Course on stereochemistry
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Mod05 Lecture 22
Energy Changes During Flipping

Okay, welcome back to thistopicon stereochemistry namely the conformational analysis of cyclic molecules, okay. We have seen that the cyclic molecules, the initial conceptabout its conformation was given by Bayer and he considered all these cyclic moleculesas planar molecules and based on that he proposed a theory which is called Bayer strain theory and as per his strain, this isstrain means angle strain and this angle strain is highest for cyclopropane and then it is decreasesto cyclobutane, it got decreased then cyclopentanealmost hasvery little angle strain and then cyclohexane as per Bayersplanar theory that it should again thestartsas we increase the number of carbons beyond cyclopentane.

If you consider all the cycloalkanes as regular polygon then the angle strain again starts to increase, okay. Now we have seen that this theorybecame untenable, because it was mount from heat of combustion data that cyclohexane is the most stable of all these cyclic compounds amongst all these cyclic compounds and Bayer strain theory could not explain the stability of cyclohexane and beyond, okay.

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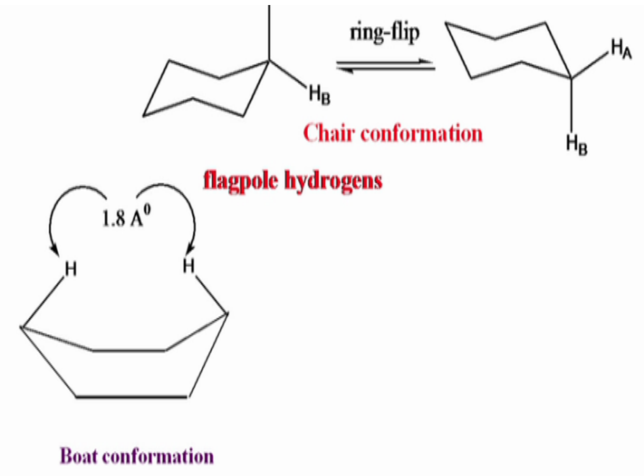

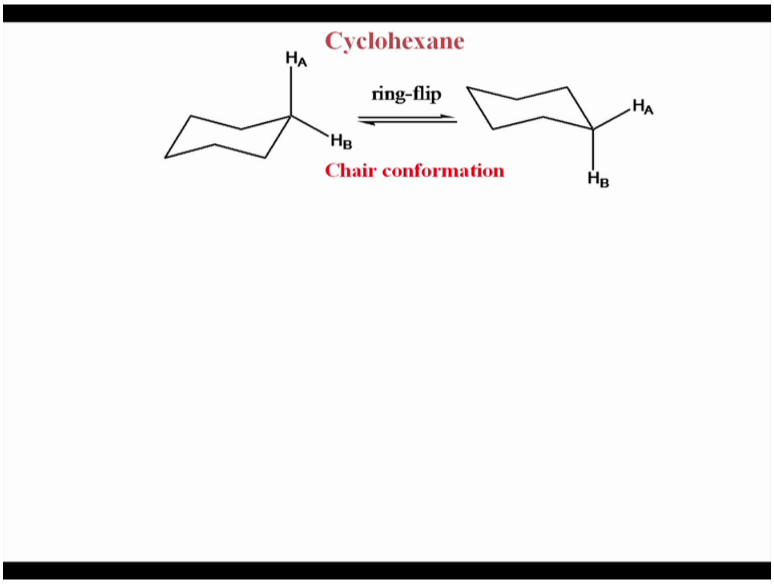

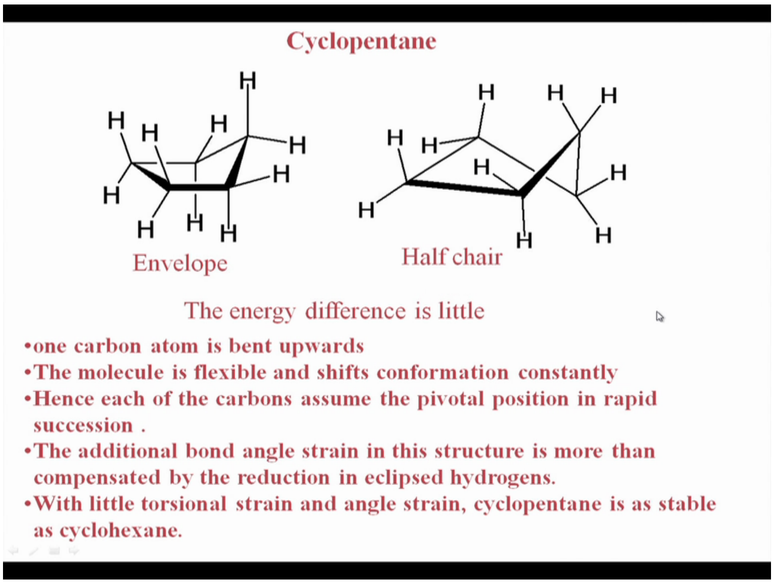

Up to cyclopentane strain theoryis perhaps applicable; however still we have seen in cyclopentane, the molecule is not planar. The molecule although angle strain is very little, but still the molecule prefers to adapt a geometry, which is not planar that Is called puckered form. So itexist in the puckered form. This is the cyclopentane I am showing it, yesterday we havediscuss this. This cyclopentane exist in two types of conformations, one is call the envelop another is called the half chair form, okay.

In the envelop 4 carbon atoms I am showing these, these 4 carbon atoms are in a plane and one carbon is up. So this is the flap of the envelop, okay. This is the envelop, this is the flap of envelop and this carbonis not very, it is not a fixed that this is the carbon which has to be up, it just the it goes down and then the next carbon goes up, so becomes the flap or tip of the flap of the envelop and then it actually oscillates between all the carbon atoms.

So at ait you cannot say thatthis is the only carbon which is at the occupying the tip of the envelop. It is just fluctuating between all the or oscillating between all the carbon atoms in the cyclopentane. This is the envelop conformation where all the 4 carbon atoms in the plane and there is another one which is called the half chair conformation. Half chair where the 3 carbon atoms are in a plane. These 3 carbon atoms and one carbon is above this plane and another car bon is below the plane, okay.

Now ifin this two conformations again angle strain is very minimal. It has minimal angle strain. So also in the planar conformation, but it does not adapt planar conformation. So question wasdiscussed yesterday, it does not at the planar conformation, because in the planar conformation, there will be what are call eclipsing interactions or you can say the torsional strain which is associated, because if it is a planar molecule then all these hydrogens, adjacent hydrogens will eclipsed each other and in order to avoid that torsional strain the molecule adapts the puckered conformation.

So it isit is all writurn here, the energy difference between these two is very little, the magnitudeis perhaps not known. It is very little, so it alwaysoscillates between the two and more over that as in I said there another oscillation going on that which carbon is up thatthat is also not fixed. All the carbonscan be up one after another. Here also which two carbons are up and down that is also not fixed? It is always oscillating between adjacent carbon atoms okay. So this is what is called pseudo rotation. This phenomena ofconformational flexibility where the carbon is going up and down that is what is called pseudo rotation and I saidthis happens, because the torsional strain gets reduced as it adopts the puckered conformation.

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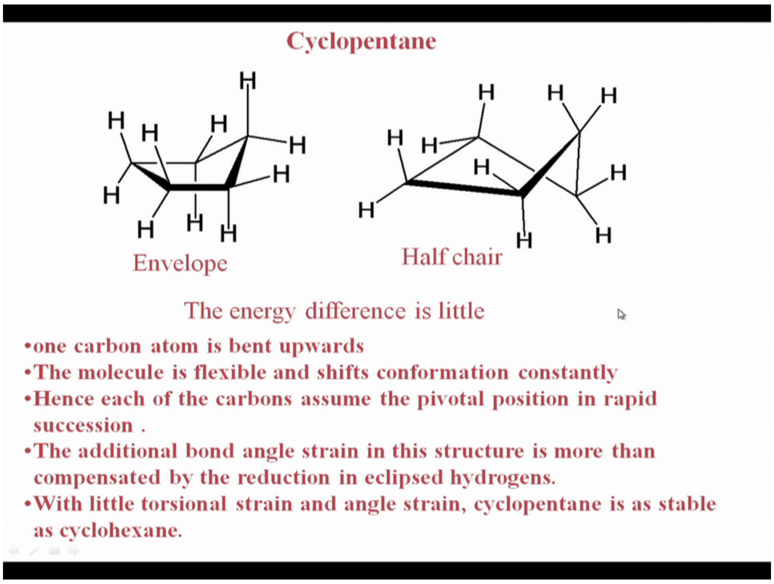

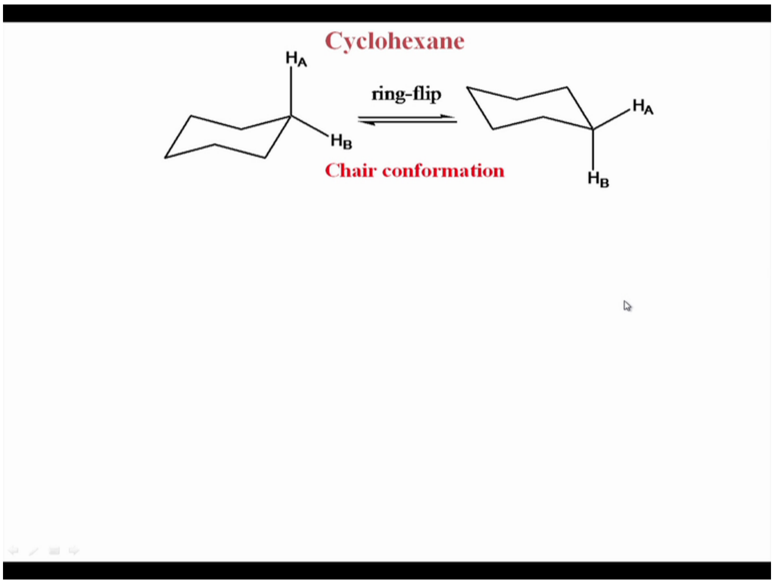

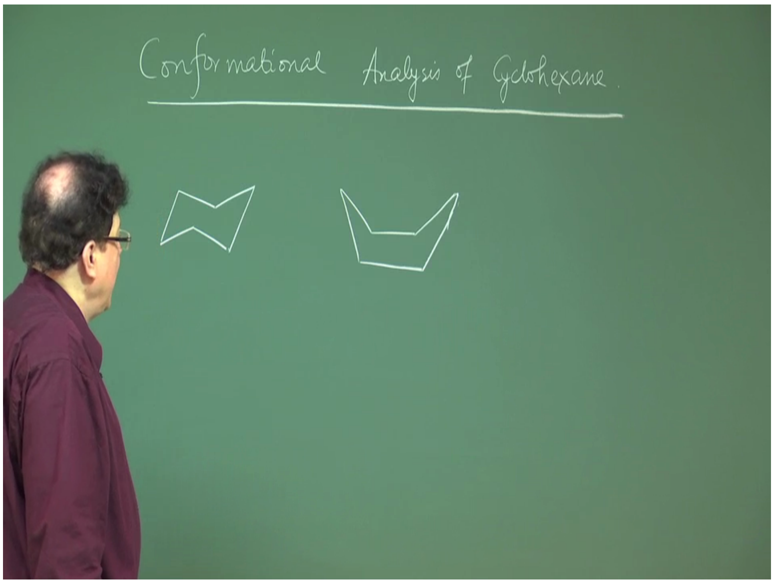

Then we started the cyclohexane, okay. Now in cyclohexane we have seen that it was (()) (5:30) mode who gave the first proposed that cyclohexane exist in two extreme conformations, one is call the chair conformation and the other is called the boat conformation and the name arises, because of the geometry. So it looks like a boat and this looks like a chair.

Now these are the two extremesand amongst these two we will discuss the reasons later on.the chair conformation is more stable than the boat conformation, okay and we decided that first we inspect the chair conformation then we will move on to the boat conformation and we will explain why this is unstable or this is less stable than the chair conformation.

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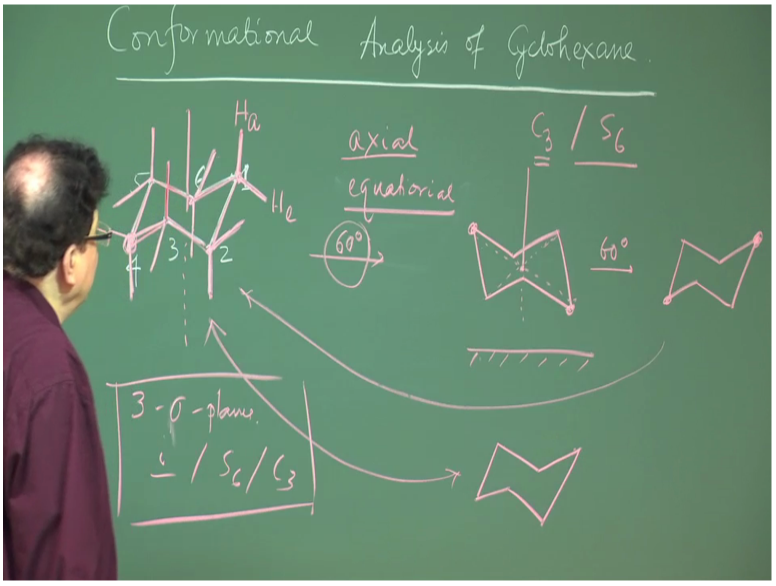

So for the time being let us just concentrated on the chair conformation. Now remember last time what I said that in the chair conformation if we number these, 1, 2, 3, 4, 5 and 6. These are the carbon numbering of the carbons. So in this case what happens? There are 3 carbon atoms C1, C3 and C5, they occupy one plane and the other carbon 3 carbon atoms namely C4, C6 and C2, they occupy another planeand the middle these two planes are actually parallel to each other and you can think of an average plane going through the which is in between these two planes, okay and then what we have identified is that there are, because apart from these carbon-carbon bonds every carbon has two other substituents, okay every carbon has two other substituents.

Now how to draw these substituents? If the carbon is occupying the top positions, so these are the top positions and these are C2, C6 and C4 occupying the bottom positions, okay and at the top carbon the if the carbon is happens to beoccupying a top position then the shapes of bonds that will be there are the carbon one will be pointing upwards vertically upwards if the chair is drawn in this fashion. So this C1, C3 and C5 we will have 3 bonds, which will be vertically upwards and the other bonds at C1, C3 and C5 will be parallel to the next adjacent carbon-carbon bond. So this is the next adjacent carbon-carbon bond for this carbon and this bond will be parallel to this and so while drawing the bond here, so this bond should be parallel to this bond and at C6 you have this is the way to write the other substituent, okay.this will be parallel to the next adjacent I repeat next adjacent carbon-carbon bond, okay.

So thebut C6 we have not of course identified here the other bond what I first said that consider the top carbons. So there will be 3 vertical bonds,which are pointing upwards and there will be other 3 bonds which will be parallel to the next adjacent carbon-carbon bond, regarding C2, C4 and C6, because they are occupying the bottom of the chair. So here they also have vertical bonds, but they will be pointing downwards. So there will be a bond here, there will be a bond there a vertical line and there will be a vertical line at C2. So C2 going down, C4 going down and C6 going down and the other bonds will be again follow the same rules they will be parallel to the next adjacent carbon-carbon bond. So this will be parallel to this.

Then C6 will be parallel to this one and C2, this will be parallel to this one, okay and in the chair another parallel system is there, set of parallel systems and that is C4-C5 is parallel to C1-C2 we have discussed that yesterday, C1-C6 parallel to C3-C4 and C2-C3 is parallel to C5-C6, okay. So this is the characteristics of the chair form. So at each carbon, there are two sets of bonds two sets (())(10:16) of substituents.If it is cyclohexane then these are all hydrogens.

Let us concentrate on a particular carbon, say C1 where I could see that, because C1 was occupying the top of the chair. So the vertical bond has gone upwards. This is what is call axial hydrogen and this is what is called equatorial hydrogen. Axial so at each carbon, you will have an axial bond and an equatorial bond or axial substituent and an equatorial substituents.The definition of the axial substituent isI told you yesterday, the cyclohexane has a symmetry has many symmetry elements if it is plane cyclohexane. So it has got a C3 axis and it has got a C3 axis, because see this is the chair then if you rotate it, remember this is the head of the chair. This is theleg of the chair. So if you rotate by 120 degree, so this is a if you rotate by again I go back to the origin of this is the starting point, so I rotate along this axis.

So this is the chair that I view now after 60 degree rotation. This is 60 degree rotation, because this carbon now occupies the position of the carbon little bit up, but at the samevertical point okay. So this goes there and the chair looks like.

Now the chair is opposite, the head is up and the leg is down on the right side. So after 60 degree rotation you come to a chair, which appears to be different where head and the leg are interchanged, but if you now again give another rotation say of 60 degree then you see then the head has come back to the right side and the leg has come to the left side, okay. That means it after every 120 degree rotation, it becomes a safe (())(12:21), so that is what is that means it has got a C3 axis, okay. So the C3 axis it is right going into the middle and perpendicular to the average plane of the ring.

Axial bonds are parallel to this C3 axis okay, so axial bonds you see all these axial bonds they are parallel to the C3 axis. So the definition of axial bonds is not that they are vertical, they are parallel to the axial, the C3 axis that a cyclohexane possesses, okay. Now interestingly when you rotate by 60 degree, the head goes up and the leg just interchanges head and theleg of the chair interchanges.So if that is that be the case, so what I am saying that if you rotate it by 60 degree then what happens? The chair will look like this, so it is just looking like the mirror image of the earlier one. So this was the head of the chair on the right side. Now this is the head of the chair on the left side. This is the leg of the chair in this form on the left side and this is the leg of the chair on the line. So it looks like the mirror image.

Now what was your axis of rotation that is the rotation is this, okay? Now so that means it does not have a C6 axis, because it looks different okay. If you give another 60 degree rotation you get the original one. So another 60 degree rotation, so you come to your previous chair from the starting point, again the head is to the right and the leg is to the left, okay. So this is now same as that, so that what I said, but in addition I want to point out that after 60 degree rotation (if now take a) if you place a mirror and take mirror image, the mirror is placed perpendicular to the axis, so what will happen?

Now you draw the mirror image of this the mirror is like placed here. So now it will look like this. So this point is here and that point and that pointis here, okay you have to maintain the object distance image distance. So now you see the mirror image is now same as the original, so what I am saying, suppose this is the axis I rotate it by 60 place a mirror perpendicular to that axis and then get the mirror image and I see the mirror image same as that chair (()) (15:04). So what does it mean that means the same axis is also can be called as S6 axis?

So this if it is cyclohexane then it possess as C3, it possess S6 okay. So you can also say that axial bonds are the bonds which are coaxial with either C3 or you can say coaxial with S6 axis. It has got, if it is cyclohexane, it has got a center of symmetry and inversion point also, because this is these are the points which match with each other. So it has got an inversion point and it has got ofcourse 3 planes of symmetry and going through this planes of symmetry are going through this and this bifurcatingI will (())(15:57) show you in in the model.

So this is the chair formthe plane ofsymmetry can be visualize best if you hold it in this fashion not like the way we have drawn it in the board if you hold it, this is a same molecule and if you bisect now from this C1 and C4. These are 1, 4 positions. If you bisect this you see, this is the mirror image of that point and becomes a mirror image of this point. So it has the 3, so there will be 3 planes symmetry, one will go through this and that this if it is one then this is 4. If it is 2 then this is 6, so it will go C1, C4, C2, C6 and C3this is 1, 2, 3, 4, 5, 6 C3-C6 and C2-C5, okay, I can write it here.

So there planes of symmetry, again I have already put it as one. So the planes of symmetries are going through C1 and C4 vertically like this or C3 and C6 or C2 and C5. So there are 3 planes of symmetry, 3 sigma planes 1 (())(17:21) is present and then S6 and C3. So these are the symmetry elements that was that are present in the chair form of cyclohexane,remember there is no substituent here, because the moment you start putting substituents these thingsthese things start will get changed also the moment you put substituent (())(17:45). So that is so we have identified this axially equatorial we knowwhich arehow to define them and how to write them also we know that, okay.

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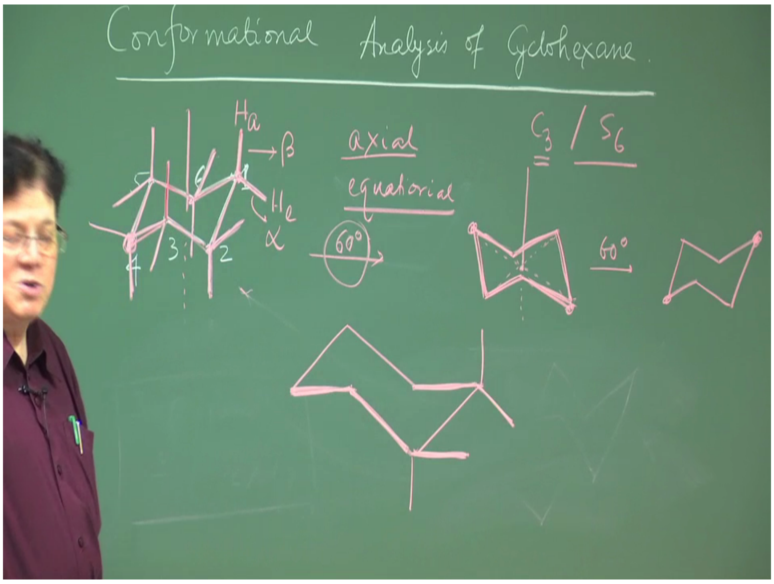

Now there areas I said some students find it difficult to write the chair form and I can give you a very simple way to draw the chair form and that isthat was published in a journal which is call journal of chemical education a very good journalregardingto add the teaching of chemistry and according to thatjournal somebody wrote (())(18:26) that because students find it difficult to write to draw a chair correctly, because I have seen students writing chair like all this deformed like this. So this is not correct , this looks like a chair, but it is the deformed chair, soyou have to maintain the law of parallel parallelism that means this is parallel, so this is parallel to that and this bond is parallel to that, but sometimes you cannot they cannot write proper. So how to make it very easily?

So in that journal of chemical education what they said that you take 4 points at equal distance, okay. So 4 point distance between them as same and you take one point above the second one and one point below the third one and then you draw it you join all these you get a chair that was in the journal of chemical education that you draw this 4 line; however I modified little bit, it is better that you modify a little, because here the problem isI told you that this is also a beta bond, because it is above the plane containing the C1, C3, C5. So this is a beta bond and this is below that plane, so that is an alpha bond, because we know we have this alpha-beta concept that a reference plane you have to take and if some bond is above that plane that is called beta and if it is below that plane that is called alpha.

So we have this beta and alpha. If you draw the chair in this fashion the problem is the beta-alpha will be very difficult, because the axial bonds if you draw that the equatorial bonds arein same cases what will happen, because this is now in the horizontal direction.So the equatorial bonds here is a problem, because that almost lies in the plane that you are considering.So I so it is better thatthis is not a problem, because this is now going awaythis is parallel to this, so this will not create a problem, the problem is created by these bonds, because they are the now placed horizontally.

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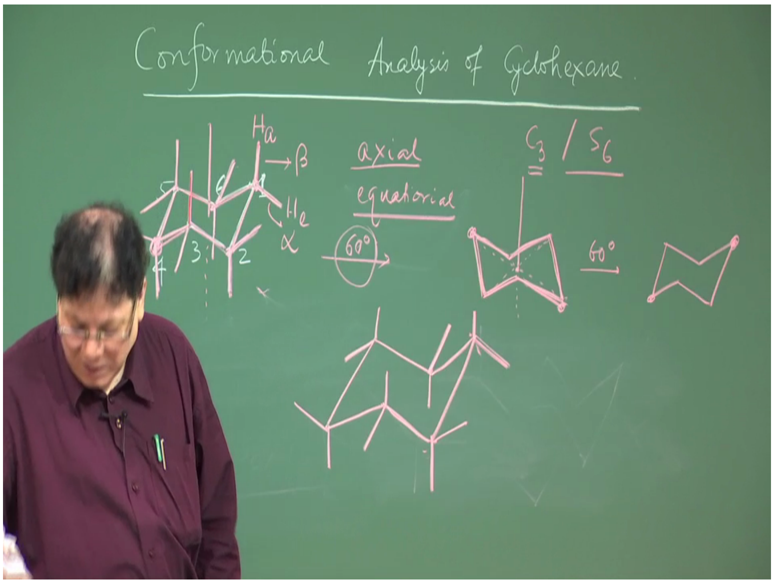

So the equatorial bonds, now it sometimes students get confused whether this is the alpha or beta, because it appears that it is laying in that average plane of the system, okay. So that is why you modify that mnemonic way of writing a chair, the best way is to you take again the 4 points, but in a little inclined fashion not in the horizontal fashion and then put one at the top and one at the bottom and now you join and you get the chair, okay then you bypass that problem. Now you do not have problem the atthe beta and alpha can be very easily distinguished, okay. So is up to you how to draw the chair, but I have given you a way to bypass if you face any problem you adapt this system of drawing 4 points in a line, but little bit inclined not in a horizontal fashion and one point at the top one point at the bottom then you just join them and you get the perfect chair okay. So that might help, because you are the beginners so that might help you in drawing the chair form.So far so we have identified some of the features of the chair form.

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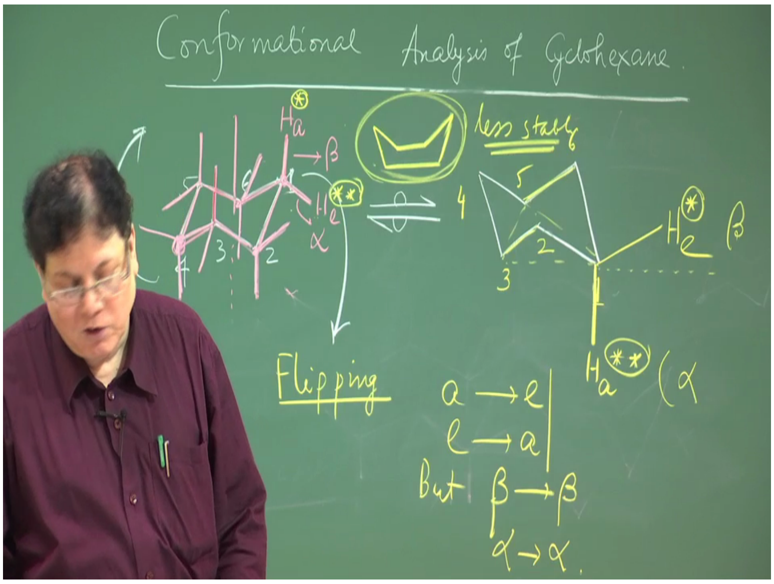

Now another feature of the chair form is that one chair form can by rotation what you are saying that I can interchange the head and the leg of the chair by rotation, by just rotation around the axis, I am not rotating any bond I am just moving the molecule as a hole. The other way you can change this is like the pseudo rotation I have told in cyclopropane, sorry cyclopentane.this alsohas a pseudo rotation (())(22:47) that the one which is down that goes up and the one which was up that goes down. So this is all the time happening in the chair, not all chairs have this propertyif there is substitution is there then sometimes this movement is restricted, but in cyclohexane this is what is happening that this goes down and that goes up you get the you get one chair and the other one is that this goes up and that goes down, okay.

So basically this is continuously happening and you see the relationship between these two chair forms that as you take it up and bring this down your head of the chair is changed, earlier the head of the chair was on the left side now the head of the chair on the right side. Now this process is what is called flipping of the chair. So the chair is flipped, the head becomes leg and the leg becomes head.So there are two ways to do that I said, one is if you rotate the molecule you rotate the entire molecule and in this case you are not rotating the entire molecule you are actually rotating these along these bonds you are rotating the system, so that is half of the operation and the second operation is you rotate the other two bonds and then you get the mirror image here. This is what is called flipping of the chair.

Now in flipping, this is a very important conceptand it is happeningit in the chair form as I said, in some chair forms, it isrestricted. There is a sign to indicate chairthis flipping. This of sign for flipping equilibrium sign, but then a semicircle on the top of the lines and then as you flip it that means you bring this down and you bring this C4 arm. So what you get is a chair for, which looks like this, okay up to that point is simple.

The next question is what happens to this Ha He, so first you identify the carbon atoms. The best way is to put the numbersagain. Now C1 was earlier arm, now after inversion this is the C1 and this is C2 then C3, C4, C5, C6, because this clock wise you have numbered it in a clockwise fashion. So that has to be maintained. So this 1, 2, 3, 4, 5, 6that clockwise fashion is maintained.Then the question is that C1to consider the C1 carbon. So there are two substituents. Interestingly earlier this was top of the chair, so the axial bond was up was vertically upwards. Now this is the bottom of the chair. So the axial bond will be now vertically down and the equatorial bonds again follow the same parallel principle that the equatorial bond will be parallel to the next adjacent carbon-carbon bond, okay. So this is parallel to this or this, because they are mutually parallel. So this what happens?

Now question is suppose this is I put a star here, okay and I put a double star on this hydrogen. So this is a star hydrogen, this is double star hydrogen; question is where at these hydrogens now? So the this is the star hydrogen, so that is now here and this is hydrogen which is double star, okay. The question is what is the big deal about it. There is a great change that has happened when you have flip this molecule.The change is that the axial hydrogen now has become equatorial hydrogen and the equatorial hydrogen has become axial hydrogen that is the change that has happened. So axial becomes equatorial, equatorial becomes axial. What about the alpha beta nature of this? This is stillbeta, because if you take the average plane if you take the plane of theplane containing C1, C3 and C5 you see that He is still He, now this was the star carbon, it is still above that plane,so this is still beta and this is astill alpha that is below that reference plane, okay.

So (what is the) what are the changes that in flipping what are the changes that happen or the changes that do not happen? What happens? Axial becomes equatorial, equatorial becomes axial, but beta remains beta and alpha remains alpha, okay, so that iswhat important, okay. Now we started with the chair form, because I told you that for the time being let us assume that chair form is a more stable of this two chair and the boatwe have assume that, but now we have tosee what is the why this is so.

Now if I again go back to the model for the time being, see what is again go back to what is flipping? In flipping you take the leg of the chair up and the head of the chair down, okay. So when you do this flipping you have notice possibly is that if you do reverse of that earlier stage that when the flipping was half done that means I have taken the bottom carbon at the top then what I end up is what is the boat form.So it has to go the flipping process has gone through the boat form, so we have to involve the boat form during flipping. So this is a chair we start suppose is suppose we start with this chair and thenwe can show many things with this model.first of all in flipping what happens? This goes up; okay it could be the reverse also. This goes down first, but they do not actually happen at the same time, because there is a problem.

If they happen at the same time, so you will go through at some point you will get through a system where all the 6 carbons are in the plane and which is not the stable form. The torsional strain will be very high as I told you that when it iswhen all the carbons are in a plane then you see the torsional strain between the adjacent hydrogens okay.So if so system we prefer the less energetic pathway that means less energy involve pathway.

So first take one arm and then take the other down okay, but you see while doing so, so this is basically done in stages. One goes up you get what is call the boat form and then you bring this down you get the flip form of the chair, okay. You seeI told you I can show you, now that (the) what happens to this axial-equatorial bonds. This red one is now occupying an axial position and beta pointing upwards.

Now if you do the flipping concentrate on only one the red that I amshowing this red one. So when you complete the flipping process you see now this has become equatorial, but it still remains beta okay. So now what we have learn we have learned the process of flipping and we have now involve that when this goes to that form you have to involve this form what si call the boat form, okay.

So now we will inspect that why flipping is just not stopped at this point why it again that this goes up that will give this form the boat form, it could have stop there but if there it does not stop there. This goes down and then getthe mirror image here or what is the flipped form. So basicallythis requires energy and it does not stop here, because this is less stable than the chair form. So the flipping process does not stop at the boat form, the boat form is occupying a higher energy.So in the next lecture we will discuss that why (the) there is energy difference between these two? Why the chair form is more stable than the boat form, okay. Thank you.