**Introductory Organic Chemistry**
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**Lecture - 08**
**Conformational Analysis of Cyclohexane Part - 1**

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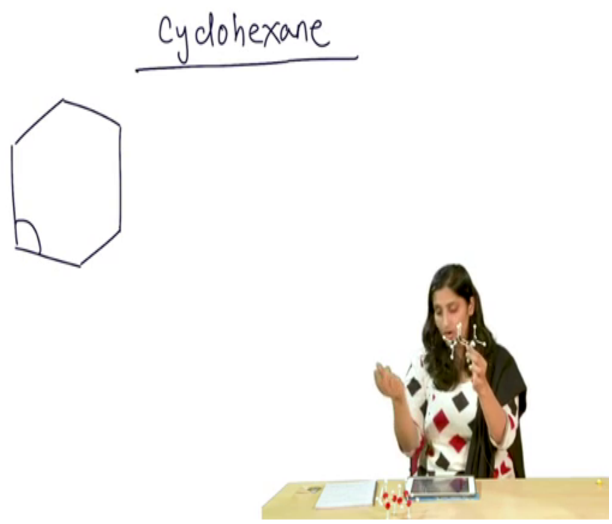


Hi, so far we have looked at different cycloalkanes, cyclopropanes, cyclobutane, cyclopentane and we have studied how their conformations are. Today we are going to have a detailed look at cyclohexanes and why I am saying detailed is that in cyclohexanes in particular, you will see that the conformations play a huge role in how the molecule reacts. So, we are going to have a detailed look at cyclohexanes now.

So cyclohexane, this is a model of cyclohexane and if I want to make this molecule in one plane such that all the carbons are in one plane, there is a lot of torsional strain because now I have six pairs of C-H eclipsing interactions, right. So, and also the bond angle as you can see if I start getting all of these carbons in one plane, the bond angle is kind of more than 109 degrees. It goes close to 120 degrees and which is not something that is very favourable.

So, cyclohexanes do adopt a lot of different conformations in order to achieve that stability. So, one of the most stable conformation of cyclohexane is actually a chair formation. So, this is one of the cyclohexane chairs and you can imagine that a person is sitting here with his head on this carbon and the legs on this carbon.

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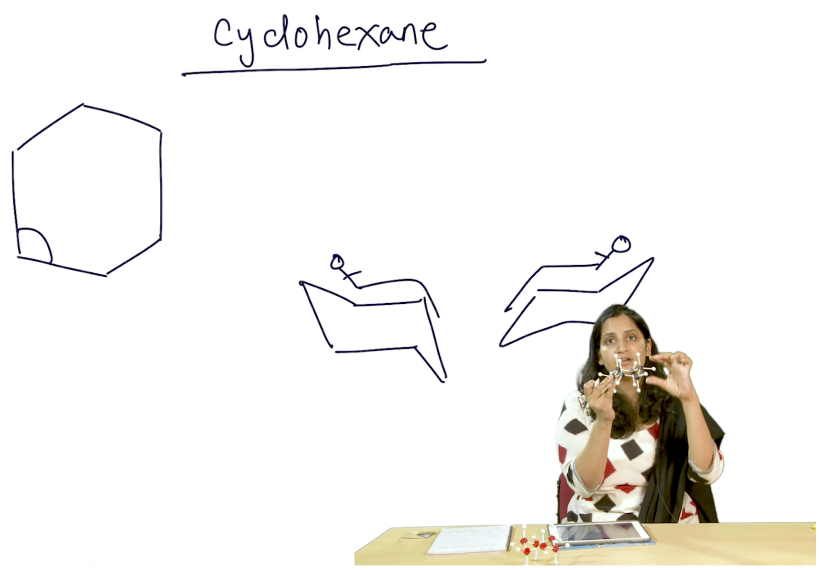


So, I am just going to draw it. In a representation, cyclohexanes are typically drawn such that they are drawn like in the form of chair, ok. So, this is a chair representation of cyclohexane and you can imagine that a person is sitting like this with his head on one side and the legs other carbon.

On the other hand I can also draw a corresponding mirror image of this chair and which will also have the same person sitting like this. I am going to refer a chair, cyclohexane as one of the head of the chair and a legs of the chair. So, in order for you to locate a head and the legs are opposite to each other on the chair.

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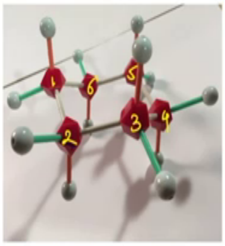 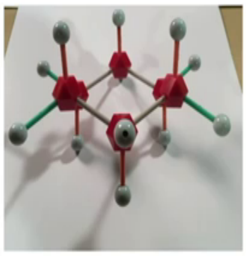

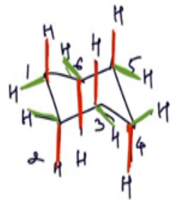 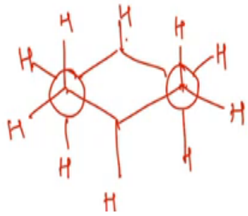

Okay, so now we are going to look at how chemists actually represent cyclohexanes on paper. So, in 3D the molecule looks like this, but how do I convert this particular 3D form on the 2D paper such that it is correctly represented. So, what I am going to do now is I am going to use this photograph and I am going to convert this particular 3D structure into a 2D form.

Now, as you can see I have these carbon numbers 1, 2, 3, 4, 5 and 6. So, now if I look at carbon numbers 1 and 3 and 5, all of these carbons have, as you can see these bonds going up, the C-H bonds on these carbons are going up and the bonds on 2, 4 and 6th carbon those C-H bonds are going down.

If you look at the pink bonds here, these pink bonds are called as axial bonds because they are going vertically up and down. So, I am going to draw this chair. Okay, so I have 1, 2, 3, 4, 5 and 6 and on carbon number 1 as you can see, the vertical bond C-H goes up, on carbon number 2 it goes down, on carbon number 3 it goes up again and down, then up and then down, right.

So, as you can see these vertical bonds which are axial bonds, they are alternating as up and down on all the carbons. If you look at the other bond on the first carbon, so this is going axial up, this particular green bond here is the equatorial bond. So, I am going to draw an equatorial bond here, on the carbon number 2 so, you have equatorial bond going in this fashion. So, I am going to draw all the equatorial bonds. On each carbon you have one axial bond and one equatorial bond present. So, that is how the skeleton of cyclohexane is going to look.

Now, just pay attention to this model. Axial bonds are going up and down as we said they are alternating going up and down, equatorial bonds are also going up and down. So, if you really see this is an axial up bond on the first carbon, if you see the direction in which this equatorial bond is going, it is going in the downward direction. So, for every axial up bond, there is an equatorial down bond that is accompanying it. So, this is carbon number 1, 3 and 5 have all an axial up and an equatorial down bond.

On the other hand if you see carbon number 2, 4 and 6, let us focus on carbon number 2. Carbon number 2 has an axial bond going down, but if you look at the direction of this equatorial bond, it is kind of going up, right. So, 2, 4 and 6 have an axial down and equatorial up bond.

Okay, so I am going to redraw this such that I highlight the axial bonds and the equatorial bonds. So, I am going to colour code here. So, let's make our axial groups as red and let's make all our equatorial groups as green. So, as you can see every carbon has an up bond and a down bond and it could be equatorial or axial, but it has a combination of either equatorial up axial down or axial up equatorial down and vice versa. So, as you can see, similarly as the axial bonds could be going up or down, equatorial bonds can also go up and down. One thing I want to point out here is that on each carbon there is a bond going up and a bond going down, that is something we want to remember, okay.

So, now why are cyclohexane chairs so much more stable that it becomes one of the most stable conformation of cyclohexanes. So, in order to show you the stability, firstly we need to understand the bond angle in a cyclohexane chair is very close to 109.5 degrees. So, there is very little angle strain involved. The other type of strain that we had looked at was the torsional strain. So, now in order to show that there is minimum torsional strain involved, let us look at this other photograph.

So, in order to visualize this what I am going to ask you to do is kind of look at this particular image like this such that these four carbons kind of appear, such that they are in sync with each other. So, if you want to look at it from this angle, this is what it is going to look like right.

If I now draw the Newman projection, let us try and draw the Newman projections on the first, the front carbons. So, remember I am only able to see just the four carbons because these four are kind of eclipsing with each other, you cannot see these back, two of these back carbons, right.

So, as you can see in this particular conformation which is the chair conformation, there are no interaction such that anytime the two hydrogens or the two carbon hydrogen bonds are nowhere eclipsing with each other. So, there are no eclipsing interactions and the entire conformation becomes more like a staggered conformation. As a result of which there is no torsional strain and the chair becomes one of the most stable conformers of cyclohexane.

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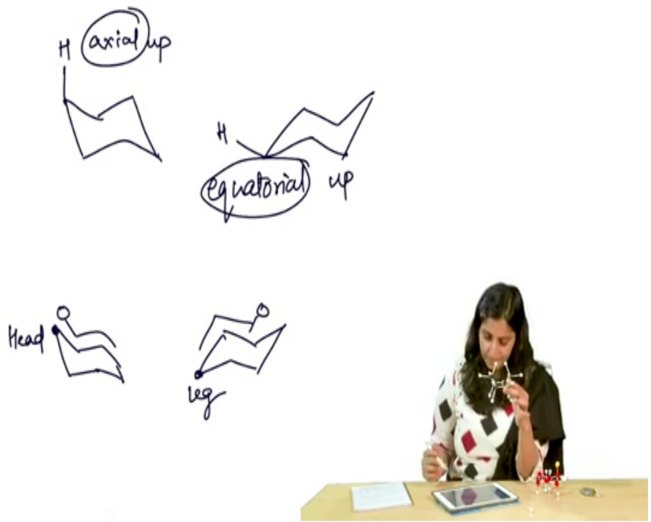


So, now let us look at the cyclohexane chair in detail. So, this is one of the chairs, but as we talked about, its mirror image is also another possibility of a chair, right. So, this is also one of the other possible chairs of the same molecule. In fact, what cyclohexane does is, it has number of confirmations in which you have these two chairs kind of inter converting between each other. So, at room temperature cyclohexane is not going to stay stable in one particular chair conformation, but it is going to constantly keep moving such that it inter converts between one chair and the other chair, okay.

So, I am going to show you both the chairs here with the help of models, ok. So, this is one of the chair and then its mirror image will be this particular chair. So, for example as you can see these two chairs are going to constantly keep on inter converting between each other at room temperature.

But how does that affect the orientation of groups that are attached to the cyclohexane? So, let me draw one group here. We are only going to draw one of these hydrogens because I do not want to draw all of them such that it becomes messy, okay. So, let's look at this particular hydrogen which is currently in the axial up form, right. So, this is the hydrogen which is currently in the axial up form, ok. So, this is the particular hydrogen here the yellow one, okay. So, that's the one we are talking about. Now what happens as this chair interconverts is that the head will become the leg of the chair and the leg will become the head of the chair. So, if you remember these two diagrams, so this particular head here has become the leg of this particular chair, right.

So, if you remember these diagram in this particular, as the chair interconverts, the head has become the leg. Now, the same way if I want to interconvert this chair, as you can see as I twist this and make the head become the leg what has happened the bond that was axial up before, okay. So, this was the situation before the yellow molecule here or the yellow hydrogen you can call it is axial up, but as I interconvert it, it becomes equatorial up, okay. So, I am going to write this as axial up and as it interconverts to the other chair, this becomes equatorial up.

Now, let us try to put it on some other position. So, I am going to put it on one of those equatorial positions. So, let's put it here. So, now let us look at this particular situation. If this chair interconverts, what's going to happen is that this is going to go up and this is going to go down as a result of which the bond that was equatorial will become axial as the chair flips.

So, as you can imagine as the chair interconverts, what happens is that the groups that are axial turn to equatorial, the groups that are equatorial will turn to axial, but if you have noticed something, the axial up still remains equatorial up, and axial down will go to equatorial down, okay. So, up and up will still be constant as the chair interconverts down and down will still be constant as chair interconverts, what changes the notation of axial to equatorial.

One of the good things to note; so, here I have a proper kind of a chair and you can imagine a person sitting like this. One of the good things to notice is that as the chair interconverts, the four carbons which are the seat of the chair. So, 1, 2, 3 and 4, these four carbons are not going to change their place, okay.

So, for example when the chair interconverts, this particular head carbon will become the leg carbon and this particular leg carbon will become the head of carbon. So, that's how the chair will look after inter conversion, before it was like this, after inter conversion it's going to go like that. So, as a result of which the middle seat of the chair, the four carbons of the chair do not really change their position, okay. When I say they do not change their position, understand that the groups on those carbons are going to change their orientation though, okay.

So, I am going to look at a couple of flips here and we are going to practice how to draw cyclohexanes first, then we are going to practice how to draw the flips, okay. But before we go ahead and do all those things I want to focus on how this flip really affects the energetics of the system. To begin with, we had a cyclohexane which was in the chair form and then we said that it is going to go to this opposite chair which is the mirror image of the same chair.

But remember that as this molecule interconverts, it is going to go through multiple conformations in between and if you really see, if I start from one chair what the molecule goes through, I cannot directly achieve the other chair. I have to do a couple of conformations in between. So, first I am going to start with something called as a half-chair, okay. So, this is kind of the representation of a half-chair.

Now, half-chair is one of the most unstable conformations of the cyclohexane. In the half-chair as you can see there are lot of torsional strain. There is a lot of torsional strain because of the C-H eclipsing interactions. So, as I start from a chair, I first have to go through this half chair, but half chair is one of the most energetic forms of the or conformers of the cyclohexane.

So, what's going to happen is that the molecule is not going to be stable in this half-chair form and in fact, it is going to go to, it is going to try and twist and get these. So, this is what it will look like. It will try and twist in order to avoid those eclipsing interactions. This particular form is called as a twist boat form, okay. So, twist boat is also unstable. It is still not the most stable form, okay. I think this is the twist boat form.

This is still not the most stable form right, but it is a little more stable than half-chair in which we had 5 pairs of C-H eclipsing interactions. In order to further convert this particular inter conversion, remember that the leg has to become the head and the head has to become the leg. So, now we have moved the leg from here all the way up to the upper position such that it will become the head of the next chair. But in the meanwhile look at what you achieve. This particular conformation is called as a boat conformation, okay.

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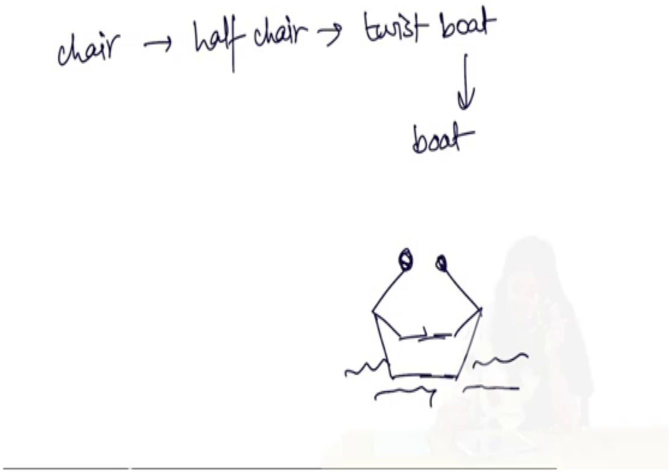


We have started from chair, we have gone to half chair, we have gone to after that we looked at a twist boat conformation followed by which the molecule achieves a boat conformation. Now, boat conformation is again one of the more unstable conformers of cyclohexane as you can imagine what is happening in the boat conformation is that firstly, you have these eclipsing interactions between these C-H groups, okay. These, this is one pair; this is another pair. So, you have two pairs of C-H eclipsing interactions, but you also have something which is because of these flagpoles, okay.

So, you can imagine that on a boat if a person is sitting like that on a boat is kind of you know in the bottle something like that, but as you can imagine this particular boat here has flagpoles which are going to come closer to each other, okay. These two hydrogens for example are going to come closer to each other and they are going to start repelling each other, okay. So, there is a lot of steric strain; especially, if the group is something other than hydrogen. So, hydrogens are really small size, but if you want to go further like a methyl group, ethyl group any other group that is present on these carbons, they are really not going to find it easy to accommodate themselves into this small space.

So, what happens is that in the boat you have a lot of steric strain, as a result of which boat is not really the most stable conformer and the energy goes up. Again, in order to avoid this kind of unfavourable situation, the molecule undergoes a twist boat conformation somewhat like this, then it undergoes the half chair in the other direction, and then you have the chair forming in the other direction. So, now we have interconverted one chair to another going through all the conformations that typically take place.

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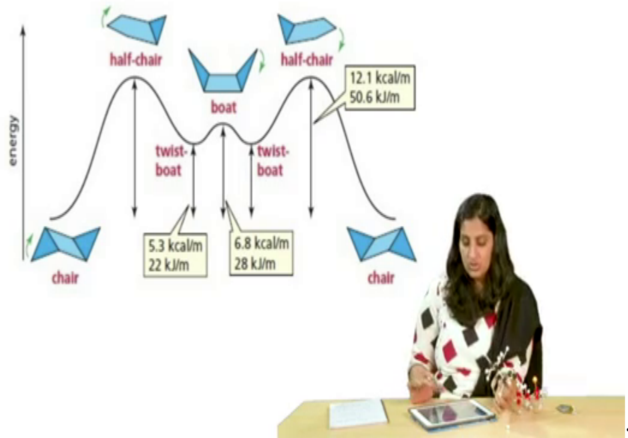


So, I have a graph here which goes through chair, half chair, twist boat and so on and it also shows you the energies of these conformers. So, we assume the chair to be the lower most energy conformation of cyclohexane and we start and as I said half chair because of the torsional strain is approximately 12.1 kilocalories per mole higher in energy than the chair. Twist boat becomes around 5.3 kilocalories higher, boat on the other hand because of these flagpole interactions as you can imagine becomes 6.8 kilo calories more unstable than the chair, okay.

So, if I go on interconverting the chair from one chair to another, the molecule goes through this entire cycle and the energy of the molecule keeps on changing as it goes from one conformer to another. If I ask you a question that at room temperature what is happening? Is the molecule locked in a chair form; is the molecule locked in a boat form; is the molecule kind of moving around and the true answer to this question is depending on the temperature the molecule is going to choose, what is going to happen? So, at room temperature the molecule is constantly moving such that we are going from one chair to another in fact, each of these carbons is taking their turn in order to become the head carbon of the chair.

In order to detect this, chemists used something called as NMR spectroscopy which is nuclear magnetic resonance spectroscopy and NMR helps you to determine if there are different types of a particular atom. So, for example in hydrogen NMR, they are going to tell you if you have different types of hydrogen in the molecule; in carbon NMR they are going to tell you if you have different kinds of carbon in the molecule. For a cyclohexane wherein all the carbons are the same you expect to see just one particular peak in the NMR. In fact, that is what you observe is that you just observe one peak, all the carbons appear and give you one single peak.

What about the Hydrogen? So, if I want to look at the hydrogen NMR of cyclohexane, ideally I should be able to see two peaks right because as we saw axial bonds are different than the equatorial bonds, they are in a different environment as compared to the equatorial bonds. But if you really do the cyclohexane NMR, hydrogen NMR at room temperature, you just see one single peak at around 1.4 ppm basically meaning that all of these hydrogens are giving me just one signal.

So, why is that? That is because the molecule is constantly inter converting between each other and you clearly have no way to detect one particular hydrogen different from the other. So, this is like if you are moving around very quickly and if you are and trying to capture a photo at the same time and the shutter speed is really really low, what is going to happen is that the camera is not going to be able to detect one particular pose compared to the other and you are going to get a very fuzzy picture.

So, at room temperature that is what is happening is that the NMR camera is not precise enough to click pictures of these particular cyclohexane conformations; but now what if I lower the temperature and I take away the energy of this molecule. Remember, the molecule has to go through all of these energetic conformations as we saw on this particular graph here, right. If I take away that energy that it has in order to go through the half chair to the boat and then to the other chair, I may be able to lock this particular molecule in a chair form.

And once this molecule is locked in a particular chair form, you can see that the axial bonds will be different from the equatorial bonds.

So, in fact cyclohexane does show a temperature dependent NMR, meaning depending on the temperature as I go on lowering the temperature I start seeing that there are two types of hydrogens in this particular cyclohexane really indicating the axial and the equatorial positions, okay.

So, now we are going to quickly go over how to draw a cyclohexane properly and how to assign groups on the cyclohexane, such that they correctly represent the 2D structure on the chair. So, what I am going to first do is, I am going to give you a quick tutorial on how to draw a cyclohexane chair, okay.

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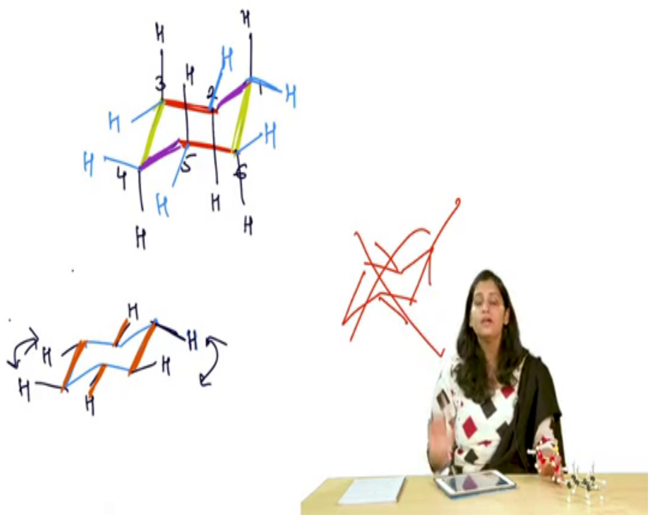

So, what we are going to do first is, we are going to draw two parallel lines such that they are a little apart from each other and then, I am going to join these two lines using a V, okay. So, these two will get together and these two will get together. Now, if you really pay attention to this particular cyclohexane, you will notice that there are various lines which are very parallel to each other. So, for example these two lines will be parallel to each other, then we have these two lines will be parallel to each other and then we also have these two lines parallel to each other, somewhat parallel to each other. So, that’s how the chair should really look, okay.

Now, in order to assign groups on the cyclohexane; one of the things I want to always you guys to remember is that let's say this is the head of the chair, right. You want to remember that the head points high. So, the axial group on the chair head as always has to point high which means it has to go up.

So, what I am going to do here is that I am going to draw an axial up on this particular chair. Firstly, that is my head carbon. So, I am going to number it as 1. Now, what you want to do is ideally have a habit of labelling all your carbons because when you have to convert a 2D structure into a 3D structure, it helps to have the labels on the carbon, so that you know which carbon is which. So, I am going to go 1, 2, 3, 4, 5, 6; typically, either go clockwise or anti clockwise, it is your choice, but follow the same direction. So, if I start clockwise on one chair, I go clockwise. On the other chair as well I do not change the direction randomly, okay.

So, now on carbon number 1, we have this axial up. Now remember that the alternating carbons have the same groups going up. So, carbon number 3 and 5 will also have axial up; carbon numbers 2, 4 and 6 will have the groups going axial down, okay. So, now we are sorted with the axial group. What you do is, you start with the chair head that carbon is always axial up all of those alternating positions, then go up and down and so forth, ok.

Now remember that every up group has a down equatorial group, right. So, what I indeed have here is that the equatorial groups, okay. So, carbon number 1 will have an equatorial down right, carbon number 2 will have an equatorial up, carbon number 3 will have an equatorial down, carbon number 4 will have an equatorial up, down and up again. So, that's how the chair skeleton looks like.

Now, one of the things that I have always seen students go wrong with is the positions of these equatorial groups. Remember that the equatorial groups have a very particular orientation. So, this particular bond is going in this direction, it is not going like this or like this or like this or inside, right. So, it is going in this direction only meaning that I should be able to draw it in that particular direction.

So, here is a good trick is that if this is my cyclohexane chair, right and this is the axial up of this particular carbon, if I want to place the equatorial groups look at their orientation. So, I am only drawing the equatorial groups now, so that it is easier for you to see. Okay, so all of these carbon hydrogen bonds here are only equatorial carbon hydrogen bonds that I have drawn.

So, now if you see this, these two on the end carbons, these two groups are kind of like they are claws of a crab, okay. So, that’s how  I remember is that those two directions are such that they look like claws of a crab and these two hydrogens this one is parallel to this line. They are parallel to those orange colored lines as I have shown. So, that direction is also fixed, it is not so, I am going to also draw some representations of what is not right. So, I am going to draw them all in red color. So, you can kind of remember that this is something you do not want to do.

So, if this is the chair right, the axial group on this one does not go down or it does not go like this, right or in this case it does not go like this, right. So, all of these are the wrong representations of the equatorial bonds, okay. So, this is something you do not want to do. You want to draw the orientation right because that’s how the particular atom is oriented and that’s where it is going to do the reaction. So, it is going to be very important to know how to draw these cyclohexane molecules, okay.

So, now we know how to draw a particular cyclohexane skeleton. Now, let us understand how do I convert a 2D structure into a cyclohexane chair.

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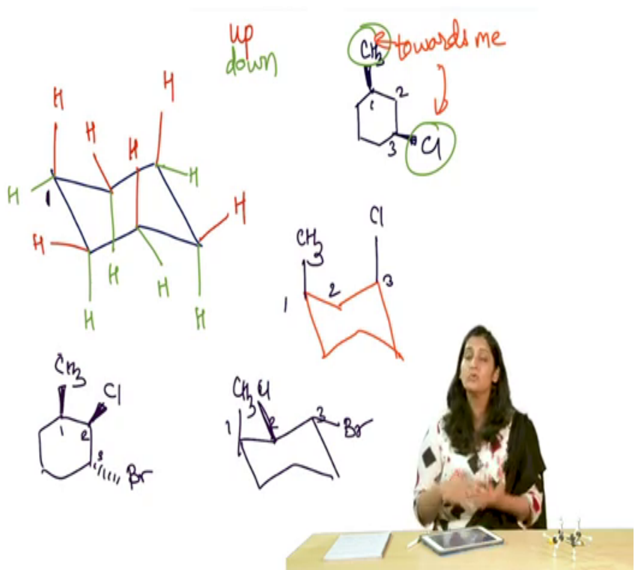

So, in order to do that I have drawn the skeleton, the same skeleton here, but as you can see this skeleton is a little different. What I have done here is that all the groups that are going up are drawn in red and all the groups that are going down are drawn in green, okay. Now, does that mean remember that every carbon has an up group and a down group, it may be axial, it may be equatorial, but we need to understand which is the up group which is a down group. More importantly if I look at this particular cyclohexane chair such I am looking at it from the top what I see is that, there are a couple of groups that are coming towards me and a couple of groups are going away from me.

So, for example, these three groups are definitely coming towards me, then these three groups are coming towards me right because they are oriented upwards whereas, these three groups on this carbon, this carbon and this carbon they are pointed down. So, if I view a particular skeleton like this what I see is that some of the groups are coming towards you, some of the groups are going away from you. So, this becomes very important in converting the 2D structure to a 3D chair structure. I have this example here which is that of chloromethyl cyclohexane.

Now, in this particular example as you can see the methyl group and the chlorine are both coming towards you. How do I know they are both coming towards you? So, that is with the help of another notation. Whenever there is a wedge, that means a dark line that is attached to the group that means that the group is coming towards you, right. So, this is, let me change the ink. So, this is coming towards me and this as well, right both of these groups are coming towards me.

So, now when I want to place them on the cyclohexane, let us take a cyclohexane, right. Now, when I want to place them, remember first thing is always number your carbons. So, it becomes easier, okay. So, I am going to start numbering 1, 2, 3, I am going clockwise on the 2D structure, I will also go clockwise on the 3D chair structure.

So, I am going to start with 1, 2, 3. Now, it does not matter where on the chair you start, I typically like to start from the head of the chair because it's the easiest position to remember, but you can start from any position because remember that at room temperature the head is not fixed. It's going to keep on moving such that it keeps on interchanging such that the chair keeps on interconverting, right.

So, we are going to start from the head and name it as the carbon number 1. Now, on carbon number 1, on this head carbon here the group that is coming towards you is actually the axial up, right. So, the up group is coming towards you, the down group is going away from you and methyl has to be thus axial up, okay.

On carbon number 3, now the group that is coming towards you is chlorine and the group that is coming towards you here is the axial group, right. So, again it has to be an axial up group. So, this is probably the right representation of this particular 2D form. I am going to do one more example such that it becomes clear.

So, now I am going to place three groups on this cyclohexane molecule. So, now in order to draw this particular, let's place another group; a different name, so it becomes clearer ok. So, now I am going to draw the chair again, again first number your carbon so, 1, 2 and 3. So, on 1, 2 and 3 I am going to draw them. You can start from any carbon. Methyl is coming towards you, chlorine is coming towards you, but the bromine is going away from you. So, whenever there is a dash, the atom goes away from you.

So, in this case methyl goes up, as we said in the previous example, the group that comes towards you on the head carbon especially is the axial up group. On the second carbon, however the group that comes towards you is this equatorial group. So, on the second carbon the chlorine I am going to draw an equatorial up group.

On the third carbon, the group that goes away from you, okay. So, this is carbon number 1, 2 and I am on carbon number 3, the group that comes towards me is axial up, the group that goes away from me is equatorial down. So, bromine is going away from me so, I need to draw it equatorial down and that is what it will look like.

So, as you can see that I did not pay attention while converting a 2D structure to a 3D chair structure, I did not pay attention to whether it was equatorial or axial, but rather I kept on thinking whether it is coming towards me or going away from me and coming towards me meaning it is up; going away from me meaning it is down.

So, more often I see students confused because they try to associate equatorial as up and axial is down or vice versa. Do not get confused; always think of whether the group is coming towards you or going away from you and on that carbon whichever group is coming towards you, it could be an equatorial group, it could be an axial group. You have to draw that molecule or that part of the molecule fragment of the molecule on that particular carbon, such that it fits to the description.