Chemical Applications of Symmetry and Group Theory
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Lecture - 09

Hello, welcome to the day 4 of our second week of this lecture series. I hope all of you are doing well. We have been trying to figure out whether we can find out the point groups of different molecular structure. So, in the last class we looked at the structures of hydrogen peroxides and we saw that for hydrogen peroxide I can have two different structures, one is the plane axis when we consider the planar configuration.

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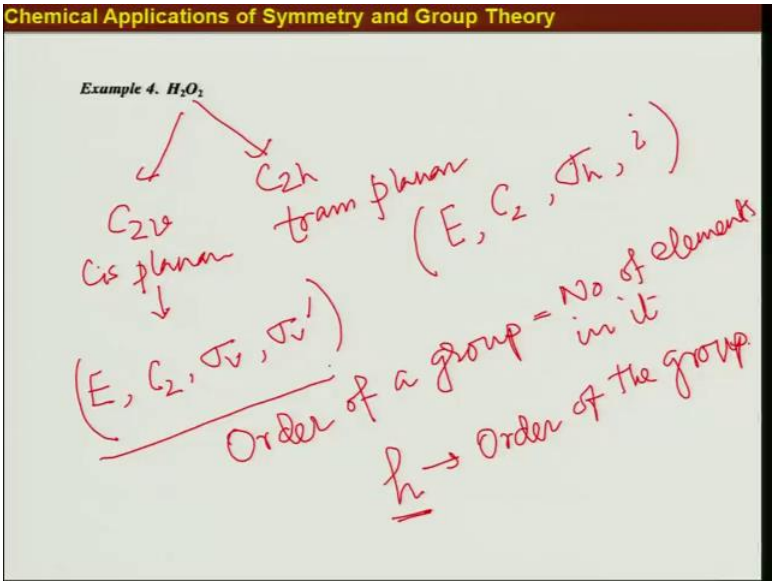

So, we got C 2 V point group for Cis planar while we got C 2 h point group for trans planar right. So, I guess you still remember what were the symmetry operations? In case you have not then, let us again look at those. So, for C 2 V that we got for planar Cis planar configuration of H 2 O 2 we got the following symmetry operations. So, we had E, we got C 2, we got 2 sigma vs which are differentiated as sigma V sigma V prime while. So, this is a group and for trans planar configuration we got identity, we got C 2, we got sigma h and we got the inversion symmetry.

Now, if I ask you can you tell me what are the orders of these groups? Both of them have four elements. In a group there are four elements and each element is a symmetry

operation. So, the answer is 4 for both for them. So, order we have mentioned it earlier of a group, this equals to the number of elements in it. So, in case of symmetry point groups also, all the symmetry operations when you have found all the symmetry operations belonging to that particular group. So, you form a close group and the number of such symmetry operations including identity will give you the order of the group.

And in many cases you will be using notation called h; h stands for order of the group. In some books you will find out that point group for order, but it does not matter. We mostly will use this term h to define the order of the group. Now one more thing have you noticed about this particular groups? Some kind of relations that you can figure out which exists among the symmetry operations. So, we should think a little bit about it. Later on we will come back to this topic again. So, what we will do today? We will continue looking at some more molecules, so molecular structures and we find out their point group symmetries systematically. You remember we had shown nice future which is a systematic procedure which describes systematic procedure to find out the point group of any given molecular structure, when you know all the symmetry operations for that particular molecular structure. So, we will use the same scheme and try to find out point groups of certain molecules. We will go from simpler to little harder problems.

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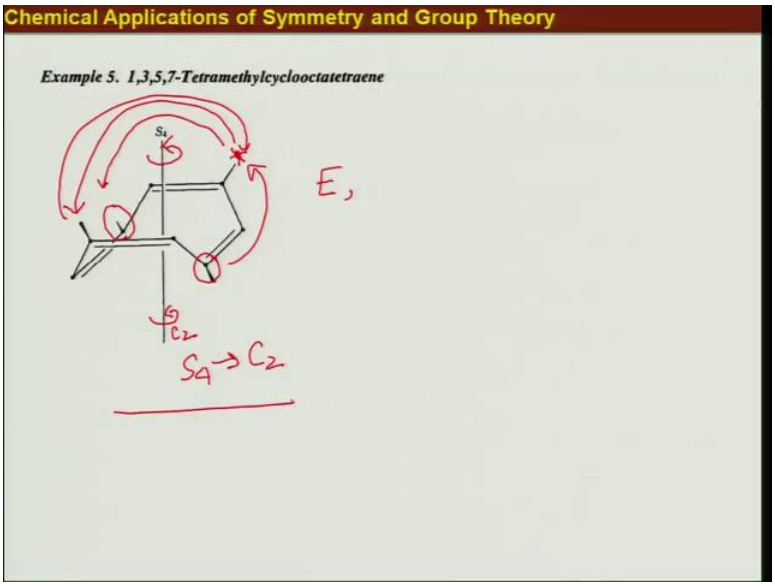

So, index molecule that we will look at is on your screen. So, this is 1 3 5 7 Tetramethylcyclooctatetraene the structure is giving here. So, for this molecule you what

are the symmetry elements you can find out? The symmetry elements or if you say here directly symmetry operations identity is into by default is present there. What do the other element that you can think of? Does it have any proper axis of symmetry, proper axis of rotation? We do not really see proper axis of rotation, which is not consequence of something else. By something else, what I mean is an improper axis of symmetry which is indicated here. So rotation about this axis by 90 degree followed, by a reflection perpendicular to this axis. We give you an indistinguishable structure. You can just verify that one.

So, if I put a star on this particular ethyl group then, 90 degree will take it to somewhere here right. So, from here to somewhere there and then when you invert it, so the one the carbon which was protruding outside, it will be going in below the plane of the paper. So, that will actually you know come here while the guy sitting here will now move up here. So, ultimately you will get back an indistinguishable structure. So, there is a valid S 4. Now if there is an S 4 we have learned in the one of the previous classes that for even order improper axis of symmetry when, N is greater than 2. In that case one always will have a proper axis of symmetry which is like C N by 2. So, here we have S 4. So, S 4 will automatically give you C 2. So, C 2 must be present. So, if you again think about this particular axis is S 4, if you imagine C 2 axis there you will see that really there exists a C 2 above the same axis.

So, you know you can figure it out like this portion which I have made this given this star symbol. So, this will come over to this place and this guy will go here. So, ultimately you are getting the indistinguishable structure. So, there exists a C 2, but this C 2 is not proper axis of symmetry. A principle axis of symmetry by its own merit, but this is consequence of having even order improper axis of symmetry. So, by rule you know, we had the step 1 2 and 3. So, if you remember that step 3 that will looked at. So, found that is it like S 4 is or only S N axis of even order is an only symmetry axis that is possible? Yes. So, I can generate C 2 from S 4 itself. So, this point group, you can easily now figure out for this particular molecule.

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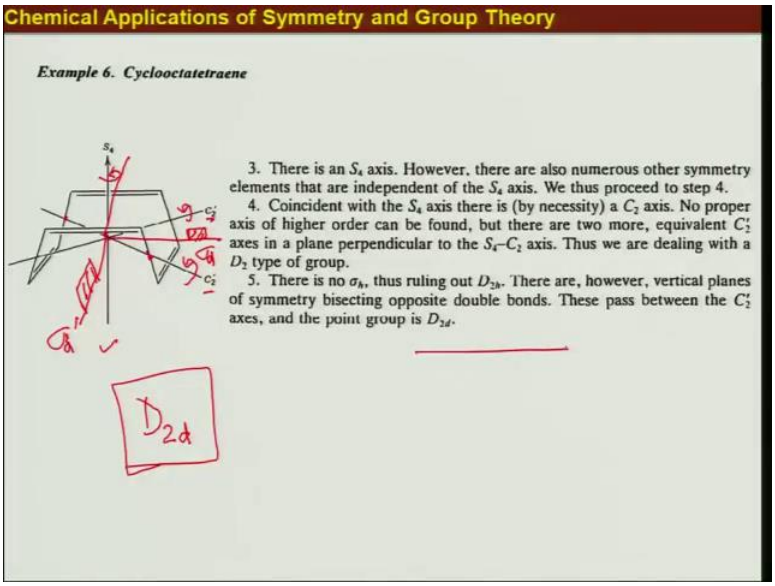

So, let us move on to another molecule, which is Cyclooctatetraene. Now you see in the previous example as well as this current example it is very vital to know the structure and that is why I you know one of this previous classes I mentioned that in order to find out the point group. First thing you have to do; you have to find out the structure of the molecule or the shape of the molecule. For that you can use this you know the (Refer Time: 09:00) structure and apply (Refer Time: 09:02) theory and find out the structure and the shape, then only you can actually visualize the symmetry operations that may exist in those molecular structure. So, here like when I look at this Cyclooctatetraene, you need to know that this is a 3 dimensional structure like what is shown on your screen. So, it is like a boat right. So, the Cyclooctatetraene also it has an alternative double bounds.

Now, if you look at this structure, what you have here just like the previous case you have an S 4, but here other than S 4 there are other symmetry elements. So, you can see that we have pointed out here. Here is one axis, which joints this point and this point. This is C 2 axis so if you rotate 120 degree you will get back the indistinguishable structure and so is this axis. So, you have two C 2s and this C 2 is perpendicular to this axis which is S 4 and; obviously, it will have C 2 axis as well coinciding on the same axis. So, you essentially have now C 2 and two perpendicular C 2 primes. So, this molecule definitely belongs to t type of point group right. So, without worrying about

anything I can write it is D and here the principle axis of symmetry, I have because it is not the S, which is only present here. So, other than S also are there.

So, I have a C 2 and two perpendicular C 2s to this original C 2 axis. So, it belongs to D and since the principle axis has an order 2 because C 2 means the order of rotation is 2. So, immediately you can write up to D 2. Now then you have to ask the next question that whether there is a sigma h? So, now, looking at this molecule do a C any plane which is perpendicular to this C 2 or S 4 axis that can give you an indistinguishable structure? And answer an obvious yes no right. So, I cannot really have this reflection symmetry which is based on the plane perpendicular to C 2 axis. So, there is no sigma h, but there are sigma Ds. So, the moment I know that there are sigma ds I have to find out; how many sigma ds? So, it demands that I should have 2 sigma ds, and then I can call this point group as D 2 d.

So, let us find out. So, I have this 2 C 2 prime set here and here and the definition of a sigma D that is for a sigma plane to be called sigma D, that plane has to bisect the and Dihedral angle formed by the principle axis and the 2 perpendicular C 2s or you can say that it can also you know bisect this C 2 prime the angle created by 2 C 2 prime axis. So, I can have a plane. So, if I can draw the plane symbol like this. So, one plane will be here and another plane will be on this plane. So, if I can draw the plane like this. So, I have 2 sigma Ds. So, I write sigma D and sigma d prime. So, I have 2 sigma ds. So, now, my point group is complete. So, this molecule belongs to point D 2 d. So, you have everything explicitly written here also. So, you can go through this one. So that you can understand it better.

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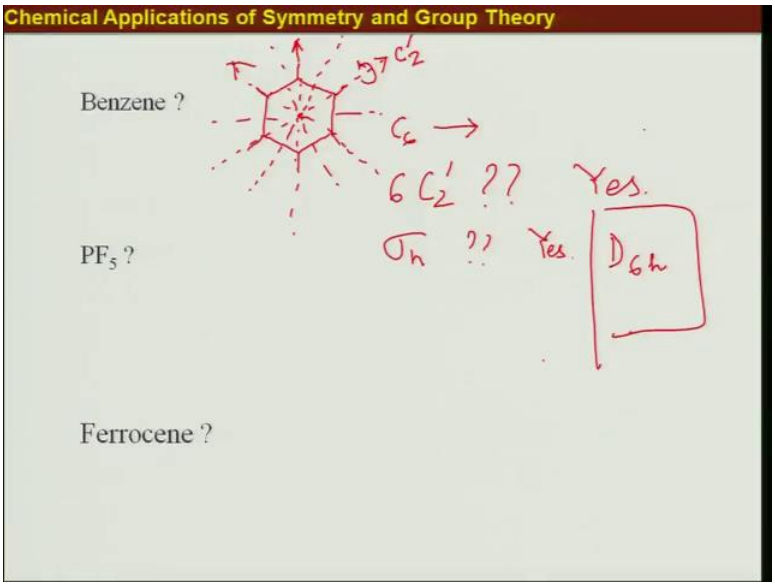

So, let us move on to some other molecules. Benzene we have been showing you the benzene models and this is probably one of the simplest thing that you know. So, the benzene we have already seen that it has a principle axis of symmetry, which is you know perpendicular to the plane of this screen. So, there are you know hydrogen atoms. I am not drawing the Pi cloud here. So, assume that Pi cloud is there that is in symmetry. So, it should be implied. So, now, you have along you know, if I can imagine an axis which is passing through this point and perpendicular to this plane of the molecule then that is my C 6 axis right and I do not have any other C 6 axis fine. So, C 6 is my principle axis of symmetry. So, proper rotation is there and; obviously, for this molecule I do not have to care about possibility of any special groups because it is not that on this you know sigma, S there or only I is there is not linear molecule and since I can see that you know C 6 is there. So, it can generate lot of other symmetry elements. I can see lot of planes there, lot of perpendicular C 2 is there. So, they have many other symmetry operations.

So, we directly go to state 4 and 5. So, in order to go to step 4 and 5, what we have to do? We have to ask a question. Are there 6 C 2s perpendicular to this C 6? So, the question we ask is 6 C 2 primes let us see. So, I can you know imagine an axis here. So, this is very very obvious to ask right. So, if I give a 180 degree I get the equivalent structure. So, this is 1 C 2 prime because this is perpendicular my C 6. Similarly I can add this two opposite hydrogen atoms. So, already I got 3 C 2 primes. Now similar to

this C 2s, there are other C 2s right. So, like this, like this and like this. So, I got my 6 C 2s. So, the answer is yes. So, automatically my point group will be D 6. I had not completed yet, but it will be D 6 followed by something either h or d or nothing. Let us figure that out.

So, now the following question will be is there a sigma h? And answer is pretty obvious because this molecule is planar. So, you know and your principle axis of symmetry is perpendicular to that molecular plane. So, the molecular plane what a planar molecule always host up between a planes of symmetry. So, this kind of symmetry is perpendicular to the principle axis of symmetry C 6 hence I have sigma h. So, if that question is ask sigma h. So, the answer is again yes. So, ultimately my point group is D 6 h.

So, that is very easy. Now you can see that there are lot of symmetry elements present there and then there will be lot of symmetry operations generated from that. We can now find out what is a point group for a given molecular structure and in many cases we do not have to even go and find out all the symmetry operations because now we have learned a little bit that what are the main things that we should looked at in order to find out what is the point group. So, that is why I did not look at any other possibilities, but you can have a quick look at this structure again for benzene and you can see there is an inversion centre right. You start from any hydrogen passed through the origin the centre point of the benzene molecule, go to the other direction the same distance, you will find identical hydrogen there. So, there is an I. So, there will be improper axis of symmetries there will be a many other sigma planes which are not in the molecular plane, but perpendicular of the molecular plane. So, there will be 6 sigma planes there. So, there are so many other symmetry operations.

Now, there will be a question that if someone tells me a point group. Can I you know find out what are the symmetry operations that this particular group can have? The answer is yes; obviously, yes. So, there are techniques by which you can find out. So, which are you know I will talk about in the following week. So, you will remember that we will be discussing about the possibility of finding out the symmetry operations from the point group symbol. So, one thing I forgot to tell you, I should have this rotations that we are using to symbolize a particular point group like C 2 V, C 2 S, D 2 S, 2 D

whatever these rotations are called (Refer Time: 19:43) rotation. So, that is for your information.

So, let us move on to other some other molecules again PF 5 that must be now by now very very easy for you right PF 5 what will be structure? You know first lecture you can think of is triangle by parameter. So, let me erase the rest of the part. So, PF 5 will have a structure something like this.

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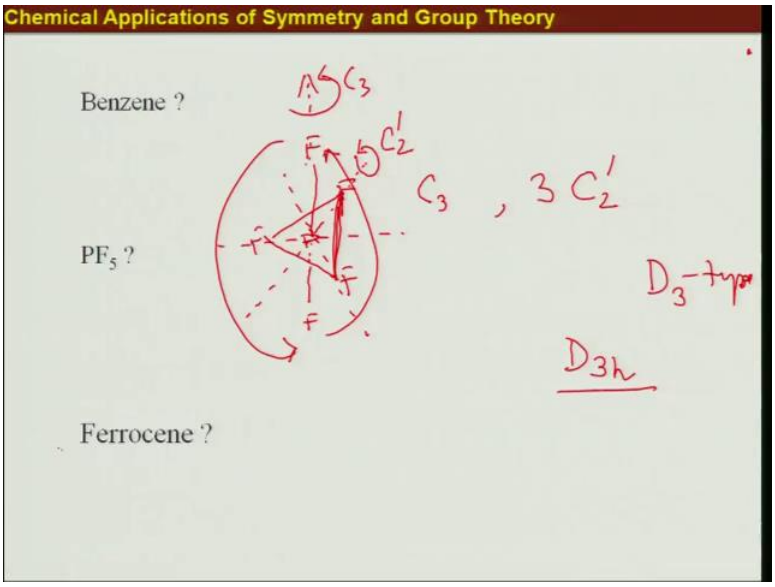

So, if we call and there will be one fluorine and in axial direction there will be one fluorine, while here there will be one more fluorine and prosperous will be sitting here. So, now, what are the symmetry operations first? Like, we will look at the principle axis of symmetry. What is the principle axis of symmetry? We can see for every 120 degree rotation I can get an equivalent structure. So, there is C 3 right.

Now, next question to be asked is; is there any perpendicular C two? So, what will be the answer? Answer is easy right. So, I can see one C 2 here because this 3 x in the equatorial plane will form as if an equilateral triangle. So, you start from one tip of the equilateral triangle and go till the mid of the base, you get an axis which is nothing, but a C 2 right. So, this is one C 2 prime, prime because it is perpendicular to the principle axis of symmetry. So, principle axis of symmetry is along this as we wrote already C 3. So, since I have started with one tip of the equilateral triangle and got you know extend it to the base and got my C 2 prime. So, I can similarly find other C 2 primes, if I start from

other 2 tips and raise to the respective basis right. So, similarly I get 1 C 2 here, another C 2 here. So, I got 3 perpendicular C 2s that is C 2 primes. So, my point groups belongs D type that must you know and it will be also D 3 type.

Now, is there is sigma h? Yes this equatorial plane act as a mirror plane right. So, the top fluorine will be reflected here and this will go here. So, I have a mirror plane which is in the molecular plane and perpendicular to the principle axis of symmetry. So, I have the point group right now, which is D 3 h. That was easy right. Now you will see how important is to know the structure in this and even in some of the following examples.

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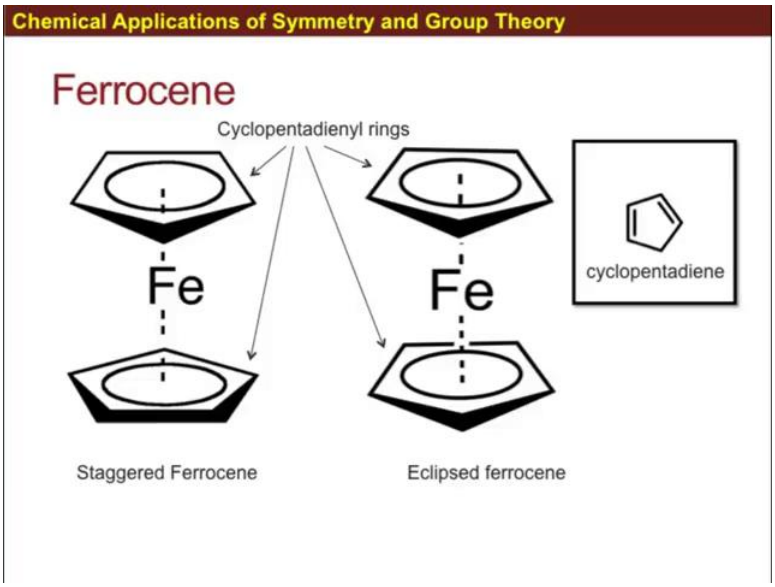

So, we are going to talk about Ferrocene. Ferrocene is he have an iron and then 2 cycle Cyclopentyl groups. So, how it will look like? So, it depends right. So, 2 Cyclopentane rings (Refer Time: 23:26) the iron in a center. Now this 2 Cyclopentane they can rotate freely. So, they can have an eclipse configuration and they can have a staggered confirmation. So, if I take this Ferrocene molecule and look from the top and if the molecule is in eclipse confirmation.

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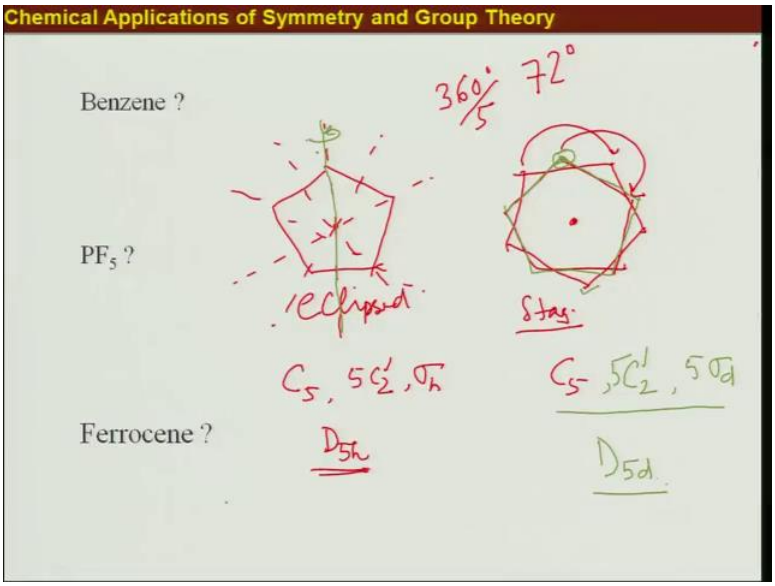

What do I have? I have something like this right because I am looking for the top. In reality it will have a structure which is like you know almost like you know (Refer Time: 24:00) kind of shape right, a (Refer Time: 24:05) structure. On the other hand, the staggered configuration will have something like this.

So, now, we have to find out the point groups for eclipse and staggered confirmations. Let us start with the eclipse, which is the easiest. I tell you at the way beginning this will have D 5 h point group why? It is a Pentagon, Cyclopentane group and all the C C bond distance are same right. So, for every, it will be what will be the angle? It should be 360 by 5. So, it should be 72 degrees. So, every 72 degree rotation will give me an indistinguishable position about this axis. So, this is my Ferrocene molecule, so axis passing through the center of one Cyclopentyl group iron and then the center another Cyclopentyl group that will my C 5.

So, this 2 are eclipse. So, a plane which is perpendicular to this C 5and containing the iron will reflect the top part the top Cyclopentyl group to the bottom and vice versa. So, I have a sigma h right and this is Cyclopentyl group. So, just like the PF 3, I can have C 2s which are perpendicular right.

So, I can find out all the possible C 2s. So, there will be total 5, C 2s which are perpendicular. So, I have C 5 as a principle axis of symmetry. I have 5, C 2 primes and I have sigma h. So, this becomes D 5 h point group for it gives a confirmation. Now what

about the staggered confirmation? Here what do I have? Do I still have C 5? Answer is yes, I have C 5. So, you can figure this one out because this one will move here. Similarly this one will move here right. So, I will not find any distinguishable change there. So, C 5 still exist in this staggered confirmation.

Now what about perpendicular C 2s? So, now, let me use another color, so that I can separate this. So, let me use something like green. So, now, say this is my top Cyclopentyl group and the other one that is in red colour that is at the bottom. So, I am discussing the possibility of having a C 2 prime here. Now we had C 2 prime for this eclipse confirmation right. So, along this, there was a C 2 correct. Now do I have a same kind of possibility here? Suppose I draw axis through this. Now what will happen? After performing a C 2 type of rotation along an axis which is similar to this here also this top green part will now go to the bottom and this red part which was in the bottom will come up here. So, this green part, it will go to the bottom not only go to the bottom. So, like this tip of my this finger is this point I am talking about. So, this will now flip completely and this part which was projecting toward you will now come in this side that is projecting toward me and it is in the bottom hemisphere. Just like this similarly the red part which is like (Refer Time: 29:03) the red part which was like a tip here. So, that will go above here. So, ultimately I have a C 2 which is perpendicular.

So, very easily I can find out other 4, C 2 primes. So, I have essentially 5, C 2 primes. Now the question is sigma h. Here I do not see a plane which will give me an indistinguishable structure upon reflection on that plane and particularly the plane which is perpendicular to the C 5 axis here. So, I do not have any sigma h. Do I have a sigma d? Yes I do. So, any of this sigma ds will be very easily found because I have the C 2s now. So, if I find out any two adjacent C 1s, if you have a plane which contains the principle axis of symmetry and bisects that you know angle formed by 2 C 2 primes, you have got your sigma d and you should be able to do that using pen and paper very easily. So, you will see if you perform that you will there are 5 sigma ds. So, that is sufficient to get the point group. So, I have D 5 d point group for the staggered confirmation of Ferrocene molecule.

So, we will stop here today and in the following class I will look at few more, a quite complicated molecules and then we will also learn about some properties of the symmetry operations and we also will try to find out, if the certain physical properties

like polarity or you know (Refer Time: 31:16) and hence optical isomerism with the symmetries of the molecules and therefore, with the point group of the molecule. So, see you tomorrow again.

Thank you very much.