Course on Stereochemistry
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Mod06 Lecture 26
Conformational Analysis of Substituted Cyclohexanes (Contd.)

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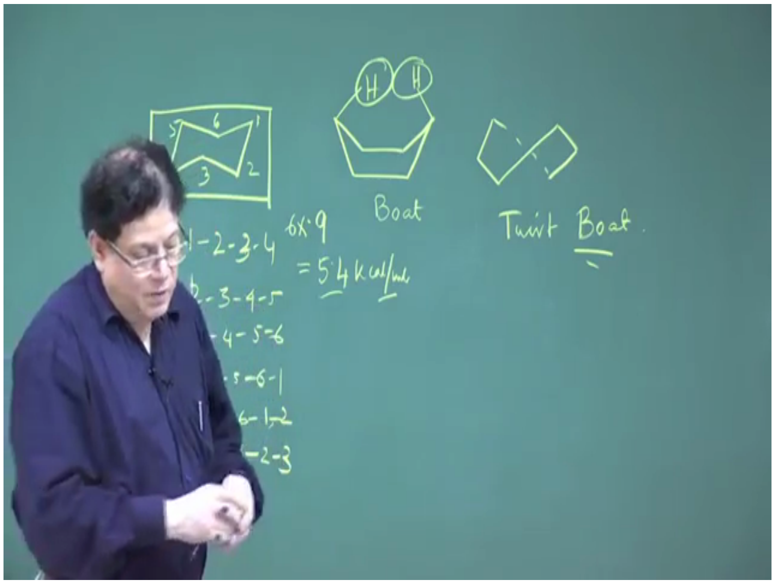

Okay welcome back to the to this topic which was the conformational analysis of substituted cyclohexane systems, remember last time we have seen the energy variation in a cyclohexane system, cyclohexane just to repeat cyclohexane is this in the mainly in the chair conformation and there are again extreme conformation and there are again stream conformation like this is a boat conformation that was told by (())(0:51), but then it was realized that this boat conformation is not a conformer. What is a conformer that is a what is called a twist boat okay, but in most of the cases it is the chair conformation, which is the predominant form. So in our discussion this boat or twist boat will come very rarely.

Now we also have seen that what is the energy how to calculate the energy of the boat form over a anti butane unit. The anti-butane unit is regarded as a zero point energy and the starting point and then from above that if something is unstable than that then you calculate try calculate the energy on the basis of what are called the butane interactions. Butane interactions can be of three types and anti-butane interaction is regarded as zero there is, because the two methyls are just exactly opposite to each other. So there was no torsional strain and there was no steric strain. So nothing is there. So it is regarded as the zero point energy.

Now as the dihedral angle decreases then they increases the there will be increases in energy okay and accordingly, we have identified methyl hydrogen eclipsing interactions then methyl then gauche butane interactions where the two methyls having a dihedral angle of 60 degree okay. Gauche butane is **is** unstable to with respect to anti by an amount of 0.9 kilo calorie per mol and based on that we have regarded cyclohexane as consisting of 4 butane units, 6 butane you units 1-2-3-4 and then 2-3-4-5 then 3-4-5-6 then 4-5-6-1, 5-6-1-2 and then 6-1-2-3 okay and then after that you come back to that 1-2-3-4. So these are the 6 1-2-3-4-5-6 6 butane units that you can think of present in a cyclohexane and these all these 6 butane units are in the gauche form that I have told you, so that becomes that means energy of 5.4 kilo calorie per mol okay and then the boat form as I shown.

In the boat form there are on the contrary 4 butane units, which are in the gauche conformation and there are 2 butane units which are in the eclipse form. So the eclipse form has higher energy than the than the gauche form. So two eclipse forms at quite a large amount of energy and along with that there is another kind of interaction present in the boat form and that is the interactions between this flagpole hydrogen. So that makes the boat unstable, I think we have covered these things.

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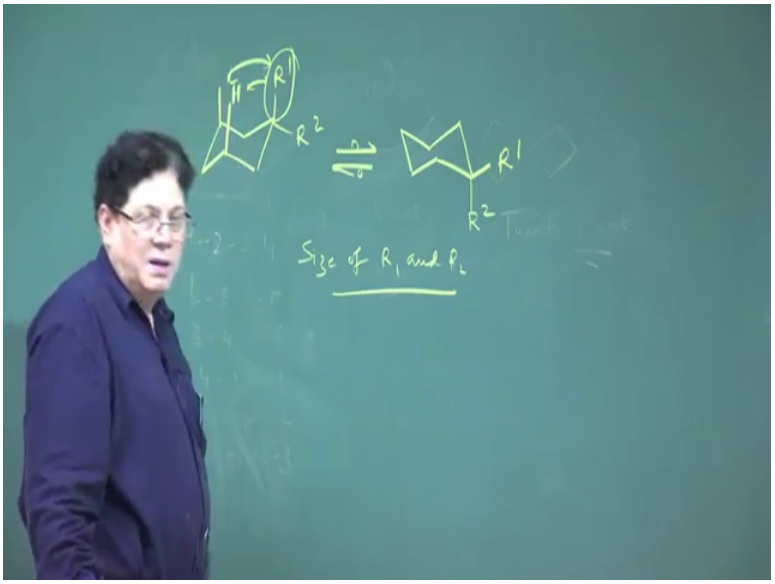

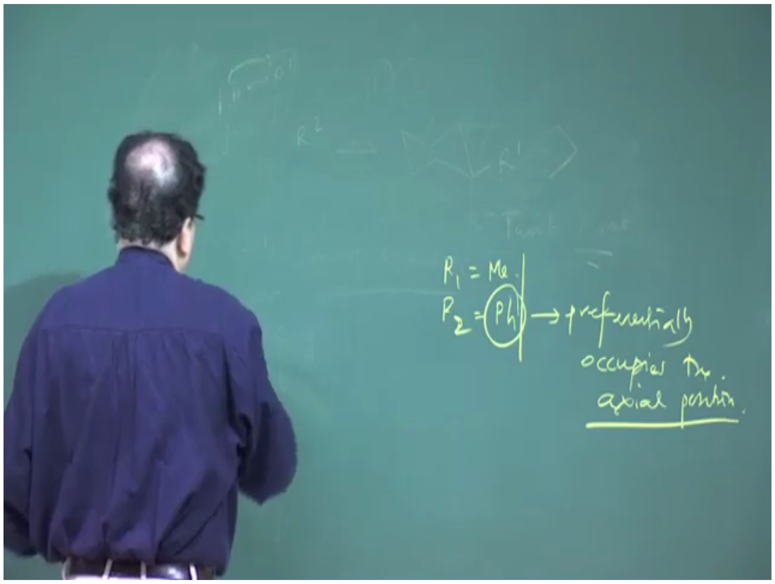

Then we went to the conformation analysis of we went to the conformation analysis of disubstituted cyclohexane. Now in disubstituted cyclohexane, the first one that we **we** have covered, the first one was that you have a R1 and you have R2 okay. So (())(4:19) substituted cyclohexane exist in the chair form, but by inversion you can get the other chair form and what is the difference between these two? R1 see in inversion again in flipping you should remember in flipping, the axial becomes equatorial equatorial becomes axial, but the alpha beta nature remain the same. So this is the situation R1, R2, R1 has become equatorial.

Now which one will predominate that will depend on the size of R1 and R2. The rule of thumb says that the bigger group always occupies the rule of thumb says that bigger group occupies the equatorial position. In order to avoid the interaction which is call 1,3-diaxail interaction with the axial, okay. So the bigger the group these interaction will be will be more; however I give you an example you should when you go through this presentation you will see that this in case of R1 equal to methyl and R1 equal to phenyl, it is the phenyl, they are preferentially occupies the axial position and I have given you the reason for that okay.

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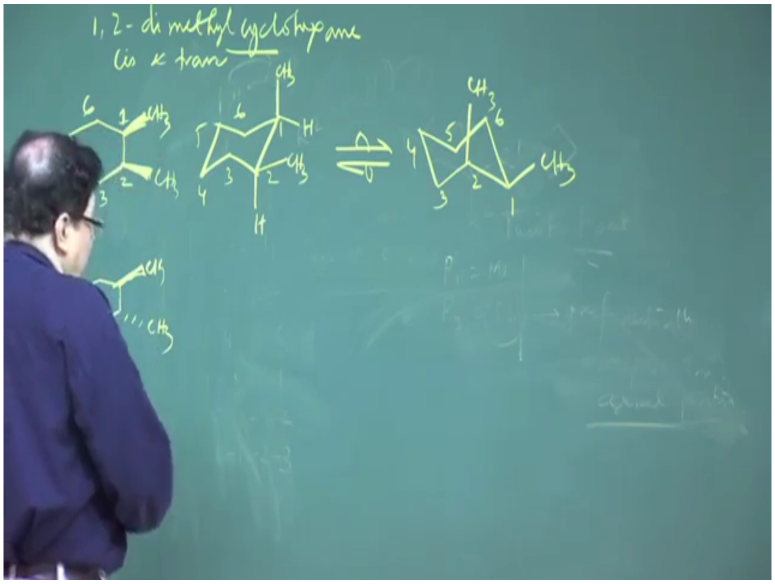

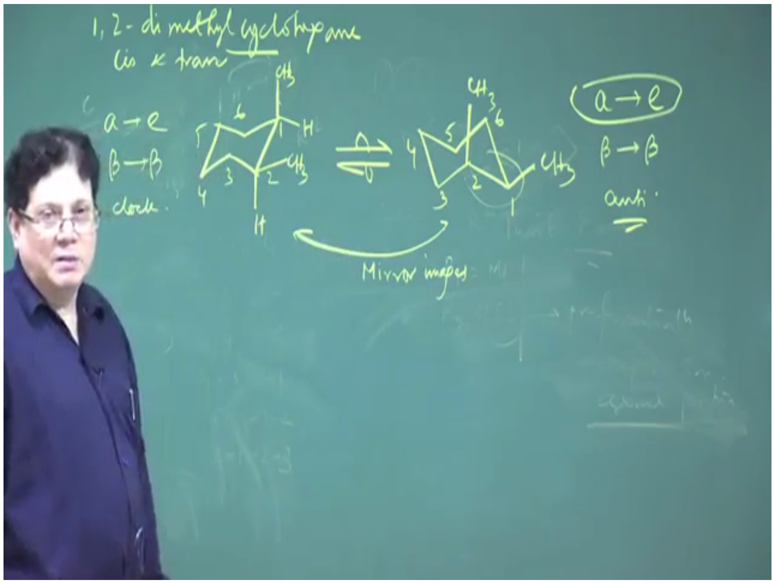

The next is the substitution there is not 1,1 substitution. Substitution which are 1,2 and I quietly o through what we have done the see the way to do it, first you draw a planar formula, a planar formula where there is a methyl here, suppose we take 1,2-dimethyl cyclohexane 1,2-dimethyl cyclohexane. So there will be a methyl, because now we have the possibility of Cis and trans isomerism. How, because this methyl can be beta and the other methyl also can be beta. There is another isomer where 1 methyl is alpha and the other methyl is beta, okay. So when we did this. This analysis was done last time when we did this, this methyl so how to do it.

Now you convert it into the chair you write the chair form, suppose this is a number 1 carbon, this is number 2, 3,4,5,6, so this will be a 1,2,3,4,5,6, okay. So let us see at one you have a beta methyl group to so to make the beta group you have to make it axial, I think with practice you will be immediately you can it will be easier for you to write this. So how do I do it? I know that the axial group here is beta and I required a beta methyl. So I put the axial the methyl has to be axial here. At 2 position again the methyl is beta and the two bonds amongst the two bonds the equatorial bond is beta, so I have to put the methyl in the beta position, okay.

So this is hydrogen that is hydrogen, then what I did? I said that okay you can flip it and if you flipped what will happen. This methyl will be here that is the number 1 methyl and this methyl will now be on this side, okay. So this is 1, 2, 3,4,5,6 then an interesting thing came (())(8:05) and interesting concept the interesting thing about these two molecules two flip form is that. This is the mirror image, their relationship between these two are mirror images.

Now I gave you mnemonic device to compare this and that remember that I give you a mnemonic device which was that you go from you pick up a particular direction that I will go from an axial methyl group to an equatorial methyl group okay, while traversing the entire cyclohexane molecule while doing that axial to equatorial I do for both the molecules and then I see what will be my beta alpha relationship and what is the direction that I take. So beta alpha relationship is beta we are going to beta to a beta no problem, but the direction you see ultimately the direction is a clockwise relation.

Here you will do the same thing axial to equatorial, now you have beta to beta, beta axial to beta equatorial, but the direction you see is now anticlockwise. So if I I say that this is always same because that is fix prefix by you, the other two parameters, if both the parameters are same then the systems 2 systems are there. If one parameter is different than they are mirror images of each other. If both the parameters are different here, then again they are back to the same molecule, okay.

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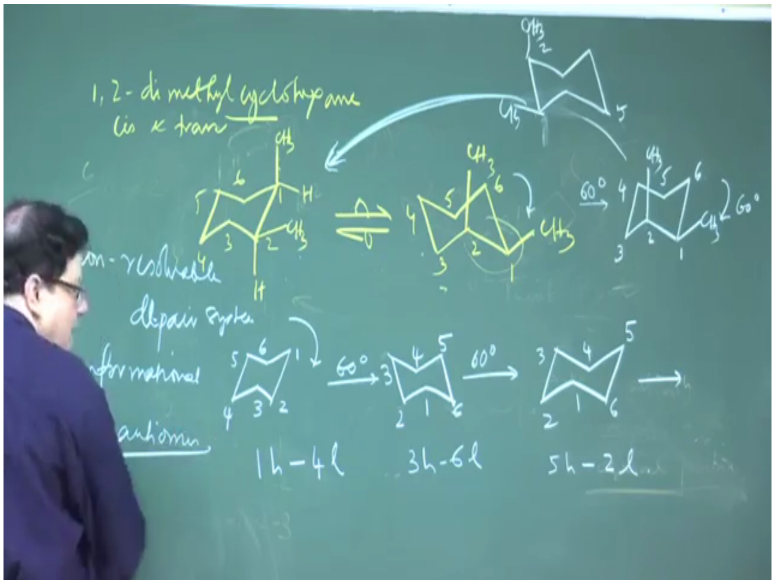

Now this is a mnemonic device you can say that, sir why cannot we in other way just to show that this is the mirror image of the other. Why cannot to you rotate this molecule and try to bring it to the similar looking molecule, okay. So today I will do that, see when you have a chair form like this, suppose this is my heard carbon and this is the, so this is my chair the starting chair is this if you can see it. So this will be my head, the head of the chair and this is the leg of the chair okay.

Now this has got a C3 axis around this. So if I rotate the molecule by C3 if you rotate the molecule by 60 degree you see, earlier the chair was the head of the chair was on this side and the leg bottom of the chair was on this side. Now the head of the chair is here and the bottom of the chair is here. So by 60 degree rotation you have changed the appearance of the chair form. Now if you do another rotation that means the 120 degree, you see I come back to the head on the top on this side right side and leg on the and the leg on the left side, okay.

So you do it constantly, so the chair if you do 60 degree chair constantly goes from one form to its mirror image form. So basically what I am saying that if you have a chair like this okay. This is really conceptual if you have a chair like this 1, 2,3,4,5,6 and if I start rotating it into the clockwise direction, suppose I do it around 60 then the chair will not look like this, the chair will look like this, mirror image chair. The question is which group has one where, okay.

So now see one can never be at the bottom carbon, right one is always 1,3,5 where at the where the top carbons okay. So what happens here? Now you have push the whole thing 60 degree, so you have 5 here and this is your 6 and this is your 1. So this is the these are the position so 1 will come at this position and I will just again explain it how to completely visualize it, okay. So initially when you have started your 1 was the head and 4 was the tail of the chair or leg of the chair whatever leg of the chair okay, 1 head 4 L now what you have 3 head and 6 leg, 3 at the top head of the chair and 6 at the leg of and 3 at the top of the chair, 6 at the leg of the chair, okay. Now if you do another 60 degree rotation the chair should look like the original question is which one is where which carbon is where. So we have rotated it now you have just again rotated it by 60 degree. So what will happen now?

Now the now your 5 see earlier what happens 1 was at the top, so next was 3 at the top. Now the third time it will be 5 than the top, because these are the 3 top groups, 5 and then this is the 6th group. This is 1, this is 2, this is 3, this is 4, hopefully this is okay. So when you rotate it by 60 degree then what happens 5 goes to the head of the chair and 2 goes to the leg of the chair? So now it is 5 head and 2 leg okay, see 2 at the leg position. So this way it happens means this is the way. So 1 and 4 where the head and the leg then it was 3 and 6 and finally, so this keeps on jumping by 2 units , 1,3,5 the head and the leg also 4,6,2 okay. So you can do it like this and complete the rotation okay, you see the (())(14:19) that is why I gave you the mnemonic device, but you should also understand the basics of it, the if you rotate it.

So if I start rotating this now, the same thing, suppose I rotate this by 60 degree. So what was the 60 degree, so chair will found this form take this form okay the mirror image form and where will be 6 now. The 6 will be still here and one will be here, 2 will be there, 3 will be here, 4 will be here, 5 will be there, okay. So 1 equatorial is this and 2 axial is this are so now look at these two. Are they mirror images of each other, no not yet, because this chair is not the mirror image of this chair they have the same chair. So in order to do that you again turn it, so this was turn by 60 degree. So now you turn it by another 60 degree. So what will happen? The chair will take a form which will look like this. Now which will be the bottom carbon now? The bottom carbon is the 5 here, the bottom carbon is the 5, okay. So 5 then this is which one will be the top carbon. The top carbon will be the two carbons and this is the 1 carbon, okay.

So as I said earlier it was 3, say 6, 3 now it will be 5, 2 system, so 5, 2 is there and then you put the groups. So at 1 there is the methyl and 2 there is the methyl, okay. So now you see the relationship between this two. This is exactly the mirror image of that okay but you have to come all the way after rotating base. Now it is up to you whether you use the mnemonic system or if you look at the by rotation you can come out to the same conclusion that by flipping you get the mirror image of the original form. So what I said the that day that this molecule Cis 1,2-dimethyl cyclohexane exist as a non-resolvable dl-pair, it is chiral but it exist as a non-resolvable dl-pair. Why, because this is the moment you try to isolate this 50 percent of it will go to this form, because these two forms are mirror images and they have the same energy, okay.

So and because this is done by flipping. Flipping is **is** always going on at room temperature. So it will not be possible to separate under ambient condition, okay again the question comes if you lower the temperature to a very low temperature to a very low condition then possibly they may this flipping you can slow down. So if you can slow down flipping then it is possible to separate them otherwise under normal conditions they are not separated, because this flipping is continuously happening.

So these cases are called these are non-resolvable dl-pair systems another terminology you can introduce non-resolvable dl-pairs system or you can call it conformational enantiomers. They are conformational enantiomers. So usually what happens? The enantiomers that we know to go from one enantiomers to the other you have to break a bond, by rotation you cannot go from one to the other, but here these are these enantiomers they are enantiomers definitely, but they cannot be resolve, why because 1 goes to the other simply by rotation by flipping and that is why they are call conformational enantiomers, okay.

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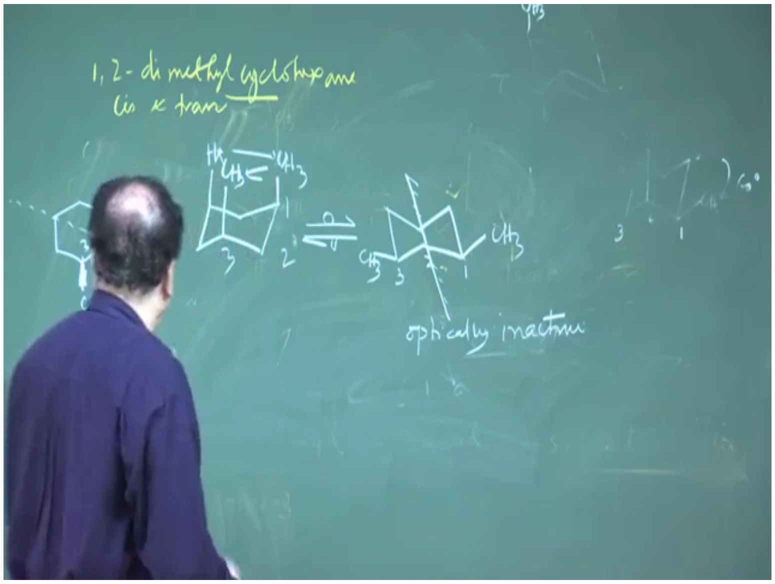

So we have seen that, now how to **o** rotate and get to the original position. In case of 1, 3 system 1,3 system means okay, first draw the planar structure. So this is methyl, suppose I want the Cis compound, this is methyl okay. So in 1, 3 system, this is again this has to be put in the this is 1, 2,3, because both are beta , so this is beta and this is beta form. So this is 1 conformation, but looks to be very unstable, because both the methyls are in the axial position. So you have lot of interactions now between methyl-methyl which is huge, which is the very high amount then you have methyl hydrogen and then this methyl hydrogen. So this will be really unstable and what it flips into the flipped one is **is** quiet stable. This carbon comes here, so that will be here. So that your 1, 2,3. So this carbon comes here and this carbon these are the 3 positions, so that will be there. So there will be huge difference in the population between this and that.

The molecule mostly exist in this form, because this is so unstable, okay you can calculate like the earlier you can calculate the energies that are associated with this systems like you calculate the methyl as axial. So that introduces 2 gauche butane interactions. So this methyl puts to this axial methyl puts 2 gauche butane interactions, in a addition you have this methyl-methyl which has to be counted here methyl-methyl, okay. So that gives it a much higher energy than this form. What about the optical activity?

The optical activity you do not have to draw, the way to do it either you if you see any plane of symmetry or center of symmetry those type of elements then you can immediately say, it is optically inactive, okay, which is you can see that if you bisect this, so this becomes a plane of symmetry, okay. This becomes a plane of symmetry. Interestingly that plane of symmetry is also (())(20:50) visible in the planar form that planar symmetry visible in the planar form, okay. So this molecule is optically inactive. So no question up checking the optical activity optically inactive, okay.

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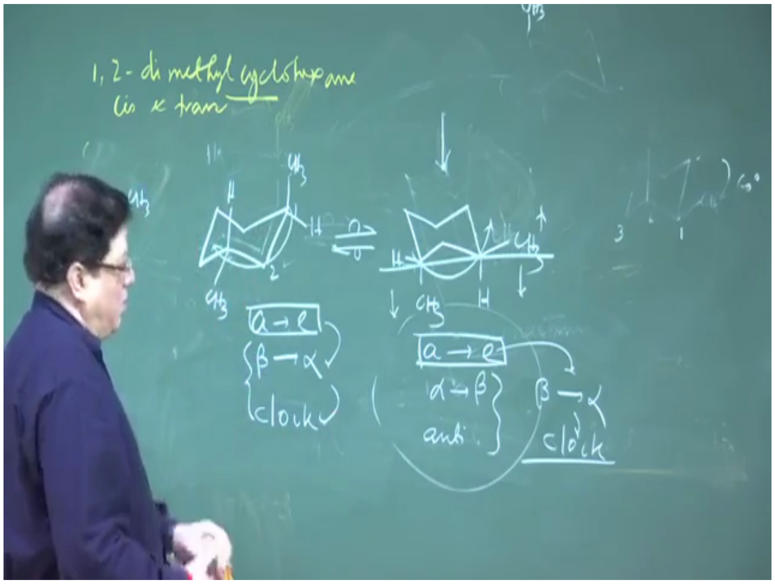

Now the next one is the trans isomer, so you make one of the methyl a the alpha. So immediately this is gone right. This plane of symmetry is gone. So you write the conformation, so this is beta this is the methyl 1 and this is 2, this is 3. So 3 is alpha, so methyl is here, hydrogen-hydrogen. Now this is a this is an interesting situation more interesting than the Cis one. The trans one, now you can flipped and they will have the same energy in the trans one, because in both the cases one will be axial and the other will be equatorial. So if you flip this methyl becomes beta equatorial and this methyl becomes and 3 that becomes beta axial, okay.

Now the question is by flipping what we get. There is no energy difference between the two. So in the system we expect that there will be 50-50 mixture of these two, provided they are different, because there is a possibility that they are same, okay. Now to check whether this is same as this or this is mirror image than that, remember your Cis 1, 2-dimethyl cyclohexane flipping gives the mirror image and that makes it a non-resolvable di-pair. So is the same thing happening in trans in trans 1,3 that is the question, trans 1,3 what is optical activity? Does it remain as a dl-pair which is separable or non-resolvable?

So in order to know that you have to know the we have to decide the similarity between this and that. Now it is up to you what you have to do? The mnemonic device you can apply. So if you apply the mnemonic device, now what is happening, suppose I go to axial to equatorial, the same one that I did for the Cis 1,2 , so axial to equatorial that means I am going from here to there, okay. So then I check the alpha beta. Where is the alpha beta, the axial to equatorial this is beta, so I go from a beta to a alpha and in this case what I do beta to a alpha, I am going from axial to equatorial, I go from alpha to beta a change, okay and the third one is the direction that I did from I did go from here to there, so that was clockwise and I went from there is to there, so that is anti-clockwise.

Basically I am traversing the whole chair system. So the shortest possible path shortest means the shortest connectivity between the substituents, okay. So that is anti. So now again you check these 3 parameter, this is always identical, because that is your prefixed you have decided to take it from axial to equatorial if (())(24:19) done the other way around, equatorial to axial, but then you have to do for both okay. So this was same I have fixed it.(24:18)

Now you see these two both are different, I told you in this mnemonic device if one is different than that becomes mirror image of each other. If two are same then that is they are same. If two are different then also they are same, okay then also they are same. A very interesting thing you can say how they are same, I can tell you that if you change your reference plane, see this alpha beta is basically based on the reference plane that these average plane of cyclohexane, based on the average plane of the cyclohexane.

So what you do here if I change my reference plane that the I think that this the down position thinking that any group which is below this plane becomes beta and any groups which are above, which are towards me they are alpha, they are, so my reference plane I have just changed, because I my (())(25:37) other world that we have a vertical (())(25:41) like this, so it is other (())(25:42) that I am looking from the top and I change the all the references now. The groups which are away from the plane going bottom are the beta and those which are lower than that plane will be alpha. So if I do that if I look from that and change my reference things axial remains as axial equatorial remains as axial and problem is the alpha beta. Now the alpha becomes beta according to the new convention that the lower groups are beta and this becomes alpha, because my reference is now just reverse, I say that all the down groups are the beta up groups are alpha then if I do that, so beta becomes alpha becomes beta and the direction was earlier anti.

So now the direction will become clockwise, because I (())(26:35) from the top as I said any direction looking from this looks clockwise, but if somebody looks the same from the top it becomes the other way anticlockwise. So now it will be clockwise so you see, now the three parameters are same, so without going into the complexity what I say that if you see the two parameters of these are same then all the three are same basically then the two things are same if of the parameter is different alpha beta are anti-direction then they are mirror images of each other. If both are different then they come back to the similarity issue, okay they becomes similar.

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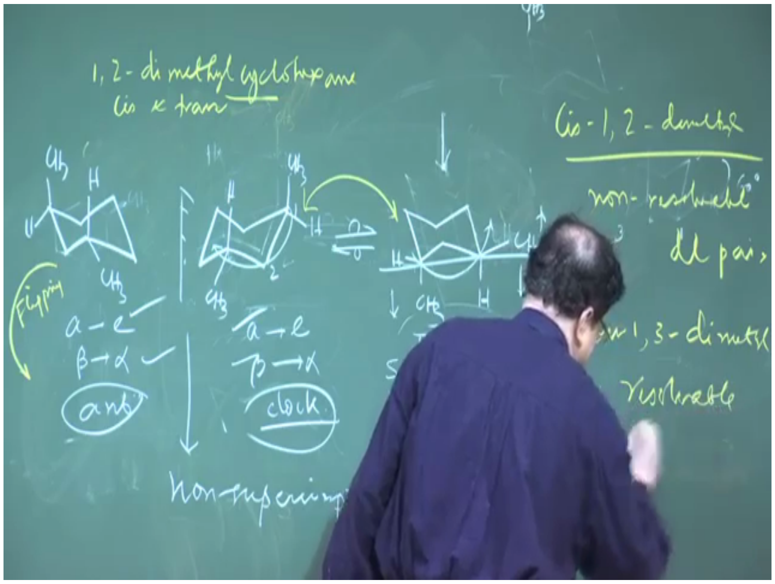

So in this case what hap ultimately what is the conclusion that these two are same molecules. So flipping here, does not give the same molecule. So then you take the mirror image, so at least it next question is whether it is chiral or not. So you take the mirror image not this way suppose I take the mirror image this way, so I get this the methyl is here and this methyl is here. Apply your mnemonic device that I have given you, now whether this mirror image is same with this. What you do? You go from axial to equatorial then it goes from beta to alpha and the direction is anti-clockwise, so direction is anti-clockwise, okay.

So here I have already erased those things. Here it was axial to equatorial, beta to alpha and this is beta to alpha and this was beta to alpha that was clockwise, okay and this flip form now we forget, because this is a same as that one. The question is between these two. So if you now check the relationship between these two, what you are saying, this is identical, this is identical only this is different from this. So they are non-superimposable mirror images. So what does it mean that means these are optically active.

Now the question is can you separate them, yes they are separable, because here unlike the situation in Cis 1, 2-dimethyl cyclohexane. Here flipping does not give the mirror image. Here this by flipping it goes to itself and this mirror image also by flipping mirror image as also the ability of flipping mirror image by flipping also will remain the as the mirror image, okay. So these two are separate entities. These two are not and here the flipped form of this and the than the and the original one of mirror image they are not, okay. They are these are same, but these and these are not same, okay.

So now the final conclusion is Cis 1,2-dimethyl non-resolvable dl-pair and trans 1,3-dimethyl resolvable dl-pair, okay and I hope you have understood what is the basis of this okay. So to check all these chirality’s in these systems we have to flip and we have check the mirror image and see the similarity between all these three systems, then you can come to the conclusion , okay. Thank you.