Symmetry, Stereochemistry and Applications
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Module No # 05
Lecture No # 27
Diastereomerism in Ring System – Part 02

Welcome back to the course entitled symmetry stereochemistry and applications. In the previous lecture we were discussing about the diastereoisomers in cyclic systems. So we were discussing about the derivatives of cyclobutane when we have seen the case with 1, 2 and 1, 3 di-substituted cyclobutanes in the last lecture. So now we will continue our lecture in this direction and we will see what happens when you have 3 substitutions in cyclobutane.

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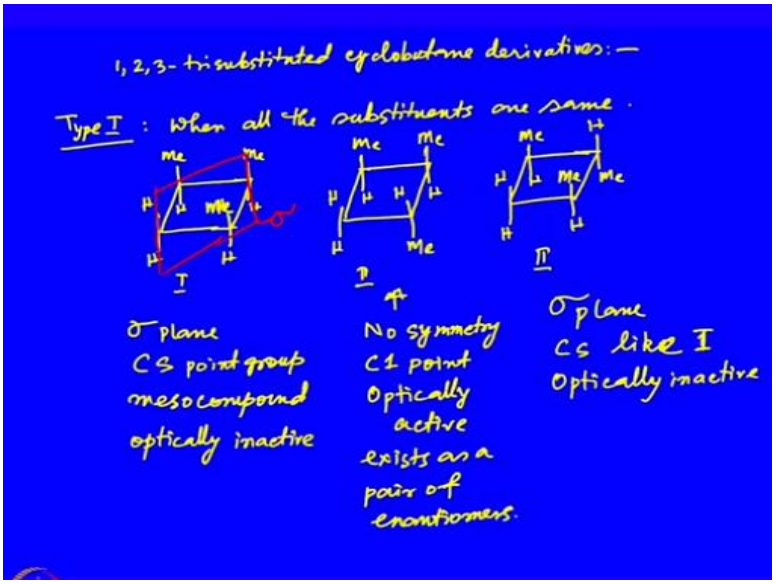

1, 2, 3- trisubstituted cyclobutane derivatives:—

Type I : When all the substituents are same.

I: σ plane
Cs point group
meso compound
optically inactive

II: No symmetry
C1 point
Optically active
exists as a pair of enantiomers.

III: σ plane
Cs like I
Optically inactive

So that is 1, 2, 3 trisubstituted cyclobutane. So there are also a few types possible, type 1 when all the substitutions are same. So let us try to draw those molecules which are the possible isomers of 1, 2, 3 trisubstituted cyclobutane. I am just taking one example with methyl this is 1, this is the second one and this is the third one that is possible for this type of molecule where you have 3 equivalent or similar substitutions.

So what we see in 1 we have a sigma plane that sigma plane contains the unsubstituted carbon atom this plane which is here. So therefore this molecule is having a symmetry Cs, so Cs point group and therefore it is again a meso compound and optically inactive. If you look at the third compound this third compound also has the same sigma plane therefore belongs to Cs point group like 1 so it is also optically inactive like 1 so it is optically inactive.

But when we look at the compound number 2 this compound 2 does not have any symmetry therefore this belongs to C1 point group. And hence it is optically active and exists as a pair of enantiomers right.

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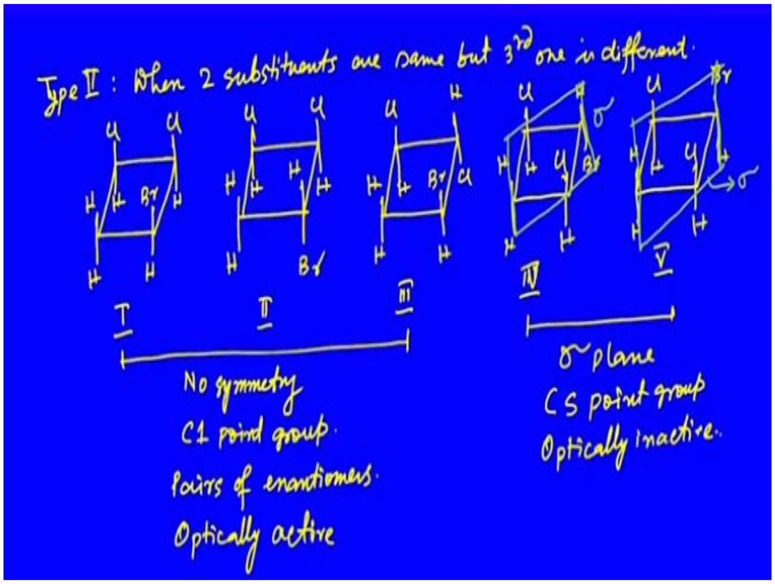

Type II : When 2 substituents are same but 3rd one is different.

No symmetry
C1 point group.
Pairs of enantiomers.
Optically active

σ plane
Cs point group
Optically inactive.

Let us see the next type which is type 2 when two substitutions are same and third one is different, when 2 substituents are same but third one is different. So here what we have are these isomers so if we look at these isomers carefully from 1 to 3 these 3 isomers do not have any symmetry. So they belong to point group C1 therefore they exist as pairs of enantiomers and they are optically active. When you look the other two, 4 and 5, both of them contain sigma plane I hope if you are able to identify the sigma plane very easily and the sigma plane is this one.

Therefore they as usual belong to point group Cs and hence they are optically inactive so this is how one can try to draw different isomers of substituted cyclobutanes and find out how many isomers are possible and which ones are optically active and which are optically inactive. So these isomers 1, 2, 3, 4 and 5 are distereomers of one particular compound. The third type of these compounds are where the all the 3 groups are different.

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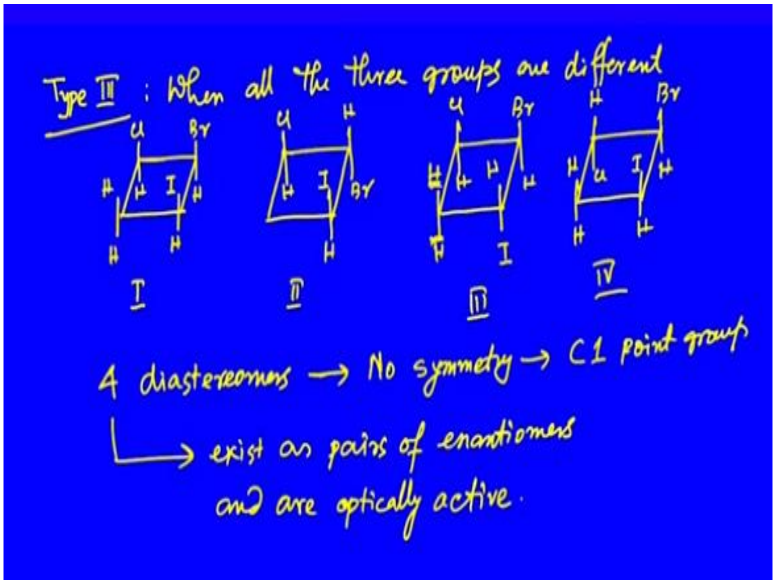

Type III : When all the three groups are different

4 diastereomers → No symmetry → C1 point group

↳ exist as pairs of enantiomers and are optically active.

So let us draw those isomers of the compound where all the 3 substituents are different. What we can see in all these 4 diastereomers is that they have no symmetry and hence they belong to point group C1. So all 4 of them would exist as pairs of enantiomers and are optically active so now we can extend this to tetra substituted cyclobutane derivatives.

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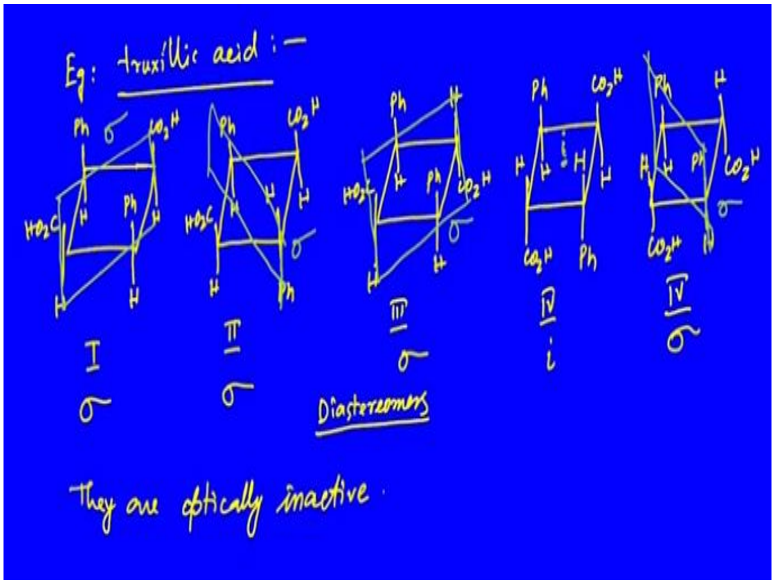

Eg: truxillic acid :-

Diastereomers

They are optically inactive.

And in that the known example is truxillic acid. Let us see the possible different isomers of truxillic acid which is tetra substituted cyclobutane derivative. So let us quickly draw the isomers that are possible for truxillic acid. So if you look at these 5 isomers very carefully of course they are all diastereomers why? Because they are not mirror images of one another therefore they should be termed as diastereomers.

But then what we see is that all these 5 diastereomers have some or the other symmetry that is present in the molecule. What symmetry do we see in the molecules? We see in case of 1, 2, 3 and 5 the sigma plane which I am drawing like this, 5 has again a sigma plane. So 1, 2, 3 and 5 they have sigma plane but the molecule 4 has inversion center i. Therefore all the molecules are one or the other way symmetric therefore they are optically inactive.

So even if this particular molecule has 4 chiral centers but they are all optically inactive because the molecules contain either a sigma plane or an inversion center. So this is how we can draw several isomers of tetra substituted cyclobutane real example is truxillic acid. So let us move to the next part of the course where we will discuss about the isomerism in cyclohexane derivatives.

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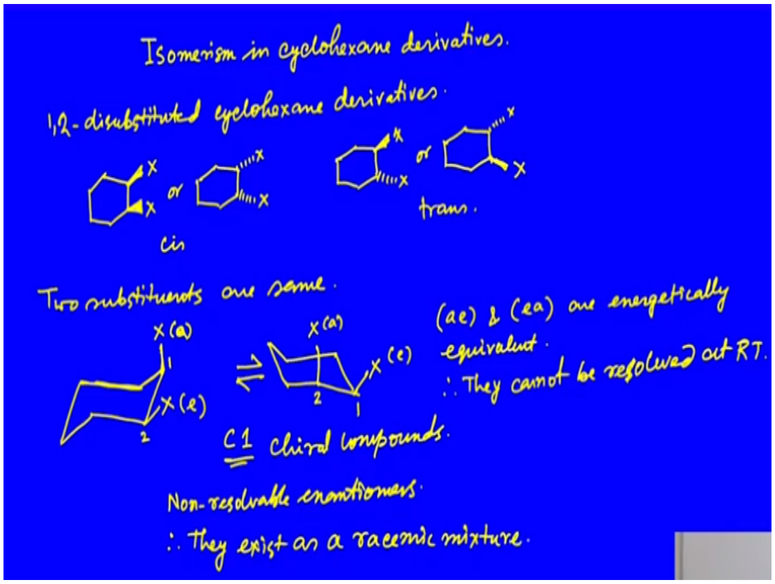

Isomerism in cyclohexane derivatives.

1,2-disubstituted cyclohexane derivatives.

Two substituents are same.

(ae) & (ea) are energetically equivalent.

∴ They cannot be resolved at RT.

C1 chiral compounds.

Non-resolvable enantiomers.

∴ They exist as a racemic mixture.

So again as usual we were discussing when while discussing about cyclobutane derivatives we have taken 1, 2 1, 3 and so on. So in case of cyclohexane also let us start by considering the 1, 2 disubtituted cyclohexanes. So if we draw this cyclohexane in planar form the Cis isomers can be drawn like that or like this and the trans isomer will be drawn like this 1 methyl group upwards or 1 substitution upwards 1 substitution downwards.

So now here there are 2 possibilities suppose the 2 substituents are same so if we draw these 2 substituents as same in the chair form which we have learnt earlier then this X is up. And here the axial bond is upwards and it is very this is axial and this is equatorial so the axial bond is up and the equatorial bond here is up. So both are up and if you do this flipping of the ring what we get is the following.

So this becomes axial and that becomes equatorial if this is carbon 1 and 2 here the carbon 1 and 2. So here ae and ea that is axial equatorial and equatorial axial are energetically equivalent. Therefore they cannot be resolved at room temperature although they belong to the point groups C1 they are chiral compounds. But since the flipping energy barrier is achievable at room temperature.

So both the isomers both the conformations are possible at room temperature therefore they are non-resolvable enantiomers. And hence therefore they exist as a racemic mixture. So let us try to draw the mirror images of these molecules.

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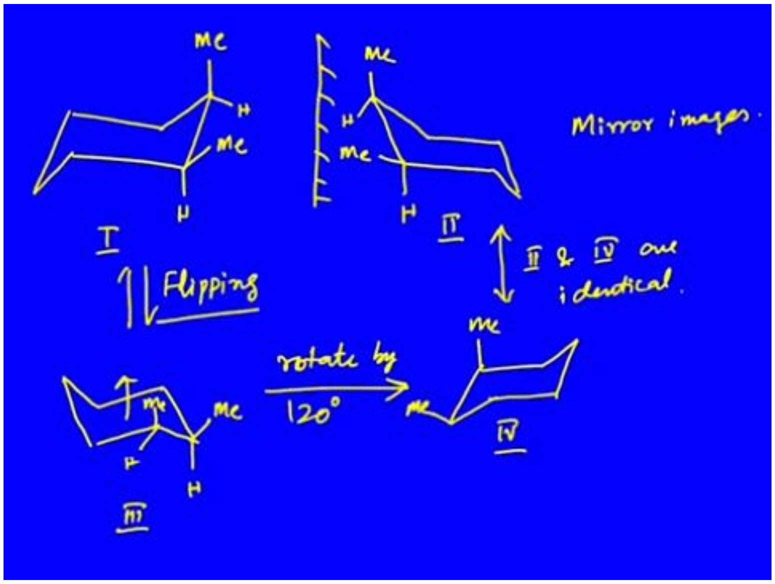

And then if we try to do a flipping of this molecule we would see this one, that is the flip structure of 1, 2 dimethyl cyclohexane. And then if you rotate the molecule by 120 degree about this central axis what we would get is this one. So therefore what we see is the structures 2 and 4 are identical and therefore 1 and 4 which are mirror images. You have flipped the structure 1 and made structure 3 and simply rotated the molecule by 120 degree you have arrived at the structure 4 which is identical to 2.

And therefore 1 and 3 are enantiomers and they are not resolvable enantiomers because this flipping that occurs at room temperature spontaneously what happens when the 2 substituents are different.

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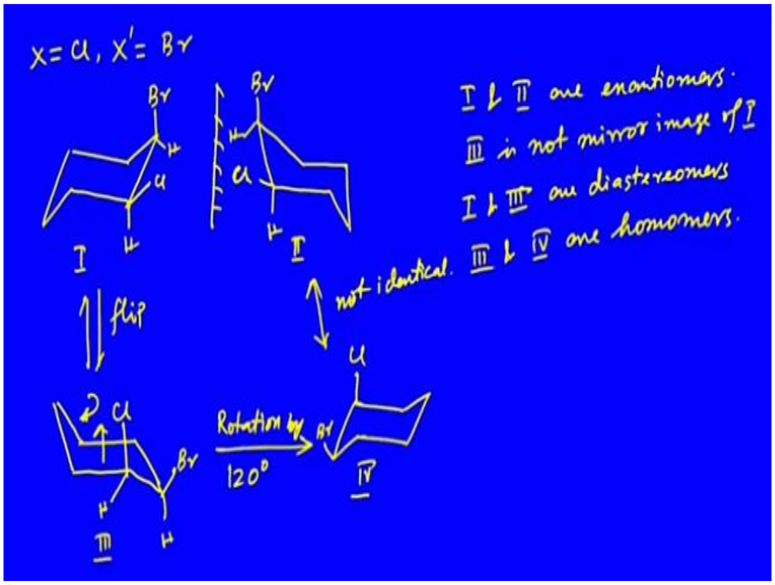

X = Cl, X' = Br

I & II are enantiomers.

III is not mirror image of I

I & III are diastereomers

III & IV are homomers.

Suppose X is equal to chlorine and X prime is equal to bromine so let us draw the molecule in its chair form and the corresponding mirror image. Now just like before if we flip this 1 what we would get is the following structure number 3. Now if you rotate the structure 3 by this axis about 120 degree what we would get is this new structure. So what we see is that, this 2 and 4 are not identical and what we see is that 1 and 2 are enantiomers 3 is not mirror image of 1 therefore 1 and 3 are diastereomers.

And what we see are that 3 and 4 are homomers, right. So in this lecture we have seen 2 different variations of Cis 1, 2 di-substituted cyclohexane derivatives and their possible isomers. So we will continue from here in the next lecture.