**Course on Stereochemistry**
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**Mod06 Lecture 27**

# Conformational Analysis of Substituted Cyclohexanes (Contd.)

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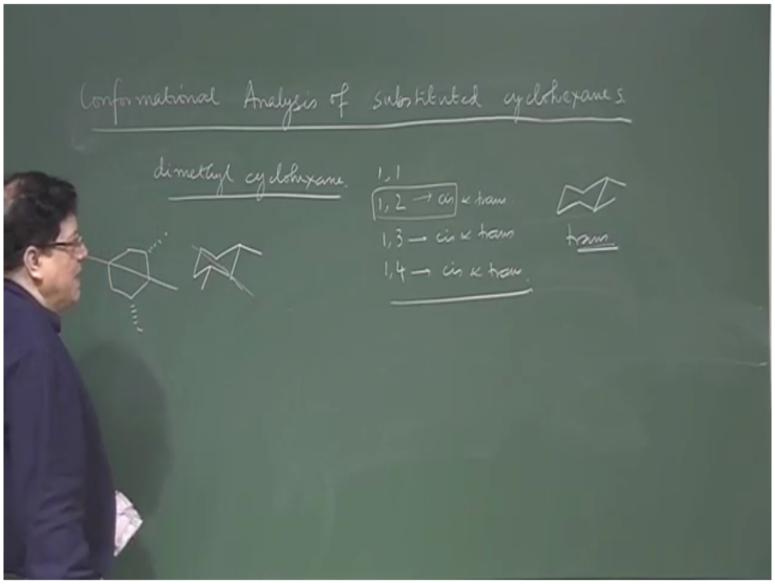

So let us again come back and do the conformational analysis of substituted cyclohexane s, so far we have done the dimethyl cyclohexanes that is our representative example and this can be 1,1, this can be 1,2, this can be 1,3 and this can be 1,4 and in 1,1 there is no question of Cis or trans arrangement, in 1,2 you have Cis and trans dimethyl cyclohexane here also Cis and trans and this is also Cis and trans, okay. So the Cis and trans they differ in energy, they differ in their optical activity just to summarize a little bit what you I have told you that 1,2 Cis-dimethyl cyclohexane exist as a non-resolvable dl-pair, because by flipping it goes to its mirror image and the trans compound is however optically active. This is the trans compound. The preferred configuration of the trans that is optically active.

For the 1,3 system what is the 1,3 system that you have suppose Cis, so Cis means the best uh arrangement is both equatorial and in the both equatorial system you have a plane of symmetry. So if you write it in the planar for, so you have this is alpha and that is alpha, because that is Cis, so you have a plane of symmetry passing through it. Here a plane of symmetry which passes through this carbon and this carbon, so a plane of symmetry is there, okay.

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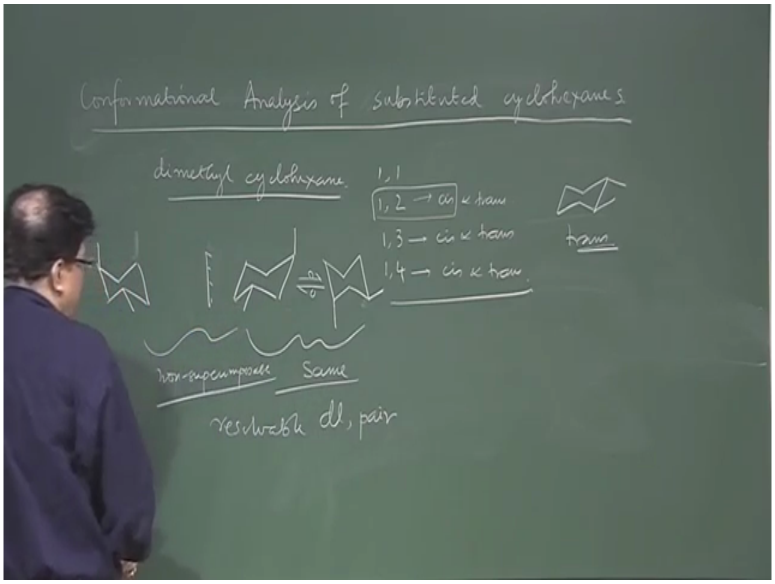

So this is optically inactive that is the Cis compound. The trans compound if you draw the planar form we will see that one beta and one alpha. So it does not have the plane of symmetry. What it has is a C2 symmetry if you make a 180 degree inversion you will get the this methyl in the beta position, okay and so the preferred conformation is see either this axial and this is equatorial. Now you can invert it very easily, because inversion gives the same type of arrangement one axial one equatorial. So this is there and now the equatorial is, sorry this is here and the equatorial is here and ultimately I have shown that earlier that these two are same by having that mnemonic formula and them finally I showed that the mirror image is different. This is the mirror image, sorry this is the mirror image here and there and these are non-superimposable. This is entirely different from the Cis 1,2-dimethyl cyclohexane where flipping gives the mirror image. Here flipping gives the same molecule, but the mirror image is different. So this will be optically active. So this is a resolvable dl-pair then we come to the 1,4 system , a resolvable dl-pair okay.

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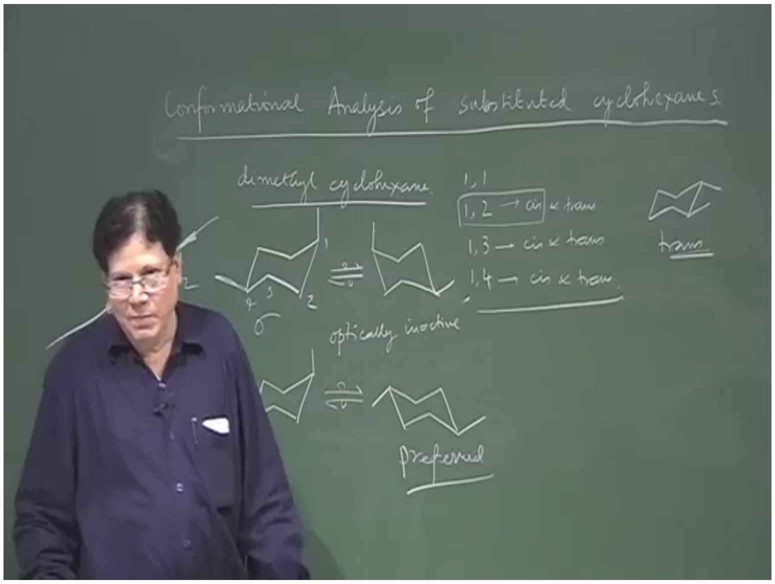

Now let us come to the 1,4 system. So 1,4 dimethyl. Now first of all, it is a it can be Cis or it can be trans so 1,4 means either you put 1 methyl here if it is beta then the Cis is another beta. So this is one form the other form is this is beta and this is alpha. So this is Cis and this is trans. Now what is their conformation? The conformation is you write the chair form and then you see where are the groups, so this is suppose the number 1,2,3,4,5,6, so 1 is there that is methyl and to make beta at the 4 position, so you have to have the this second methyl group in the equatorial position. So this is the Cis compound, because both are beta if you invert it what you get say inversion looks like this, so that is the compound, see these are the same again the same molecule they are topomers.

They are same molecules they are topomers and this is optically inactive you do not have to draw a mirror image, because I could see a plane of symmetry passing through this, see this is the planar symmetry between 1 and 4 that means the vertical plane containing these methyl groups and passing through 1 and 4 if the sigma plane, okay. So this is optically inactive, the same is the trans compound. Here also there is a plane of symmetry passing through 1, only the conformation is different. The conformation is, so now this is beta, so this methyl is here and the 4 th methyl is also here. So this is not the proper conformation, because this suffers from the 4 gauche butane interactions, because 1 one axial gives 2, so 2 axial is give 4. So it immediately flips and then major form will be the will be this one. This is the major, sorry preferred conformation, simply, because both the groups are in the equatorial position.

So this does not introduce any additional energy because the anti-form of the butane is regarded as having the zero point energy, okay. So that finishes of this 1 this dimethyl systems.

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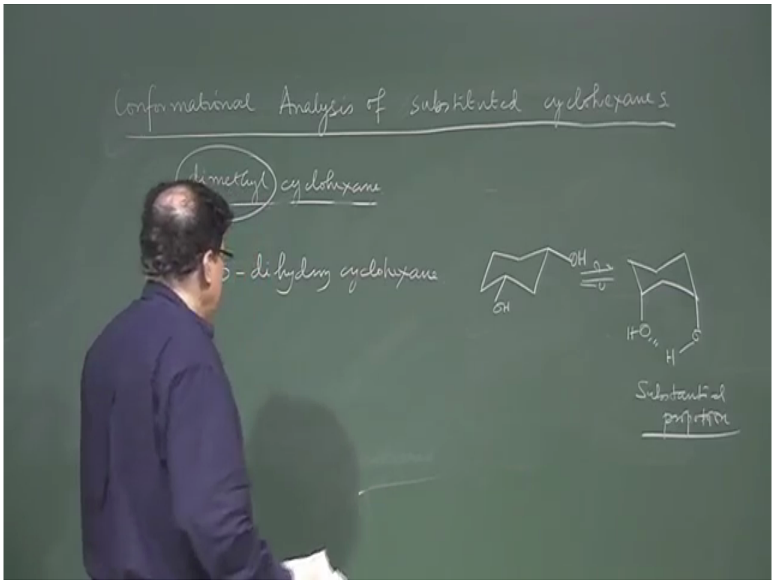

Now it is not always true that the same thing will be followed if you have other substituents instead of dimethyl, okay like suppose there is 1, 3-dihydroxy cyclohexane, now what happens in case of Cis 1,2-dimehyl that means one is Cis means both are equatorial, right, because that is the Cis and that is will be that will be the most stable form, because if you invert both the groups will be axial okay.

So in dimethyl system, this is the major form and this is the minor form, okay. So where are the methyls now? The methyls are one is here and the other is there, okay, but this is in the dimethyl system again I repeat, this is the preferred, but when these methyls are replaced by OH (())(7:45) then it is seen that there is a substantial proportion of the diaxial conformation also and the reason is that these diaxial conformation is stabilized by intra-molecular hydrogen bond. So now different forces when there are methyls, there is no such in intra-molecular forces, but here because they both OHs (())(8:22), so there is a possibility of a hydrogen bond, but only when they are in the axial conformation. So when both are diaxial that is diaxial conformation. So now there will be a substantial proportion, I do not know the exact proportion of this, but I can say there is a substantial proportion of diaxial conformer that is for 1, 3-dihydroxy.

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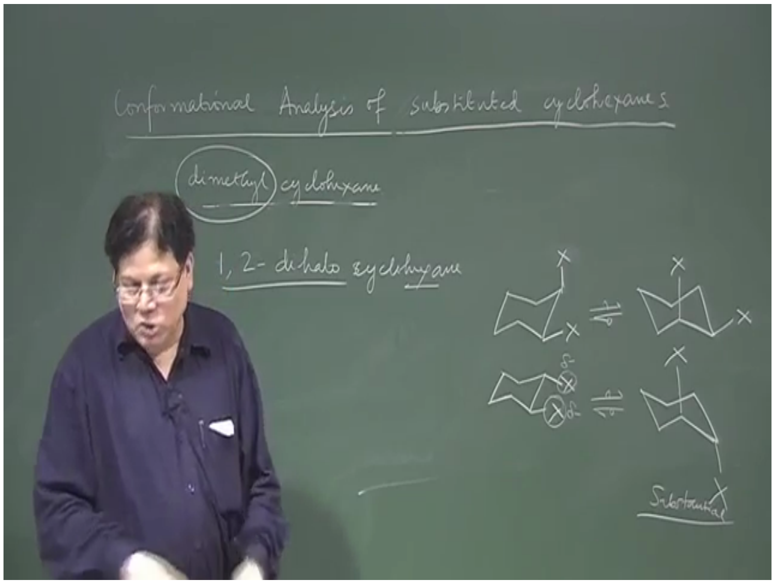

So similarly so it is not always true that the diaxial or the conformation where the number of axial groups are more are always less stable that is not true. It depends on the type of substituents like 1 example like a this 1,3-dihydroxy cyclohexane, okay or cyclohexane 1,3 (())(9:14). Now if we have the halogen compound, suppose I have 1, 2-dihalo systems cyclohexane. Now if I have the Cis compound then what happens then one will be this, suppose it is x is (())(9:38) and this is x okay and if I write the trans compound. So these are the preferred conformations, of course Cis if you flip it can flip and it if we if you flip the relative the relationship that does not change, because the dihedral angle still remains the dihedral angle still remain 60 degree, this CX and CX only this X becomes equatorial and this X becomes axial. So the energy remains a same, because this is a same situation, one axial one equatorial, but if you come to this one, so if you flip now, so what happens you get a diaxial x here and X there, okay.

Now interestingly here the question is here both are 50-50 okay. It is a same like 1,3-dimethyl cyclohexane case, it exist as a non-resolvable dl-pair. Here usually what happens in dimethyl system? This is the preferred conformation and this is the least preferred I told you about by showing the I told you about this by showing you number of gauche butane interactions that are present in this systems, okay when these are methyl. So you have one extra gauche butane unit when you have diaxial then you have 4 extra gauche butane unit and so ultimately the difference becomes 3 gauche butane interactions is the difference in energy when one x (())(11:27) methyl, but when X is halogen then what happens there is now repulsion. This is delta minus that is delta minus.

So now there will be repulsion between these two XX and that will make again the same thing that we because in this conformation that repulsion is gone, because they are anti to each other. So there will be again a substantial proportion of this substantial, because of the that intra molecular repulsion between the XX that dipole-dipole repulsion is no longer there if you put in the diaxial conformation. So there are cases where diaxial can be also a present in significant manner, okay.

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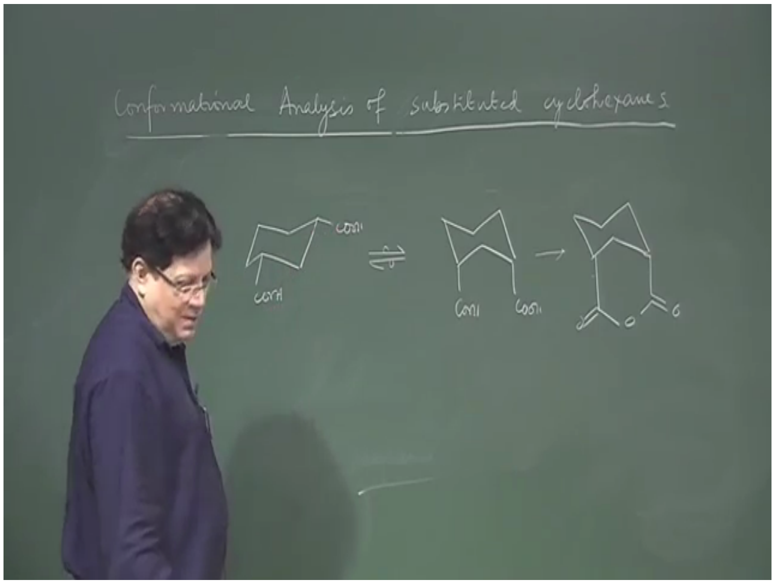

And also there are molecules where the reaction meets the substituents in the diaxial conformation like if you have a CO2H here and the CO2H there, okay. This is a Cis cyclohexane 1,3-dicarboxilic acid. If I want to make an anhydrate out of this, because they are far apart and intra-molecular anhydrate formation. So what it will do? It will flip and this becomes CO2H and this also becomes CO2H. Now you see they are close in close proximity, so they can easily form the anhydrate. So this anhydrite both these are in the axil conformation or in the axial orientation, because that is the way to make the anhydrite for anhydrate formation they have to be close by and this is the only way they can interact with each other, but actually the stable conformer is the diaxial is a diequitorail cyclohexane, okay. So there are cases where the axial orientation also can be important. So I give a few examples, okay.

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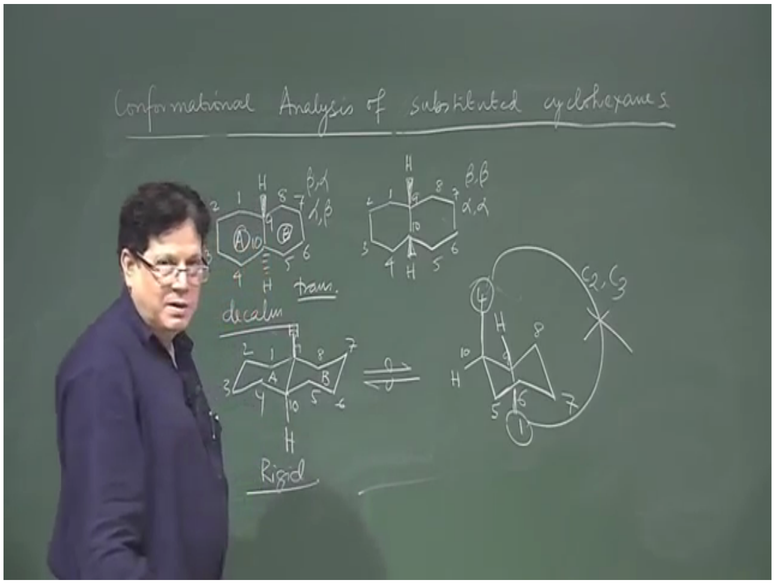

Now let us go to another system just increases our knowledge a little bit about this, do not restrict it as in the cyclohexane system. let us complicate the situation a little bit, add another cyclohexane which looks like, okay. So another cyclohexane I added on to this. This fused cyclohexane systems is called decalin, they are called decalin, you can call them as per hydro naphthalene that is also possible, because it comes from naphthalene. So if you have naphthalene and if you completely, reduce completely reduce means per hydro per hydrogenation that means you fully saturate the molecule. So then you can get what is called also decalin.

Now decalin can exist in two forms, one is a Cis decalin. This is what is a trans-decalin at the Cis. So the trans one I first added then I write the Cis one. So in the Cis both the hydrogens are either beta or alpha you can write the alpha also, both alpha or both beta. So a trans, it is beta alpha or alpha-beta and here it is beta-beta or alpha-alpha, I have added the I have just drawn the beta-beta and here beta. The numbering system in decalin is like this, 1, 2,3,4,5,6,7,8,9,10. So it follows the numbering that is used for the naphthalene system, remember naphthalene system we jumps of here 4 goes then 5. So the ring junction get was given the numbering at the last, okay. So this is how the numbering system goes in case of decalin. So that will be the same here 1,2,3,4,5,6,7,8,9,10.

Now let us try to draw the conformation of this. How do you do? Suppose this is my A ring and this is my B ring. So first write the B ring in the chair form, okay. So this is the B ring in the chair form and suppose this is my 9th carbon or this is the 10 th carbon, okay. So this will be 8,7,6,5. Now I have to see what is the status of the hydrogens at the 9 and the 10th carbon. The 9th carbon the hydrogen is beta that means you put the hydrogen, so that is hydrogen and that is beta, so it is a beta axial and that is alpha axial. So what are the remaining bonds? The remaining bonds are there like this.

So now you complete the other chair form. So this is the A ring, so that is what is trans-decalin. Now an interesting point of trans-decalin is that if you want (())(16:47) the very rigid molecule if you want to flip it, it is not possible, it just stays(())(16:53) into it, you cannot flip this molecule means you cannot really flip into other chair forms. Flipping means conversion of one chair into the other. So if I want to flip this that means if is suppose try to flip it, so concentrate on the ring B. so flip the ring B, so B if you flip the ring B, so what will happen 7 will come here and 10 will go to the top and where is your 9. This is your 9, this is your 8, this is 7, this is 6 and this is your 5, okay.

So after flipping this is a seen arrow, so where are the hydrogens now? The 10 hydrogen was beta ,10 hydrogen with respect to this , the 10 th hydrogen was beta axial with respect to B. now after flipping, the 10 hydrogen let us see whether I am in the correct path 10, 10 goes here 9 is there. So we are talking about the 9th hydrogen here. 9th hydrogen is beta axial. So now it will become beta equatorial, this is okay (())(18:08) and the 10th hydrogen was alpha axial. So the 10th hydrogen will be this hydrogen, okay. So that is alpha equatorial now and this is beta equatorial, axial becomes equatorial, equatorial becomes axial, but the beta remains beta, alpha remains alpha, okay.

Now you have this carbon bond left and these are another carbon-carbon bonds on this side, okay. So your task is to now, so this is the carbon 10, so this is your 1,2,3,4. So this one carbon is here, which is attached to sorry, one carbon is attached to the 9 and your 4th carbon is attached to 10. So now this C4 and C1 you have to attach , but they are moving towards opposite direction, so it will be not possible, because here only 2 more carbons that is C2 and C3, to attach this two carbons C4 and C1 via only two carbons. So the distance is much more than that. So you cannot have a only 2 carbon chain to connect C4 and C1 and that is why you cannot flip this form. So this is a completely rigid molecule, okay. There is no question of flipping, because this connection needs a longer chain but you have only C2 and C3. So that is a very short chain, so you cannot connect this particularly okay. So that is a trans- decalin.

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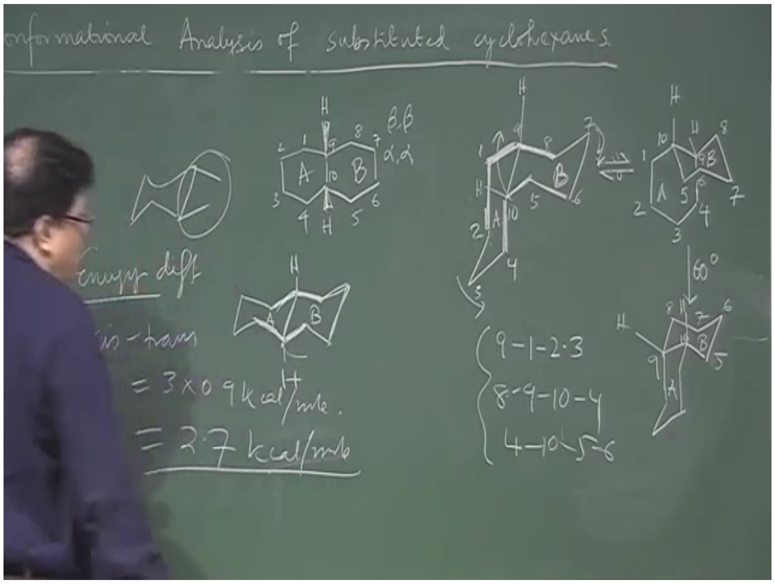

In case of Cis-decalin, the situation is little different. In case of Cis-decalin the situation is little different, let us see. So again suppose this is the B ring and this is the A ring. So you draw the B ring and then you put the numbering also, suppose this is your suppose this your 9, this is the 10 and this is 8,7,6,5. So at 9 you have beta hydrogen. So beta hydrogen means it has to be axial, in in order to have a beta and then at 10 you have beta, also beta hydrogen, so this will be like this. Now you have the carbon-carbon bonds, okay. So this is the way you draw the rest of the, it is little tricky, but I think with practice you can do it.

So what I have done, first draw the (())(20:56) and then put the numberings put the hydrogens the according to the alpha beta nature and according to then alpha beta nature these are already fixed that means the axial or equatorial is determine by their axial alpha-beta nature. So once you have the hydrogens you connect the other carbons and you get the other ring of that ring A. so Ring A is in this type of chair. So it is lying in a vertical fashion and this is lying in a horizontal fashion, okay. Now this molecule question is whether this molecule is rigid or not. This molecule is not that rigid. This molecule if you flip it, so you flip the first the B ring, so when you flip the B ring, so it will look like this is your B ring. So 7 goes here and then 6 is here, 7 comes here 6 is here, 5 is there then you have 10 you have 9 you have 8, okay.

First you have to put the hydrogens, the hydrogens at 9 with respect to the ring B now the axial beta axial. So 9 we will now be beta equatorial and 10 with respect to this ring B. Here it is very important that which is your reference ring, because if you look carefully this hydrogen is actually equatorial with respect to ring A, but and this hydrogen is axial with respect to ring A. on the other hand with respect to ring B, they are completely different. This is axial with respect to ring B; this is equatorial with respect to ring A.

So what will happens now 10, it was earlier beta equatorial, now it will become beta axial, okay. So now you have two at other atoms okay. So to now you have the other ring atoms, so unfortunately the way it is drawn that will be, 1 is connected to 1, a 10 is connected to 1 then 2 then 3 then 4. So it does not look like a chair, but it is a chair actually what happens? A chair if you look from the front side like this. So it will look like a hexagon. So this is exactly like that, so because this is like this I can make a model of this and then show you exact situation what is happening here.

So let us make the Cis-decalin, so Cis-decalin means Cis-decalin, so you have you have this is cyclohexane, but you have only, the five minutes, okay. So I will try to be quick let us say if I can make the this Cis-decalin, I can show you the Cis-decalin then that will be clear. So 4 carbons are needed 4 carbons I have put, sorry (())(24:00). So this is 6 carbon this is 1,2,3,4,5,6,7, so one extra that is why this looks little bit deformed. So now it will look like, this is 1, 3. So there are some mistake here again I have to make 1,2, because Cis-decalin, the decalin is so, so carbon atoms where okay, only it was 1,3, okay. I think this is now fine. So let see what is this molecule? This is a Cis-decalin molecule, how do you know? The way it was presented earlier was like this, the red let the red ones be hydrogen. So I put the hydrogens here, so 1 hydrogen at the ring junction, the ring junctions I put the red balls okay. So they are the hydrogens.

So these hydrogens we will change, they are axial-equatorial orientation. So this was the our starting compound and once I do the flipping, so this went up this sorry, once I do the flipping, so flipping means, this is okay 7 (())(25:38) so the I am drawing the right one taking the right one or not if I am taking this one may be, it is difficult to match with this. This is the this is the cyclohexane, but you can see the Cis form, because this is a cyclohexane chair. So they are both Cis, now you can flip this molecule. How to flip this you take this up and you take you have to take this down, so this chair is now **is now** inverted and you have to invert the other chair. So this is little complicated like a simple cyclohexane. So when you do this flipping, so again I repeat, so what I do? I take this down, I take this up and then I take this down. So all these things when I do then I have this changed figure, okay.

So this is the flipped form, again I do the original one you have to bring it down and bring it up okay and this is becoming a chair, but yes now this becoming a this is becoming a boat. Now it is becoming a chair. So this is the original one, this is beta axial with respect to this ring, beta equatorial with respect to this ring, but this is with respect to the A ring. This is equatorial and that is axial. So when you flip, this is flappable molecule, so you can flip this goes to the chair boat form and then you do this a change the other carbon yes. This is little not that flexible like the cyclohexane, simple cyclohexane and make sure that the other is in the chair. So this is the case, okay. So this is flip up, this can flip up; this can be flipped, okay. However difficult to show both the rings in the chair form, in order to do that what you do?

If you now give it a 60 degree rotation of the B ring, if you give a 60 degree rotation you know I have shown that it changes in this direction. It goes into the mirror image chair and if it goes into the mirror image chair then where is the carbon 9? This is the carbon 9 and this is the carbon 10 after a 60 degree rotation and then this will be you can complete the other things. This is 10, this is, so that will be 8 that will be 7 that will be 6, sorry that will be 7 that will be 6 that will be 5 okay and now what you have in 9 you have a equatorial hydrogen, no problem at 10 you have a axial hydrogen that is also okay, but the beauty is that now you can show the whole thing in both the rings in the chair form. So this is your B ring and this is your A ring, okay both the rings in the chair form.

So this is a seen arrow. So this is Cis-decalin is can be flipped whereas the trans decalin cannot be flip, regarding their energy difference, in trans-decalin if you think of this ring B and if you ring I you think this ring as A, so these substituents and these substituents are like the two methyls when you have dimethyl cyclohexane, but Cis these two methyls are in a equatorial position, so they are not putting any extra gauche butane interactions here. Similarly these two this and this are the di-equatorial substituent of this ring, but because they are in the equatorial dimethyl substituent of B ring, but since they are in the equatorial conformation, in the equatorial orientation. So they will not put any extra butane units there, okay. Now extra butane unit whatever butane units are there, remember this is already taken care by the cyclohexane ring and this part in the mutual, earlier in the in the dimethyl cyclohexane you have a mutual gauche butane system, but here that is taken a care by the whole cyclohexane ring.

So you do not have any extra gauche butane over the two cyclohexane rings. What about here you have, now this is interesting, this is axial with respect to this chair form. So this is one gauche butane unit, so that is 1,2,3,4, so you have 9,1,2,3 this 1 gauche butane unit and you have 8,9,10,4 8,9,10,4 is another gauche butane unit, okay and this is equatorial. So that will not give any extra on the other hand, now this substituent this substituent is axial substituent with respect to B ring, earlier we have consider the substituent these and that with respect to A ring. This is equatorial, so it did not impose any gauche butane unit, this is axial.

So this introduce 2 units and what about this one, now consider the other substituents consider the B ring and think in that 1 is (())(31:01) C1 is a substituent and C4 is a substituent. So C1 is equatorial no problem, it does not introduce any extra, but C4 introduces 4,10,5,6,5,6 and the other one is 4, 10, 9,8, but that is already there, 4,10,9,8, so that is a common. So you do not take the common. So the ultimately what happens the energy difference is basically, so which one is more unstable the Cis is more unstable, because it has got a excess energy. So the energy difference Cis minus trans is equal to 3 into 0.9 kilo calorie per mol or that becomes 2.7 kilo calorie per mol, okay. So that is the conformation analysis of just at the very preliminary stage of Cis and Trans decalin, okay. So you have you need lot of practice in order to draw the conformation and then turn it around to show both the in the chair form, okay I think as the time passes as you go as you will become matured with practice and finally, it will be much easier for you to draw this molecules in the proper geometric shape, thank you.