Structure, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A Problem-Solving Approach
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Lecture No. 03
Examples of Various Point Groups Notations, Chiral and Achiral Point Groups, Examples of Various Point Groups

So, welcome back to this course. In the last lecture we were we finished? We will continue from there we said that the point groups can be chiral point group or it can be achiral point group.

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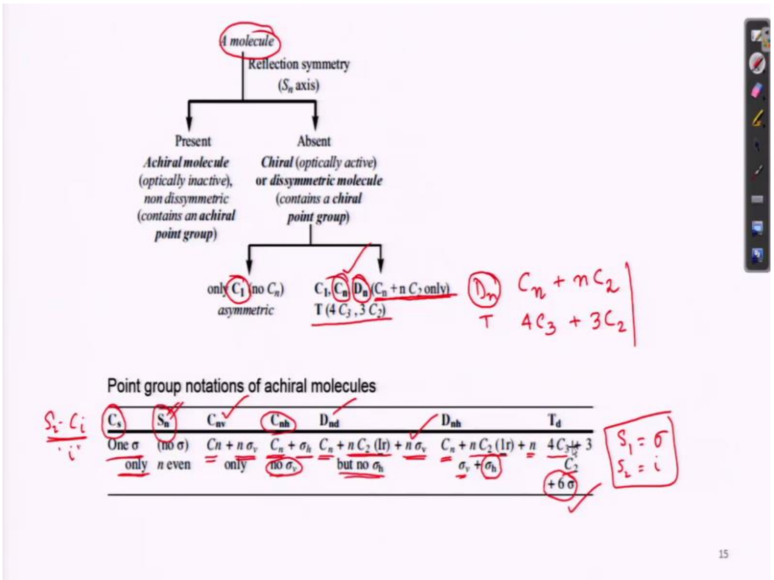

So, amongst the chiral point group we have C1 that means molecule which has got only identity element and then it can be Cn it can be Dn, Dn means dihedral point group. Dn can be equated as that means, when something has Dn that means that it has got a Cn n plus n number of C2, C2 axis and then you have tetrahedral point group which means that it has got 4C3 axis and plus 3C2 axis. Will give you examples one by one.

On the other hand, for achiral molecules or achiral point group, I said that will be more complicated because now you have combination of all 4, the simplest one the simplest achiral point group is CS that is containing only sigma one sigma containing only one sigma that means, one plane of symmetry. Then you have you have a Sn where there is no sigma remember when Sn is equal to 1 S1 is actually equal to sigma. And S2 is actually equivalent to i these two you should remember. So, but beyond that you can have other, other number of n’s. So, there is a point group which can be called Sn.

Then you have here something is not given you can also write CS or Ci. Ci is the one which has got a S2 axis, S2 axis or you can say that it has got an inversion point I think it is clear there is CS which got one only plane of symmetry one plane of symmetry nothing else then there is Ci which has got a center of symmetry nothing else but center of symmetry you can see that it has got an S2 axis that you can say of course, CS also you could have said that it has got an S1 you can you could have said a point group S1. But usually it is denoted by CS then Ci then Sn where, where n is not these numbers 1 or 2 and then Cnv which means that it has got a Cn axis then n sigma v planes. So, n number of sigma v planes Cnv.

Then you have Cnh these are different point groups achiral because now you are bringing in sigma once you are bringing in sigmoid I that means, you are talking about achiral point group. So, Cnh which means that it has got Cn and a sigma h but no sigma v that is Cnh. Then you have dihedral symmetry element that is Dnd. Dnd means it has got Cn it has got nC2 which is perpendicular to the Can, then it has got n sigma v but it does not have any sigma h and initially you have to it will be a little bit difficult you have to remember 6 is notations. What it means, what it signifies what I think it is with practice, ultimately it will be it will set in your mind.

Then you have Dnh, Dnh is Cn very similar to the earlier one nC2 perpendicular in sigma v that is up to this point is identical, but then in addition it has got a sigma h and there is a Td, Td is earlier we had T here and now Td that contents 4C3 plus 3C2 that is implied in a tetrahedral point group in addition it has got now 6 sigma planes. So, what is basically you are doing that for chiral point group if you look at carefully very carefully that ends up with either Cn or Dn or only T.

And when you are having these plane of symmetry vertical plane of symmetry, horizontal plane of symmetry, then you have to add these v or h alongside that, like Cn in case of chiral point group for achiral point group Cnv that means, you are now adding sigma v to the system Cnh that means you are adding sigma h to the system to make it achiral. Dnd, Dnd you are adding basically again sigma v to the plane but D means the diagonal, diagonal plane of symmetry.

So, sometimes you can say is sigma D here also but the without writing that you can here it is written sigma v you can do that, but remember these D stands for Dnd that means the that there is n sigma v elements which are present and it is bisecting the angle between the 2C2 axis and then Dnh Dnh you add one more sigma h in addition to all whatever is present in Dnd and finally, Td you add again sigma to make it achiral.

So, these are the some of the achiral point group this is not the entire list, but for our organic chemistry I think this is for organic molecules studying the point group system in organic molecules I think this will be the this will be sufficient to know. Now, let us go to the give some example where I told you about that apart from this point group notation you have something which is called symmetry number and order of point groups.

Some students actually to find the order that is a little tricky, but there is a shortcut number mnemonic way to remember the number of the order of a molecule that the order means a number order means again I repeat what is order? Order is the total number of symmetry operations that you can perform on a molecule, what is the symmetry number? The symmetry number is the number of indistinguishable forms that a molecule can take or can adapt while doing the on the basis of only the simple axis of rotation.

Simple axis of rotation that is the symmetry number. Symmetry number is not very hard to find what is little difficult is the order. However, I can give you an a mnemonic way of telling the order.

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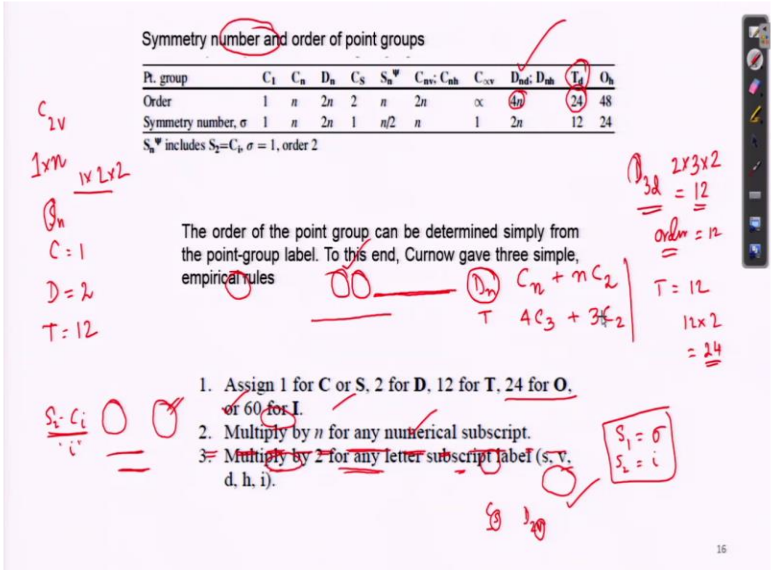

And it says that to find the order of a, of a point group what do you do you take because all these notations you see start from either c all these notations have C or D or T actually there is octahedral also we have we have not considered that D. So, this is the scenario now, C or D or T and so, the mnemonic says that if you have a point group which says that it is C2v. So, you take 1 for C so for C you take 1 or even there is this is Sn also so for if the point group starts with S, so for C or S, you assigned 1 for that.

And then there is this suffix, in the suffix if you see that in the suffix there could be n like C2v, Cnv so, n is the, is a number. So, 1 into n so, in this case C2v that means 1 into 2 and then for this for this label like v or D or all these all these levels letters basically C2v. So, it could be what CS CS means, you have a alphabet here or you could have D 2v So, you have an alphabet here. So, for these alphabets, if alphabets are present in the suffix, then you also multiply this by another 2.

So, in case of if what is the order of D3d suppose, this mnemonic says that for D you have 2 because I did not say this for D you take 2 for T you take 12 and then 24 for octahedral icosahedral 16. So, these are all written here this is the way because it is sometimes difficult that when you try to find a number of symmetry operations that can be performed on a molecule you never know whether you have actually finished all the symmetry operations or not.

So, it will be nice if you from the very beginning you know the highest thing you can do the actual number actual number that means the actual order by having some mnemonic device like this, what the device says that all point group starts with an alphabet capital alphabet, either it could be C or it could be S or it could be D or it could be T or it could be O.

We have done only up to T so, for C and S you assign or ascribe the value 1. Then if there is this for n the suffix there could be two things in the suffix there could be a number n or and there could be an alphabet. So, if we have the number multiply 1 with that number, if you have if you have the letter alphabet, then you multiply that by 2. So, what is the order of D3d? So, for D you take 2 for this is the number which is 3 and for any alphabet you will again multiply by 2.

So, that is 12 so, the order of D3d is 12 if you see in this list, it should be given here Dnd is there. So, if it is D3 as it says 4n so, 4 into 3 D3d 4 into 3 that will be 12. So, if it is TD, TD for T already you have to take 12 and then if there is an alphabet here, no number here, so 12 into 2 so, that means 24. So, the order that is number of symmetry of a number of operations that you can perform on a molecule which is TD is total order is 24. Symmetry number is little bit easy, because it is based on only on the C axis. And I will show you the examples, let us go to the examples.

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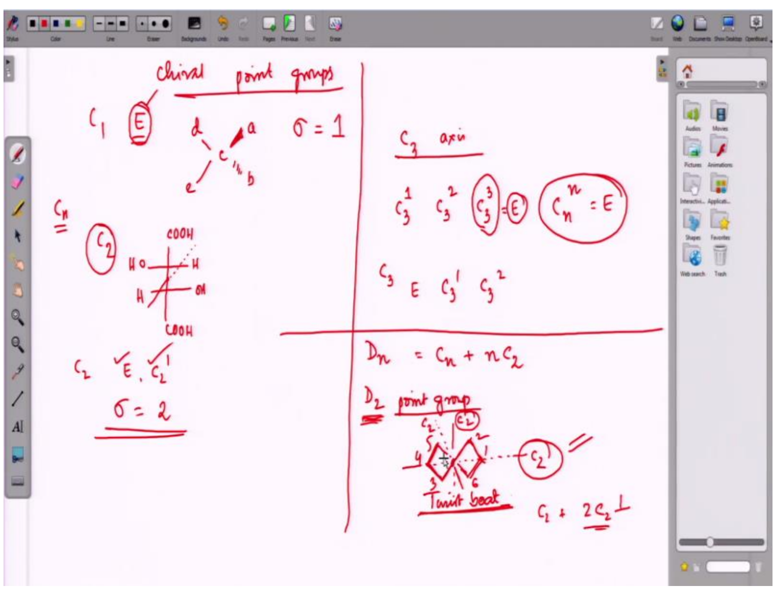

Let us consider our first chiral. So, we are talking about the chiral point groups. So, our first chiral point group is C1. C1 is basically, basically an asymmetric molecule means earlier definition asymmetric. So, if you do not take the identity operator as a symmetry element otherwise it is basically as symmetric. So, each has got so, if C1 is there, that means it has only the identity and which is defined by E. So, C1 chiral point group has this identity operator that is E. The example is very simple that if you have a carbon and if we have 4 different groups a, b, d and e then this has got only C1 nothing else, no other symmetry operation can be performed on this. So, it has got only E.

So, it is so, basically what is the sigma for this you can do only one operation that is the C1 operation. So, that means it is sigma is equal to 1. Now, the next one is suppose we have we want to see what is C2 because the next one is Cn. So, suppose n equal to 2 so, let us take a molecule which shows C2 this is molecule this molecule we know very well I will write see always remember this is achiral point group. So, whatever example you have to take they should be chiral molecule.

So, I take achiral tartaric acid in the Fischer projection form. So, this is a Fischer projection of a chiral tartaric acid and you see that it has got a C2 because this is the axis and if you turn it 180 degree it becomes the same. So, that is C2. So, now, C2 means basically see when this is also another important issue we should talk about this that if I say that a molecule has a say C3 axis the question is how many operations or how many each indistinguishable forms you are getting using this C3 axis.

C3 axis means that you rotate the molecule by 120 degrees 360 by 3 and you get an indistinguishable form. So, you have to see that how many times you get this indistinguishable forms by doing a complete turn complete turn this 360 degree. So, the first indistinguishable form you get after turning it while 120 degrees around that axis. So, that is what is called C3 we give a superscript that is 1 so, C3 1 that means you have turned only (one) once that is 120 degree.

Then you give another 120 degree rotation. So, you again come to an indistinguishable form. So, that will be called C3 2 that means you have turned by 2 times of 120 degree and finally, what you have another turn of 120 degree means you have completed the full turn that means 360 degree so, you can say C3 C3 the third one, but the third one is nothing but bringing back the original you are coming to the original position all the atoms then come back to their original position where they were at the beginning.

So, this is nothing but an identity operation. Identity operation means as I said one fold C1 means identity operation. So, rotating by 360 degree all molecules will come to the same form. So, same form that was all at arms will again regain their original position. So, any we can say that Cn if you turn it n times, if something has Cn axis started n times that means you are completing the full cycle of rotation. So, that is basically an identity operation.

So, basically when you have C3 axis and then the if a molecule has C3 then what it has it actually or how many operations you have to do you can do one is this identity operation from the very beginning you can write that that is actually C3 3 and then you have C3 1 that means 120 degree rotation and you have C3 2. C3 3 is E means the identity operation. So basically, now you have C3 1, C3 2 here, if you have C2 that means here you have E and that is identity operation is always there for every molecule and because it is C2 so, you can turn only once that means C2 1, C2 1 is the one turn that you can give.

Because 180 degree for the first operation and the next operation it brings to a 360 degree that was identity operation. So, it has got an identity operation and the C2. So, what is the sigma is the symmetry number basically is that number of operations that you can have the number of indistinguishable forms that you can generate that is basically the identity operation creates one and the C2 1creates another one. So, that will be 2 sigma will be 2.

Our next one is Dn, remember what is Dn? Dn is nothing but Cn plus nC2. So, let us take a take an example of Dn Cn plus nC2. Let us take a one example of D2, D2 point group we want to find out a system which has got D2 point group. So, remember that cyclohexane can exist preferentially in the chair form that we know unless there are some other constraints the chair form they actually one chair from flips to the another chair form and while doing so, it goes to a form which is also a confirmer much higher energy confirmer but that is what is called a twist boat.

And twist boat is, is represented by this structure this is what is a twist boat, this is a twist boat. Now in twist boat if you want to identify let us see what is the twist boat?

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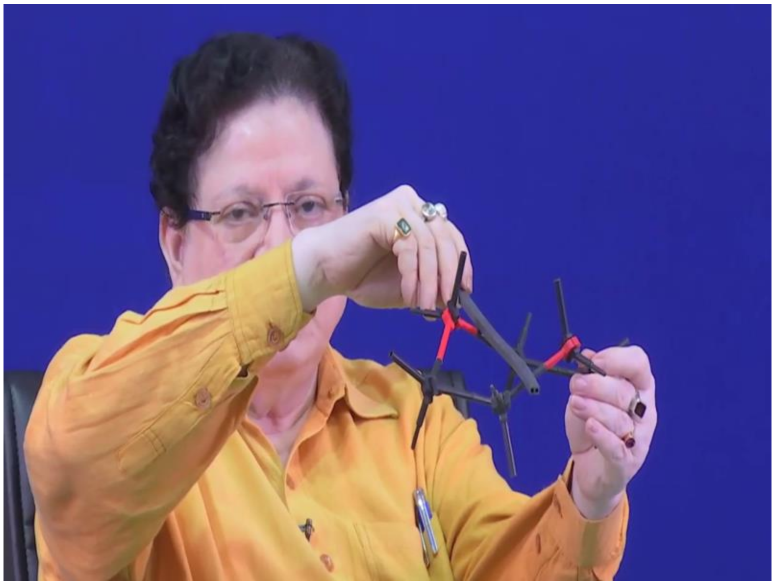

Now let us take the formed when one shear form is, is flipped and going to the other chair form in between you have a you have what is called a twist boat, in the twist what you know the bowsprit flagpole interactions are lace. And it is if you can see it, let us see I want to put it in the correct perspective. So, this is what is the twist just a second yes, this is the twist boat. So, in the twist boat form, what you have is actually I can actually there is a plane up a C2 there is no question of a plane, the circle it is a chiral geometric.

So in the here, there is a C2 axis going through going through these points, I will again show you the points. Let us see, I want to make it a little clear in the screen from here, let us see. It is not the way actually what happens when you project on the screen that is little bit different. So, that is little difficult to do. I will try to do it. Let us see again bring the yes this is the twist boat form and in the twist boat form there is 2 atoms are basically in the plane of the in the plane of the paper.

If I have these, this one and that one so, basically what you are saying you are seeing actually 2 quadrilateral and as if they are they have a common point although they do not have a common point. They do not have a common point but it appears that projection says that almost there is a common point actually one is above and the other is below. So, there is one C2 axis going through this atom, this atom and this atom.

That means this is a C2 axis and there is other C2 axis one is going from the from the top and then you can rotate it by 180 degree you will see that you will get the same system that is another one and there is a third one which goes through the apparent cross section of these bonds of this quadrilaterals apparent cross section of these quadrilaterals through that you can get another axis.

So, basically there are 3 C2 axis, one is between these 2 carbons, I will show you in the diagram when I go to the diagram. Another is basically this one and a third one, which goes through the apparent inter cross section between the between these quadrilaterals the bonds between the quadrilaterals. So, let us come to the diagram now. So, what I am saying so, this is the twist boat form, so, one axis is this another axis is going from the top and there is a third axis which goes through this point and the point behind it. So, that is basically difficult to something like this.

So, this is one C2 this is another C2 this is a third C2. Now, remember this all are C2 so, how to find the principal axis that is the first question. If you look at this whatever I said that when the fold is the same for the C axis, then you have to take that C axis as the principal axis which goes through the maximum number of atoms. So, in that case, these C2 axis basically suppose this is your number 1 carbon 2 3 4 5 6 so, this C2 axis goes through 1 and 4 C1 and 4.

This C2 axis does not go through any of the atoms it is through going through the central point of the molecule which is empty by the way that that part and then the other C2 axis the third C2 axis is going through the middle point of C2 C3 bond and C5 C6 one the middle point of that. So, C2 this is the principal axis and then the other C2 axis are there. So, it fulfills that this is a D2 system there is a C2 plus 2C2 and these C2s are actually perpendicular to the principal axis.

If you look at this, this is perpendicular to this C2 axis and this is also perpendicular to the axis, mutually these 3 axis are basically forming the x y and z coordinate a z axis of it of the cartesian geometry. So, that is the D2 point group let us go to the tetrahedral point group where is that now.

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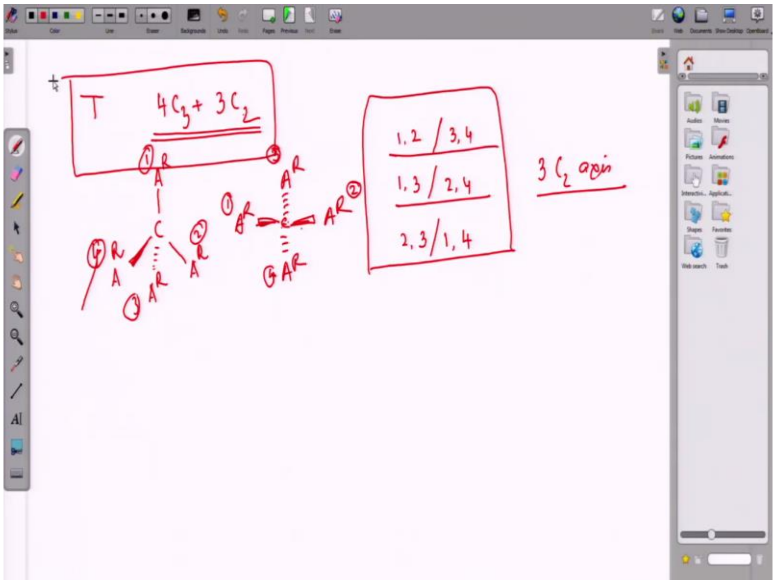

Let us go to the T the T1 is basically what we said that when it is a T point group then it will be 4C3 plus 3C2 that should be the case for C3 plus 3C2. So, what, what type of system we are talking about? It is a carbon weight attached to it 4 groups 4 identical groups identical but if it is for identical in all respect then what will happen then it will be it will not be chiral. Here, these groups are special that they contain a stereo generic center and a nSC stereo generic center like the original chiral center or you can say chirality center and suppose all are in the R configuration.

So, if that be the case then it is chiral of because you can argue that the mirror image in all the Rs are as, so they cannot merge on each other. So, it is chiral and this is a system which has got these 4C3 and 3C2. I can show you again with a possibly with a model.

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Suppose these red groups there are four red groups and these red groups are one I am actually holding with my hand these 4 groups suppose they are the stereogenic elements represented by A or n in the R configuration. Now what will happen see, you can find out the C3s, which are going through this take this as the particle like this and then you rotate it by 120 degree and you will get a C3 but going through this one. So, now, there are basically four A's.

So, this is the number 1A, this is the number 2A this is number 3 and this is number 4. So, because there are 4 A groups so, how many so, you will have C3 axis 4 C3 axis because, first you bring the number 1A group on the top and you get a C3 axis then you bring the number 2 group on the top you get another C3 axis, then number 3 group on the top like way and then number 4 group on the top. So, there are 4C3 axis no doubt about that.

Now, the question of finding the C2, the C 2 axis you see that if you hold the molecule this way, suppose I hold the molecule this way, I rotated this way. So, basically what I am doing, I am having an axis like this I hold the molecule this way the 2 molecules like the Fischer projection and I have this axis and then I rotate this molecule let us show this tetrahedral point group by taking this model this model it is a tetrahedral carbon in the middle and you have 4 groups which are ident which are signified by these red balls.

Just think of these red balls are basically representing the, the A groups not only A groups and in the in the A group the stereochemistry of the stereogenic center of the SP3 chirality center is R.

So, that is a situation So, these are all A's in the R configuration, first of all finding the C3 axis C3 axis that you bring 1A to the top and then you rotate it and you get the C3 axis you see these 3.

So, the axis is actually aligned to this C and this number one AR bond since you have 4 type Ar bonds, so, there will be four C3 groups. So, first bring this first AR on the top you get one C3, then you can bring the other one at the top you get another C3, you do not have to actually bring it like this what you can say that since there are 4 bonds connected to AR’s, so, each bond actually is the direction of the 4C3 axis because there are 4C3, 4C AR bonds. So, that is all about the C3.

Now, in case of C2, because it has got tetrahedral symmetry so, there must be 3C2 axis here, we have to find that C2 axis. So, if you take the molecule as his as his hold held in case of Fischer projection, so, what do you do you keep it in the Fisher projection and then suppose this is the axis I think this is. Now, you give it a rotation by 180 degree. So, this left part goes to the right part and the right part comes to the left part.

Similarly, the bottom part goes to the top part and the top part goes to the bottom part, but the molecule is indistinguishable with the original because all groups all these groups are AR representing AR. So, basically, that means, this axis suppose this is your one AR group and this is your secondary AR group. So, your axis goes if it forms a plane, your axis is basically in the plane bisecting the angle between these 2 boards that is the axis.

Now, this is a C2 axis because you are giving you a 180 degree rotation and because you can have 3 pairs like that 1 2, 2 3 and 3 4, so, you can have 3 C2 axis, again I repeat, because these access is basically going is bisecting the angle between 2C AR bonds, if that be the case, then you have only 3 pairs 1 2, 2 3 and 3 4. Now, somebody might ask that what about 4 1 or what about the 4 3, we are not considering that actually we are considering that remember, when we bisect the angle between the 2 bonds, we are actually bisecting the angle between the other 2 bonds at the same time.

So, you should not duplicate this. So, when I am bisecting this 1 and 2 bond angle between 1 and 2, so, I am actually bisecting the angle between 3 and 4. So, basically what we should we should say that see this is what I am saying AR, AR, AR and AR suppose this is your number 1 number

2 just arbitrarily I am giving some number and this is 3 and this is 4. So, the C2 axis is going through this through vertically here perpendicular to the plane of this tablet and then give it a 180 degree rotation.

So, when you bisect this angle between these two, you are bisecting the angle between 3 4. So, basically here this axis involves 1 2 and 3 4 this pair, this is a better way of representation. The other one will be when you are bisecting between 1 3 and 2 4 that forms another pair and you can have only one more pair that is 2 3 and 1 4. So, this is the these are the 3C2 axis that can be present here.

So, this is the tetrahedral symmetry tetrahedral point group sorry tetrahedral point group, it is not a symmetric tetrahedral point group. And it is exhibited by this special class of molecules a tetrahedral carbon with having same stereogenic units attached to the carbon. So, that completes the point group for the for chiral point groups that we have covered the next is the achiral we have to deal with Achiral point groups.

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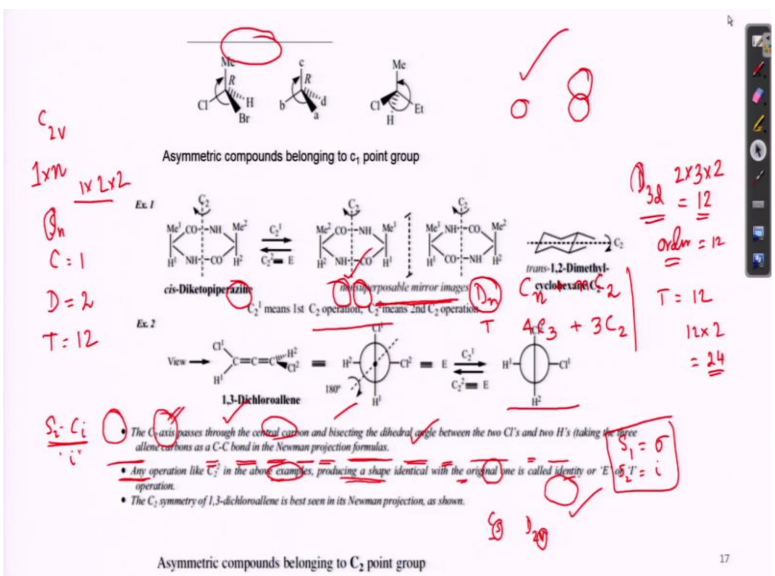

Let us I think that this Achiral point group will take much more time. So, we will do it in the next lecture, because that will take a lot of time, we have to abruptly stop in the middle if we want to start now. So, we have now seen what are the point groups we have seen what is meant by order, what is meant by the symmetry number and then we have defined the point group of chiral and achiral molecules these are called chiral point groups and achiral point groups.

We have not shown all but we have shown the important ones which are required in organic which are generally shown by the organic molecules and then we have covered the we have covered this the chiral point groups, different types of chiral point groups maybe we can what we can do in this short whatever time we have.

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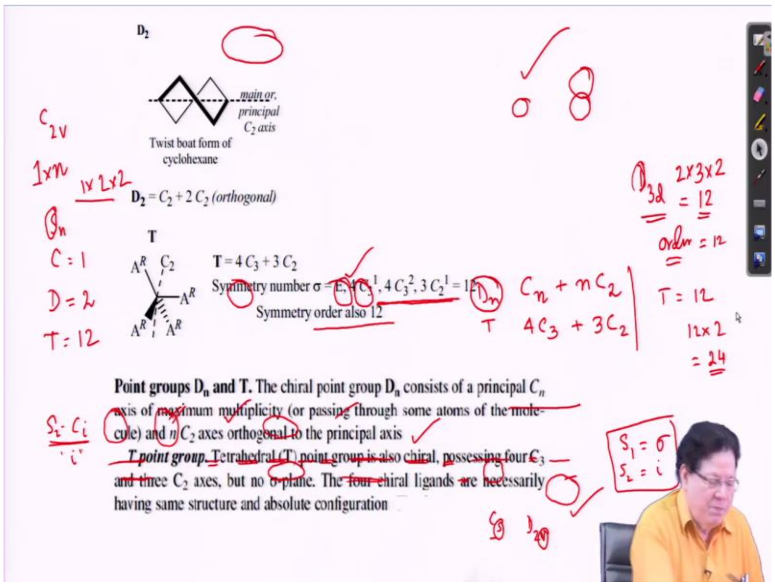

We let us try to find out the order we can find by adopting the what I have said is by adopting that mnemonic formula. But symmetry number let us try to find the symmetry number of a tetrahedral point group, chiral tetrahedral point group that means T point group.

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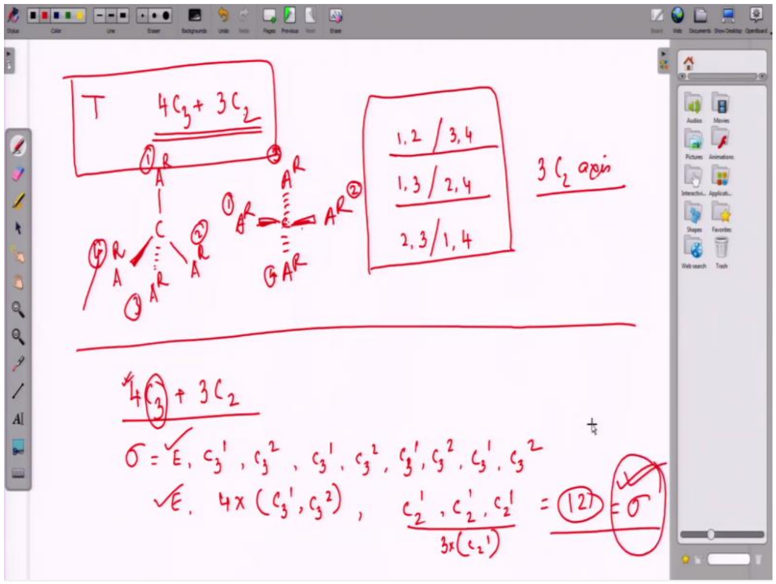

Now T point group is we are talking about a T point group. So, it is 4C3 plus 3C2, I will show you how to find the symmetry number, sigma. Now C3 just forget about this number first, consider one C3. If we consider one C3 it starts with C3 1 that is the 120 degree rotation. Then you have C3 2 and after that it is the identity operation, so, that you can always write in the front. So, identity operation and then C3 1 and C3 2. Then you have there are 4C3s, so, you have C3 1, C32, then you have another C3 1, C3 2. So, then another C3 1, C3 2 and a fourth one C3 1 and C3 2.

So, an identity operation and then according to the number of the C3s, you have C3 1, C3 2, C3 1, C3 2, C3 1, C3 2 and C3 1 that means, basically you can say E and 4 into the C3 1 and C3 2. And in case of the C2, what you have in case of C2 you have C2 C2 is 180 degree so, you can have only one operation here. So, C2 1 and C2, C2 1 now, there are there are basically 3 C2 ones here. Because there are 3 C2 axis. So, you can write this as 3 into C2 1. So, the total number becomes how many see this is the symmetry number.

So, you have E that is one then 4 into 2 that means 8 plus 1 9 plus 3 so, that makes it 12. So, symmetry number is equal to 12, I think it is clear to you. Well, so, first is the E you do not repeat II remember because there are so many C3 axis you are going to repeat E. E is only once and then according to the fold you have different number of operations, if it is C3 then you have 1 and 2 if it is C2 then you have only 1. So, if it is C4 you can tell that I will have C4 1, I will have C4 2 and I will have C4 3, the other is the identity operation. So, that is a good way to start that how to find the symmetry number. Thank you.