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

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Lecture No. 06

Concept Clearing Session on Achiral Point Groups

Welcome back, will continue from where we ended last time that is we are doing some clarifications on the point group the symmetry number and the order. So, we have seen that first of all molecules are divided into chiral and achiral, chiral point group system and then achiral point group system. Achiral point group you can divide it into two, one is having Sn and the other is where n is even and the other is different types of combinations like Cnv, Cnh, Dnd and whatever this Dh and that Td so, we have done the Sn, now let us take the suppose the sub-group 2.

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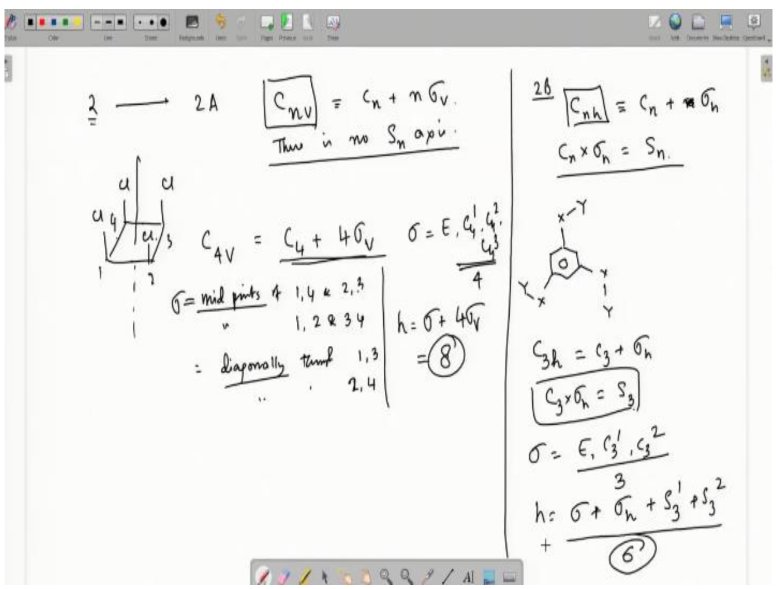

That sub-group and in the 2 this 2A group, 2A group is nothing but Cnv now, what is Cnv, Cnv is basically you have Cn plus n sigma v actually there is no remember there is no Sn axis present in this system, Cnv does not have any Sn axis. On the other hand, in the 2B system, 2B is Cnh so that is equal to Cn plus n now plus only sigma h only sigma h. Now, you know Cn and then sigma h combination gives rise to Sn basically you are rotating by using the C and then taking the perpendicular plane taking a mid-image that gives a nothing but an Sn axis.

So, Cn into sigma h is Sn, so there is Sn in Cnh but there is no Sn in Cnv. Now, how to calculate the order and all those things order and the number, number is easier one because it only involves C. So, let us see take an example say all C's tetrachloroethylene. Now this has got this belongs to C4 v because it has got a C4 axis that is visible it has got C4 axis and then it has got how many it has got sigma v so sigma v how many, one is basically going through the mid-point of this and that vertical plane, another is going through the mid-point of this and that suppose 1, 2, 3, 4 so, one is going through the mid-point sigma basically one is going through midpoint, midpoints of 1, 4 and 2, 3.

Similarly, another will be midpoints of 1, 2 and 3, 4 and then diagonal another is the diagonal going diagonally through but vertical through 1, 3 is one possibility, another is 1, another is 2 and 4 so, that gives you 4 sigma v because there is no Sn, so it is now easy to write the what is the symmetry number that is identity element then C4 1, C4 2 and C4 3 so that is 4 and then what is h, h is the order that is sigma plus 4 sigma v so that makes it 8.

So, it is very easy because there is no Sn, things become little complicated when you have Sn so, let us sort this out. So, Cnh take a molecule a benzene molecule x, y, x, y, x, y so, that is this is a molecule which belongs to Cnh it has got a C3 you can see very easily that it has got a C3 going perpendicular to the benzene ring so, it is actually nothing but it is a C3h molecule C3h molecule that means it has got a C3 plus a sigma h so, since C3 into sigma h is equal to S3 so it has got an S3.

So, now what will happen to the symmetry number that means identity C3 1, C3 2 so that is 3 and then order sigma plus, sigma h is 1 then you have this S3 so you have to consider now successive operations of S3 so S3 1 and S3 2 so, that makes it 6 so that is equal to h. So, let us go to another one little bit more elaborate let us see we take the we take a cyclohexane, we take a benzene again but all carbons are substituted.

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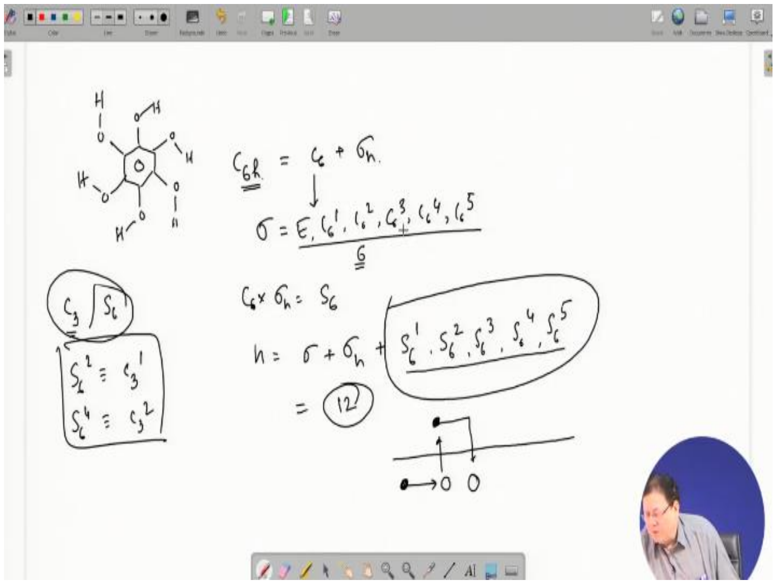

Like OH, H in this direction, OH in this direction, OH in this direction, H, so this is the hexahydroxy benzene and it has got C6 you can see, C6 so it actually and then h sigma a nothing else is there so, this will be 6C, 6h system so, that means it has got a C6 plus s sigma h now, C 6 will give the sigma that will be identity and then C6 1, C6 2, C6 3, C6 4 and C6 5 so, that means it has got 6, symmetry number is 6.

Now, because C6 into sigma h equal to S6 so it has got S6 now let us see how many successive operations of S6, unique operations of S6 are possible. So, one is so now let us see h is equal to sigma plus one sigma h is already there so that makes it 7 plus S6 1, then S6 2, then S6 3, then S6 4, then S6 5 now here unlike the last time. Last time means when we have seen that a molecule having C3 and S6 then what happens this is important if a molecule has C3 and S6, then S6 2 is equivalent to C3 1 and S6 4 is equivalent to C3 2.

But, it is not true when they both the when you have the fold the number n fold that means the fold number is same for S and C so that is no longer true if, you have C6 and S6. So, for C6 and S6 all these are unique operations so that makes it one this is 6, 7, 8, 9, 10, 11, 12 so that means it is equal to 12 so you understood that important thing is if you have this type of combination C3, S6 or C4 S8 then some of the successive operations of S coincides with the successive operations of C ,but here if the folds are same then that does not happen.

You can prove this by drawing that whatever I have shown that systematically you can start with a molecule and then take rotate and get a form then take a mirror image. So, you go to the original because, it is S axis so you continue to do that and if you do that you will find out that which are the ones that matches with the C axis for C6 and S6 you will never find that C6 and S6 you will not find all the S6 successive operations are distinct and unique so now let us go to the other sub-group.

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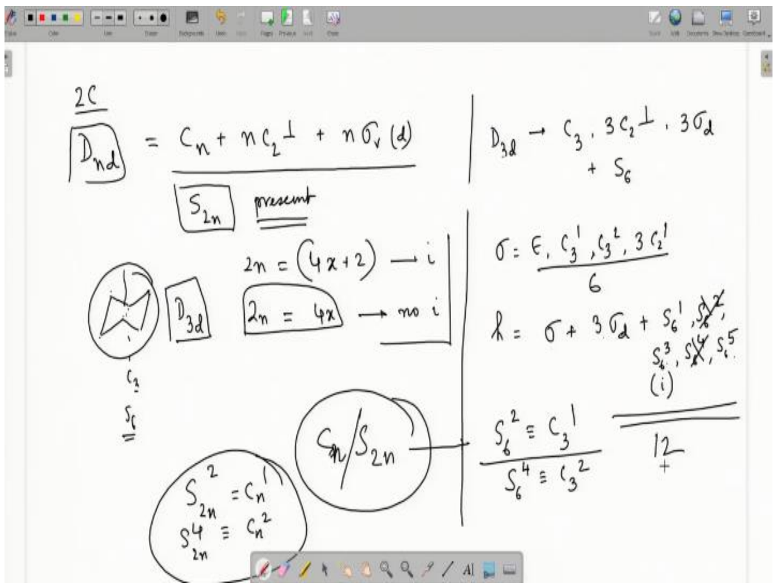

That is other sub-group is 2C that means Dd so D nd means again is basically Cn plus Cn plus n C2 perpendicular plus n sigma you can write v actually they are diagonal also and then that is that is all that is Dnd. In nd, that here in the Dnd system you have the existence of S2 n so S2 n is present that is the scenario like if you have a system like this cyclohexane you know that it has got a C3 but in addition it has got up down, up down, up down that type of system so it will have C3 in addition you will have S6 because, up down, up down this type of system what will happen once you give a twist where up becomes up carbon occupies a position which was earlier occupied by the down carbon and it happens to every position then the mirror image will bring it to the original.

So, what will happen that like in cyclohexane you have C3 but you also have S6 as I say explain so this is actually cyclohexane belongs to a group which is point group which is D3d so Dnd we are taking about so in general whenever you have Dnd system Cn axis is there so you will have in addition S2 n axis present.

Now, let us take a particular molecule or again the same thing some of the successive operations that if this 2n belongs to that 4x plus 2 series where x equal to 0, 1, 2, excetra then you have an i and if n can be expressed in terms of 4x then no i, it is very similar to the earlier when we discuss the point group of Sn. So, now example, example is suppose let us see take an example D2 say take a system D3d we do not have much time we will just take some specific examples.

So, for a D3d system you have C3, you have 3 C2 perpendicular, you have 3 sigma, sigma d and in addition you have S2 n that means S6 so now you have to perform the you have to first see what is sigma, sigma is basically C3 that means you have 3 S sigma is 3, 3 plus 3 C2, 3 C2 so that means sigma is 6 again I write sigma is basically just elaborate C identity C3 1, C3 2, then 3 C2 1 so that makes it 6 question is what is h, h is equal to sigma plus now you already have 3 sigma d that is there.

Now, you have to come back to the consider the S6 now S6 you can write as S6 1, S6 2 write everything whatever is means possible in successive operations 4 S6 5. So, here I already told you that in case these two do not match S2 n so here it is a system which S Cn S 2 n for this system what happens here this S6 2, S6 2 is equivalent to C3 1 I told you already and then S6 4 is equivalent to C3 2 so, you can have a generalized rule like that S6 2 that means you can have S2n 2 is equal to Cn 1 and then S2n 4 is equal to Cn 2 so that you can say.

So, basically you are crossing out this and that and this is by the way is i. because as I said if 2n is equal to 4x plus 2 because it is 6 so this is also equivalent to i. So number of the order is basically 6 plus 3, 9, 10, 11, 12 so that becomes 12 so that is the Dd. Then we have other molecules I think there is you can we I have shown that how S 6 2 becomes equal to C3 1 or S6 4 becomes equal to C3 4.

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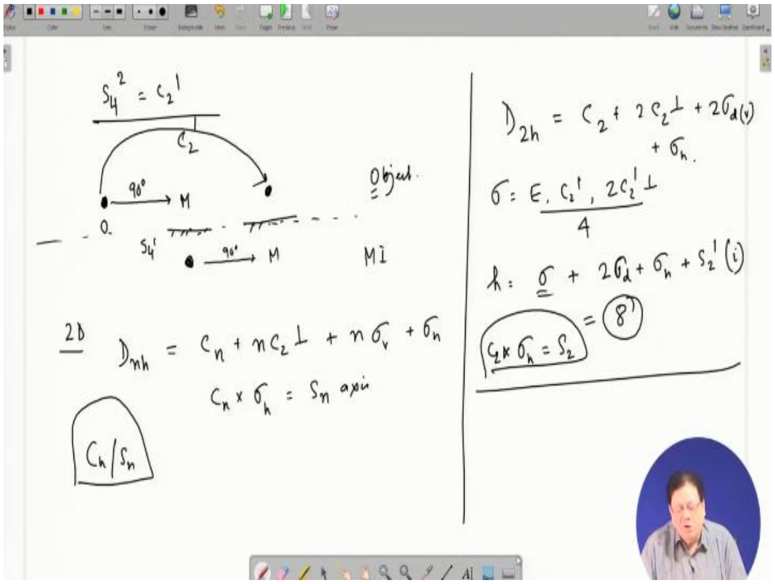

Similarly you can also prove, prove that S4 2 is nothing but equals to C2 1 a quick revisit of what we do here if that question comes what we do is basically we start with the original molecule suppose this is the original molecule so you rotate it, it gives it goes to the mirror image as I said in order to rotate means rotate by 90 degree so you get the mirror image and then you take the image of that plaster through a mirror you get the original so that is your S4 1 and then you again rotate it by 90 and if you rotate it by ninety you go to the again to the mirror image by the same analogy like this and then take the image and you go to the original.

So, now you see your original is on the side of the side before mirror image position so there are two sides this is the mirror image side and this is the original side the object side you can say the object side. So, what will happen now you can go from this to this simply by rotation of 290 degrees that means you have a C2 operation this is the C2 1 so that makes that tells you that S4 2 is equal to C2 1. So, you can have different increase the fold and try to do this exercise and then prove the analogy between C2 and the S axis.

Now, let us take the sub groups in 2D what is 2D, 2D is nothing but the Dnh, Dnh means Cn plus n C2 perpendicular plus n sigma v or you can say d the same thing and then plus sigma h so in addition to that you have a sigma h but presence of this sigma h makes the makes it mandatory that there is Sn axis. So, this is a system Cn Sn that is not the type of n S 2 n this Cn Sn type of system.

So, let us quickly have a particular say D2h say D2h system, what is D2h so that means C2, C 2, 2 sigma d and then these are vertical so you can say v and then plus sigma h so the symmetry number is equal to identity C2 1 then 2 C2 1 which are perpendicular so that makes it 4 what about the symmetry what is the order of the point group that means h is equal to sigma plus 2 sigma d plus sigma h so one is missing.

Now, if you have as I said if you have C2 and sigma h then that makes it S2 so you have S2, S2 has only one type of only one operation S2 1, S2 2 means it is nothing but Cn n, C2 2 so that means it is again the identity operation so that matches with the C2 2 or matches with the identity operation so you should not you do not consider that so only S2 1, S2 1 is nothing but again i, it is inversion center or this center of symmety.

So, now that makes it 4 plus 4 that is 8 so that is how to calculate the different if the point group is given then how to calculate the symmetry number and the element so only thing that makes it little bit complicated is the you have to always consider whether Sn axis is present or not that is the important one I said I can again just if time permits.

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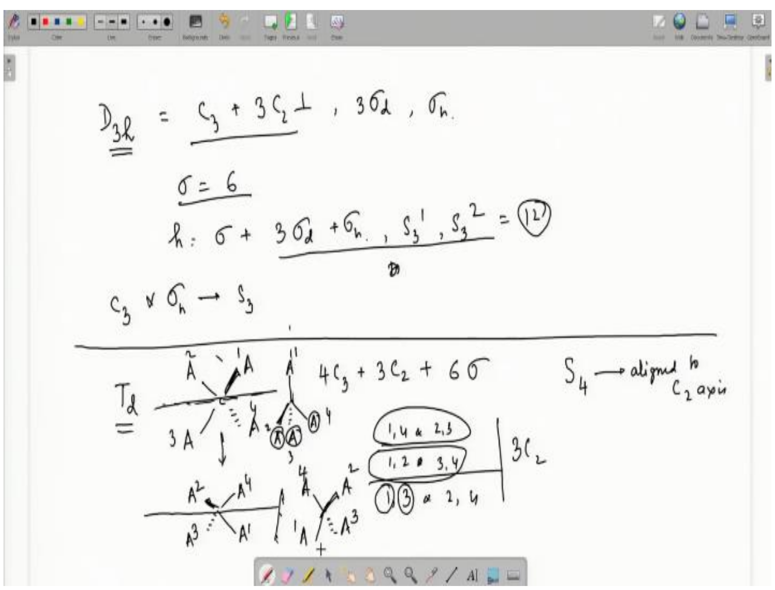

Say D3h, D3h means C3, 3 C2 perpendicular 3 sigma d and S sigma h. So, let us quickly we know that the symmetry number will be 3 plus 3 that will be 6 and symmetry and the order will be sigma plus 3 sigma d is already there plus sigma h is there now sigma h and C3 combination gives rise to S3 so what you have is here S3 1 and S3 2 o that means that makes it 12 total h is equal to 12.

So, I think that clears the point so if you have these type of groupings like what I did and then try to figure out at that point that whether S axis is present or not so again I summarize that there is a class which is Sn axis n is even this is for achiral point groups and then there is a class where you have this Cnh, Cnv, Dnd, Dnh and the tetrahedral.

So, what you do you when you have these any class of that belonging to the class two type, then you have to be careful from the very beginning that whether Sn axis is present or not if, it is not present only in D if you have noticed it, it is not present in Dnv, Dnv it is not present but in others it is present Dnv does not Cnv, Cnv does not have any Sn axis all others have Sn axis.

But again the considering the fold of the Sn axis you have to be careful for D n d what happens the fold of the C axis is doubled in case of S axis like in cyclohexane and then in some other in many cases the successive operations of S axis becomes equal to the identical with the successive operations of C axis so that you have to be careful that happens only when you have a combination of Cn and S2 n present then you have this similarity or identity of the successive operation of C versus successive operations of S.

So, one more is remaining I think that is what is the tetrahedral one so, tetrahedral achiral point group is Td tetrahedral that means it is a tetrahedral molecule like a carbon attached to four groups say 4 A's, so, it has got what 4 C3, 3 C2 plus 6 sigma so, if that be the case now where are these C3, the C3 are basically you have to look it into this form that 1 A and then you can write it in this form so, these are the A's.

So, here AC 3 is basically aligned with this carbon and the top e so, that is 1 C 3 so you can have you can bring the other one this is A1, this is A2, this is A3, 4 so you bring a 4 at the top and view it in the same similar way so you will get basically each for each CA bond you get 1 C3 axis which is aligned to that bond so, that there will be 4 C3 axis, there will be 3 C2 axis, 3 C2 you can get from here suppose this is your 1, this is your 2, this is your 3, this is your 4 so you take an axis like this and you give a 180 degree rotation out of plane rotation.

So, the A will 2 will come here 3 will go there and this A will replace will come to the position of A4 and A4 will come to the position of A1 but they are their appearance is the same so that is the C2 so, C2 will go basically what C2 will involve 1 and 4 and 2 and 3 so that is S axis then you have 1 and 2 and you have 3 and 4 so then you have so, these 2 are there C2 and you have one more that is 1 and 3 and 2 and 4.

So, going through the actually this axis is going through the middle of the angle bisecting the angle between the A's the A 's which are basically attached to these specific carbons so, that gives your 3 C2 and there are this 6 sigma however, apart from these it has got S axis also it has got S axis and this S axis is S4 axis what is S4, S4 is that you take it take this molecule rotate this molecule along this S4 axis by the way is aligned to C2 axis.

So, what happens here that if you give it a 90-degree rotation, then this will be beta and that will be alpha, so this will be A2 so we are talking about the 90-degree rotation if we look from this side clockwise so A2 will go up and A3 will go down and now A4, A1 will come into plane here and A4 will also come into the plane, this one. Now, this is your axis so you put the mirror here and if you put the mirror, then it again looks like the form what was originally depicted for the molecule. So, this is the scenario all is only they look same always remember this fact they look the same but, the same atom is not there in the different forms.

Like, here earlier on the left side it was A2 now it is A4, on the right side earlier it was A2 now it is A4, earlier it was A1 here now you look this is A2 and earlier if this was A3 here now it is A1 and here A3. So, the basically it appears the same but it is not having the same atoms at the identical positions that is what is very important in understanding the symmetry operation, the symmetry operation that is very important issue here so, let us I think there let us do one more just a general problem.

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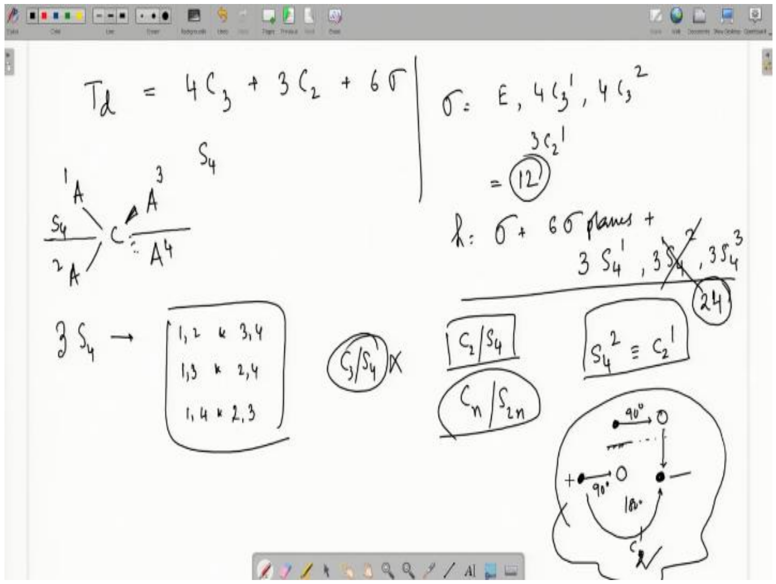

So, let us do this symmetry order and symmetry number determination for Td. Again just remember Td is basically that having 4 C3, 3 C2 and 6 sigma in addition as I told you it has got S4 axis as I again I write that molecule C A4, A, A so, one now there how many S4's are there that is important this is what is S4 that means you give it a turn by 90 degree and then place a mirror perpendicular to that axis so, one will be suppose this is 1, this is 2, this is 3, this is 4, so 1 S4 will go through the will bisect the angle between 1, 2 and 3, 4 another one will bisect the angle between 1, 3 and 2, 4 and third one will bisect between 1, 4 and 2, 3 so, these are three possible ones.

So, you have 1, 2; 1, 3; 1, 4 no other possibility because the others are already taken care of by the right side. So, there are 3 S4's then so your sigma that means symmetry number will be 4 will be identity, operation and then 4 C3 1, 4 C3 2 and then you have 3 C2 1 so that makes it 1, 5, 9, 12 so sigma is equal to 12 so what about the h, h will be your sigma plus 6 sigma plane plus S4 how many S4 you have, 3 S4.

Now, you have to do successive operations on S4 so 3 S4 1, 3 S4 now you have to have 3 S4 2, 3 S4 2 let us proceed just let me see try to find out which whether something is matching with the one with the C axis and 3S 43. Now, this is a system which is having C2 S4 remember the C axis is the one which is aligned to the 4 not the C 3. So, it is not a C3 S4 system means not the when I talk about this that means they are aligned with each other that is not it is aligned to Ct C4 so that means it is the same type of story Cnh 2 n.

So, if you have this type of system then some of the operations of S axis are nothing but operations done through A C axis so, what is that operation actually the S4 2 is identical to your C2 1 is identical to C2 1, S4 2 is identical to C2 1 you can do this again by the same token that if this is the original then the mirror image this is the mirror image, then take the 1 you get the original then again 90 degree rotation, this is 90 degree rotation so you get the original and then you take the mirror image, mirror image original and you take this you get to the original.

So, that is 180 degree rotation so that means from here to here you can have any way you have a C2 operation from here to there and that is C2 1 so that means S4 2 is equal to C2 1 so basically you have to cross this out. If you cross this out then you have 12, 6, 18 3, 21, 3, 24 so, h is equal to 24. I think that should make it clear you can actually this is one way of as I said this is one way of understanding this similarity between some of the S axis operation versus the C axis operation.

So, we have done the, we have clarified this symmetry point group for different systems and then we have done how to calculate the different parameters, this symmetry number and the symmetry order. These are important as I told you symmetry is very important in understanding the molecular orbitals of designing the molecular orbitals of the system as well as understanding the spectral properties and the third one is what we are interested is basically understanding the a chirality of a molecule that decides whether a chirality is present or not.

So, I think that ends up this type of practice session. We will do some more practice later on, on the tricyclic cyclohexane system which is that parahydroanthocyanin but that is at the appropriate time, once we go through the next topic which is basically determination of absolute configuration and conformation by spectroscopic technique and the technique that will be used is not a is basically what is called circular CD spectroscopy circular dichroism spectroscopy or it is also called ORD optical rotation, Optical Rotatory Dispersion.

So, we will talk about these in the next lecture and once we are through with that, that ORD and CD, then we will do again problems and at that time bicyclic systems or tricyclic systems or even pentacyclic systems are going to come. So, that will cover that aspect the problem solving session on the perhydrophene or parahydra anthracene. Thank you.