Symmetry, Stereochemistry and Applications
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Module No # 05
Lecture No # 28
Diastereomerism in Ring System – Part 03

Welcome back to the course entitled symmetry, stereochemistry and applications. In the previous lecture we were discussing about the isomerism of 1, 2 di-substituted cyclohexane derivatives. So while discussing that we had talked about the Cis isomers of 1, 2 di-substituted cyclohexane derivatives. So now let us start talking about the trans isomers. As you know the 1, 2 di-substituted compounds can have Cis and trans 2 isomers and we are discussed only about Cis.

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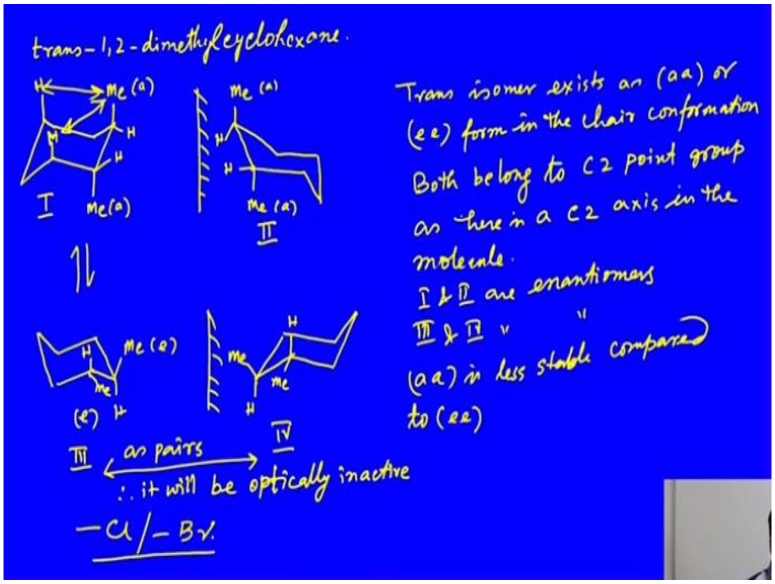

trans-1,2-dimethylcyclohexane.

Trans isomer exists as (aa) or (ee) form in the chair conformation Both belong to C2 point group as there is a C2 axis in the molecule.
I & II are enantiomers
III & IV " "
(aa) is less stable compared to (ee)

III ← as pairs → IV
∴ it will be optically inactive
−a/−B✓.

So let us see what happens when we have trans 1, 2-dimethyl cyclohexane. So if we draw the molecule in the chair confirmation the 2 methyl groups which are trans are always up and down that means in the chair conformation both are either axial and otherwise both are equatorial. So first we try to draw the mirror image of this compound of this molecule and see what happens? So this molecule which was di-axial still remains di-axial as its mirror image and then when we try to flip the di-axial conformer what we get is this one.

We get the corresponding di-equatorial so now this is ee and the corresponding mirror image of that ee would look like this. So the trans isomer exist as either aa or, ee form in the chair conformation and both belong to C2 point group as there is a C2 axis in the molecule. So if we number these molecules which we have generated the 1 and 2 and here after flipping it is 3 and 4 this 1 and 2 are enantiomers.

Similarly 3 and 4 are enantiomers so now we need to find out which one is more stable. So as we know that when we have methyl groups in axial position they can interact by 1, 3 di-axial interactions like that. And therefore the aa is less stable compared to ee so we will always have in the solution or in the liquid state at room temperature the excess of this ee conformers ee isomers and this will also always exist as pairs.

And therefore it will be optically inactive because these 2 cannot be resolved and we cannot separate 1 enantiomer from the other. So that is why this 1, 2-dimethyl cyclohexane in trans form although will have 4 enantiomers. But it since they are not resolvable at room temperature therefore will be optically inactive. So I would like you to see what happens if you have 2 different groups suppose instead of methyl groups you have 1 chlorine and 1 bromine in trans form and see which one is more stable and all that.

And then decide yourself whether they will be separable or not whether they will be isolated and they can show optical activity or not.

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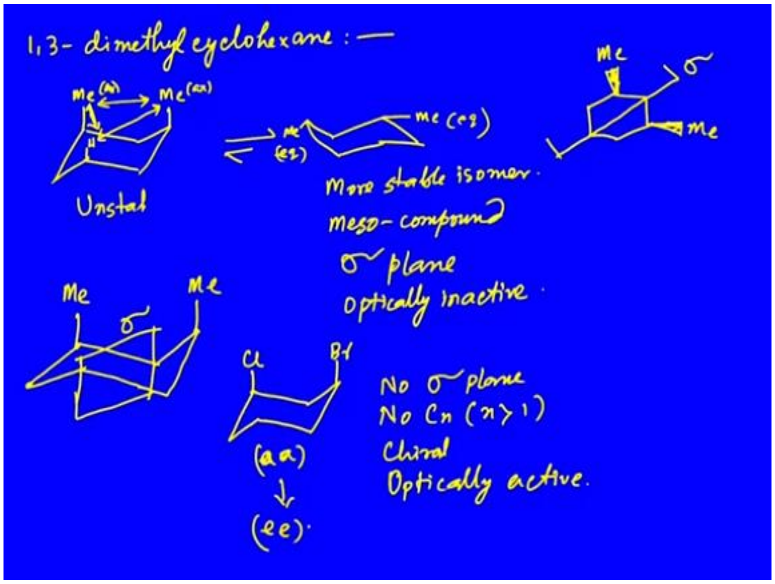

1,3- dimethyl cyclohexane :—

Unstabl

More stable isomer.

meso- compound

σ plane

optically inactive.

No σ plane

No Cn (n>1)

Chiral

Optically active.

Now let us try to see what happens when we have 1, 3-dimethyl cyclohexane. The dimethyl cyclohexane in 1, 3 position can have the Cis isomer where the 2 methyl groups are up and if we flip, the other possibility is you have both in the equatorial position. So this is axial-axial and this is equatorial-equatorial see I have drawn the equilibrium shifted towards di- equatorial. Because when you have 2 methyl groups in the axial position both of them will have very strong 1, 3 di-axial, interaction and also the methyl and hydrogen will have di-axial interaction.

So this will be unstable and we will always get the more stable isomer now we will see the Cis compound. This Cis compound is a meso compound as it as a sigma plane if you try to see this molecule in the planar form the cis isomer is suppose this one. Then this is the plane which exists in the molecule that is the plane which contains the carbon in between, let us try to draw it for your easy understanding. This is the mirror plane which bisects the molecule and methyl and methyl are mirrors, this carbon and that carbon are mirrors, this carbon and that carbon are mirrors image.

Therefore this compound is optically inactive but when the substituents are different suppose you have a bromo and chloro substitution, then there is no sigma plane, no Cn where n greater than 1. Therefore this compound is chiral and hence should be optically active. So if you draw the mirror image of this compound they will be a pair of enantiomers and also this one is aa we will have the corresponding ee isomer as well.

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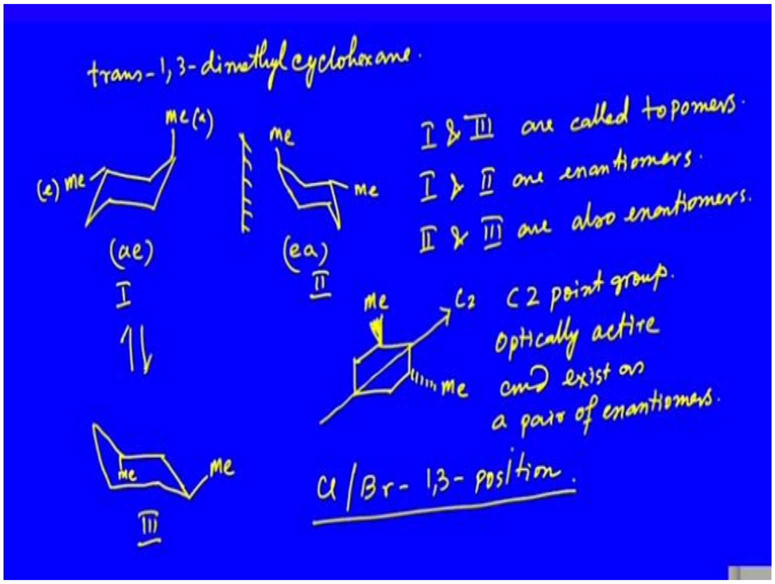
trans-1,3-dimethyl cyclohexane.

I & III are called topomers.

I & II are enantiomers.

II & III are also enantiomers.

C2 point group.

optically active and exist as a pair of enantiomers.

Cl/Br- 1,3- position.

So if we consider the trans 1, 3-dimethyl cyclohexane you can understand that the 2 groups it will be one is axial the other one will be equatorial. So this isomer is termed as ae if we draw the corresponding mirror of this we should get another ae isomer. Rather we should name it as ea. And then if we do a ring flip of this first isomer ae what we get is this. So this 2 forms 1 and 3 are called topomers you can see that 1 and 2 are non-super imposable mirror images.

So they are enantiomers, similarly 2 and 3 are also enantiomers and in the planar form if we try to draw this trans 1, 3 what we get is a C2 axis. Therefore this molecule belongs to a point group C2 and this will be optically active and exist as a pair of enantiomers. So please do it yourself when you have 2 different substitutions. Suppose Cl and Br at 1, 3 position in cyclohexane what will be the possible isomers of that compound.

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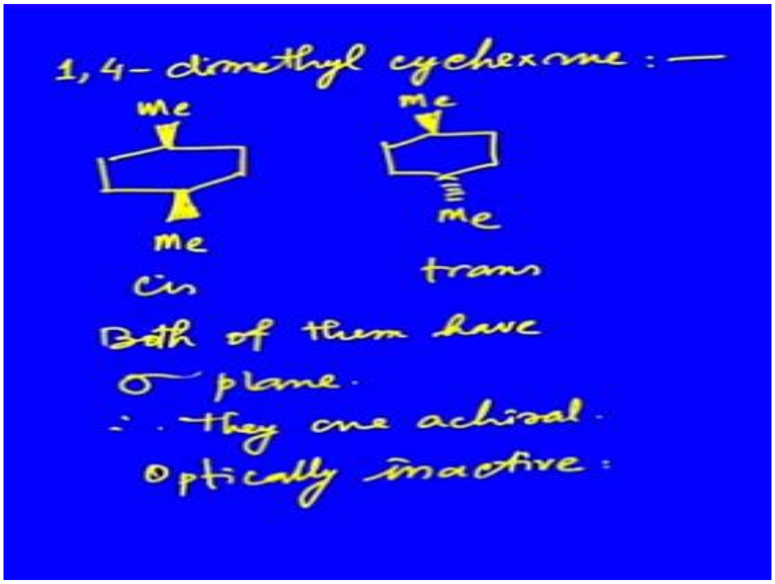
1, 4- dimethyl cyclohexane :—

Both of them have σ plane.

∴ they are achiral.

optically inactive.

Now let us see this situation with 1, 4 dimethyl cyclohexane, so in the planar structure if we draw dimethyl cyclohexane in the Cis isomer or dimethyl cyclohexane in the planar form if we draw the trans isomer what do we see? We see that both of them have sigma plane therefore they are achiral and optically inactive right. So let us then try to see what happens when you have 2 cyclohexane ring connected together.

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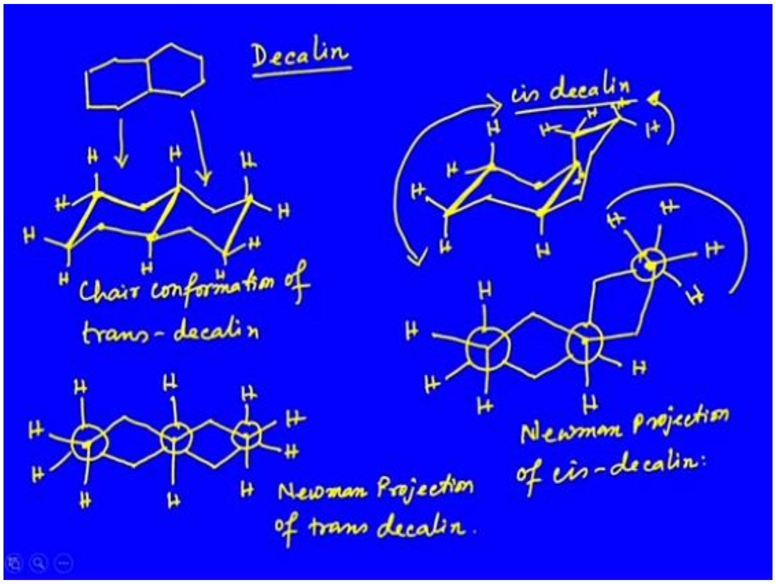

So I am talking about a compound which essentially looks like this so this is called Decalin. So if we try to draw this molecule in the chair form how it should look like is very interesting. We first draw the cyclohexane in the chair form for the first cyclohexane ring which is this one and then the second cyclohexane ring as to be drawn next to it. So now this is the chair conformation of trans decalin, why is it trans?

Because if you see these 2 hydrogens are trans so if you try to draw this trans decaline in newman projection by looking through this bond, this bond and this bond one after another. So when you draw that newman projection we draw 3 C-C bonds which we have marked. So on the front carbon here you have hydrogen down 1 hydrogen on the left hand side and it is connected to the next carbon there which has 1 hydrogen here and 1 hydrogen there.

So we draw that these hydrogens like this, now the front carbon is connected through the middle carbon to the next carbon. So we draw this, the back carbon is connected to this third carbon to that carbon. So we draw these and then the second this third carbon we have 1 hydrogen down and is connected to the other carbon like this. Similarly the back carbon has 1 hydrogen up and connected to the other carbon like this.

So we have these hydrogens which are here and other 2 hydrogens which are those, so this is the newman projection of trans decalin. So then what is Cis decalin as usual we should first draw the first cyclohexane and then the axial and equatorial bonds would join. So this is the Cis decaline isomer so now if we try to draw the newman projection of that again we take these 3 bonds to look at it.

So from the first carbon point of view we have 2 hydrogens third is connected to carbon here we have one hydrogen and there is 1 hydrogen like this is the second carbon in which is the bridging carbon and then this carbon has 1 hydrogen down. And here 1 equatorial hydrogen and the axial bond is connected to the next carbon, so we should draw first 2's carbon centers and draw the corresponding hydrogens here.

These are those 4 hydrogen in the front and back carbon then the front carbon is connected to this carbon here the back carbon is connected to this carbon there. Now what we see is that on the back carbon the hydrogen which is top is going through a bond and goes and gets connected to a carbon there. This has the hydrogen and also this gets connected, this goes to the back carbon and this goes to the front carbon which then has hydrogens like that.

And here we have 1 hydrogen which is that one, so the 4 hydrogen that we have shown here are hydrogens which are present on that side. Those 4 hydrogens at the back so this is the newman projection of Cis decaline. I would like you to practice this projections yourself then you will understand better, so we will continue from here in the next lecture where we will discuss about the diastereomerism in Pi systems.