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

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Lecture No. 02

Introduction to Point Group Notation, Classification, Symmetry Number and Order

Hello, welcome back to this course on Structure Stereochemistry and Reactivity of Organic Molecules and Reactive Intermediates: A Problem Solving Approach. We have just kick started this course, by recording one lecture and in the in that lecture, we briefly described the what is meant by structure of a molecule especially the 3 dimensional structure and with reference to Chirality and then what makes a molecule chiral then we deliberated on the symmetry elements namely the 4 elements of symmetry.

And we have just highlighted some important points, which will be required for the subsequent classes like when we talk about the simple axis of symmetry, then we have mentioned that what is meant by that are how to select the principal axis which is also regarded as pointing towards the vertical direction. So, any plane which is containing this principal axis will be regarded as a vertical plane like a plane of symmetry, which is containing the principal axis is called sigma v and the orthogonal plane is called sigma h.

So, identification of principal axis is very important then, we have seen that there are 3 kinds of planes of symmetry sigma v, sigma h and sigma d. The definition remains the same that the Sigma plane divides the molecule into two half's so, that one half is the mirror image of the other half. The then we went to deliberate upon the center of symmetry. And the important point to note here is that the definition is precise if you say that it is a point which when any atom is joined to that point and extended in the reverse direction, which is an identical atom, an identical atom.

If you say that it reaches an identical substituent that is that is not correct in case the substituent has a stereo generic center SP3 stereo generic center, so, you have to be careful. So, it is better that you say atom join to that point them extended in the reverse direction meets the same atom and this is true for all the atoms that are present in the molecule. Then, we said something about the alternating axis of symmetry which is basically composed of two operations, one is reflection and there is rotation.

Now, this can be the original definition is that it is rotation followed by reflection that means, you rotate the molecule through 360 by n and then take the mirror image through a mirror which is placed perpendicular to the to the axis of rotation and you get the an indistinguishable form of the molecule. That is, otherwise you can also say that first you take a reflection that means, you would form a mirror image again the mirror has to be placed perpendicular to the intended axis of rotation and then you rotate that reflected molecule by 360 by n degrees and you end up having an a form which is indistinguishable from the original form.

So, I think we ended up at that point, today we are going to discuss, go to the to the point groups that that defines the symmetry elements of a molecule. But before that, I think we will have missed a few points and that those points need to be clarified and then we will go to the point group section. The point that was important is that is generally we do not highlight this aspect when we say that a molecule is chiral when it is non even when it has a non super imposable mirror image.

Now, a molecule can exhibit in different confirmations, depending on the structure of the molecule. So, if the molecule is flexible connected by CC single bonds, then it is possible that it is possible that there will be free rotation around the carbon, carbon bond unless it is highly restricted by some other some other process by steric effects, but otherwise there is this rotation.

So, basically what we are saying that a molecule has different conformation so, when we talk about chirality, what conformation are we talking about which conformation we should take? In fact, a molecule for a molecule to be chiral every possible confirmations has to be chiral. Every possible confirmation divides the alternating axis of symmetry or every conformation of the molecule is chiral.

On the other hand, if a molecule you take a particular conformation of a molecule and you see that this conformation is chiral you cannot immediately jump into conclusion that the molecule is chiral because this conformation of the molecule is chiral that is the important point I want to make.

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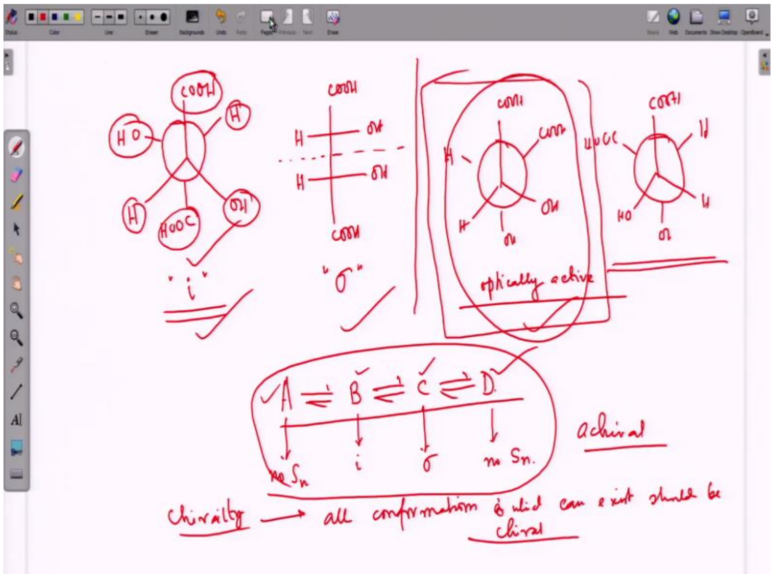

And so, basically what we are saying that suppose I take the meso tartaric acid confirmation, one Newman Projection I draw for meso tartaric acid we know that meso tartaric acid we say that it is optical, we know that it is optically inactive because of the fact that it is usually represented in Fischer projection and in the Fischer projection it appears that it has got a plane of symmetry. This is the plane of symmetry. So, the general answer the students give that meso tartaric acid is optically inactive due to the presence of a plane of symmetry and that causes internal compensation.

However, that meso tartaric acid can exist in different confirmations like the confirmation that I have written the Newman projection that is that is also a chiral confirmation because it has got a center of symmetry as you can see that CO2H opposite to that CO2H, H opposite to that this H and this OH opposite to the OH. So, meso tartaric acid this also represents meso tartaric acid, but this now the explanation is that meso tartaric acid is optically inactive, because it has got a center of symmetry.

Earlier you are saying meso tartaric acid is optically inactive because it has got this plane of symmetry in Fischer projection and in Newman projection you are saying that it has got a center of symmetry. So, what is the actual answer? In fact, I can draw another confirmation in Newman projection of course, CO2H H, OH and then what I do that I put a OH here and bring the OH here CO2H there and H here. Now, this conformation is optically active, this conformation does not have the plane of symmetry, does not have the center of symmetry actually it does not have the other any other improper elements of symmetry. So, this conformation should be optically active.

So then what is the, so the actual answer why meso tartaric acid is optically inactive lies in the fact that out of several confirmation some meso tartaric acid in fact for any molecule if a particular conformation becomes optically inactive that means becomes a poses a improper and improper element of symmetry that means S axis, Sn axis, then that kills the optical activity whatever of any other confirmation which might be optically active. Like here I have drawn 3 confirmations some meso tartaric acid this is inactive form due because of why this is inactive form because of sigma but this is the active form.

So, somebody might say that this is active form, so, meso tartaric acid should be optically active when that is not true we know that. Now, what is the bottom line? The bottom line is that if a molecule exists in several confirmations, which is usually the case if at least if one of the confirmation is a chiral, then that kills the optical activity of the whole molecule that means the whole the molecule becomes a chiral. Actually what happens here however, there are some restrictions in this definition is that suppose you have just a second suppose you have a molecule which can exist in several confirmations A B C and D.

And suppose this does not have no Sn this has a center of symmetry this has a sigma claim and this has no Sn that is always possible then as I said I have drawn only 4 confirmations here because this D or A, because C and B both are optical inactive both are chiral so, the whole system becomes a chiral. So, the actual correct definition of chirality for a molecule is that all the confirmations that the molecule can exist should be a chiral then only the molecule becomes a chiral. If one conformation becomes a chiral, then the molecule will not show any optical activity.

So, you see that for a beginner for a beginner if he writes he or she writes meso tartaric acid in this form, then he or she might end up saying that meso tartaric acid is optically active, but which is not true because other forms as I said, the rule of thumb is that if one conformation becomes optically inactive, then the whole molecular system becomes optically inactive.

And the exact reason if you go into in detail, then what happens that this molecule has exactly the what is the mirror image of this molecule, the mirror image of this molecule is this that this your CO2H is on the H, this is H CO2H on the left side and this is OH and that will be OH and that will be H and that will be CO2 that will be CO2h. Now, these two molecules are actually inter convertible by rotation and that is the reason and since they are present in equal amount, because of the flexible barrier, the barrier is too low.

So, you will never be able to isolate any active conformation in this molecular system. So, what is the again what I have said that chirality definition must indicate that all confirmations in a molecule which molecule can pauses can exist should be chiral. That is the correct definition of chirality. If you say a molecule is chiral because it is a non super imposable, it has got a non super imposable mirror image you may miss this point because as I said if somebody starts with this form of tartaric acid he or she might end up saying that tartaric acid, meso tartaric acid is optically active that is not true.

So, while defining chirality remember you have to you have to consider all the confirmations that a molecule can exist. And once you find a confirmation, which is a chiral that means the molecule is a chiral. You do not have to search many because sometimes intuition can tell that way that the molecule is going to possess a form where there is some i or sigma or Sn.

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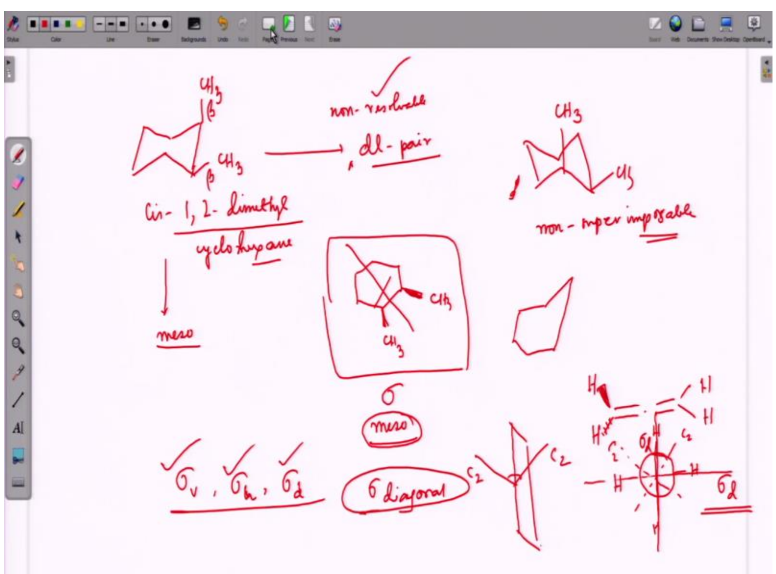

The one more point that in connection with this is that we know that C is 1 2-dimethylcyclohexane. This is C is 1 2-dimethylcyclohexane this many times it is a what is asked is what is the optical activity of this molecule cyclo-hexane. Some books are a majority of the books are correct it says that it exists as a non resolvable dl pair. But there are some books it says that it is it exists as it is inactive it is a mess of forms it is optical inactive.

Now which is correct, non dissolvable dl pair or is it a meso form? You have to decide on the different confirmations that are available for this molecule. Now, when this C is dimethylcyclohexane you know that it can undergo flipping. Now, when it flips you can you get basically in this case when it flips you get the mirror image of this you get the mirror image form of this molecule. So, methyl is here and methyl is there. So, if you try to overlap this onto that one that is not possible. So, this is the non super imposable mirror image.

And since this conversion is happening has a low energy barrier happening at the room temperature very fast, so it is not possible to separate these molecules that is why this is a non disability dl pair. Now you can always also you can also think that that during this adopting different confirmations, a confirmation might arise where the whole thing is cleaner and then both the methyl’s will be like this. So, all the carbons became planar once it bought the methyl’s are beta here because we started with beta so, we can think of a confirmation of this 1 2-dimethylcyclohexane says in this form that all the is a plain hexagon, if it can adopt to a plain hexagon, then what happens it has got a plane of symmetry, then it becomes meso.

However, you know that this molecule while going from one form to the other that means the flipping, it never adopts this six member trainer 6 member dream because that has got the highest energy because of this CPR angle strain and also the Torsional strain and just said Torsional strain. So, during flipping what exactly happens is that at some point of time, you have a system which is like a half chair, but it will never add up to this confirmation. So, if it does not add up this confirmation, so question of meso does not arise.

So, I want to clarify this thing that may this one 2 diameter cyclohexane in the C form is exactly is a non resolvability dl pair do not be mistaken that it is actually existing in a meso form. This is again basically the concept is based on the various confirmations that are available for a molecular system. So, that is what is I wanted to say and I think that there are 3 types of sigma plane of symmetry sigma v sigma, sigma v, sigma h and another which is called sigma d. This is the vertical plane of symmetry, horizontal plane of symmetry and this is diagonal plane of symmetry.

Vertical plane of symmetry is basically aligned with the principal axis of the molecule. Sigma h is the orthogonal plane to the vertical axis and sigma d is that which is which bisects the angle between two C2 axis. So, this d stands for diagonal sigma diagonal it is not always present it is present in molecules where C2 axis are present two C2 axis has to be present.

And this angle the sigma d is basically bisecting the angle between the two C2 axis like I gave you an example, very quickly I did that that in the Allene system plane allene that you have this sigma d in Allene you know that this is orthogonal the plane in which these two hydrogen's lie is orthogonal to the plane containing these two hydrogen's. So, if you draw a Neumann projection, it will be looking like this hydrogen, hydrogen and hydrogen and hydrogen.

So, you see that here is a there is a C2 axis here and there is a C2 axis there and the Sigma plane passes through this or sigma plane passes through these are anyway this is both are actually bisecting the angle between the two C2 axis. So, this will be sigma d that will be sigma d.

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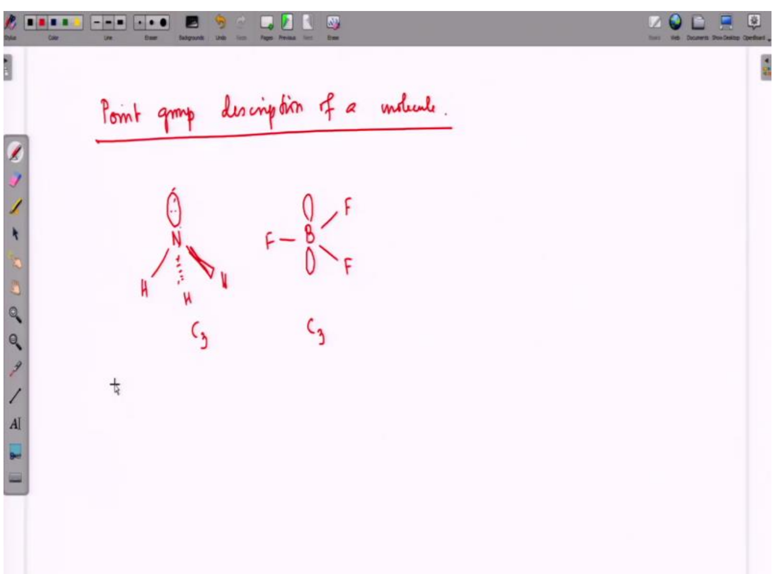

The next we will go to the, we will go to the Point group description of a molecule. Now what happens that when we do perform these when we determine the symmetry elements of a molecule we do one by one like plane of symmetry, center of symmetry we try to find out whether the molecule poses possesses these or not or simple axis of symmetry or alternative axis of symmetry. And if I say that a molecule poses a C3 axis. It just gives it just says it is a statement of fact statement of fact means it does not provide a good stereo chemical feature of that molecule by only saying that the molecule has a C3 axis.

I give you an example that if you take ammonia, we know ammonia is pyramidal with the lone pair occupying the fourth vertex of the of the tetrahedron whereas BF 3 is planar here the this is a P this is a P orbital. Now, both of these containing a C3 axis, a C3 axis passing through this passing through this the boron so vertical like this. Here it is going through the nitrogen. So, both are possess C3 axis, but it you see that the molecules are totally different. There is their geometry is totally different. So, by saying only this phenomenon that only when defining only one type of symmetry does not give you the complete picture, the studio chemical picture of the molecule.

So, scientists thought that it would be better that if some norm is found where or a notation can be found that where by simply providing a notation or giving a notation to a molecule you can actually, you can immediately give that what type of symmetry elements it has. So, basically what I am saying is that just a second that a point group and this is what is called a Point group. Point group is basically a defines the symmetry class of a molecule and also it which provides the number of symmetry elements that the molecule can possess or molecule actually has.

This is based on the on a particular type of notation, which was devised by Schoenflies the scientist Schoenflies that he gave a way to depict the different symmetry elements by in notation which is called a point group for a molecule. Now, why it is called a point group when you club all the all the symmetry elements that the molecule can possess, because, when you talk about symmetry element, you are talking about some operation like we call symmetry operation like when you say a molecule has C3 axis that means, you imagine an axis and along that axis or about that axis you are rotating the molecule you are performing an operation. So, that is why symmetry elements can also be equated that equated to symmetry operation.

So, these symmetry operations the number of symmetry operations that you can you can have or you can apply to a molecule that is basically defined by this notation what is called the point group. So, the precise definition is that the point group defines the symmetry class to which a molecule belongs. The symmetry operations or the elements are combined to form a point group and the notation has been given by Schoenflies.

See each operation why it is called a now the question is why it is called point group? Because each operation that I was talking about symmetry with each operation, what it does, it leaves the difference substituent's, it perturb of the difference substituent's changes their original position bring it to a new position, but one point remains the same which is unperturbed and that is the center of gravity of the molecule. So, it leaves a point which is unchanged and unperturbed and that is why this is called a point group.

Now different so, basically point group is nothing but clubbing of all the symmetry elements that a molecule can pauses and give a type of notation like C to B, you have my you must have heard DnD, DnD, then DnH, TD, all these symbols are there. So, we will discuss what are these symbols are these symbols what they really mean. Now, it is true that a molecule can have 4 types of symmetry elements or you can perform four type of symmetry operations on a molecule.

However, for chiral molecules, we must remember for chiral molecules, 3 of the symmetry operations are absent that means the eye operation the sigma and the Sn, these 3 are absent. Only thing that can be present is the simple axis of symmetry because simple axis of symmetry does not have any bearing on the chirality of a molecule.

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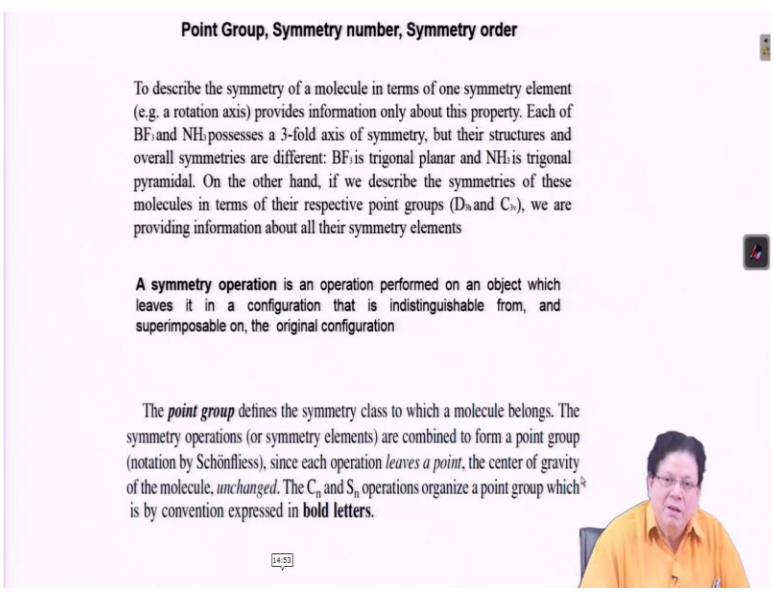

Here it is, everything is written that I said about BF 3, and NH3, it says that to describe the symmetry of a molecule in terms of one symmetry element provides information only about particular of that symmetry element only, like BF3 and NH3, each possesses a 3 fold axis of symmetry, 3 fold axis of symmetry, but 3 fold axes of symmetry, but their structures and overall symmetries are different. BF3 trigonal and NH3 pyramidal.

On the other hand, if we describe the symmetries of these molecules in terms of their outcomes the respective point groups that means a particular notation, which actually has inbuilt character of all the symmetry elements that the molecule can possess then we are we can we are providing information about all the symmetry elements that the molecule has. As I said this is already I have already told you what is the point group?

Point group defines the symmetry class to which the molecule belongs the symmetry operations or the symmetry elements are combined to form the point group notation by Schoenflies, since each operation leaves a point the center of gravity of the molecule unchanged. So, this is called a point group.

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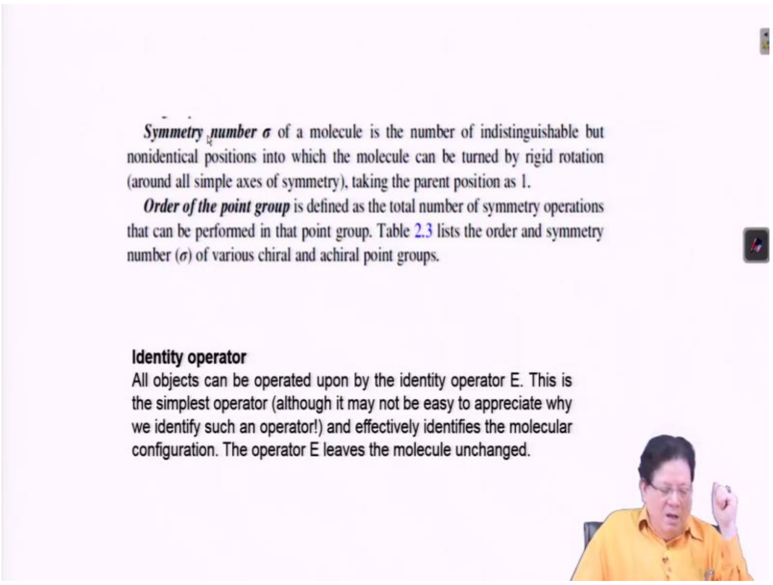

Now, another important concept from the point group actually basically what we are saying that from the point group it is possible to know how many symmetry elements and how many operations you can actually perform on the molecule. So, there are two other important things which are connected to point group is called symmetry number that is sigma that is written here symmetry number symmetry number of a molecule basically is the number of indistinguishable forms indistinguishable from the original indistinguishable forms.

So, you have an original molecule it is looking like a particular form and then from that, how many indistinguishable forms can you generate by performing the symmetry operations, but this symmetry number remember is connected only by to the indistinguishable forms that you can generate by only simple rotation via simple access. So, only using simple axis of rotation that means, Cn axis how many indistinguishable forms you can generate that gives you the symmetric number.

So, symmetry number is basically you have to find out different types of C axis that are different types of C operations that you can apply to that molecule on the other hand order of the point group there is another term which is symmetry number is denoted by sigma and there is another one which is called order of the point group. Order of the point group is defined here is defined as the total number of symmetry operations total number now. Now, it is not only C now, it includes C it includes sigma it includes S it includes i, all these symmetry operations that can be performed in that point group and that gives the order which is which is denoted by H.

So, you have two different thing, first of all point group clubbing of all the symmetry elements or symmetry operations and giving a notation. Number 2 is that symmetry number that number of indistinguishable forms that a molecule can have by applying the simple axis of rotation all possible simple axes of rotation and number 3 is the is the order of the point group which is basically the total number of symmetry operations that you can perform on the molecule which is belonging to a particular point group. So, the order sigma includes only the sigma is only including the C axis operation whereas, the order that is H that includes all types of operations including C, sigma, i and Sn.

So, let us start this point group how it has been classified? Now, you know that as I said just previously, that molecules can be chiral or molecules can be a chiral. So, it is much simpler to actually put classify chiral molecules and assign the point group to them. Chiral molecules we know that they only have C axis. They can have they may have, they may not have. That is why the dissymmetry term has been used. Dissymmetry is basically devoid of these improper elements of symmetry whereas, a chiral molecules can have different types of symmetry.

So, that is little bit more complicated, but for chiral molecules it is easier because it only has either it has got C or it may not have C however, I just have one important point that there is something called identity operator. Identity Operator means basically one fold simple axis of symmetry. One fold simple axis of symmetry means, if you rotate a molecule by 360 degree, then the molecule comes back to the original form.

Now, this is also included in the point group this is also considered as a symmetry operation in the point group and this is called identity operator. So, identity operator identity operation is nothing but the C1 that means one fold simple axis of symmetry, so, 360 degree rotation remember, every molecule should have must have actually has one this identity, this identity element that means this C1 axis that every molecule or every object has. So, that is the identity operator.

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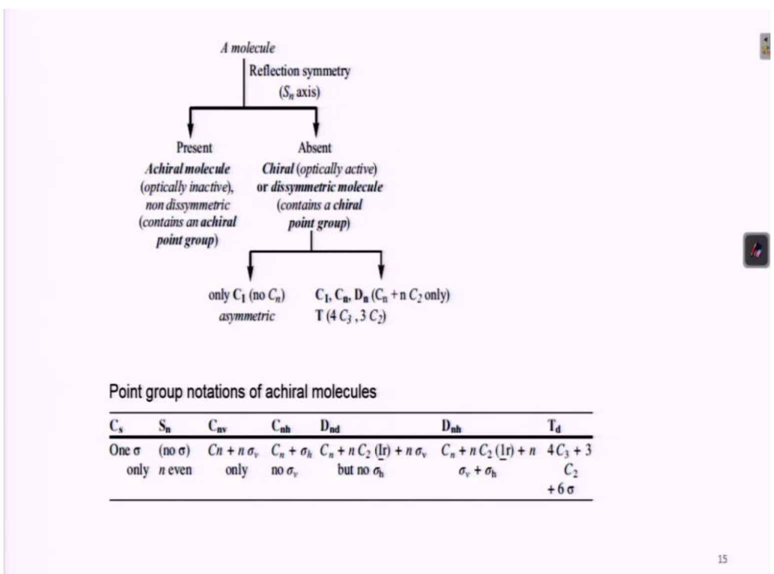

So, now, we go to the classification. So, take that this is a molecule, a molecule is here. Now, this is it is shown here that this is the molecule and so, if we just got reflection symmetry that this element improper element of symmetry Sn axis, if it is absent then it is chiral and it contains what is called chiral point group. And if it is a chiral that means, if reflection symmetry is present, it is a chiral, then it is say that it has got a chiral point group.

Now, in the chiral just quickly classify the chiral point group that there are molecules which will not have any type of symmetry element, but remember every molecule has identity element that means the C1. So, there is one class of chiral molecules which will be only say that they are they belong to the point group C1 and no other no Cn where n is greater than 1. And the other class of chiral point groups are Cn that means, something has C2 axis or C3 axis simple axis of symmetry. So, it could be Cn or it could be Dn. What is Dn? Dn is basically dihedrals point group, Dn is basically equivalent to having Cn plus nC2.

So, when something has a Dn point group that means that it has got a Cn access plus in nC2 axis, n number of C2 axis only, no other here no question of any sigma i or Sn because it is chiral and there is a there is a another one which is called T. T is tetrahedral point group, simple tetrahedral point group which will have 4C3, 4 number of C3 axis and 3 number of C2 axis. So, what are what we are saying that a chiral, chiral point groups are C1or it could be Cn or it could be Dn or it could be T. And so we will discuss the molecules which are showing these type of point groups in our next lecture. Thank you.