Course on Stereochemistry

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Mod05 Lecture23

Energy Comparison between Chair and Boat Conformations

Okay, welcome back, so we will continue with the conformation of cyclohexane, so far what we know that cyclohexane can exist into a stream conformations, one is the chair form another is the boat form. let and then this chair form is the more stable of the two and we are going to explain that in this lecture we are going to discuss the energy differences between the chair and the boat form, but before that I again remind you that this boat form is involved when we flip one chair into the other form, okay and during flipping the rules are very clear axial becomes equatorial and equatorial becomes axial, but the beta or alpha nature of the bonds remains the same, okay. This concept will be useful when we come to the substituted cyclohexanes.

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Now let you inspect the energy of the two forms. In the chair form, if we again see the chair form, the chair form of the cyclohexane obviously, it has got 6 carbon atoms forming the ring, okay. Now when I look between any two carbon-carbon bonds. If I look between two carbon-carbon bonds and then what I if I want to know that what is the dihedral angle between the connected carbon-carbon bond to these two carbon atoms.

So now what happens you forget this part suppose, this part I do not I do not want to see, I just want to see if I look between any two carbon atoms what is the dihedral angle between the carbon-carbon bonds that are attached to these two carbons atoms, okay. So basically what I am saying, I am shadowing this part, so what I see that it is kind of a butane unit 1, 2, 3, 4, so that consist of the butane unit here and what I am doing? I am trying to figure out that this butane unit is it in the staggered conformation or is it in the eclipse conformation? If it is in the a staggered conformation then whether it is the gauche form or whether it is the anti-form that what I am trying to figure out, okay.

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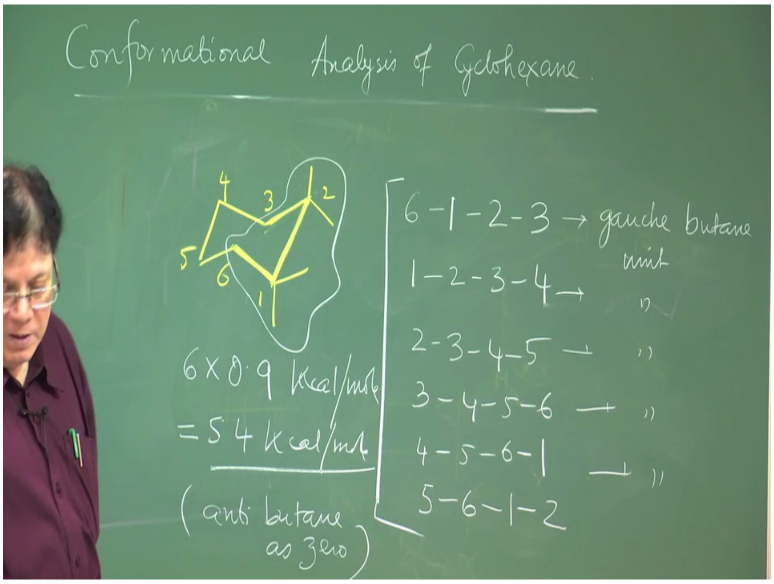

Now first of all there are 6 carbon atoms, so when I look through any two bonds, so question is how many butane units I can find out in this way in the chair form. So suppose this is your number one carbon and this is number two. So if I look from the number one to two I see one butane unit. So if it is one that has has to be 6. So 6, 1, 2 and 3 that is one butane unit. Then if I look through 2 and 3 I see another butane unit. So this is this was your 1 and this was your 1 and this is 2, this is 3, this is 4. So in this way you can think of bisecting a by dissecting not bisecting dissecting this cyclohexane into butane units, the question is how many butane units are present in cyclohexane. So I draw this way again I draw the chair form. So what I am saying that if this is your number 1 carbon suppose, this is 2, this is 3 , this is 4 , 5 and 6, so when I look from look through these two bonds 1 and 2 then I see what is the dihedral angle between these C2-C3 and C1-C6, because that makes one butane unit. So this is one butane unit, okay.

So my first butane unit is 6, 1, 2 and 3 and then what I will look I will look into the dihedral angle between C1-C6 and C2-C3 and it is clear what is the dihedral angle you do not need the model here. It is very clear that they are not empty, because these two carbons are not this anti is this if this carbon is in this direction carbon-carbon bond and if the other carbon-carbon bond is in this (())(4:50) that is the angle. So that is not there that is very clear and this is a staggered form that is also very clear, because you see the nothing is eclipsing each other. So it is not a and not the eclipse form.

So it is in the staggered form, but it is not anti (())(5:06). So it has to be in the gauche form them, because this is the logic, but you can see the model also if you see between 1 and 2 suppose, so I see and angle of 60 degree, so I this is 60 degree that means this is a this butane unit is in the gauche form and likewise you can find other butane units, if I look through 2 and 3 then I get another butane unit 1-2-3-4 then the question comes that what is a dihedral angle between C2-C1 and C3-C4 and it will be again 60 degree. So this is one gauche butane unit and this is another gauche butane unit, so likewise how many you can find. So just but combination you can tell that the next one will be, this is 1-2-3-4 the next one will be 2-3-4-5 then you will have 3-4-5-6, then 4, 5, 6, 1 okay and then 5-6-1-2, after that you come back to the origin the first one 6-1-2-3, okay.

So these are the you can consider cyclohexane as considering these butane units, so it dissect it in such a way that you can see all these 4 butane units and all these 4 butane units are in the, gauche butane conformation, okay that 6 butane units just (())(6:59) if I have said something wrong, this is 6 butane units and all these 6 butane units are in the gauche form correct it and the energy associated we know the what is the energy excess energy a gauche butane unit has over the staggered where the anti-form okay and that was I am just remind you that was 0.9 kilo calorie per mol okay.

So this cyclohexane in the chair form has an energy of 6 into 0.9 kilo calorie per mol, so that becomes 5.4 kilo calorie per mol remember this is not absolute energy. This is taking anti-butane as zero as the 0. (())(7:57). So if you think anti has zero then that is my starting point. So cyclohexane chair has energy, because it has got 6 gauche butane interactions 6 gauche butane units, so the energy is 5.4 kilo calorie per mol okay. So that is the chair form.

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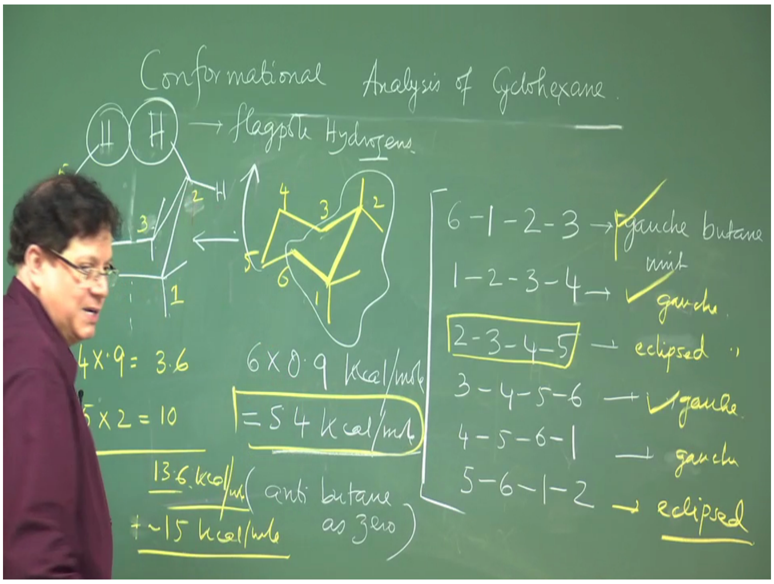

Now we inspect the boat form. So how the boat form is arrived, see you what you do? You take this arm and you get the boat form. This is the boat form, okay. Now in the boat form we have to write the hydrogens, the substituents look like this and so these are the substituents, so you see there are these are kind of the axial bonds which are present in the, which were preset in the cyclohexane chair, but now instead of the C3 axis what it has is a C2 axis if you rotate it 180 degree you get the you come to the original if you rotate it by 180 degree you come to the original appearance okay. So it as got a C2 axis.

So these are not no longer parallel, but quite closed to the 2, it is not parallel, but almost parallel this down bond so they are called axial bonds okay and these are the equatorial bonds. Now what happens to these two bonds, okay? These two bonds have a special name the bonds here, these two hydrogens are the very important hydrogens, because they are within the some of their (())(9:59) radii, okay. So that means they will now heat (())(10:04) each other okay. So this is first of all these hydrogens are call the flagpole hydrogens and they heat each other. So there is a steric strain associated by having this flagpole hydrogen. So the boat form already has a problem which was which is not present in the chair form already there is this hydrogen-hydrogen interaction. The flagpole these are called flagpole earlier it is used to call (())(10:35) flagpole interactions, but actually has are flagpole hydrogens.

Flagpole is basically what that you have in the boat you have a flag you can have a pole in the boat and then you can have a flag attached to them also (())(10:50). So from that it the name has originated the flagpole. Flagpole is basically we host a flag on a stand, so the boat has a stand this is the stand and you attach a flag, so the hydrogens occupying the flagpole position. So this is the flagpole hydrogen-hydrogen interactions, okay. So that is in the boat form.

Now you can say, because of that flagpole flag hydrogen interaction boat form is less stable, but that is not the entire picture, there is flagpole hydrogen interactions true, but that does not contribute much to the instability of the boat form, we have to again inspect the boat form and dissect it into the butane into the units and then see what is the status of these butane units, okay I can show you in the model that in the chair form, the butane units are all in the gauche conformation, whereas in the boat form you see, suppose this is my number 1 carbon, this is number 2 carbon, if I look through this 1 and 2, I again see a dihedral angle of 60 degree that means this one that means this C6 , 1, 2 and 3, so this is a butane unit that is in the gauche conformation, okay.

If you look through this also the next pair of carbon atoms you see again an angle of 60 degree okay. So now I can come here and the number it again, so suppose this is your 1, this is 2, this is 3, this is 4, this is 5 and this is 6, do not actually (())(12:40), this is not as per the numbering system here if I may be if I restrict to that numbering system, because it is derived from that, so better than this is 1 and this is 2, this is 3, this is your 4 carbon, this is the 5 th one which has gone up and this is your 6.

So now the butane units are one is again that 6-1-2-3, this is in the gauche form I have already showed that to you then the next one is 1-2-3-4 that is also in the gauche form, okay. Now what happens after that? So this is again I come back to the model. So this is the first one is between these two I see and angle of 60 degree. So this is a gauche form then I see between these two, I see again there is an angle of 60 degree, so that is in a gauche form, but then when I come to this is these two, the next set what I see that these carbon-carbon bonds are eclipsing each other, okay and the same is true if you are careful enough now, you see on the left side also there is another pair of butane units, which are eclipsing each other okay.

So what are these? These are the these are this 2-3-4-5, so 2-3-4-5 in the boat conformation is not a gauche (())(14:18), it is a eclipsed eclipse butane and then likewise another one will be there 5-6-1-2, 5-6-1-2 that is also in the in a eclipsed butane. So now what we have we have 1 gauche then second one then there is an eclipsed, so forget about that this is the this is gauche and this is also like here also this is gauche form. So you have 4 gauche butane units in the boat form and the remaining two are in the eclipse form, okay. So now you try to calculate the energy. So what is the energy, because there are 4 butane units which are in the gauche form, so you have 4 into 0.9 a that becomes 3.6 kilo calorie per mol and you have two eclipsed butane unit, eclipse butane unit is almost is having an energy of excess energy of about say roughly about 5, okay.

So if it is roughly about 5, 5 into 2, so that makes it 10. Now this is approximate okay, because there is range nobody really could accurately measure this eclipse butane interactions that gives an energy between about 4 to 6, so I take the middle value 5, so that will be 10 and if we add this of 13.6 kilo calorie per mol that is just as per the butane units plus you have to add this steric interaction between the flagpole hydrogens, okay. So if it is at least 13.6, but it is greater than 13.6, so it will be around I can say it will be around suppose 15 kilo calorie per mole considering that the flag pole hydrogens interaction is about 1.4 kilo calorie. These are approximate times, but even if it is approximate if anybody is not 15, it could be 16 or 14, but it is way above the value that we have for the cyclohexane. So this is the energy of the cyclohexane chair and this is the energy of the cyclohexane boat.

So now you can see, what is energy difference between the two, so the boat form is **is** highly energy has much higher energy than the chair form and this is the reason why the boat form is unstable and cyclohexane exists mostly in the chair form, okay. Now in between the, so I hope this is clear.

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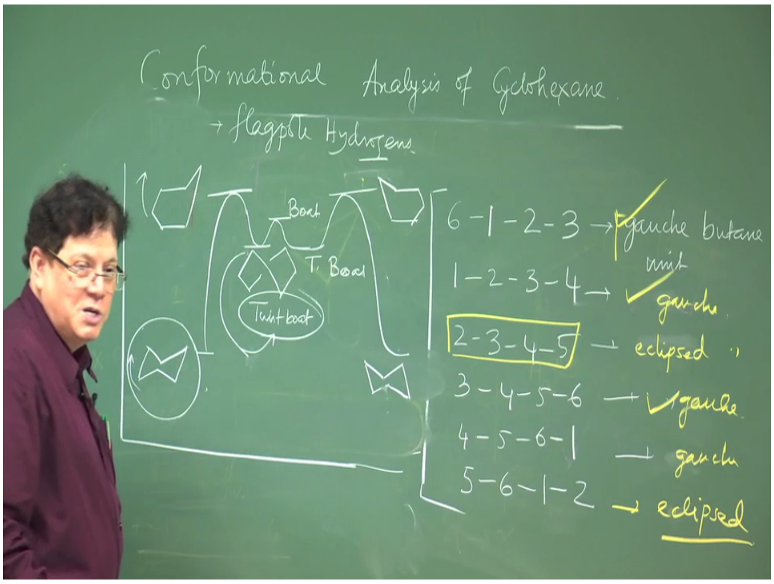

Now in between the when you do the flipping there is something else that how the energy changes then. The energy if the boat form has we know the boat form has higher energy that is true. So if this is the energy and these are the forms. So what happens this is suppose this is the chair form, one chair form I draw here and I am doing the process of flipping. So what will happen?

First I suppose the way I do the flipping there are two options I have, I can bring this down and then later take this up or I can do the reverse I can take this up and bring this down, okay suppose I am taking this up okay. Now what will happen? This is interesting that , so this is my starting chair. So first what I am doing? I am doing an operation where I take the leg of that the bottom of the chair and trying to bring it to the top okay, while doing so I end up with a system where 5 carbon atoms are in the plane and very similar the envelop conformation that we have seen in cyclopentane.

So I see a form I have to go through this form if I want to take this arm. So I go through this form. This form has very high energy, because now you have so many eclipsing interactions, because 4 5 carbons atoms are in the plane. So there will lot of eclipsing interactions involved in this form. So 5 carbon atoms in a plane then you have the top of the chair that is still remaining here. Now this is what is call half chair conformation the half chair okay. The half chair is so when you make it up, so you go through a form which looks like this. So the energy we will rise like this. So this is the half chair energy of the half chair, okay and then you bring it further up. So this is the half chair and now you so you have the highest energy point. Now you have cross the highest energy point, so you are bringing it further up, okay.

So as you complete the competes operation means take it to the point where it occupies the ultimately it will occupy the head of the chair. What happens these two hydrogens which are the flagpole hydrogens, they began to strike each other. So what is happening say this form has the highest energy then the energy starts decreasing**,** it start decreasing, but at some point, it again starts increasing, because when the hydrogen start heating each other, so that the increase the system again the energy increases. So this is that means before you reach the boat form the perfect boat form you have something which you will look like this where the flagpole hydrogens are not close enough like a and not that close enough in the like in the boat form.

Now this is what is called this is not the boat. This is what is call the twist boat form and it is it is usually drawn in this fashion means not in this fashion it is usually drawn in this fashion where you look through these crosswise between the between these opposing bonds and if you do this is, it will look like something like this. This is the way to draw the half chair twist boat sorry, not the half chair, this is the twist boat, I hope is this clear that means before you reach the boat you have a point where the energy, so it goes down, first it goes up, because you are making lot of eclipsing interactions creating lot of eclipsing interactions.

So it has grown up. This is the half chair then you again continue the operation move it further up energy goes down, but energy goes down up to a point which call the twist boat form and then it goes to the boat form. So this is the boat form and this is the form which I have drawn this what is called the twist bond, okay and then the next half of the operation will be just the whatever you have drawn then what you have, this is the boat then it starts moving out. So the flagpole hydrogen interaction starts decreasing. So the energy decreases.

So once you reach the boat then again the energy decreases and you come to the point which called the twist boat, okay. So you go to another twist boat and then you come to a point where all again all the 5 carbon atoms are in plane that is just a mirror image of the half chair that you have drawn. So mirror image of the half chair will be now will look like this and ultimately you come to the flipped form in the flip form may be this. So I hope this is clear now. So first you have this chair then you have the half chair which is the highest energy point, then you have twist boat then you have boat then you have another twist boat then you have the mirror image of chair and then finally the mirror image chair okay that is the twisted form okay.

Now if I ask that what are the conformers of cyclohexane? The conformers of cyclohexane are the chair form and the twist boat, because twist boat is occupying that is the definition of the definition of twist boat, okay, definition of conformers, which occupying the occupying the minima of the energy profile diagram. So according to that this is a conformer that is a conformer, but interestingly boat is not a conformer, okay. It is so whenever we talk about the conformers; it is the chair form and the twist boat; however for just simplicity we do not discriminate this twist boat and boat that much, because the energy difference is not very high. It is only the flagpole interactions that contribute about one kilo calorie or 1.23 something approximately.

so that is not much energy, so we generally equate this do not discriminate between the boat and the twist boat, but truly speaking if you are very rigorous stereo chemist scientist then you have to say that boat is not a conformer, the conformer is the twist boat and obviously the chair form okay. So that is the energy profile diagram. How the energy changes as you go from as you do the process of flipping, oaky I hope this is clear.

So we have now learned that the axial-equatorial concept we have learned the what happens to the flipping? Why chair form is more stable than the boat form that we have learned and we have also learned the different learn the very important concept that boat is not a conformer. It is the twist boat that is the conformer, so cyclohexane ideally has two types of conformers, one is the chair another is the twist boat, okay. Thank you.