Structure, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A Problem-Solving Approach

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Lecture No. 04

Solving Problems on Point Groups
(Cn, Cnv, Cnh, Dnd)

Hello everyone, welcome to this course on Structures Stereochemistry and Reactivity of Organic Molecules and Intermediates: A Problem Solving approach. In the last lecture we have introduced or I have introduced to you the concept of mind group, but we have not elaborated that much. So, today I plan to elaborate this concept of point group and also the associated parameters that is symmetry number and symmetry order and then we will solve some examples.

Now, let us again start from the very beginning that if you have if you see that a molecule has a C axis some C axis some C3 axis, then it really does not tell you the complete information about all the possible symmetry elements or the structure of the molecule. So, basically what I am saying that if you are telling a particular presence of a particular symmetry element that does not allow you to grasp the structure of the compound, the structure of the molecule and also the number of symmetry elements that are present in the molecule.

So, that actually is the genesis of this concept point group. So, what is point group? Point group is basically a notation that is used to describe a molecule, but that notation will specify exactly how many symmetry elements it has and how many distinguish indistinguishable forms that the molecule can adapt while you are performing a symmetry operation.

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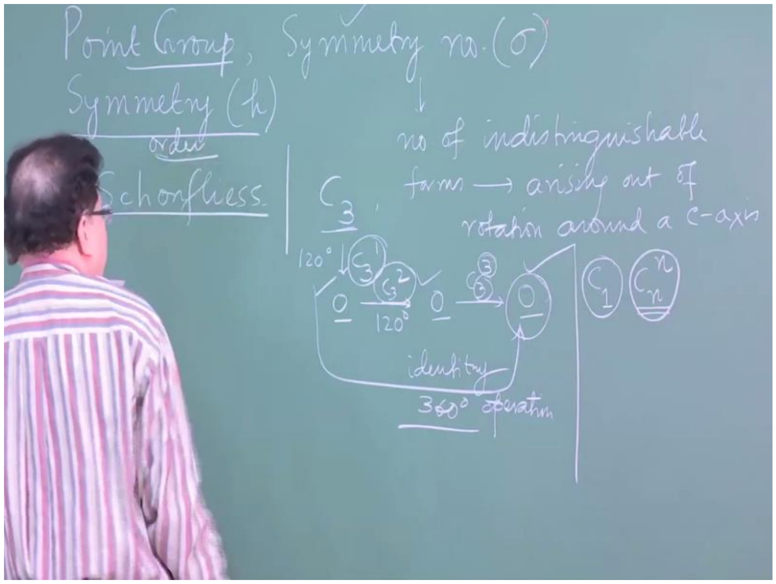

So, we are again back to the concept of point group then we will also elaborate on symmetry number remember the symmetry number is denoted by sigma and will also tell about the symmetry order, the symmetry order is denoted by h. So, what is a point group? Point group again I repeat is a, is a notation that is used to describe the all possible symmetry elements in a molecule. And this notation has been introduced by Schoenflies.

So, he is a scientist who introduced the point group notation for a molecule. Now, the question that can arise is that why it is called a point group? What is this point all about? This actually this point group concept is that basically you are it tells you how many symmetry elements it has the molecule has and you can perform any of those symmetry element. While performing you can perform any of the symmetry operations, the operations based on the symmetry element.

So, when you do these operations, basically one point remains unchanged remained at the same position all the time, and that is what is the center of gravity for the molecule. So, that is why this is what is called a point group because performing the symmetry operations does not change that point, namely, the center of gravity for the molecule. That is why this is called the point group.

Now, this so, we know what this point group look like some examples, like if you have if I say that a point group for a molecule is C3, that means that the molecule is only having a 3 fold simple axis of symmetry. We will come to various notations before that will also describe or define what is a symmetry number? The symmetry number is the number of indistinguishable forms that a molecule can adopt while you are performing symmetry operations only based on the simple axis of symmetry.

So, basically the simple when you rotate around an axis, which is a simple axis of symmetry of this president in a molecule, you actually get before you complete before the complete rotation of 360 degree you can get different forms which are indistinguishable from the original although some atoms have changed their positions, but the atoms being same, so it is you cannot actually differentiate between these between these 2 forms.

So, so, that is what is the symmetry number? So, symmetry number is basically the number of what I am saying number of indistinguishable forms, but remember these indistinguishable forms are actually arising out of rotation around a C axis, a simple axis of rotation so, that is what is symmetry number that means, the symmetry number is basically you can find it out by trying to find out they what are the symmetry the simple axis of symmetries that are present in the molecule and then you try to find out what are the different indistinguishable forms.

Like again coming back to this C3 point group that means, the molecule is having a C3 axis it tells you that each 120 degree rotation around that axis that molecule looks like the same as the original. So, that means that when you give a 120 degree rotation then you get one form which is identical with the original. So, that is called C3 1 that means we have perform the operation only once only 1 120 degree rotation. Then you can have another 120 degree rotation which is now called C3 2 and that brings the molecule again as looks like the original.

And finally, if you give a third 120 degree notation that means, which is denoted by C3 3 to the it is basically the suffix is it is a subscript and the superscript. So, you again come back to the original however, this basically is meaning that you have not you have done a 360 degree rotation and each 360 view rotation we know that the molecule remains the same. So, this is basically is called an identity operation, identity operation.

And so, basically the atoms again come back to their original position and this is the this is the successive C3 symmetry elements which are denoted by C3 1 and C3 2. So, the number of indistinguishable forms from a C3 operation and you get this is 1 this is 2 and the identity that identity that means the complete rotation of 360 degree. So, these are called successive C3 axis

C3 1 and C3 2. So, that means that what is an identity operation you can say it is C1, C1 means 360 degree divided by 1 that means you are rotating by 360.

So, the molecule will definitely become the same as the original and basically nothing has changed the atoms are the atoms remain at the same position, each atom remains at the same position you can also denoted by if you have an n fold symbol acts of symmetry, then by rotating in times you get back to 360 degree. Like here, C3 3 that means you have given 3 times rotation. So, you bring to the so, that completes one complete term that mean 360 degree. So, you can say that Cn n is identity opposition or C1.

Now, one more important point is there that is the symmetry order, symmetry order the symmetry order. So, what is a symmetry order? The symmetry order is basically the number of possible symmetry operations that you can perform on a molecule.

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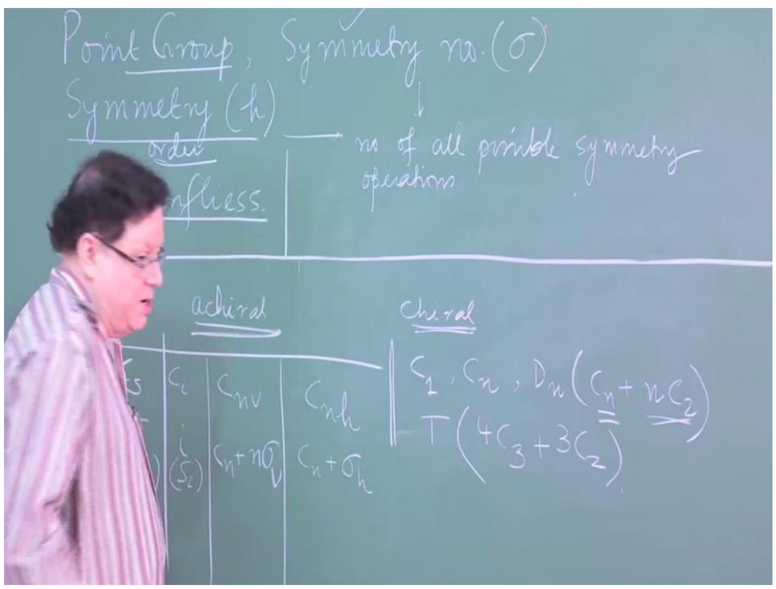

So, symmetry order is basically the number of all possible symmetry operations. So, basically symmetry order tells you the complete picture, the symmetry number on the other hand is only based on the C axis. Now let us come to the different classes of point groups. Now we know that molecules are classified either Achiral or Chiral. So Achiral so that we will have a set of point groups and then chiral.

Now, when a molecule is chiral, we know that the molecule cannot have the Sigma I or S axis, it can only have C axis or that C axis that Cn which is n greater than 1 that may be absent also, but remember every molecule has got a C1 axis. So, for chiral entities chiral molecules, which lacks all possible symmetry elements, which we call as asymmetric that will belong to the point group of C1 because that is the only possible symmetry operation that you can perform on that molecule that means rotation by 360.

And then you have a possibility of Cn that means a molecule can have only C2 axis or C3 axis or whatever. And we know that if the molecule is Chiral, but still pauses Cn axis where n is greater than 1 that is called a dissymmetric molecule. Remember that our earlier course on stereochemistry we have discussed all these asymmetry and the dissymmetry. So that is a dissymmetric molecule. So, a dissymmetric molecule can have can have a Cn axis. So, it can belong to a point group of Cn.

Then you have what is called a dihedral symmetry Dn, what is Dn? Dn is basically you have Cn plus n sigma v. This is n C2 Dn is v will come when we have it when we have a subscript, which is a v or like Dnv or Dnh when sigma h will come. So, dn is basically Cn plus nC2. And then you have another one which is called tetrahedral symmetry and that a chiral molecule can have T symmetry or T point group it can belong to so, that means, it has got 4C3 axis and 3C2. So, these are the possible chiral point groups. So, C1 or Cn then you have Dn, Dn is C n plus MC 2 and then you have T that is a your 4C3 axis and 3C2 axis.

On the other hand achiral point groups will be will be large in number because now there is a possibility of presence of all four elements of symmetry C and as well as plane of symmetry, then center of symmetry and all possible alternatively axis of symmetry. And based on that some of the point group notations I will tell set there could be Cs, Cs means now it has got only sigma plane. So, if I draw a table like this, so, Cs means that it has got a sigma plane only and then it can have Ci so, that means it has got i.

Now i is also you know is equivalent to S2 and sigma also is equivalent to S1. However, this point of notation is Cs, if you have only plane of symmetry Ci if you have only center of symmetry. And then you have so C symmetry and then you have Cnv that is one possibility. And then you can have Cnh. So, what is Cnv? Cnv basically, you have Cn plus n sigma v Cn plus n sigma v and the other one is Cn plus sigma h only sigma h.

Remember, because there can be only one horizontal symmetry element because only one horizontal plane is possible against the principal axis of symmetry. So, sigma h can only 1, but sigma v can be large in number it could be in finite in numbers also.

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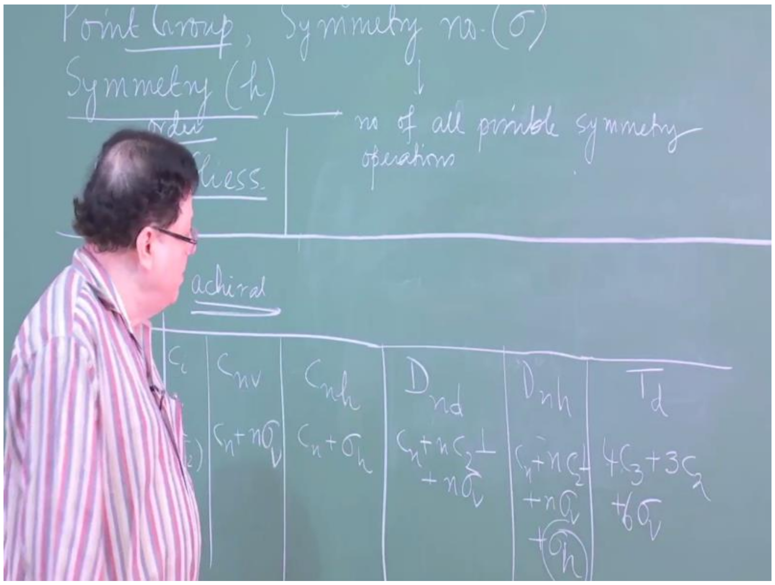

Then you have let me erase this then you have the D symmetry that means the dihedral symmetry So, here you can have here you can have Dnd or you can have Dnh and finally, we have the T symmetry but T Td symmetry point group Td point group apart from this there are other ones octahedral we are not considering it because that is for organic chemists that may not be required unless you are handling with molecules like Cubans. They can have octahedral symmetry otherwise, I think these symmetry elements are sufficient to describe the types of organic molecules that we are dealing with.

Now, what is Dnd? Dnd is basically you have Cn plus nC2 which is perpendicular to this Cn axis, the principal axis and then you have n sigma v that is Dnd. And then you have Dnh, Dnh is basically everything what is there in Dnd but apart from that you have a sigma h. And then you have the difference between these two are basically that you have it in addition to all these whatever is present in Dnd point group you have also the sigma h and for TD the tetrahedral symmetry TD point group what you have is that 4C3.

I remember I told you 3C2 that is always present in a tetrahedral point group and then you have apart from that now, because it is an Achiral molecule, so there must be some other improper element of symmetry that this is only proper element of symmetry. So, you have 6 sigma v planes. So, that is the point group system that is usually applicable to the organic molecules. So, let us take some do some examples and try to find out the find out the number of symmetry number as well as the symmetry order.

Now, if you want to remember symmetry order is the number of all possible symmetry operations that you can perform on a molecule and sometimes what happens I also felt this problem when I was a student like you that you never know that if you have a molecule and if you try to find out the different types of symmetry operations that you can perform on the molecule, sometimes what you do sometimes think that whether I am missing any symmetry element or not.

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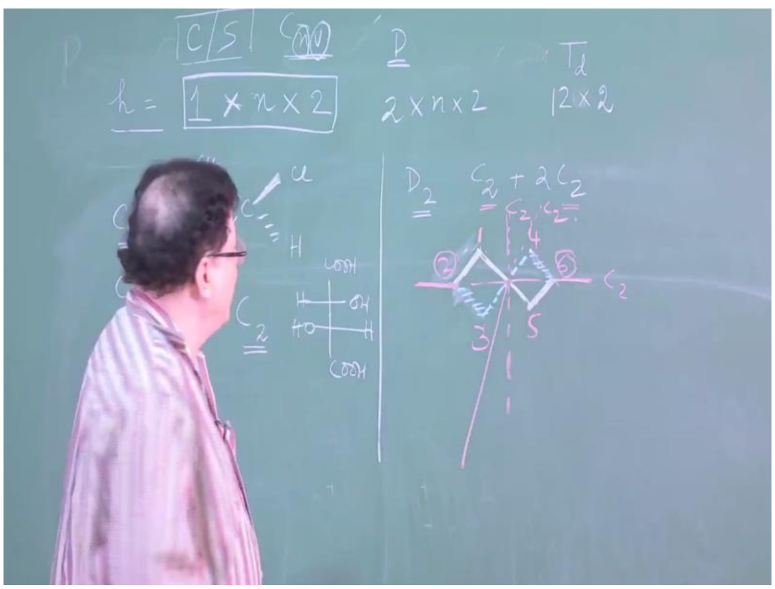

So, to overcome that, there is a empirical rule where you can calculate the symmetry order just by empirical rule, so, that you actually from the very beginning you know that what is the symmetry order of the of the molecule if the point group is given, so, when you try to find out the symmetry elements, then what you have that at some point of time you know that I have reached the target whatever is defined by the by h by applying this empirical rule and then you can stop there.

Otherwise always there is this question coming in mind that whether the symmetry elements that I have drawn whether these are sufficient or there are even further number of symmetry elements possible or not. So, what is this empirical rule the empirical rule says that if you have a C point group or like this the Cs Ci Cn Cnh so, if you have C1 point group or S like this Ci you can call S also or Sn also, Sn is also possible where n is other than 1 2.

So, if you have this these type of mind group based on C or S, then you assigned a number you assign a number 1 or a quantity 1 against that notation. So, for like Cnv if something is Cnv so, the number of the order of the symmetry order will be because it starts with C, so, it will be 1 into this whatever the number is here because that will be a number like C2v so, n is equal to 2. So, you have multiplied by n into if you have this alphabet like v or h or d, if you have the alphabet or even is all these things i, S then you multiply that by 2.

So, it is basically so, if it is this is for C if it is d then you assign 2 for D So, 2 into n into 2 So, that will be the order and if you have 3 then it will be 12 so, suddenly there is a jump so, if it is only a T So, if it is TD so, you see that I will be having 12 into 2 because the alphabets this the subscript alphabet subscript gives a value of you have to multiply by 2. So, you can always apply this before working out the problem the finding out the symmetry order. So, you know from the very beginning that what is the limit what is the correct number that you have or you have to arrive at. So, let us start with different molecules.

So, let us try to see Cs. Cs is basically of actually let us do first the chiral point group. The chiral point group the numbers are much less. So, chiral point groups is basically what C1 or Cn or Dn or T. So, C1 an example of C1 is basically a molecule containing 1 asymmetric that is a SP3C stereogenic center or what we can call it a chirality center. Remember chiral center that term we do not generally use, but still in colloquial language we still tell about chiral center that means the carbon possessing 4 different loops but in actual reality that should be called a stereogenic center.

However, the stereogenic center can be SP3 type or can be SP2 type the double ones also can show the stereo generosity. So, if you have different rules like say Cl h methyl and then suppose ethyl. So, this does not have this is truly asymmetric as symmetric means just it is dived of Cn and all other improper elements of symmetry but n is greater than 1 because C1 is universal it is present in all molecules. So, that is C1.

Then Cn means you have to assign something says suppose I have got a C2, a C2 molecule what is the C2 molecule? I can type an optically active tartaric acid and that has got a C2 axis and then you have say D suppose we have D2, D2 means what you have a C2 plus 2 C2. So, that is the twist boat the twist boat form. this is a twist what form for to cyclohexane this twist boat form if it is not visible that much I can this is also should be. So, this is the twist port form name in this twist port form you have 1 C2 axis which is going through these carbon suppose this is 1, this is 2, this is 3, this is 4, this is 5 and this is 6.

So, you have an axis going through C2 and C6 and that is the that is the principal axis because you remember that when you have similar fold the C axis where you cannot differentiate based on the number of the fold n then what you have to do you have to find out what is the principal axis the axis which is going through the maximum number of atoms. So, here these C2 is going to C this carbon number 2 and carbon number 6 in addition to this there are 2 other C2s one is this vertical one and the other is going through this C1 C5 middle point and the C3 C4 middle point, but both these are actually remember both these are perpendicular to this principal axis.

So, there is one C2 here and another C2 is basically going through that middle point of C1 C5 and C3 C4 that is another seat. Now, if you want to find out suppose the symmetry number and the symmetry order.

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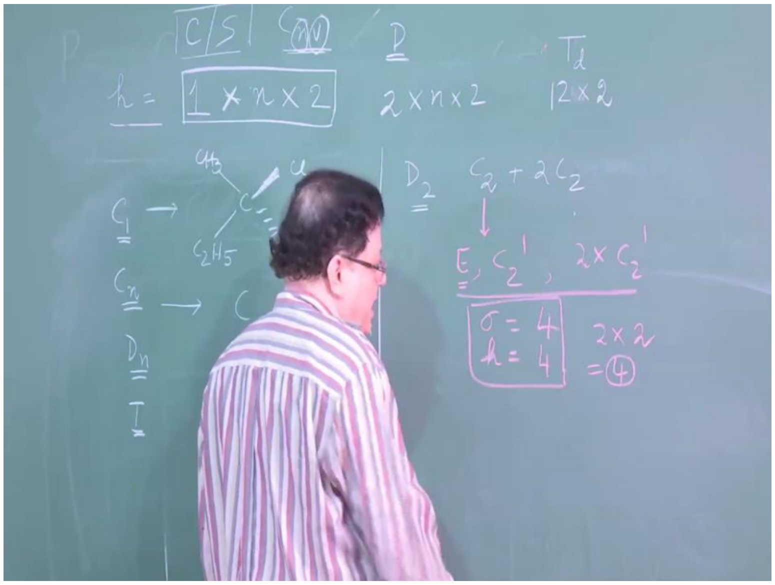

Now, a C2 means what, C2 means if you get if you give full turn that gives you that means C2 2 that gives you the identity operation. So, E is present that is present in every molecule then you have C2 1 that was one operation of 180 degree that gives you another indistinguishable form. So, from the C2 you get E and C2 1 and from this C2 you cannot see the identity operation is only unique it is only one time you can get and the other side basically that you will have from the other C2 you have 2 C2 1 types.

So, that means the symmetry number is basically now 1 2 3 4 and symmetry order because there is no other symmetry element possible. So, that is also 4. Now, if you apply that empirical formula because it is D2 what I said for D you have 2 and for this subscript number integer you would multiply that so, that becomes 4. So, that matches so, you know that I have actually got all the symmetry, symmetry elements must be 4 symmetry elements must match your operation actually.

That is the difference between the symmetry element because if I say C3 is present symmetry element that means the it has got this E it has got C3 1 it has got C3 2, so, these are different operations. So, that is what is included here in sigma as well as in h. Then you have you have this Td molecule let me see whether what other systems I can take T molecule is interesting.

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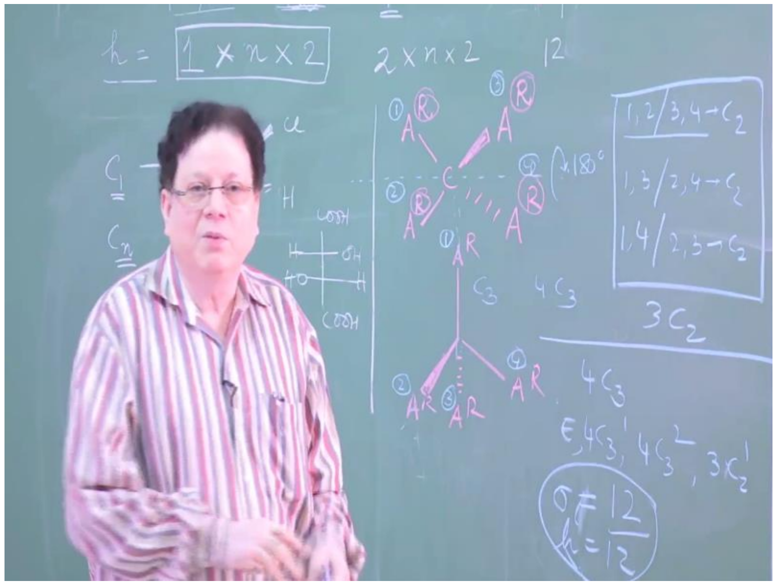

What is the T molecule? Tetrahedral that you have an AR that means, I am talking about carbon which is attached to a group containing stereogenic center. So, that is denoted by E and suppose there are 4 A's present in this molecule and that makes it chiral although these are same groups, but interestingly this molecule is chiral because these A is containing this stereogenic unit stereogenic center. And suppose that is all are in the R configuration. You can have another molecule where all are in the S configuration and there is chiral molecule optically active. There is no plane of symmetry here.

Now, this has got, this is the one which has got this T symmetry for so, I can draw it in this fashion that suppose one AR is on the top then all other AR’s are basically looks like this one will be in the plane like this AR and this AR will be above and this is so, it looks like a pyramidal at the bottom. So, now you see suppose I point out that this is your number one although they are all same. The groups are same chirality and same constitution, but you can number them, number this is suppose number 1 AR, this is number 2, this is number 3 and this is number 4.

So, now, you see that if you have an axis containing this carbon and this, this first AR and then you give a rotation by 120 so, you will get to the same indistinguishable form that means, this will be an axis which is a C3 axis. So, basically what we are saying this carbon and the line joining this A group that means, whatever carbon is here and these carbon if you join this and then that makes it that makes it a C3 axis.

And then and then you have similarly you can have 2 at the top so, you can have another C3 axis 3 at the top you can have another C3 axis and 4 at the top you can have another C3 axis you do not have to bring to the top you can think that I will have the axis between this and that just for better understanding I am trying to I am projecting it in, in such a fashion I am drawing it in such a fashion that you can understand it better.

So, basically now we have 4 C3. So, where are the C2s? Because we know that T symmetry has a C has actually 3 C2s. What are the C2s you can actually from the structure it is better suppose, this is your number 1 A this is number 2, this is number 3 and this is number 4. So, if you have an axis which is bisecting the angle between these A these 2 1 and 2 ARs, obviously, that will bisect the angle between the third and the fourth A group.

So, if you do that, and then give a rotation if you think that this is the axis and then you rotate it by 180 degree, so, you get to the same form same indistinguishable form. So, that is basically that means the axis which is dividing the angle between the number 1 and 2 or 3 and 4 is the same line. So, I can say that 1 2 and 3 4 they are associated by the same line. So, that is 1 C2 axis. So, similarly, you have 1 3 combination and 2 4, so, that gives another C2 and then 1 4 and 2 3, so, that is another C2.

So, these are the 3 C2s that are possible, so, 3 C2, so, what is the, what is the symmetry number here? What is the symmetry number? Symmetry number, remember, the symmetry number of chiral molecules actually are same as the symmetry as the symmetry order because you do not have any improper elements of symmetry. So, you do not have to bring any improper element of symmetry. So, they are they are all same.

So, what will happen now, how to find out the symmetry number because it is 4 C3 that means, you have the identity operation and then you have C3 1. So, how many C3 1s you will have 4 C3 1s and then 4 C3 2 you will have and then you have from the C2 side, you will have 3 C2 1 C2 1 that is 1, 1 180 degree rotation you can give otherwise the next one gives the identity operation. So, that means you have 1 plus 4 5 5 plus 4 9 9 plus 3 12. So, sigma is 12 and h is also 12 if we if we apply the this we have already so, this is this is 12.

So, we are talking about no, no suffix here. So, you have to assign only the value 12, there is no suffix here and we are finding that it is it is 12 if it is Td then it will be 24 remember, because D stands for another multiplication by 2. Let us work out some other have a quick look at some other molecules because we have not dealt with any of the Achiral systems.

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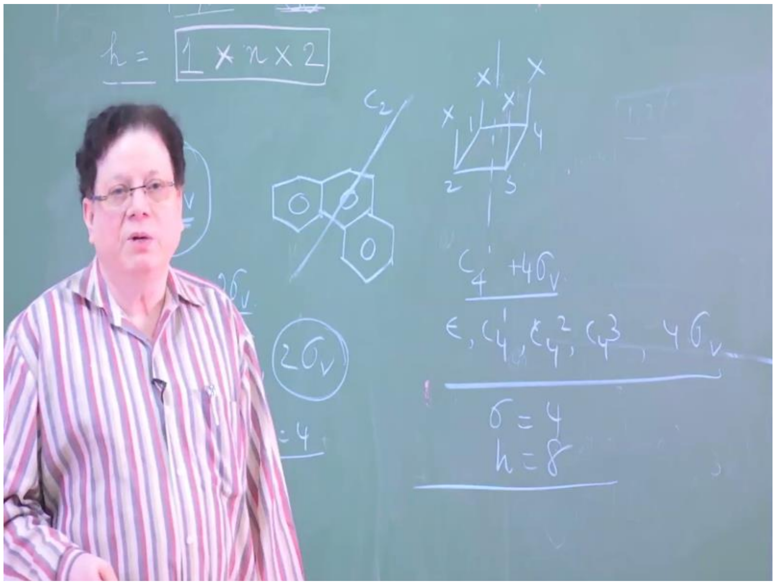

I think we will go to say C2v because it is a problem solving approach. So, we will definitely do many problems, but that is that will be at the end of the lecture series on the stereo CAD or the symmetry and stereochemistry. Once we are through with that, then we will start doing other problems. So, at this point we are only taking some, some examples to clarify that doubt. So, suppose it is C2v, C2v is a molecule like suppose phenanthrene you know what is phenanthrene this is what is phenanthrene now financing has got a C2 axis going through this so, that is your C2 and it has got C2v. So, this axis is basically the in this direction lying in the plane of this benzene ring.

Now, you have that now you have so, this is so, 1 is the plane of the benzene ring and the other is C2v means you have C2 plus 2 sigma v, just a second 2 sigma v. So, you have 1 sigma is basically this and the other is going through the is the perpendicular 1 is going through this the plane you divide it and the other is the plane of the phenanthrene ring this is actually aligned both these planes, remember both these planes are actually belonging a taking this as is going through this axis both these planes that is important point that is why it is v both are sigma v's.

So, now it is, it has got identity opposition C2 1 and 2 sigma v. So, basically now it is see this is Achiral now, there is a difference between the symmetry number and the symmetry order. Now, the symmetry number is 2 because this is based only on C axis and now, this the h is basically so, this is sigma is equal to 2 h is equal to 4, because now we have to add these two 2 plus 2 that is 4. We will have a quick, quick look at other systems like C4v. What is C4v? C4v is this is that was you take a cyclobutane and having all C's that being tetra substitution at each carbon, but all are in the C stereochemistry.

So, it has got now what is that, it has got a C4 axis I can see this and in addition to that, it has got 4 sigma v's. What are these 4 sigma v's? One is going through. So, this is 1 this is 2 this is 3 this is 4. So, 1 is going through 1 middle of the 1 4 and 2 3 another is going through middle of 1 2 and 3 4, another is the other said the diagonals 1 3 the planes which are going through 1 and 3 and the plane which are going through which is going through 2 and 4. So, that is the 4 sigma v's.

So, here the symmetry number will be identity C4 1, C4 2 remember C4 can have up to 3 because they have the same 90 degree rotation, so, 190 then 180 then 270 and finally, you return to the original position and then 4 sigma v. So, that makes it that makes it that symmetry number is equal to 4 and order is equal to 8. So, this is this is some of the examples that we have. Remember there are some tricky examples which we are not doing right now. But as I said once the class ends, this the lecture series on Stereochemistry Structure and Stereochemistry and Symmetry, then we will go to, then we will again come back and solve some other complicated problems. Thank you very much.