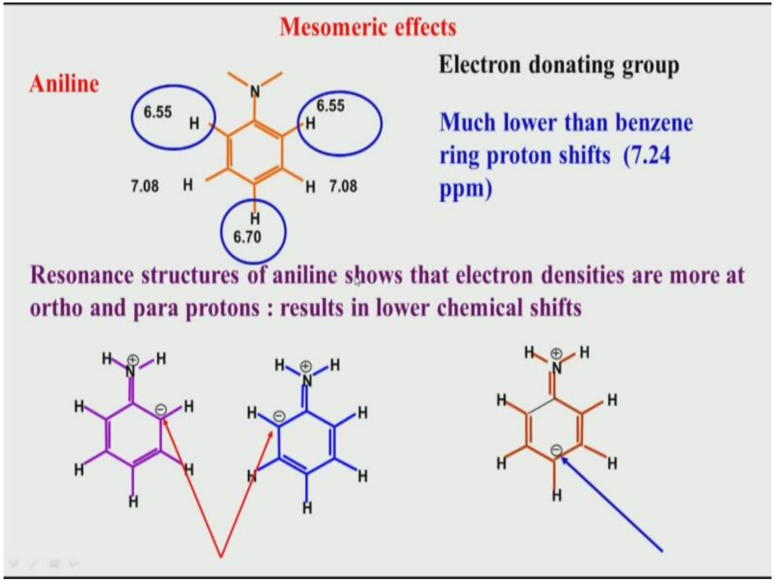

Mesomeric effects

Aniline

Electron donating group

Much lower than benzene ring proton shifts (7.24 ppm)

Resonance structures of aniline shows that electron densities are more at ortho and para protons : results in lower chemical shifts

So, here you can see the example of alanine aniline. Aniline is a well-known molecule and this is a structure so if you look at these functional group NH2, it is an electron donating group. So, it is an electron donating group so what happens is, it donates a known pair of electrons to towards this ring and because of this situation to end of with little higher electron density around this ortho-hydrogen.

So, this ortho-hydrogen accumulates electron density which in turn is transferred to this hydrogen. So, this hydrogen is also having a higher electron density compared to the case where there was no (alanine) aniline or NH2 groups (())(1:19). So, we can see because of this higher electron density, this hydrogen atom now appears de-shielded sorry, shielded. It comes at a higher that is lower chemical shift value de-shielded. So, this we can see this value here, it is around 6.5 ppm compared to the other hydrogen which is Meta hydrogen where it is de-shielded.

So, this is typically the value we will see in the benzene ring, the aromatic benzene ring. So, that is a normal 7 ppm but with respect to that value this hydrogen has got up field shifted because of this electronegative, this is because of this electron donation (())(1:55) higher density of the electrons accumulated at the ortho position.

The same thing can happen in para in para position. So, if you continue this resonance delocalization of this (())(2:07) tetron you can see even in the para position this carbon will have a higher electron density around it which in return transfers electron density to this hydrogen. So, overall this system has a very high electron density around this hydrogen and therefore, again remember if you have higher electron density, it is shielding a lower electron density is de-shielding.

So, the higher electron density called as a shielding of this hydrogen and it comes at a lower ppm value compared to the hydrogen in the Meta position. So, this is how mesomeric effects influences the chemical shifts you can get more varieties of more examples in the different books which we looked at in the very first class there. So, I would recommend to go through those examples typically this is how one can explain based on the electron withdrawing group or the electron donating groups donating nature of the functional groups.

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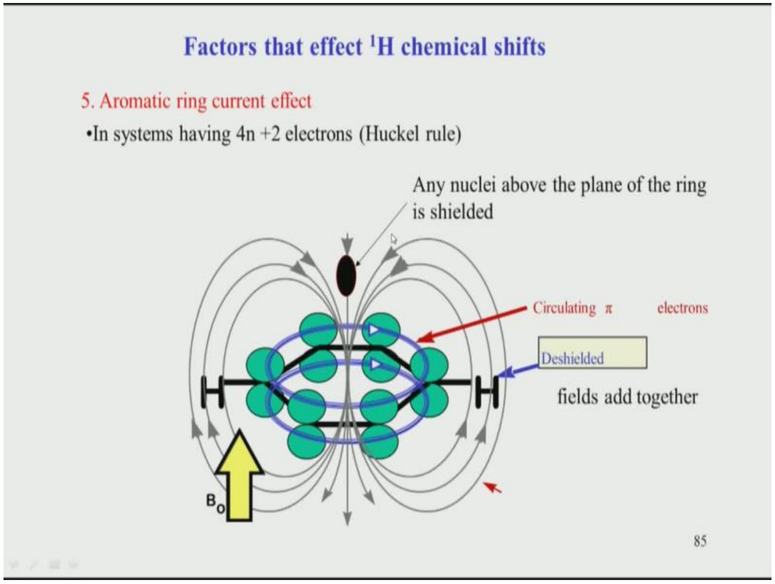

Factors that effect ^{1}H chemical shifts

5. Aromatic ring current effect

- In systems having 4n +2 electrons (Huckel rule)

Any nuclei above the plane of the ring is shielded

Circulating π electrons

Deshielded

fields add together

So, we look at another effect because of which electron chemical shift change and that is called as ring current effect. So, this is very typically observed in only the aromatic rings. This is called ring current effect. So, in aromatic systems what happens is the ring there is a delocalization of this electron around the in the aromatic ring. So, this is schematically shown here.

Now, again remember the remember the any moment of electron that is a moment of charge generates a magnetic field and therefore, because of the circulating pi electrons there is a magnetic field around this particular ring and that the magnetic lines are shown here by this grey color arrows. So, you can see the magnetic field is going into the plane of the ring then comes out and then it is.

So, if you now look at an hydrogen atom, let us say which is located at this position in that particular hydrogen atom, this magnetic field lines are coming into the ring and they are this opposite to this particular magnetic field which is shown in the yellow color. So, what is happening is that this the electron because of the circulating electron density the magnetic field around this hydrogen is being shielded, is being opposite compared to what is in the main magnetic field? Therefore, this hydrogen is which hydrogen is located here becomes shielded, shielded means it come certain up field position whereas if you look at an hydrogen atom which is located in the plane of the ring in the plane.

So, if you look at this case here this electron this magnetic field is coming in the vertical direction and it is in the same direction as this yellow color magnet the l field direction of the main magnetic field. So, you see here also, this hydrogen this electron this cloud this magnetic field is actually supporting or is it in the same direction as the main magnetic field and therefore, this magnetic field and this magnetic field they add up together and that basically increases the magnetic field. n the other words it results in de-shielding of this (hy) it is not shielded, the shielding means opposing the main magnetic field, de-shielding means supporting the main magnetic field.

So, we can see here it is a supporter of main magnetic field and therefore, this hydrogen appears de-shielded and that is the reason why in a NMR spectrum you will always see the aromatic ring protons means the one we attach to the ring always coming at around 7 to 7.5 ppm because they are in the plane of the ring but if the structure of the molecule is such that if there is any hydrogen coming on the top of the ring will appear de-shield it will be appear shielded. So, we will see examples of this type of systems in the next slide.

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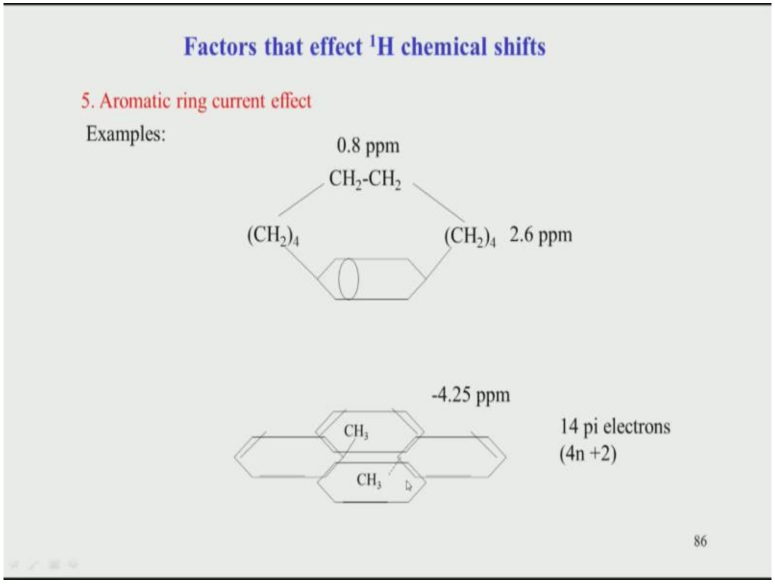

Factors that effect ^1H chemical shifts

5. Aromatic ring current effect

Examples:

14 pi electrons
(4n +2)

Here, you can see there is an aromatic system . So, here what happens is so this is an aromatic ring and you can see that this hydrogens which are away from the ring which are in ring so these are two hydrogen atoms which are on the top of the ring, because of this ring current effect, they are highly shielded. When we say highly shielded it comes at a low ppm value and that is point 0.8 ppm but those which are towards the ring the plane of the rings.

So, you can see these hydrogens are more towards the plane of the ring and if you remember the the the flux that electron the circulating pi electron, this side the main magnetic field and the field because of the ring, they add up together and therefore, they become de-shielded. So, de-shielded means they come at a lower ppm higher ppm value and that higher ppm value is because of that it comes at 2.6 ppm compared to 0.8 ppm which is at the top of the ring.

Similarly, if you look at this particular system here if you which look at this plane you can see this CH3 is right on top of this aromatic ring plane. So, this is a planar structure of aromatic ring 4 electro aromatic rings fused together and this hydrogen is located right on the top of the ring and therefore, it becomes highly shielded and in fact it comes at a very low value of - 4.25 ppm, it is negative ppm. Negative basically means it comes even more up field compared to TMS which is our reference, that is our zero ppm reference and it comes in the negative side of the TMS.

So, that can happen because this hydrogen is right on top of the ring and that is a shielding effect of because of the ring current and any hydrogen which is located on the plane of the ring will not experience that shielding effect and it will typically come at the ppm value of benzene ring which is 7 ppm. So, aromatic ring current effects are very very important for understanding the structure of molecules. In fact in bio-molecules if you consider proteins. Proteins have aromatic amino acids (())(7:38) such as the tyrosine, phenylalanine, histidine and tryptophan and so on.

So, whenever you have this aromatic rings any hydrogen atom which comes close to this ring a get very much highly influenced by this ring current effect and ring current affected chemical shifts in fact are very very important in determining the structures of lots of molecules. So, we will look at that aspect in a later time.

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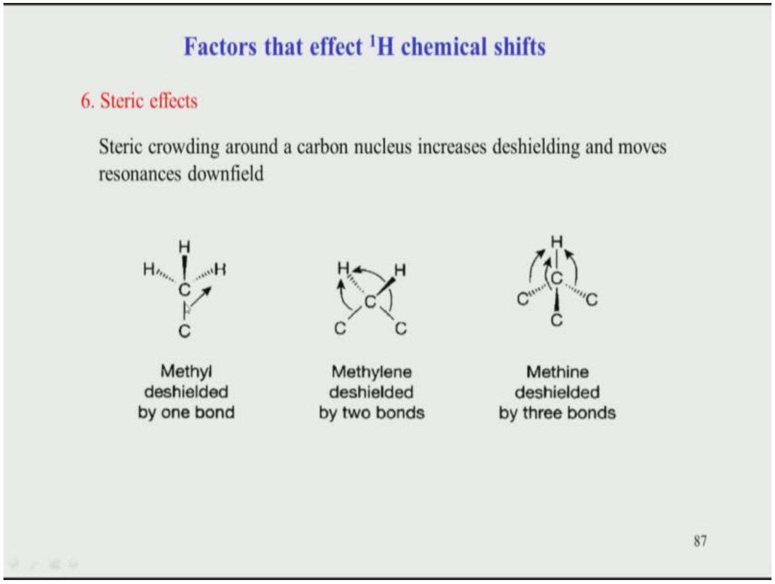

Factors that effect ^{1}H chemical shifts

6. Steric effects

Steric crowding around a carbon nucleus increases deshielding and moves resonances downfield

Methyl
deshielded
by one bond

Methylene
deshielded
by two bonds

Methine
deshielded
by three bonds

let us continue with the next effect of a chemical shift by that is called steric effect. So, steric effect as with the as we learned in chemistry is basically the crowding effect.That means any if you have two bulky groups around the molecules they cause the steric effect is influenced on the structure of the molecule. So, for example, we have can see here that the methyl group is de-shielded by one bond. So, if there is there is a two there is a carbon-carbon bond a single bond and these three hydrogens are located on one side and because of this group this is carbon shield atom sitting here this particular hydrogen is influenced and that gets de-shielded. When you say de-shielded it becomes means it comes at a higher ppm value.

So, suppose there was no carbon here if there was no carbon here you would have another hydrogen which is a methane group. A methane as we saw in the last class it comes at around point 0.23 ppm but because of this additional carbon atom, this will now affect this proton and suppose let us say you have a another methyl which is if you have two methylene groups that is a ethane molecule and in ethane we saw that the hydrogen has a chemical shift value of 0.8 ppm 0.86 ppm.

So, you see it has moved from 0.23 in methane to 0.8 in in ethylene ethane group. So, this is the effect of the steric group because of this additional carbon an atom. Similarly, if I keep adding more and more carbon atoms when we have at a secondary carbon, tertiarytertiary carbon you can see that that the hydrogen atom gets more and more de-shielded. So, in this particular example, these two hydrogen atoms are now experiencing steric effect of two more carbon atoms compared to one here and therefore, these two will be more de-shielded because compared to these hydrogen atoms.

Similarly, if you have a tertiary carbon you can see the methane group you will have further de-shielding because of three carbon atoms attached to this carbon compared to 2 n1 here. So, that is how the shielding effect is influenced, the shielding factor is influenced by the presence of multiple carbon at6om around this hydrogen.

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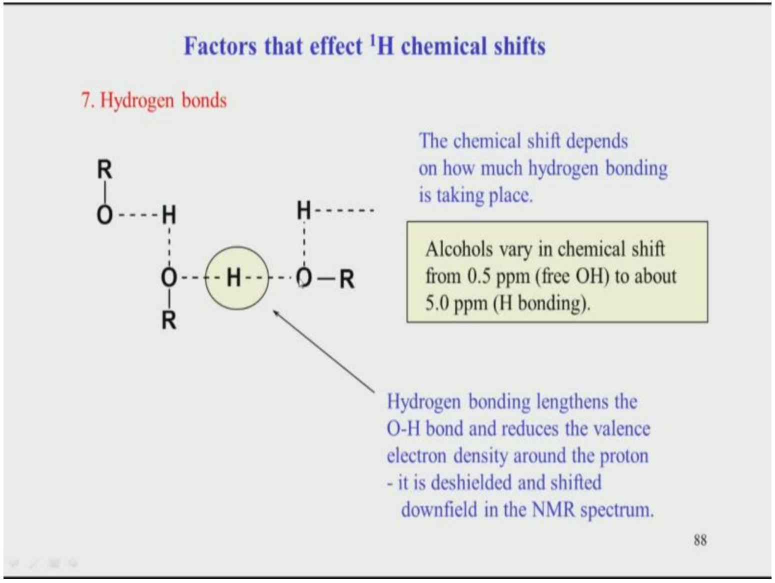

Factors that effect ^{1}H chemical shifts

7. Hydrogen bonds

The chemical shift depends on how much hydrogen bonding is taking place.

Alcohols vary in chemical shift from 0.5 ppm (free OH) to about 5.0 ppm (H bonding).

Hydrogen bonding lengthens the O-H bond and reduces the valence electron density around the proton - it is deshielded and shifted downfield in the NMR spectrum.

So, the another the another important effects is called hydrogen bonds and we have this very important because of many of the organic molecules or biomolecules have hydrogen bonds in their structures. So, all of us know what is an hydrogen bond the hydrogen bond basically is an attraction So, is basically is a donor atom which is electronegative and there is an acceptor electronegative the both of them compete or they both of them one of them is bonded to hydrogen, the other one is electrostatically attracted to this hydrogen and therefore, it forms a very weak bond between this hydrogen and there is oxygen here and because of that what happens is there is an addition.

So, this is a covalent bond here, for example, which is already attached to this oxygen but there is a weak dotted line hydrogen bond between this hydrogen and this oxygen and what happens is because of these additional extra bond, the electron density around this hydrogen is reduced because now there are two electronegative groups which are competing for the electron density around this hydrogen. So, this hydrogen experiences a low electron density which means it gets de-shielded.

So, hydrogen bond are hydrogen atoms are in a involved in hydrogen bonds are typically de-shielded and we can see that actually there is a large variation because of hydrogen bonding the alcohols OH groups because of hydrogen bonding they come at as down field de-shielding means down field and they come at as much down field shift as 5 ppm.

So, this is the effect of hydrogen bonds and it is very important to know that effect of hydrogen on de-shielding and shielding effects because again it is based on structure of the molecules and lot of information we get knowing the chemical shift based on hydrogen bonds.

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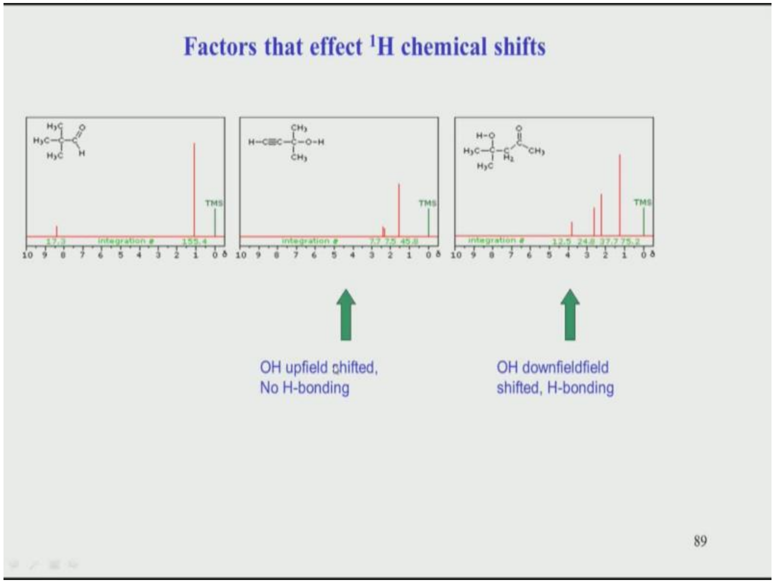

Factors that effect ^1H chemical shifts

OH upfield shifted, No H-bonding

OH downfieldfield shifted, H-bonding

So, this is an another example here. So, one of the thing what typically we do? We will look at it again in a later point of time but to tell you in a very quickly is that to one of the ways to find hydrogen bond is present in a molecule or not is to simply record the spectrum of the molecule at different temperatures.

So, as we go to higher temperatures what happens is the hydrogen bond breaks because hydrogen bond is not a very strong like covalent bond, it is weak in energy. So, as we increase the temperature , it has a tendency to break and the moment the hydrogen bond breaks, the OH chemical shift the H, the hydrogen atom which is lower in hydrogen bond suddenly experiences an up field shift meaning it basically goes towards lower ppm value it goes towards the right side and that basically indicates there is no hydrogen bond and if you go to lower temperature this hydrogen bonds becomes more strong and it goes to lower down field shifted if there is a hydrogen bond.

So, of course these are shown for different molecules but the idea is that this molec if a peak shifts because of the temperature very strongly if it shifts, it is one of the indicating indicator that that particular hydrogen may be involved in a hydrogen bond and therefore, temperature dependent effect of on chemical shift is is used as an indicator of a presence or absence of a hydrogen bond.

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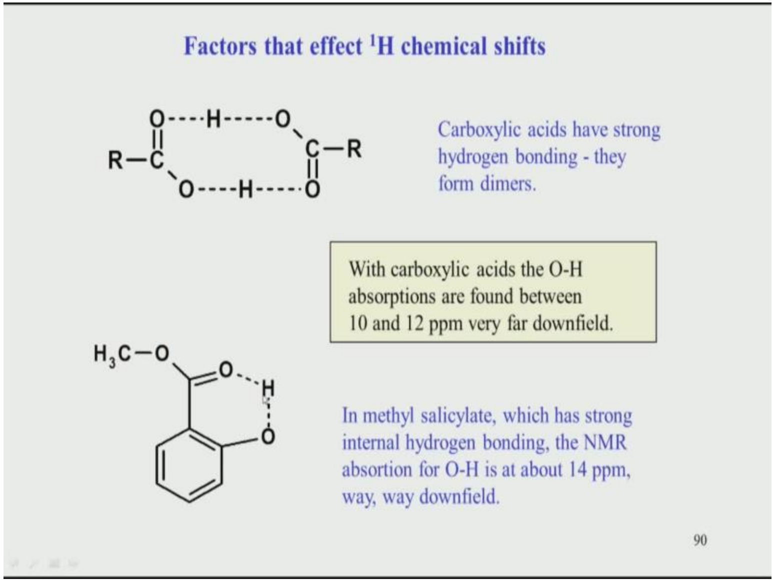

Factors that effect ^1H chemical shifts

Carboxylic acids have strong hydrogen bonding - they form dimers.

With carboxylic acids the O-H absorptions are found between 10 and 12 ppm very far downfield.

In methyl salicylate, which has strong internal hydrogen bonding, the NMR absortion for O-H is at about 14 ppm, way, way downfield.

So, this is what is shown here in carboxylic acids. So, the carboxylic acids are very strong hydrogen bonds, they form kind of diamonds that is a well-known and that is why they have a very down field shifted. You can see as I mentioned in the last class, the hydroxyl the OH H atom of the carboxylate groups they come at a very down field shift around 10 to 12 ppm and is very easy to recognize them when you see them in NMR spectrum and that it is coming from carboxylic acids. And you can also have a inramolecular hydrogen bonds such as in salicylate. Here methyl salicylate or you can have it in intermolecular hydrogen bond as shown here.

So, even in the in case of intermolecular hydrogen bond the chemical shift of this hydrogen is very much de-shielded, means it comes at a very high ppm value and that is typically you know in this particular case, it comes at around 14 ppm which is very high down field shifted proton compared to any other proton . So, that is one of the indicators of hydrogen bond but of course we cannot say directly whether there is a internal intermolecular hydrogen bond or there is a intermolecular hydrogen bond but that for that one has to do some more experiments which we will we will see in the later point.

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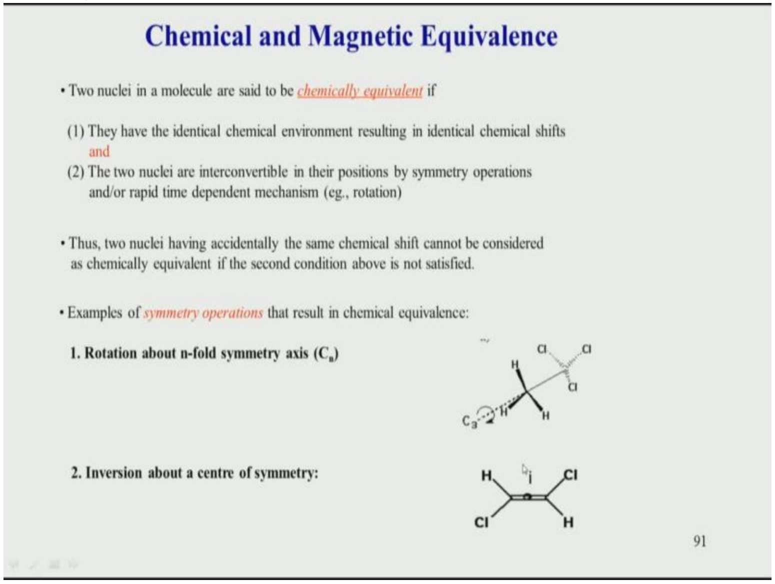

Chemical and Magnetic Equivalence

- Two nuclei in a molecule are said to be *chemically equivalent* if

  (1) They have the identical chemical environment resulting in identical chemical shifts
  and
  (2) The two nuclei are interconvertible in their positions by symmetry operations and/or rapid time dependent mechanism (eg., rotation)

- Thus, two nuclei having accidentally the same chemical shift cannot be considered as chemically equivalent if the second condition above is not satisfied.

- Examples of *symmetry operations* that result in chemical equivalence:

  1. Rotation about n-fold symmetry axis (C_n)

  2. Inversion about a centre of symmetry:

So, now we will come to a very different concept. So, we have seen how the chemical shifts are influenced by various factors major another important point or topic or concept in NMR is called chemical and magnetic equivalence. So, this is very important to know understand let us see what this means. so, what happens is many times two hydrogen atoms will have the chemical shift.

So why does it have the same chemical shift? The reason is that they have identical chemical environment around them. So, this is one of the reasons two hydrogens can have same chemical shift value. Remember chemical environment means electronic electron density. So, if two hydrogen atoms have such an electron density that the shielding factors are same for both of them then the chemical shift also will be same for both of them but that is not chemical equivalence.

Chemical equivalence means this is one of the conditions it has to satisfy, that means two hydrogens are same, at the same time the two hydrogens are interconvertible. So, this is very important point which has to be borne in mind is that the two nuclei that is two hydrogens which (())(15:47) they are interconvertible in their positions by some kind of a symmetry operation.

So, we will look at this more in detail but this is let us look at an example here, the example is shown here on this right here, the example thus let us say this these these two hydrogens these two hydrogens let us look at these two or you can look at all the three hydrogens here. So, what I can do isI can convert this hydrogen into this position by simply a rotation this is the angle between them is 120 degrees.

So, by simple rotation I can change this two (())(16:23) this hydrogen or I can take this hydrogen to this side by another rotation. So, by simple rotation I am able to interconvert these three hydrogens. So not only that they are in the same chemical environment because they are all equidistance. So, when they rotate they have the same roughly average positions with respect to these three chlorine atoms.

So, because of that these three hydrogen atoms are now chemically equivalent, meaning they have the same chemical shift, same chemical environment and they are interconvertible with respect to each other. So, one should distinguish here between two things, one is that two hydrogen atoms can accidently by chance have the same chemical shift value. That does not mean they are chemically equivalent, when you say if there are two hydrogen atoms are chemically equivalent, it means they have to satisfy both of these conditions and that is why this word and comes into picture, they are to not only have the same chemical environment at the same time they should be interconvertible in that positions by some kind of a symmetry operations such as rotation, translation i mean rotation or rotation around an axis or rotation around a bond and so on.

Only when both of these conditions are satisfied we considere that the two hydrogen atoms are a chemically equivalent, if only the first condition is satisfied if only that the chemical environment accidently is same then they are called the chemical shift de-generacy. That means they are de-generate, the two hydrogen atoms have accidently the same chemical shift value, they are de-generate or they are overlapped but they are not chemically equivalent.

So, we can look at some more examples of chemical equivalence here. So, this is one example, the second example is inversion around center of symmetry. So, for example, look at this molecule here if I taken inversion if I can invert this to this side, this hydrogen will come here, this hydrogen will go here and they are come they are chemical they are basically positionally they are come back to their positions in the sense they are interconvertible. They are interconverted into each-other's positions but there is no difference in the structure of the molecule because of this conversion and the molecule llooks the same and therefore, these two hydrogens are interconvertible.

At the same time they have the same chemical environment. This hydrogen has a chlorine next to it and a chlorine this side. Similarly, this hydrogen has a same one chlorine next to it and this side.So, you see the chemical environment around these two hydrogens are same and in the same time they can be interconverted around each other and therefore, these two hydrogen will have the same chemical shift value and they are considered as chemically equivalent. So, they will always be equivalent. So this is a trans hydrogen.

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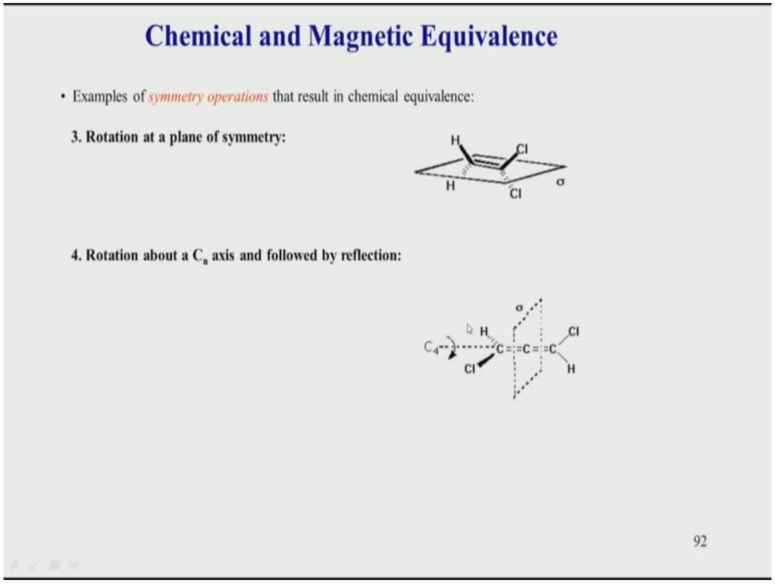

Chemical and Magnetic Equivalence

- Examples of *symmetry operations* that result in chemical equivalence:

3. Rotation at a plane of symmetry:

4. Rotation about a C_n axis and followed by reflection:

We will look at more examples of this. Let us look at this particular structure. So, you can see there is a double bond here and there is a plane of symmetry which means this is a mirror image of this. So, if you can imagine this plane as a mirror it is reflecting this hydrogen around this mirror and therefore, these two are actually mirror images means if I turn around the molecule by this around this axis I can actually interconvert this.

So, if I turn around by 180, these two hydrogens will get converted to interconvert to each other. So, there are both these condition that they are interconvertible because of a symmetry operation and in the same time they have the same chemical environment because they are at the same distance or same structurally we similar to each other. Therefore, these two hydrogens are now chemically equivalent and therefore their chemical shift value will be same. They will not have different chemical shift value. You can look at this another example here, again we can see there is an axis of symmetry here, this dotted line shown here

So, we can see that I can convert this to this hydrogen by inversion symmetry here similar to what we did in the the previous slide. So, again these two hydrogen atoms will be equivalent to the each other.

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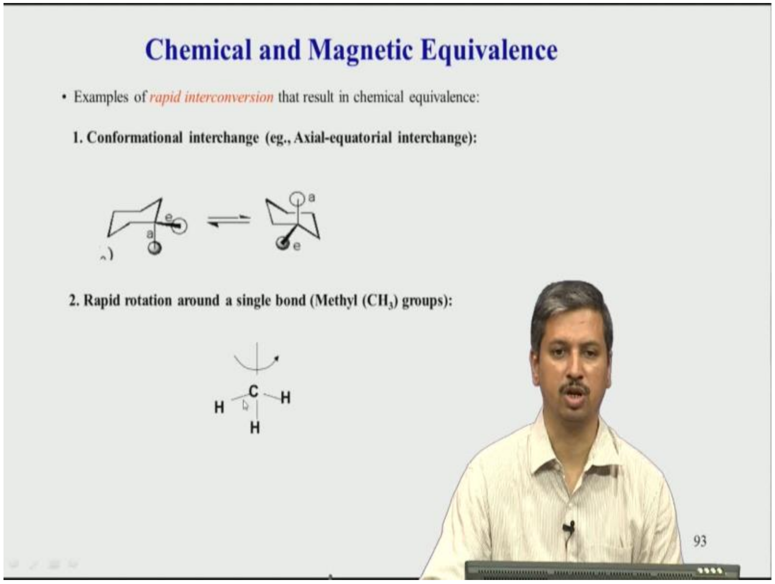

Chemical and Magnetic Equivalence

- Examples of *rapid interconversion* that result in chemical equivalence:

1. Conformational interchange (eg., Axial-equatorial interchange):

2. Rapid rotation around a single bond (Methyl (CH_3) groups):

So, we can look at some more examples. So, this is another case where there is a methyl group here, a methyl group in this a look at this particular axial equivitorial if they are interconvert.

So, another reason chemical equivalence can come if they rapidly interconvert (())(20:367) a between each other. So, this is what is shown here example we know in a methyl group. SSo, let us look at a methyl group we know that the methyl group very rapidly rotates around this bond, this particular single bond in if there is a single bond here, in fact so much so that even in a solid form this methyl groups continues to rotate at a very fast time scale.

So, this rotation is very rapid and because of this rapid rotation around this bond these three hydrogens experience the same chemical environment because they are they cannot have different if any if you have functional group here, this hydrogen, this hydrogen, this hydrogen they interconvert and they end up with the same chemical averaged chemical environment around themselves and therefore, all the three are chemically equivalence.

So, methyl groups are always chemically equivalent in NMR spectroscopy. It is very difficult to not have the methyl groups in equivalent. Thatis only possible if you freeze the methyl group but even in a solid state these methyl groups rotating very rapidly. So, therefore they can all these three hydrogens in a methyl are always interconvertible ande always are were equivalent.

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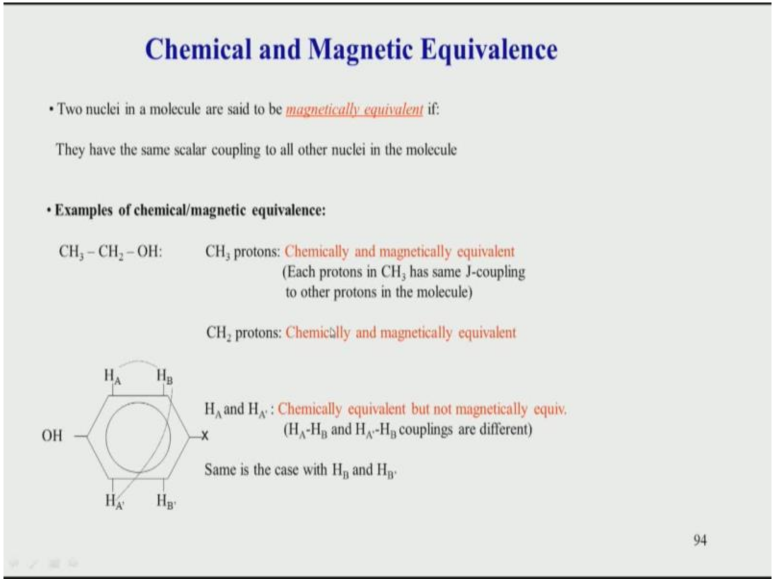

Chemical and Magnetic Equivalence

- Two nuclei in a molecule are said to be *magnetically equivalent* if:

They have the same scalar coupling to all other nuclei in the molecule

- **Examples of chemical/magnetic equivalence:**

CH_3-CH_2-OH: CH_3 protons: Chemically and magnetically equivalent (Each protons in CH_3 has same J-coupling to other protons in the molecule)

CH_2 protons: Chemically and magnetically equivalent

H_A and $H_{A'}$: Chemically equivalent but not magnetically equiv. (H_A-H_B and $H_{A'}$-H_B couplings are different)

Same is the case with H_B and $H_{B'}$.

So, this is basically the concept of chemical equivalence we will look at magnetic equivalence in the next class . so, the take home here is that chemical equivalence is a very important point. Because of chemical equivalence the shift of all the hydrogens come up to the same and it is important to know because methyl groups for example, always have the C3 three CH3 atoms the 3 3 hydrogen atoms are always chemically equivalent.

The only way to break chemical equivalence is to put them in a non in anisotropic medium but in a normal solution NMP spectroscopy these three hydrogen atoms are very strongly chemically equivalent and you can never separate them.

So, this is our concept of chemical equivalence, one has to basically look at symmetry operations we are look at we have to look in the molecule and figure out if there is any way I can convert one hydrogen atom to another hydrogen by some symmetry operation. If we can do that then basically the two hydrogen atoms become chemically equivalent.

So, we looked at chemical equivalence, now let us look at what is called as magnetic equivalent. So, this are this is another concept in NMR. so, chemical equivalent basically means that the two hydrogen atoms, two hydrogen atoms are called as chemically equivalent if they are interconvertible to each other as well as they are having the same chemical environment.

Now, what is magnetic equivalence? Magnetic equivalence is follows. For this we will have to use the concept of j-coupling which we will see in more detail in the later class but one can still understand this concept based on the structure of the molecule. So, if you look at this particular structure ethanol these CH3 hydrogen atoms, this is a methyl group. So, therefore it will be all chemically equivalent hydrogen atoms.

Now, to establish whether these three are magnetically equivalent also we will have to look at their interactions with other hydrogens in the molecule. So, chemical equivalence remember does not rely on the interaction of this hydrogen with other hydrogens. It is only based on the structure of the molecule and the symmetry operations whereas in this particular magnetic equivalence concept one has to also look at the other hydrogens in the molecule and then see how this particular one hydrogen interacts with another hydrogen.

So, in the methyl group case you have to see if they have the same j-coupling, each of this hydrogens in this methyl group whether it has the same j-coupling with the all other hydrogen atoms in the molecule. if yes if they have the same coupling then we say that this hydrogen atoms these three hydrogen atoms, they are not only chemically equivalent but they are also magnetically equivalent. So, this is the concept.

So, if you look at now this hydrogen atom here, these two hydrogen atoms are chemically equivalent. Why? Because they have the same chemical environment around the two hydrogens and they are actually it reconvertible by a rotation but they are they magnetically equivalent? For that one has to then consider their interaction with this hydrogen and this hydrogen and it turns out that these two hydrogens have the same interaction with this hydrogen, the interaction is a j-coupling interaction and they also have the same interaction with these hydrogen atoms. Therefore, these three two hydrogen atoms are bot chemically equivalent and magnetically equivalent.

So, we can look at more examples here and in aromatic system. So, let us see in the aromatic system here now if you look at the symmetry operation if you look at the symmetry if you draw a axis line here at the center of the ring you can see that these two hydrogens are interconvertible. Means they can be if I rotate the ring around this line, around this horizontal line, this hydrogen will come this side and this will go that side.

Similarly, this will interchange and because of this interconvertibility and because they have the same chemical environment this hydrogen and this hydrogen are located equally close or far from this oxygen and so on, they are chemically equivalent but are they,magnetically equivalent? For that you have to look at the interaction with all other hydrogen.

So, now if you look at this hydrogen A it has particular interaction with B, that is j-coupling. So, that is separated by one bond, two bond and three bonds but if you look at interaction of this A with this B, it is not the same because it has now one bond, two bond three bond, four and five bonds away. So, this A prime this hydrogen is five bonds away from this hydrogen. Therefore, its interaction with this is very weak but the interaction of this hydrogen with this hydrogen is relatively stronger.

So, now what happens is this two hydrogens they are chemically equivalent but their interaction with another hydrogen, you take any other hydrogen in the molecule, they are not same because this one is more closer and this one is farther. And because of that these two hydrogens are no longer magnetically equivalent. Sosimilarly this hydrogen atoms and hydrogen atom and this hydrogen atom you can consider the same way that these two are chemically equivalent but if you take any one hydrogen atomlet us take this one now it is interaction with any other hydrogen atom this one these three bonds away.

So, it has type of (intr) one particular strength of interaction j bond j-coupling but the j-coupling of this with this hydrogen is five bonds away. So, it is a different type of interaction and it is weaker interaction. So, therefore this hydrogen and this hydrogen are no longer chemically magnetically equivalent and we say that they are magnetically inequivalent even though they are chemically equivalent.

So, you see chemical equivalence and magnetic equivalence is a very important concept. Two hydrogen atoms can be chemically equivalent but they need not be magnetically equivalent but vice versa, if two hydrogen atoms are magnetically equivalent they are normally always chemically equivalent. So,chemical equivalenceI does not necessarily establish magnetic equivalence.

So, most of the time we will be worried about chemical equivalence and we will not look at so much a magnetic equivalence. So mechanically as far as they areequivalent their chemical shift values do not change and that is all be the concern as far as the structure of molecule NMR interpretation is concerned but it is very important to keep in mind this the concept of magnetic equivalence. So, we will look at the next in the next class we will look at how chemical shifts now can be further interpreted and we will look at some examples and then see how we can analyze the data. Thank you.