Course on Stereochemistry

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Mod05 Lecture 21

Conformations of Cyclohexane

Okay, now let us come back and study the next higher homologue of cyclopentane that is cyclohexane, which is actually the most interesting and most well studied of all these cyclic systems. Now we have seen that this puckering of these rings started from cyclobutane and why the puckering is takes place? The simple reason is to reduce the torsional strain, okay. In case of cyclobutane, although the angle strain increase a little bit, but the gain is more if you reduce the torsional strain. In cyclopentane, there is virtually angle strain virtually zero. So even if you make it a puckered the angle strain still remains zero, but you gain a much more, because you are reducing the torsional strain.

Now let us come to the cyclohexane, okay. Now cyclohexane according to Bayer should be planar, okay. If you try to make it planar, you see is very difficult, you cannot really straight make it planar, because it so flexible. It is very difficult, but suppose I force it and make it a planar molecule. So this is the planar molecule of cyclo sorry, still it is moving, it is very difficult, but if you try to make it planar, you see the angle starts; little bit bending , I do not know whether it is visible there.

The angle bends a little bit, because it will suffer from angle strain, because angles will be then 120 degree, but the normal angle is 109 degree. So this little bending, I hope actually, it is very difficult to hold it in that fashion, I try again yes. It does not that means it is not a stable. If it does not want to they remain in this fashion, it is not stable. So you see the bending now, the top one you can see the bending a little, okay. So what happens? You have the angel stain in the in a in the planar form and in addition, you have huge number of torsional strain, because there are now adjacent bonds increases the vicinal carbons relationships number of relationships between the vicinal carbons that increases. So you have very large number of torsional strain. So to avoid that cyclohexane adopts what is called adopt some conformations, non-planar conformations again puckered conformations where the angle strain is zero angle strain is perfectly maintained at 108.9 degree 20 (())(3:06) correct is 10928 minutes, but per approximation we can say 109.5 degrees, okay.

So the valency angles are perfectly maintained and, but still it is puckered. It is first it is there is (())(3:23) (())(3:25) mode succeed and mode, they first very predicted that cyclohexane exist into extreme conformations, there are they identify two conformations for cyclohexanes and one of them is called a chair conformation, okay. So this is one conformation which is called a chair conformation, okay. Why chair conformation, because it looks like a chair. So if you look at this molecule, so you see that there is leg of the chair then this is the handle, arm of the chair and this is the where you rest your head okay. So these looks like a chair. So this is called a chair form of cyclohexane.

Succemode (())(4:14) also identified another one which is called the boat conformation. This is what is called a boat conformation? This is you see, this is very flexible. So that is why I could get to this is conformation is very easily. So this is the chair conformation again I show and this is the boat conformation, okay. So these two they identified.

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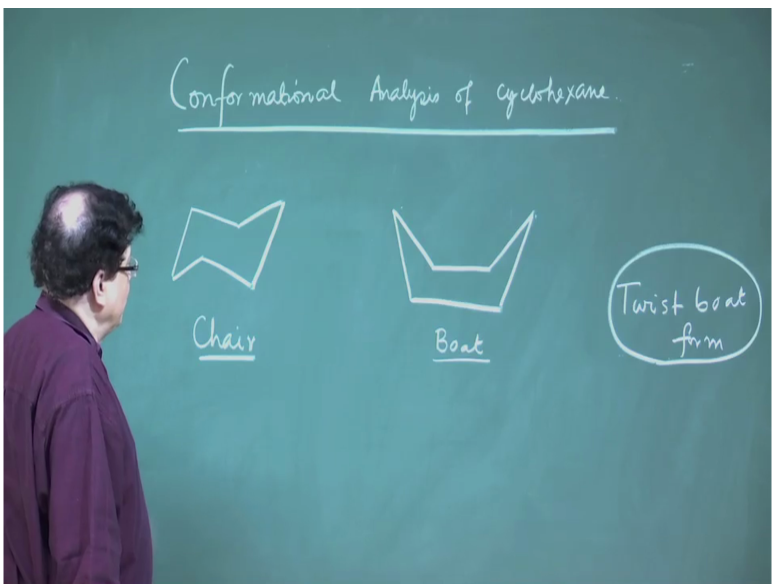

Now how to draw the chair as (())(4:42) a boat conformation of cyclohexane? I can draw it quiet quietly (())(4:47), because I have done it up till number of times. So first draw the chair conformation and this is the chair form and this is the boat conformation, okay. Now between these two conformations, it has been found that cyclohexane exist mostly in the chair conformation and there are reasons for which boat conformation is quiet unstable and we can discuss that later however; there is another form which is in between the chair and the boat and that is what is called twist boat form, we will come back to this later. This twist boat form has lower energy than the boat form, but has higher energy than the chair form and it is true that most of the cyclohexane molecule exist mostly in the chair conformation.

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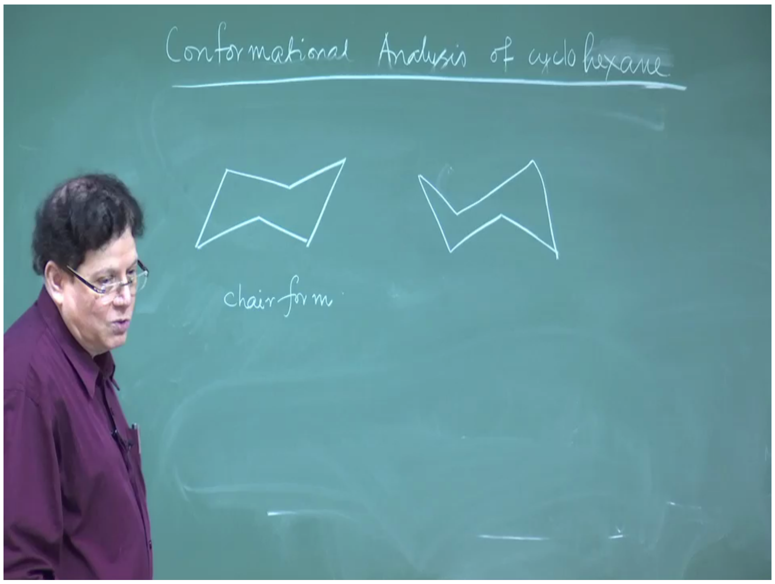

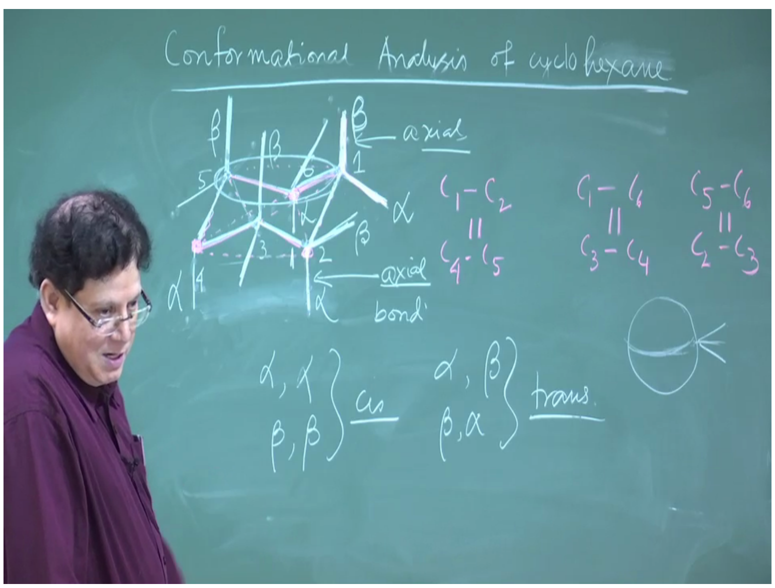

And let us inspect the chair conformation as this is the principle conformation that cyclohexane exist. So first thing that that is important in chair form while drawing this, see there are some students draw in a very bad way like this chair, so there are certain rules in drawing this chair or certain architectural pattern that this chair form follows, okay and what is this? So we have to identify that what are the important criterion or important points architectural, now architectural point of view, okay or geometric point of view. What are the criteria that it satisfying, okay. This is the chair form again we put some number carbon numbering that we have 1, 2, 3, 4, 5 and 6, oaky. So in this you see, this carbon is above this carbon that is very clear if you start from this carbon C4 carbon, so these two bonds are is going above is going upward direction, okay then these two bonds the next two bonds, they again now they come in the downward direction and then after that again these two bonds approach in an upward direction and finally meet at this point, okay.

So what happens now you have3 upward point, these three are the upward points, because these bonds are going up and these bonds are also going up and you have three downward points. Let us see whether we can use a different chock, so these are the 3 downward points, okay. So what happens here? This C1, C3 and C5**,** they lay in one plane and C4 difficult to draw here, but C4, C2 and C6, they lay in another plane, okay we can come back to this geometry to this model and then show it, so what I am saying that there are 3 top carbons which are these three. So they lay in one plane and there are 3 bottom carbons which are there three one this one that one this is the alternate each other. This is alternative, so the back carbon a bottom carbon not back a bottom carbon then a top carbon then bottom then top then bottom then top, okay. So it alternates.

So 3 top carbons lay in one plane and 3 bottom carbons lay in a other plane and these two planes are parallel to each other, okay. So there is an average plane, I can say that there is an average plane, which is going through the middle of these two planes, oaky. So this is the first thing and the second thing is now the whatever the bonds at the carbons, because you have these carbon-carbon framework, but now you have in addition you have the hydrogens if you look at the model you see or do not look at the model before you go to the model, let us try do it in a board, because as I said models are good, but you do not always have the facility of this molecular model systems. So is better to try to visualize thing.

So when there is a carbon at the top you see that there is a one bond which goes vertically upward, okay and another bond which is here, which is downward, but it is not vertically downward. It is I have drawn it in such a way that this is parallel to these bonds. So this is parallel to this bond that bond. In fact these two bonds are parallel to each other that is also due to the chair system. These bond and this bonds are parallel to each other and then this one and this one are parallel to each other. So which bonds are parallel?

Just a internal framework C1-C2 is parallel to C4-C5 parallel to each other and then C1-C6. This parallel to C3-C4 so that parallel is means parallel and then C5-C6 is parallel to C2-C3 they are parallel each other. So while drawing the chair form, you have to maintain this. This parallel relationship between these bonds you have to be you have to maintain while drawing this, okay, I will show you how to draw a chair form for beginners, because sometimes as I said some people many people draw it in a deformed form, which is not correct. So there are some ways to draw it correctly.

Now the question of these bonds the extra the outside bonds after cyclohexane. So there is a bond which is a if it is top carbon, so there are 3 top carbon C1, C5 and C3. So one bond will be vertically upwards and the other bonds will be parallel to the next adjacent carbon-carbon bond. So this bond will be parallel to the next adjacent carbon-carbon bond and in the bottom carbon you have a now instead of going upwards you again have vertical bonds like this again you have vertical bonds like this. This is the bottom carbon and this is the bottom carbon. So we have vertical bond like this.

So again vertical bonds are there, but bottom carbon the vertical bonds go downwards and the upward carbon the vertical bonds go upwards, okay and whatever the other bonds in the bottom carbon, because in the top carbon what I said this is the parallel to the next adjacent carbon-carbon bond the same thing happens here also. So when you draw the 4th ligand here that should be parallel to the next carbon-carbon bond next means next to adjacent. So this one or this one, so this should be parallel to this, okay. So if I try to draw the bond here the extra the 4th ligand that should be parallel to this okay. If I want to draw the 4th ligand here that should be parallel to this and this.

Now sometimes people ask that this parallel line I can also add in this direction. This is also parallel to this. So what is wrong with this? The wrong is that it cannot actually all these 3 bonds cannot be in the same direction in the on this side. So one bond has to come in this position, you remember the sawhorse projection formula. So what happens? This is the kind of sawhorse projection formula. So you cannot have a sawhorse projection formula where this is there, this is in the sawhorse, it is not possible okay. So that is why there is no bond in this direction although this is parallel to this bond, okay. So it is parallel but going in the opposite direction. This is parallel, but going in the opposite direction. This goes from here to there, this goes from here to the top position.

So we have identified how to draw the inward bonds as I said, these are parallel to each other and outward that means which are not making the ring. So outside the outward bonds they are we have identified some vertical and some vertical and vertical bonds like this and some bonds, which are parallel to the next adjacent carbon-carbon bond, okay.

Now there are other points which we need to remember that is we have said that there is a plane here C1-C5, C1-C3-C5 lies in one plane and this plane if it is reference plane then this bond is above that plane above the plane containing C1-C3-C5. So according to the nomenclature conventional that nomenclature system this is beta bond, okay and this bond is below this plane containing C1-C3-C5, so that must be alpha, okay. So this is a beta bond and this is an alpha bond.

So we if we come to the next carbon C2, now this belongs to the carbon which is lying at the bottom plane, so C2, C6 and C4 they form another plane. Here you see this is above that plane, so this should be beta and that should be alpha, okay and it actually this vertical bond here it is beta, next vertical bond is alpha. The following vertical bond is again beta; the next vertical bond is again alpha. So it alternate when it comes to beta and this is alpha, okay. So that means this is how the alpha beta relationship between the bonds are designated, okay. This is designated as per the plane that they carbons belong to, okay the top carbons at the plane and the bottom carbons head (())(17:02) lay in a plane and this alpha beta are basically the whether these bonds are above those planes or below these planes, okay.

This is important while drawing the Cis-trans derivatives disubstituted derivatives of cyclohexane that is important, because what is Cis as I said, alpha-alpha or beta-beta we will make a Cis relationship and alpha-beta or beta-alpha will make a trans relationship, okay. Now these bonds apart from this designation of this alpha-beta, they have some other names, okay. These vertical bonds are called axial bonds. So this is what is also called an axial bond. This is also an axial bond, okay and the other bonds see one thing is very interesting that these axial bonds is perpendicular to the plane containing these three carbons.

So it is just orthogonal to that plane however; this is going down, but it is not orthogonal to this plane. It is laying little bit closer to that plane I can go to the, now the model. So if I take the model, so you can see this is the bottom carbon. So this is going downwards very actually downwards, so that is the axial bonds and this bond is equatorial bond this is going upwards , but it is note that far away from the bond from the plane that I am talking about this carbon that carbon and this carbons are the bottom carbon that makes a plane.

So this is little bit above that plane. It is beta, but the point I want emphasize is that this is going far away from this plane, but this is slightly above the plane. So these are called equatorial bonds, because if you think this is as a, there kind of a circle if you put a circle here, a circular a plane containing a circle. So these bonds lie close to the circle, so equatorial concept came from that if you have this our mother earth, so what happens? This is the kind of (())(19:35) equatorial the equator.

So the things which lie close to the equator are called the equatorial bonds, okay. See you can always say bonds which are not axial they are equatorial, but that is not the correct way of saying, you should know the origin of equatorial bonds, because it is lies, equatorial. Basically what happens that if you consider this as a circle? Now a circular plane, so these bonds lie close to the circular plane, the plane of that circle rather than these bonds. These are actually going. These are orthogonal to the plane, so they are called axial and this is equatorial.

Now why these are called? This is equatorially we understand, because it is closer to this these are the plane, if I think it is a circular plane. So they are called equatorial, but why it is called axial? It could have been call vertical bonds, but we do not call it vertical bonds, okay we call it axial bonds. So what is a definition of axial bond? Now you can say bonds which are vertical to each other vertical, this bonds these bonds are all vertical, axial bonds are al vertical, okay. So you can define it as the vertical bonds are axial and the other bonds are equatorial, you can also tell that bonds which are mutually parallel to each other, this bond is parallel to this bond, this bond see all these bonds are parallel to each other, okay the axial bonds.

So bonds which are mutually parallel to each other they are axial bonds that is another way of looking at it; however the question is what is the origin means equatorial name has a origin, because it is close to the equatorial plane of the cyclohexane system. Axial must have a why it is called axial bonds? They must have origin the name originated from something else that is why it is called axial bonds and if you say that bonds which are vertical, they are axial bonds that si not correct, because if you hold the chair form in this fashion then the definition changes, bonds which are horizontal that becomes axial bonds, see these are axial bonds. The axial bonds the way you hold the chair that is important.

So you cannot say that bonds which are vertical, they are axial bonds, so that is the wrong concept, because it is the then you have to say I have to hold the chair in such a fashion that these bonds you look horizontal or this vertical, okay. So that is not the correct definition. The correct definition is that which also tells that why it is called axial is that. This is a cyclohexane remember all the all these are hydrogen, so assuming those two bonds. So this is cyclohexane.

So in cyclohexane, if you rotate this if you think there is an axis here and you start rotating this cyclohexane along the axis. So what you see that if I do a 60 degree rotation, again I go back to the earlier one. Earlier the head of the chair was on my left side, okay and on the right side is the leg of the chair the bottom of the chair. If I do a 60 degree rotation the whole thing changes, the bottom of the chair is now on my left side and the top most position the head of the chair is now my right side. So if the appearance changes, appearance of the chair changes.

Now if you give further 60 degree rotation, then what happens? Then again the again we come back to the original position the head of the chair is to my left and the bottom of the chair is to my right, which was my starting point. So basically what I did? I did a rotation of first 60 degree, but I did not come to the same appearance, but then I made another 60 degree rotation. So it appears the same like the earlier one, the starting point. So that means it has got what is called 360 by 120, so that gives you a number 3. So it has got a C3 axis of symmetry, C3 simple axis of symmetry, okay C means simple axis of symmetry.

So that simple axis of symmetry is here. If I rotate the chair in this fashion, the simple axis of symmetry will go through this, okay. It still there, but it changes the way you if you orient the chair in this fashion then the simple axis of symmetry will go through this point. It will be inclined okay, but what remains constant is that these bonds the axial bonds remain parallel to this simple axis of symmetry. So the simple axis of symmetry goes through this point and it will always be the bonds will always the axial bonds will always be parallel to this. So that is basically the other way to say is that they are coaxial with the simple axis of symmetry. So that is why they are called axial. So they have originated from the coaxiality of these bonds with the C3 axis, okay. So that is why.

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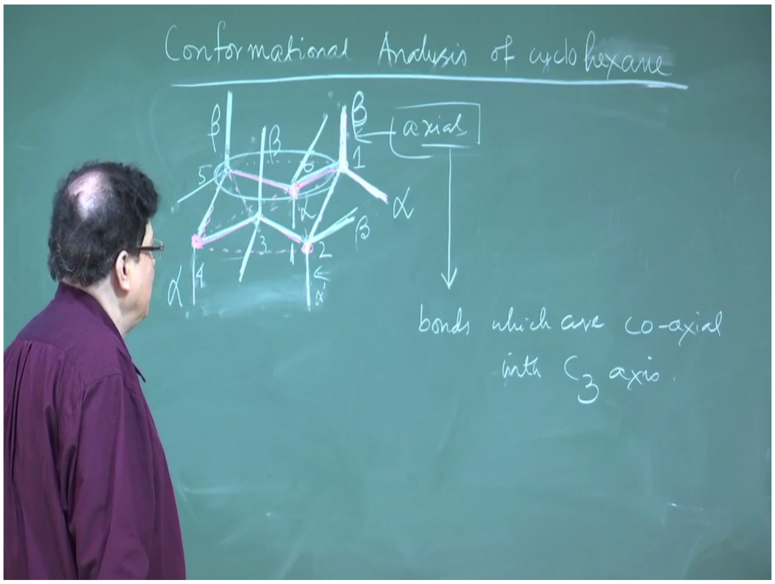

So now what we learn that there are, first of all cyclohexane chair exist mostly in the chair form as I will come back to the half chair later on when you do the energy profile analysis, but right now concentrate on the chair form that is the most common form most stable form, we have identified two types of bonds at the carbons, you can define it in two ways either axial equatorial or you can say beta-alpha. So there are two ways of descriptors, one is axial. So what is the axial bonds? Bonds which are coaxial with C3, because it has got a C3 axis, okay. So that is the correct definition of axial bonds and the bonds which are very close which are laying almost in the equatorial plane that is called the equatorial bonds. So this concepts are very important we will just end of with one more concept which, but next class we will defiantly we will elaborate that issue.

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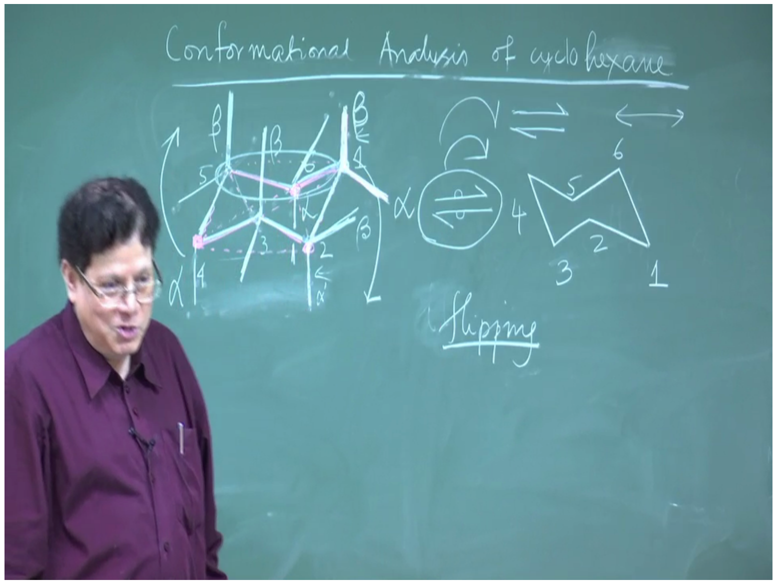

The issue is that this chair form like pseudo rotation I have told you already in cyclopenten that the bond all in cyclobutane also, that the bonds which are up they go down. Now bonds which are down they go up that is happening all the time. In chair form also very similar thing happens. The leg the bottom of the chair can go up and the head of the chair can go down. So this is again that is what is, now in this case it is called flipping. It is very similar to pseudo rotation, but you have a special term here, the chair flips. Chair flips, because why flipping, because the head of the chair becomes the bottom of the chair and the bottom of the chair becomes the head of the chair, oaky. So this is the I again show the process of flipping that the bottom of the chair goes up and the head of the chair goes down, okay and what happens the chair looks like the, looks this is the different, earlier it was looking like this, now it will look like a mirror image of this, because this goes down and this goes up, okay.

So if you follow this numbering that means this is 1, that is 2, that is 3, that is 4, that is 5 and that is 6 okay. So this is what is called flipping, sorry flipping of chair and it is, there is a sign for flipping and that sign is that you have to put a kind of half (())(28:23) circle here, see you know lot of this means 1 electron movement, this means 2 electron movement, this means equilibrium, this means resonance and now you have another type of arrows and that is that you when you put this circles here on the arrow half arrows that means flipping that means this is now flipped and go into the this form, okay.

So next we will discuss that what happens to the axial equatorial bonds? What happens to the beta and alpha nature in the chair form when it flips from one to the other and then what happens to the energy associated with it, because that is what we have discussed in butane that when you rotate what happens to the energy? In this case this is also a kind of rotation, flipping is also a kind of rotation. So when you flip what happen to the energy? How does it vary when you go from one chair to the mirror image chair that is called the flip form? So that is one aspect another is what happens to the axial-equatorial bonds and what happens to the alpha and beta nature of the bonds, oaky that will be the next class. Thank you.