**Symmetry, Stereochemistry and Applications**
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**Module No # 03**
**Lecture No # 14**
**Conformational Analysis of Disubstitued Cyclohexane Molecules**

Welcome back to the course on symmetry, stereochemistry and applications. In this course we have already discussed about the nomenclature of organic compounds. And after that we started discussing about the stereochemistry of simple organic molecules. And in the previous lecture we had understood the different conformations of cyclohexane and mono-substituted cyclohexane derivatives. So in this lecture today, we will try to understand the conformations and conformational aspects related to di-substituted cyclohexane molecules.

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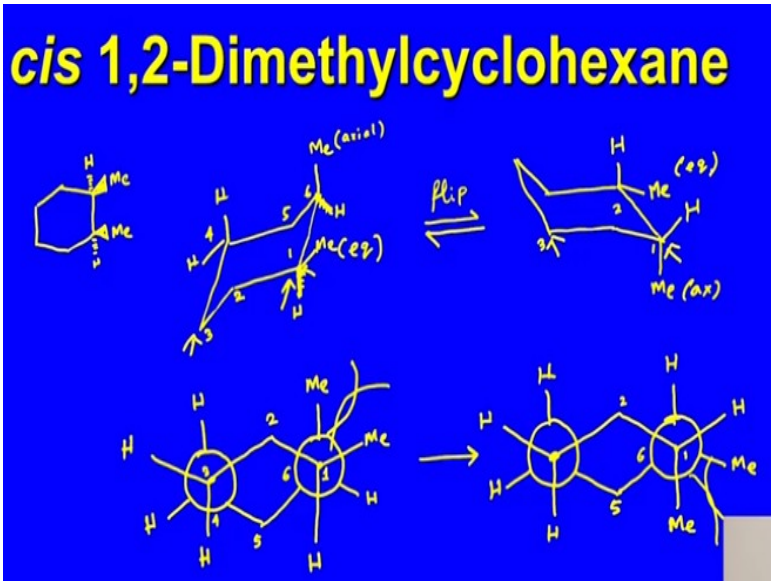


So in that we would like to start with cis 1,2- dimethylcyclohexane. So when we write cis 1,2-dimethyl cyclohexane as you may be writing from your previous knowledge, we used to write cyclohexane as a hexagon. And when you say cis that means you have 2 methyl groups on adjacent carbon atom with both of them upwards. And with the corresponding hydrogens downwards. So when we try to draw this molecule in the chair form you should remember that both the methyl groups should remain in the upward direction.

So if we try to draw this cyclohexane in chair form we should draw this 1,2 dimethyl in this fashion. So this methyl group here should be up and the other methyl group on that carbon also should be up. And here the hydrogen is down and there the hydrogen is down so this is the confirmation of cis 1,2 dimethylcyclohexane. So here this methyl group is axial and this methyl is in the equitorial position.

So if we try to flip this molecule what should happen? On flipping, this molecule should flip like that so this methyl group which is up here should come down, the hydrogen associated should be up. The methyl there should be down and the hydrogen there should be up. So this makes it same in terms of conformation because if we try to draw the Newman projection of this particular 2 conformations looking at this C-C bond and through that C-C bond.

And here through this C-C bond and that C-C bond what do we see, so here what we are trying to draw is the Newman projection of this cyclohexane conformer. So on the first problem here I have a methyl group in the equatorial position this hydrogen is in the axial position then it connects to this carbon suppose if I number it as 1, 2, 3, 4, 5 and 6. So it connects to the carbon 3 here like that and then on carbon 3 we have 1 hydrogen here and the other hydrogen there.

So then on carbon 4 this axial hydrogen is here that equatorial hydrogen is here and the bond from 4 through 5 to 6 is like this. So this is your carbon number 2, 3, 4, 5 and the back carbon 6 with this as 1. So then you have a methyl group which is present there and the hydrogen which is present here. On flipping, what do we get? On the front carbon the methyl is down, the hydrogen is up and it connects to the other carbon like that. So through if it is 1 and that is 2, this is 3 connects to 3 and 3 as 2 hydrogens, 1 axial and 1 equatorial.

And then the atom 4 will have hydrogens here there and it connects through the carbon number 5 to the back carbon 6 like this. And the back carbon has methyl downwards and this hydrogen upwards. So now if we try to remember our understanding with butane we had the n-butane Gauche interaction due to the presence of 2 methyl groups in the gauche position at the 60 degree interaction. So that interaction is present in both the conformations therefore these 2 conformers are equally stable at room temperature or any temperature.

And there is no preferential stabilization of the one or the other, because in both the cases you have 1 methyl group in the axial position and 1 methyl group in the equatorial position. So, cis 1,2 dimethylcyclohexane has only one conformation that you can find from here.

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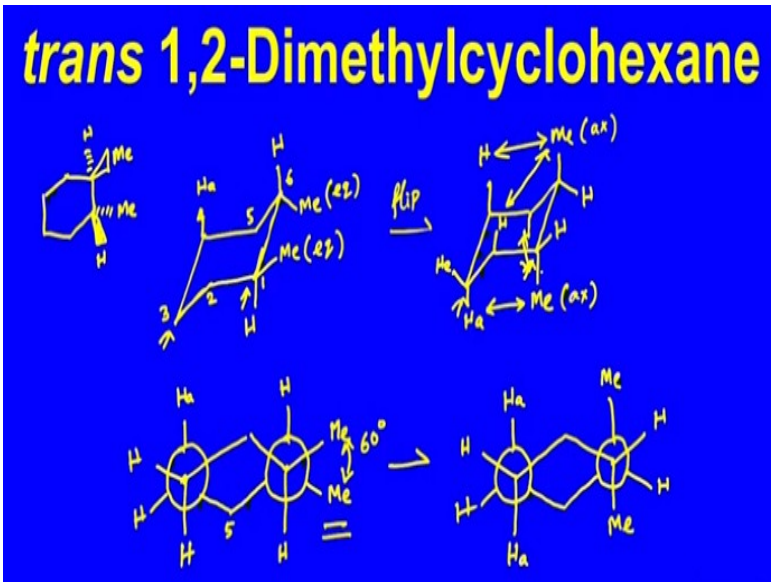


Now if we move to the trans isomer of 1,2 dimethylcyclohexane let us draw it once again as a planar molecule as we are very familiar to draw. So we write 1 methyl up and the other methyl down with the hydrogen here up and hydrogen there down. So now if we try to draw this trans 1,2-dimethylcyclohexane in the chair form it would look like this. Hydrogen down methyl up here methyl down and hydrogen up.

So this is trans 1,2 dimethylcyclohexane where 1 methyl here it is equatorial this methyl is also in the equatorial position. When we flip, what happens? On flipping the methyl here would go up the hydrogen there will come down this hydrogen will go up and this methyl will come down. So it becomes di-axial from di-equatorial. So let us now try to draw the Newman projection of these 2 looking at those bonds as we had done in the previous case.

And we try to number those atoms as usual. So on the first front carbon 1 we have a methyl group here 1 hydrogen down and this connects through 2 to 3 like that, 3 has 1 hydrogen down 1 hydrogen here. Then carbon 4 has 1 hydrogen in the axial position up and equatorial down. You should remember that the axial is here and the corresponding connectivity from 4 to 6 is through 5 like that. And in that the methyl is down and the hydrogen is up.

And then if you try to flip what we would get on the front carbon the methyl is down, the hydrogen is up, it connects through the carbon number 2 to 3 like this and this hydrogen is axial which is here this hydrogen is the equatorial hydrogen which is upward. Then the next hydrogen here is axial, this is equatorial and then you join these 2 bonds and then look at the back carbon which has methyl there and hydrogen here. So what we see now is? In this conformation again the 2 methyl groups are at 60 degree which is equivalent to that n butane Gauche interaction.

When that 2 methyl groups are empty here but they are now in di-axial orientation. So what will happen is if you see this conformer here in the di-axial conformation, you have the hydrogen which are up. There will be di-axial interaction with the methyl and hydrogen groups once the di-axial interaction. So in that case here also there will be di-axial interactions in the methyl groups. So then one has to compare the energy values associated with the n butane Gauche interaction and the corresponding 1,3 di-axial strains and decide which conformation is more stable than the other.

So this I would like to leave it to you to find out among these 2 which is going to be more stable conformation.

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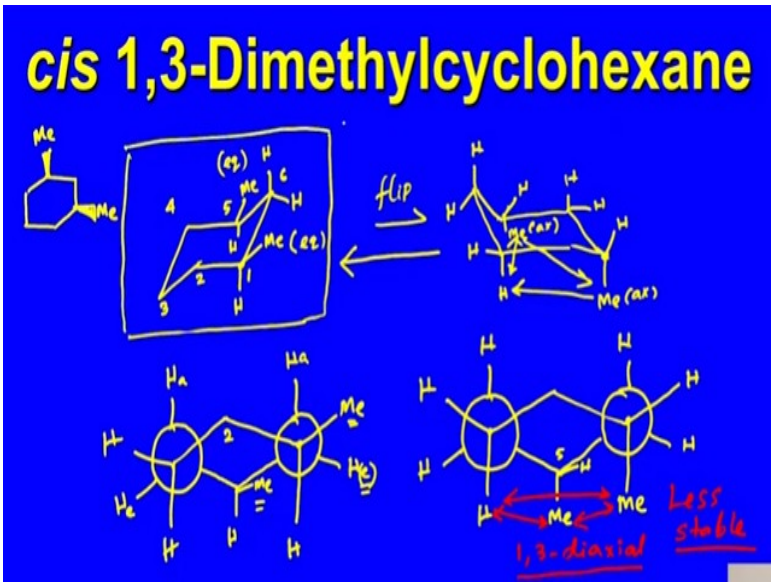


Now let us see the situation with 1,3 till now we have discussed about the 1,2 di-substituted which means 2 adjacent carbons have the substitution. Here it is 1,3 which means there is a

carbon gap between the 2 groups which are on 2 carbon atoms of cyclohexane. So if we draw it like that we can understand easily that these 2 methyl groups are both upwards. But on 1 and 3 carbon atoms, so if you try to draw the chair conformation of this molecule and we take this carbon as carbon number 1.

From then this methyl which is up should have a hydrogen down, second carbon does not have any methyl group. So 2 hydrogens and third methyl group, third carbon atom has 1 hydrogen down and methyl group in the equatorial position but up. So what we see here is that the 2 methyl groups that, we have are both in the equatorial position. So now when we try to flip the chair what would happen is that the methyl group on this carbon will come down to the axial position, this hydrogen will be in the equatorial position.

This does not have any methyl group, this has 2 hydrogens, the third carbon which is here is a methyl group down and the hydrogen in the equatorial position here is hydrogen axial, equatorial and again axial and equatorial. So what we see here is the 2 methyl groups both are in the axial position on 1,3 di-methyl cyclohexane. So what we now have is a strong 1,3 interaction between the methyl groups and the hydrogens.

And it is very obvious that this 1,3 di-axial 2 methyl groups 1,3 di-methylcyclohexane in this cis conformation, cis isomer, you have a very strong 1, 3 di-axial interaction so if we try to draw this molecule using the Newman projection as we were doing in the same way like before. On the front carbon here we have a methyl group in the equatorial position there is 1 hydrogen these 2 are connected through 2. And then you have the hydrogen here, hydrogen in the equatorial position.

Then on the carbon 4 this is the equatorial hydrogen and on the carbon 4 this is the axial hydrogen, this methyl is connected through 5 to that, this and that are the corresponding axial and equatorial hydrogens. The methyl group here is the equatorial position of the hydrogen is here and the methyl group is in the backside, this is equatorial do not mix it up. So what we see here is this methyl and that methyl are far apart so there is no question of n butane gauche type of interaction.

And this conformation does not have 1,3 di-axial strain, so therefore this conformation is always more stable compared to the other conformation. Let us try to draw the other conformer in the Newman projection for our understanding. So on the front carbon you have a methyl down hydrogen this connects to 3 like that, that has a methyl down, hydrogen down, hydrogen up. So then this and that connects through carbon number 5 which is in turn connected like that.

And in this 5 we have a methyl group downwards and the hydrogen upwards in the backside direction. So it is very clearly seen here that this groups are very close and they interacts through 1,3 di-axial interaction. And hence this is less stable. So always at room temperature, this 1, 3 dimethyl cyclohexane in this form will stabilize in this chair conformation compared to the other one.

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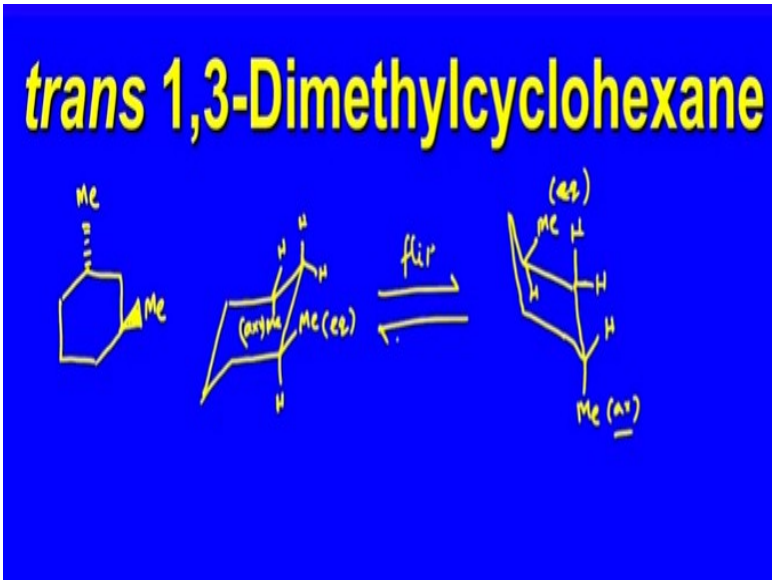


Now let us see what happens when it is trans 1, 3 dimethylcyclohexane so as usual if we draw it as a planar cyclohexane ring which we are very familiar to draw, is 1 methyl is down the other methyl is up is representation of trans 1,3 dimethylcyclohexane. So when we trying to draw the chair form of this one 1, 3 di methyl cyclohexane very efficiently we should start drawing the methyl groups first up.

Second carbon does not have any methyl group so 2 hydrogens, third carbon has a methyl group but if this methyl is up the other methyl is supposed to be down so the methyl is here and that hydrogen is there. So it is very clear that if this is in the equatorial position that is in the axial

position in the third carbon atom. Now if we try to flip this what should happen? In the flipped condition the axial one will become equatorial bonds and equatorial bonds will become axial bonds so the methyl group which was here would be down and the hydrogen may be up.

So it will become axial the second carbon does not have any hydrogen so it is up and down the third carbon which has methyl group in the axial position the hydrogen will be axial now and methyl will be equatorial like that. So what happens is now here we have a situation where one is axial and other one is equatorial and on flipping the equatorial become axial and axial becomes equatorial which means both the conformations are of same energy and they coexist in the equilibrium. So I will leave this for you to draw the Newman projection and understand yourself how that is possible.

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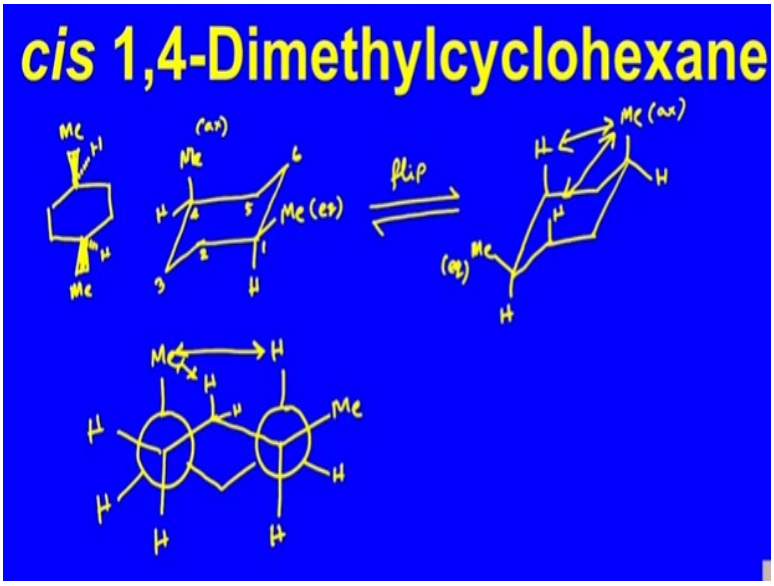


So now we will move to the next molecule which is 1,4 disubstitutedcyclohexane that is cis 1,4 dimethylcyclohexane. So when we draw that cis 2 methyl groups are up and 2 hydrogens are down on 1, 4 positions. So if we draw the corresponding molecule here in the chair conformation by making this methyl up and the hydrogen down and on the fourth carbon making the methyl up and the hydrogen on the down this is cis 1, 4 dimethylcyclohexane.

So remember that now here it is equatorial and the other one is axial, if you flip it becomes it goes like that, on flipping this carbon as the methyl up the hydrogen down and carbon 4 has hydrogen down and methyl in the up position, see here this is axial and this is equatorial. Once

again these 2 conformations have 1 methyl in the axial and 1 in the equatorial position. And in either conformation the condition does not change. So these 2 conformations again has the same energy. So if you try to now draw the Newman projection of one of those we will be able to understand what are the interaction that are present here?

So we number those atoms as usual and draw these groups as we have already done so I will quickly draw this Newman projection. So we have 1, 2, 3 this is the fourth carbon and on fourth carbon I have the methyl group in the axial position and here I have the hydrogen this connects like that for this. So here what we have is as usual the methyl-methyl 1, 3 di-axial interaction, 2 times. Similarly on that one this hydrogen and that hydrogen these 2 are up so we will again have the 1, 3 di-axial interaction present in that and that is why these 2 conformers are of same energy.

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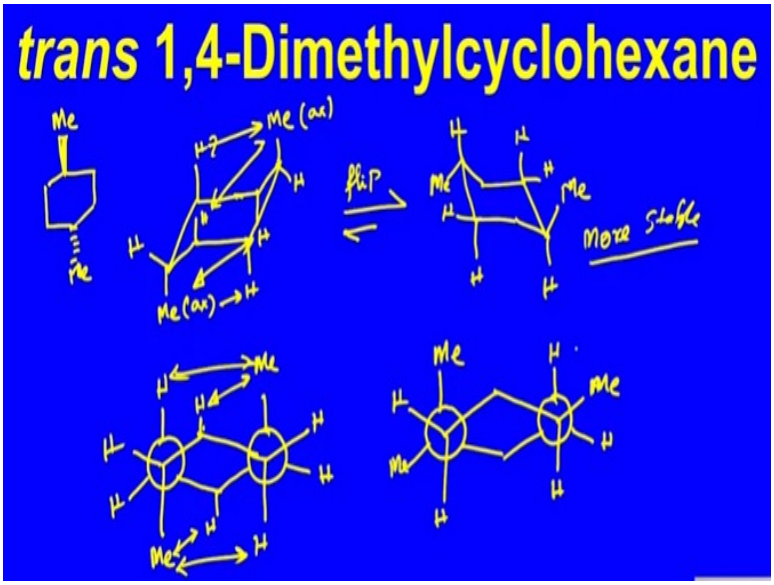


Now let us see what happens when it is the case of trans? So in the case of trans 1, 4 di-methyl cyclohexane if one methyl group is up the other methyl group is down. So if we try to draw it here this methyl group if you draw up the other methyl group you should draw as down. So now if we see here that this is axial and that is also axial which means for that particular methyl group there will be 1, 3 di-axial interactions with these axial hydrogens for the other methyl group there will be 1, 3 di-axial interaction with the other 2 hydrogens.

So it will have 2 fold effect of 1, 3 di-axial interactions with 2 methyl groups if we now flip the molecule what we should have? If we flip the molecule we would have this methyl group in

equatorial position and that methyl group once again comes to the equatorial position and that way we avoid the 1, 3 di-axial interactions. Therefore this conformation is more stable than the first conformation that we have drawn. So if you try to draw the Newman projection of the first conformation it should look like this.

You see here on the back carbon you have a methyl group, the hydrogen is here, the back carbon is connected to the back carbon here and the hydrogens on that are these. And the methyl group that we have on this front carbon is downwards, hydrogen methyl hydrogen and hydrogen. So what we have here is very easily seen that this methyl hydrogen 1,3 di-axial interaction is present on either side of the molecules and giving it a less stability.

But when you try to flip the molecule then we will see that these 2 groups have methyl groups in the equatorial position and the 1,3 di-axial strain is avoided. So in this lecture we have understood the conformation of di-substituted cyclohexane derivatives. And we have understood how to draw those in this chair form and how to convert those chair form conformations to the Newman projections and calculate the interaction energies based on whatever interactions are present.

So I would like you to go through the textbook for this part get the energy values for 1, 3 di-axial interactions and the n butane Gauche interactions and calculate yourself to find out the energy values associated with these conformational differences. So with this we would like to conclude this lecture and we will continue from here thank you.