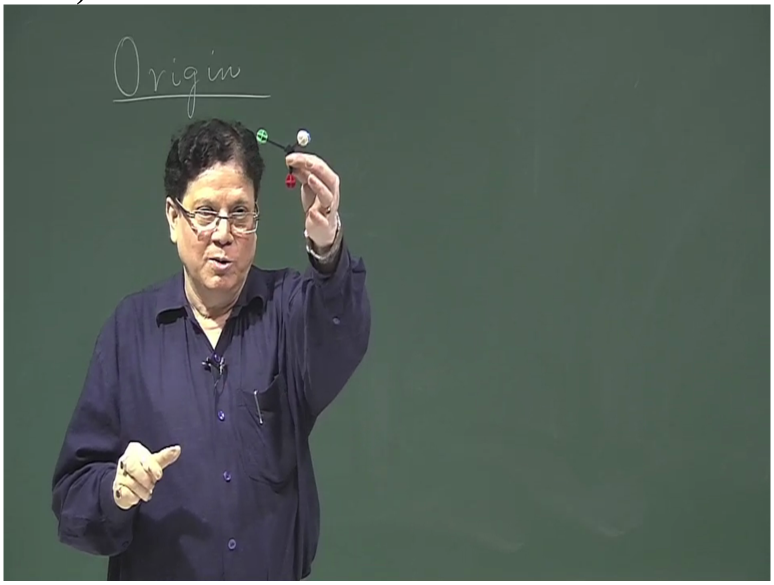
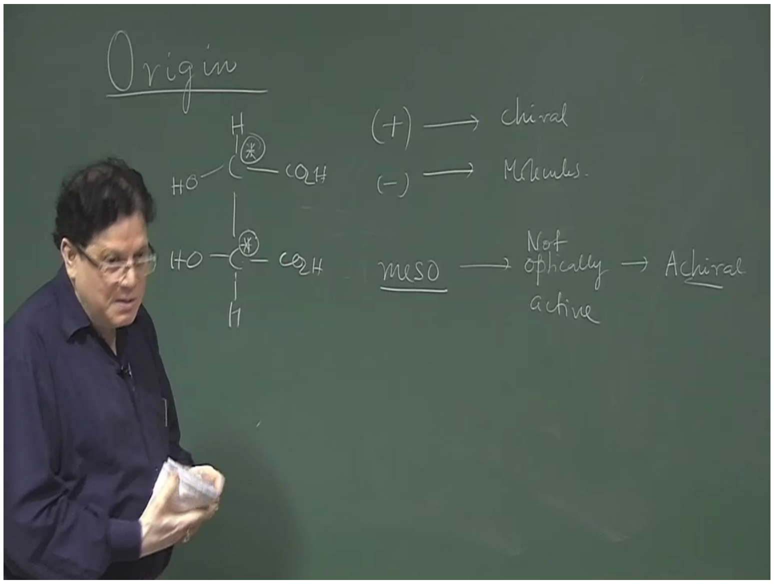
Course on Stereochemistry
Professor Amit Basak
Department of Chemistry
Indian Institute of Technology Kharagpur
Module No 01
Lecture 02: Chirality, Symmetery Elements

(Refer Slide Time: 0:20)





Okay now let us giant discuss as I was telling that wiser molecules rotate the plane of plane polarised light. Now again I repeat, molecules which rotate the plane of plane polarised light are called optically active molecules or they are chiral molecules and they can exhibit an

Enantiomeric pair and that exactly what happened with Racemic tartaric acid that exhibited, that was existing into Enantiomeric pair and what Pasteur did, he just separated the 2 types of crystals fortunately for him that the 2 Enantiomers crystallised as separate crystals and those crystals are mirror images of each other.

So he could, using a microscope, he could separate those 2 forms okay. The question is now, why molecules rotate plane of plane polarised light? Now the initial argument that was placed to support or to explain this phenomena of optical activity was based on the existence of the carbon that exactly Vant Hoff and Lebel told. They told that a carbon when attached to 4 different groups, that exhibits stereo isomerism okay and that carbon he named as an asymmetric centre.

Later on, it was called a chiral centre and in modern day, that chiral centre name has been changed but I will come back later to that modern day nomenclature of a carbon that 4 different groups are attached. But right now, let us call it a chiral centre or an asymmetric centre okay? So the initially, it was proposed that the optical, in order for a molecule to show optical activity, it should possess a carbon with 4 different groups as is shown here.

Okay? So that means existence of a chiral centre is important for a molecule to show optical activity. Okay? But the problem started when it was shown that there is a form of tartaric acid which was called mesotartaric acid which was called mesotartaric acid, see this is what is tartaric acid, it can exist in 2 forms, which can exist in 3 forms right? One is the + form, another is the - form when there is a 3rd form which is called meso which is not optically active. So this is not optically active, not optically active.

That means it is not chiral or what is called achiral whereas these are rotating the plane of plane polarised light, so they are chiral molecules. So the earlier argument that a molecule must have a carbon with 4 different groups which is called a chiral centre. It does not hold when you increase the number of chiral centres in a molecule like what happened in a in tartaric acid. Now you have two chiral centres which are marked as Tao.

So these chiral centres according to the argument earlier that existence is mandatory, existence of this type of carbon is mandatory to show optical activity does not hold good. So there is a problem in saying that optical activity arises due to the presence of chiral centre in a molecule okay? So then it was revised, this definition or this the reason for molecules showing optical activity. 1st it was said that there must a chiral centre.

Then it was revised that yes there are molecules which can assess chiral centres at they may be optically inactive, specially for molecules when the chiral centres are similar in nature. Similar in nature and means the same set of 4 groups are attached to the carbon. Okay? So you revise, you say that okay chiral centre presence is required but some molecules are there where in in spite of having this chiral centre, the molecule may be optically inactive.

So the definition got changed. Then another big problem came that there are molecules where no such chiral centres are present but they all they may be optically active. One example is what are called Aileen system. So people prepare this type of system, Aileen is named basically is that it is a 1 3 123 dial ok, not the conjugated one. The directly connected, 123 dial, they are called, they are also called cumulated systems.

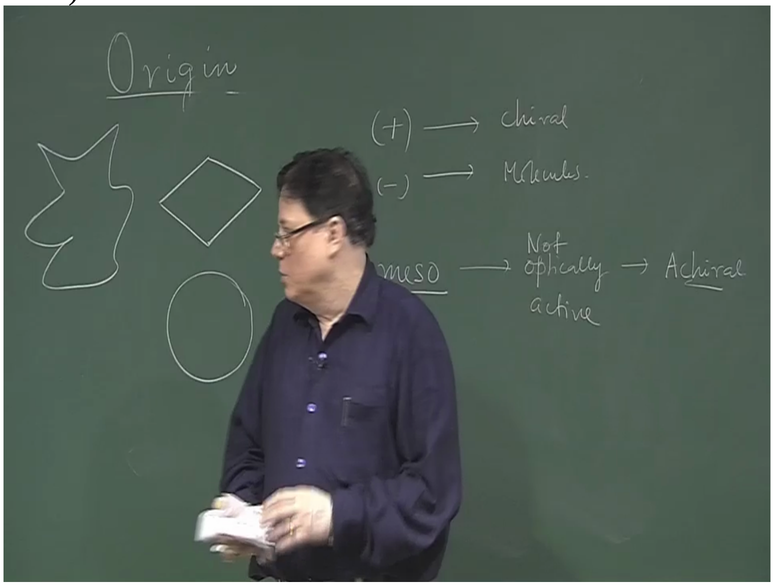
This is the Aileen system. Aileen system does not have any friends or there is no possibility of presence of this type of carbon because these carbons are now all, this is SP2, this is SP and this is SP2 but they are are Aileen systems which were optical activity. So the problem even become complicated because 1st we said that there must be presence of a chiral centre in the molecule.

Then we modified a little bit that no no, there are some molecules where the chiral centres are similar and they may destroy the optical activity. So there are some molecules, in spite of having chiral centres, they may be optically inactive. But the hard one was very difficult that there are some molecules where there is no such kind of chiral centre present but they are optically active. So there must be something wrong in the entire concept.

So then people realise, scientists again looked back and inspected this molecule and then they found that where actually the argument is going wrong. The argument is going wrong because it is based on the presence of this chiral centre. See that is not a mandatory for a molecule to be optically active. So what is then the necessary condition for a molecule to show optical activity?

That is again I repeat, that is not based on the presence of a chiral centre. The presence of chiral centre brings stereo isomerism in the molecule. When these type of centres are present, you generate what are called stereoisomers as I have already mentioned but this does this is die not directly connected to the optical activity. Okay? The optical activity is then connected to what? What is the reason for molecules to show optical activity? It is based on what is called symmetry concept okay symmetry concept.

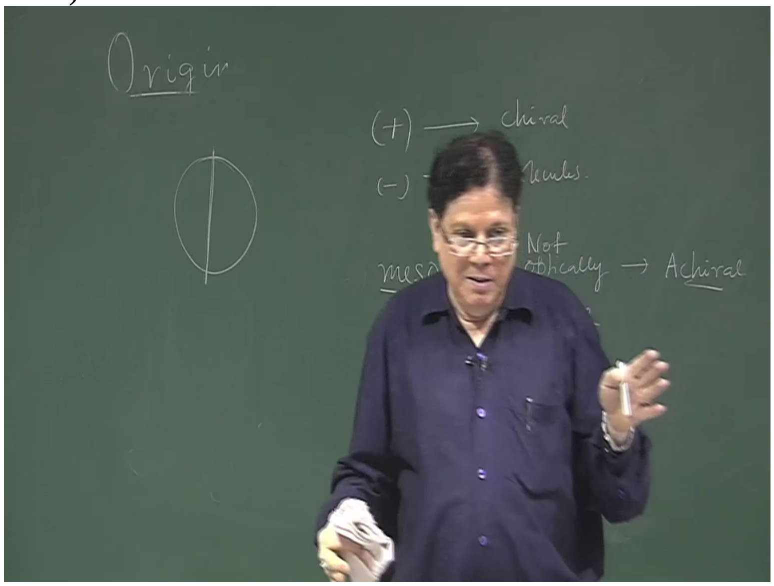
(Refer Slide Time: 8:23)



We know there are symmetric systems like if I have a square, this we call a symmetric system. If I draw a circle, this is called a symmetric system. Now why do we call this symmetric system? There must be some criteria of calling something a symmetric system. If I draw an object like this, now you will say oh, it is not symmetric it all. So there must be something in our mind which tells that something is symmetric, something is not symmetric okay.

So for molecules also, there are some molecules also we have to inspect that what is the symmetric property of this molecule and finally it was shown that these symmetry properties actually dictate the presence or absence of optical activity in a molecule. So not associate further, we have to know that what are the symmetry what are the symmetry elements.

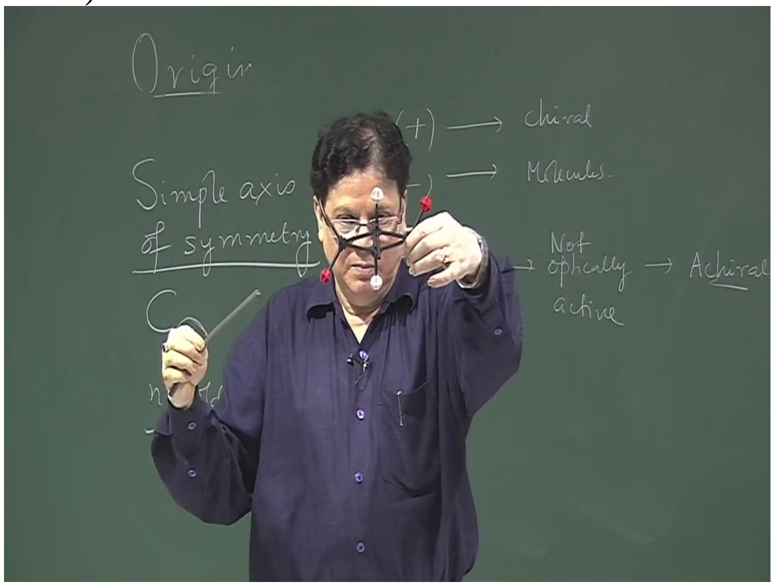
(Refer Slide Time: 9:25)

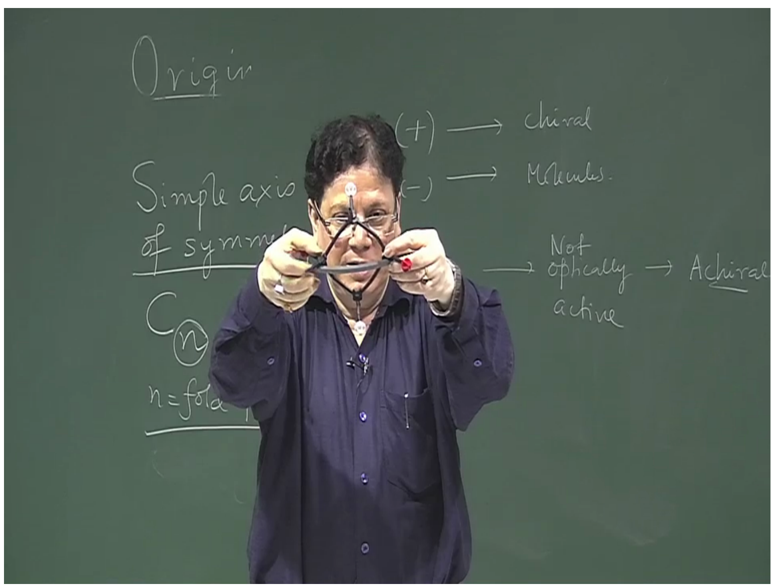


That means what we look so when I say something when I as I say I draw a circle, I immediately say, it is symmetric. Why do I say it is symmetric? Because you might say that because if I divide it into 2 by a line, vertical line, I get 2 identical mirror image kind of pieces which are, 2 pieces I get and one is the mirror image of the other. So that is what that is we call it symmetric.

But there are, this is one type of symmetry operation that you can cut it into half and then see one half is the mirror image of the other half or not. So like likewise there are 4, there are additionally 3 different symmetry elements and in total, there are 4 symmetry elements possible in a molecule. One is this what is the most obvious one that to cut the molecule into 2 halves and then see whether one half is the mirror image of the other half okay? These are called plane of symmetry but we will start from the very beginning because plane of symmetry comes little later.

(Refer Slide Time: 10:35)

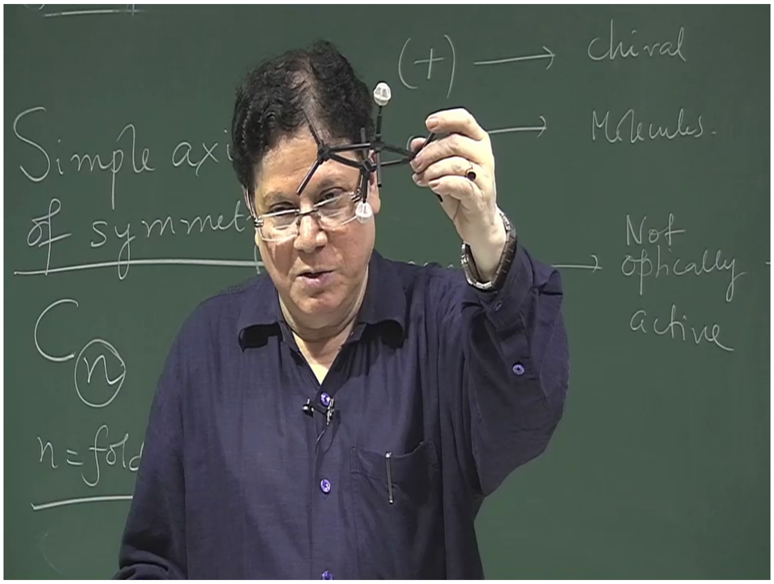




The 1st symmetry element that one should consider is what is called simple axis of symmetry, simple axis of symmetry or this is denoted as C. It has got a also another subscript which is N, this is what is called the fold, N denotes the fold of the axis. I will just explain what does it mean. Fold of the axis. Simple axis of symmetry means that if you have a molecule, simple axis of symmetry, if you have a molecule and if you rotate it along an axis, if you rotate it along an axis, suppose I have this molecule, this I am showing and I have an axis like this which is the my axis of rotation.

If a rotate it by 180 degree, what I see? I get the same molecule, identical molecule. Okay? When I rotate it by 90 degree, it appears different. It is the appearance. Because molecule remains the same, whatever I do. It is the appearance of the molecule that is more important. So if I take the molecule like this idea have an axis going through these 2 carbons which are holding this reed, atoms and now if I rotate it, remember this white is on the opposition, is above, this is below, this red is below and this red is above.

(Refer Slide Time: 12:33)



And now if I this is this is not the symmetry, I I remove the red molecules sorry. I have to remove the red ones because that is disturbing the symmetry element. Now if I do not have the red ones, I rotate it by 180 degree, so what happens, I get a similarly looking molecule, a similar looking molecule. This happens only by rotation of 180 degree. It does not happen by rotation of 90 degree okay.

So what is this N, I was talking about this fold? The N is basically that how much you have rotated to obtain the molecule which has the similar appearance and 360 divided by that angle. That means 360 divided by the angle that is required to rotate the molecule around the axis to appear the same like the original one. Okay? So in this case, because I am rotating it by 180 degree, so the fold this has got a simple axis of symmetry because I come to the same appearance appeared molecule after rotation of 180 degree.

That is before I reach the 360 degree. Remember, if a rotate the molecule by 360 degree, that means it always remains the same, it will appear to be the same. In this case, before 360 degree, if you find an angle where it appears same, the minimum rotation that is required and 360 divided by that angle gives you the fold. So here the fold is 360 divided by 180. So this molecule has a two fold simple axis of symmetry. Okay?

So what is the definition of simple axis of symmetry? That you rotate the molecule around an axis by 360 divided by N degrees or 2 pi by N degrees and you find a molecule which looks exactly like the same as the starting one. This is also called proper axis of symmetry. Simple axis of symmetry or proper axis of symmetry. That is the starting point of symmetry element. The 2nd one is what is called the plane of symmetry which I already told you. What is plane of symmetry?

(Refer Slide Time: 15:10)

The plane of symmetry is so simple axis of symmetry, now let us talk about plane of symmetry. What is plane of symmetry? Plane of symmetry is that you divide the molecule into 2 halves by an imaginary plane such that one half is the mirror image of the other half. Remember, I am not saying one half is identical with the the other half. I say one half is the mirror image of the other half, that is important.

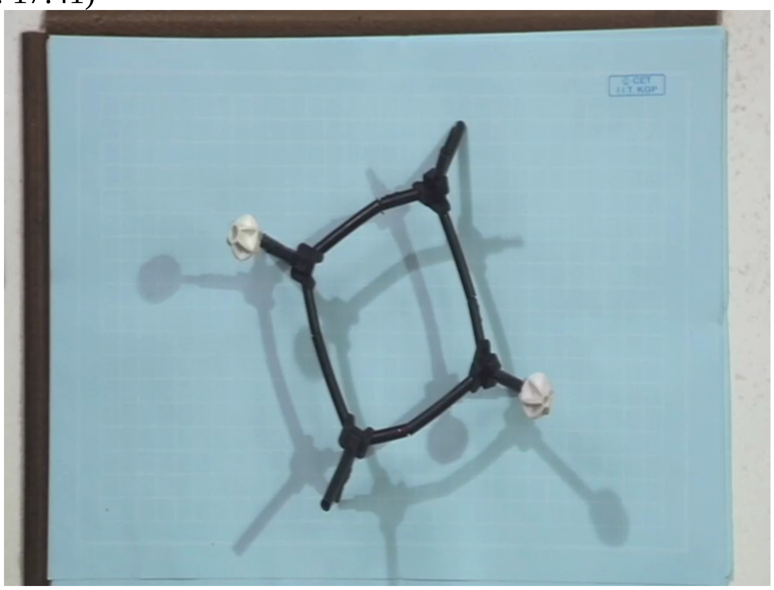
So if I take, suppose if I take a molecule like this where there is a X here on the top, and another X here, this is hydrogen and this is hydrogen, then if I have a plane here, divide the molecule and if this is supposed to be a mirror, then this half is exactly the mirror image. So then this is called that this molecule is having a plane of symmetry. Now a molecule can have multiple planes of symmetry.

I should have told you earlier that a molecule also can have multiple sets of C axis, a molecule can have C2 axis, a molecule can have C3 axis, same molecule. It is not that it will have only one plane of symmetry. There are molecules which has got one plane of symmetry. There are molecules which do not have any plane of symmetry, there are molecules which have multiple sets of plane of symmetry. Like this molecule, one plane of symmetry we have identified.

So this part is the image of this part but there is another plane of symmetry and that is going through this carbon. Suppose this is carbon 1 and this is carbon 2 and if you now bisect between this carbon and that one, then this part will be the mirror image of the other part. And I can show you because I have the luxury of having the molecular model here. Okay?

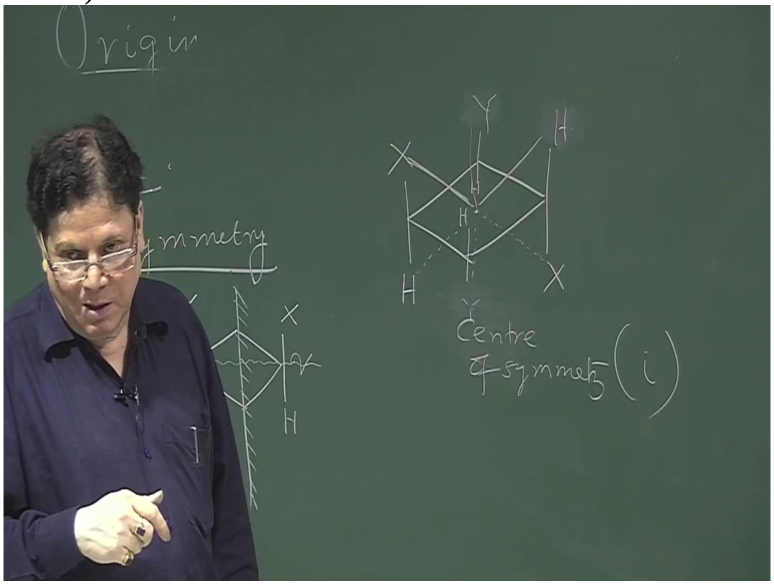
So what molecule I have shown is this that these are the 2 axis. This is hydrogen. I am not showing the hydrogens. Now one plane of symmetry is between this. You see, this is the mirror image of that one and the other plane of symmetry is this where this is the mirror image of that one. Okay? So it has got two planes of symmetry.

(Refer Slide Time: 17:41)



This plane of symmetry is designated as Sigma, Sigma plane okay. So this is the 2nd 2nd symmetry element. The 3rd symmetry element is what is called a centre of symmetry. What is the centre of symmetry?

(Refer Slide Time: 18:04)



A centre of symmetry is suppose I have again I take this cyclo butane type molecule and I have X here and I have X at the down, a hydrogen here, hydrogen there and then what I see that if I take the centre point of the molecule and then join this X to this point and then extend it backwards to an equal distance, I I reach the same atom, X. ok? The same thing happens with this hydrogen. So what is the centre of symmetry?

Central symmetry is a is a central point in the molecule which is joined to any substituent in the molecule and the line joining that substituent, if you extend it backwards, you find an identical substituent at identical distance. The more important point is that this has to be true for all the atoms present in the or or the substituent present in the molecule. Suppose I replace it by Y, now what happens, this is okay, this you join, extend it backwards you get X.

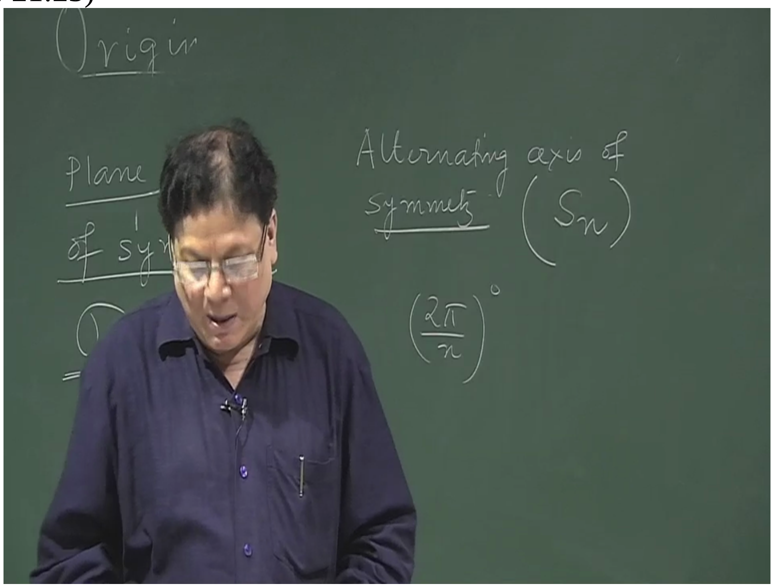
But the problem is, if you join Y to this point, and extend it backwards, you get H. So it does not have any, so your centre of symmetry is not present. By the way, this is called, designated as I, inversion point. I will talk to you about this inversion point it later because once you know the absolute configuration concept, then we can come back and then explain why this is called an inversion point. Okay?

This is donated as I. So I is present as long as this is hydrogen, that is hydrogen and also these are hydrogens. Remember you cannot neglect any of these groups. So whatever substituents are there, this criteria should be satisfied. That means, this hydrogen if you join to this point, extend it backwards, you get this hydrogen. So if you disturb this hydrogen by Y, so now the planar symmetry is gone.

So to bring back the planar symmetry, what you need? Y here and a Y there. Okay? So what is the again come back to the definition. A a centre of symmetry is a central point within a molecule that if you join any substituent to that point, and then extend the line backwards, you get an identical substituent at identical distance. And this has to be true for all the substituents or items that are present in the molecule.

Centre of symmetry cannot be many because it is the central point in the molecule which is only one point. So either 1, it has to be 1, either it is present or it is not present. So that is clear. So we have considered 3 symmetry elements so far.

(Refer Slide Time: 21:23)

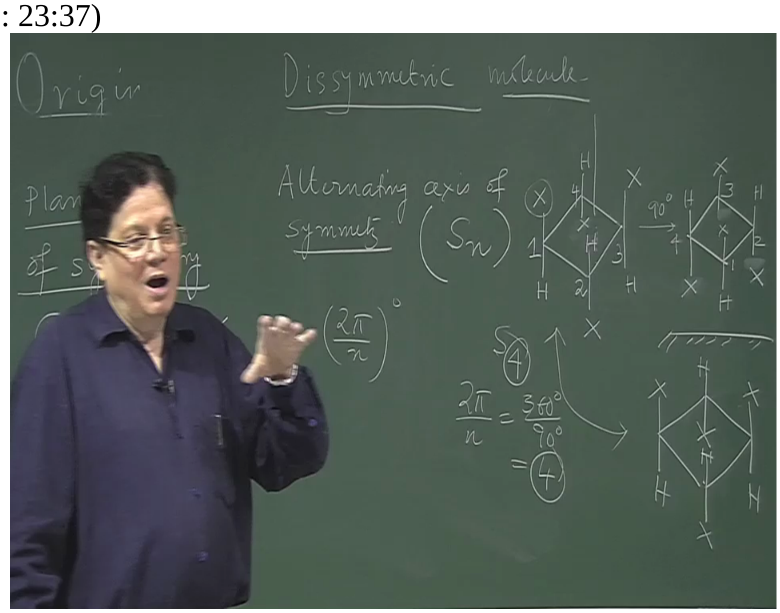


Now the 4th symmetry element which is called alternating axis of symmetry, alternating axis of symmetry. Because it is an axis of symmetry, so a fold is will be associated again because you have to rotate the molecule, rotation is needed. Okay? So this is this is designated as SN. N is the fold, S denotes alternating axis. So this SN means N fold alternating axis of symmetry. What is this? This is that you rotate the molecule by some degrees, by 2 pi by N. If it is N fold, then you have to rotate it by 2 pi by N degrees and then in case of Centre, in case of simple axis of symmetry, you rotate by 2 pi by N and you come to the same appearance of the molecule.

In alternating axis of symmetry, what happens these days that you rotate the molecule. You rotate the molecule and then stop at the 2 pi by N degree, then take another image of the molecule along the axis. The mirror has to be placed perpendicular to the axis of rotation and the mirror image now should be identical to the original. So there is the difference between CN and SN.

The difference is in CN, just 2 pi by N degree rotation will give you the molecule of same appearance. In case of alternating axis of symmetry, you rotate by 2 pi by N degrees and then along the axis, place a mirror which is perpendicular to the axis and then the mirror image that you obtain should be identical with the original one. Identical means, appearance should be identical with the original. Okay? So some example.

(Refer Slide Time: 23:37)



Example is suppose again cyclo butane acts as a very good basis for this concept that if you have supposed X here and if you have again another X, if you have X there and if you have X at the down, so suppose these are all hydrogens. So if I take this molecule and sorry this is ya this is the X for here, this is hydrogen. Now if I rotate this, if I have a acc axis like this, if I consider an axis like this which is going through the centre, by the way it is difficult because this is aligned to this line.

So it is difficult to show. But consider this line going through the centre of the system. If it goes through the centre of the system like this, so it is going through the centre of the system. And then you rotate it by 2 pi by N degrees. That means we have to find out what is the N here. Suppose I rotate it by 90 degrees okay. See if I rotate it by 90 degrees, then what will be the scenario?

The scenario will be this X will now be here, this X will come to this position, better number the carbons, then that will be better. 1, 2, 3, 4. So this will be your 1 after 90 degree rotation. So in 1, the X was up. So this is 1, this is 2, this is 3, this is for. So X is up, then t, X was down. At 3, X was up. So now X will be down and at 4, X was down, so X must be down. What happened? Sorry let us see.

1, X is up, that is okay. 2, X is down, that is okay. 3, X is up sorry 3, X is up and 4, X is down. So this will be the appearance of the molecule after, this will be the appearance of the molecule after 90 degree rotation. And then, the question is, do y look like the same or not? They are not because here X on the left, extreme corner, this is up here, so they are not appearing the same but now the axis is there.

Now if you place a mirror here and take the mirror image of this, so what will be the mirror image now? Image distances equal to object distance. That is the basic premise of mirror image. So this X will be here numbered 1 that X was up, so now the X will be down. This X will be here and this X will be down okay? The rest are all hydrogens.

So this is the mirror image. Now you check whether this is identical with this one and if you inspect, you see that these 2 are appearing the same. So if that is the case, that means now what happens? You have rotated it by 90 degree around an axis, you have taken a mirror image of that rotated molecule, the mirror should be placed perpendicular to the axis, that is very important. And then you draw the mirror image and you see it is identical with the original one.

So that that means now it has got fourfold alternating axis of symmetry. So it has, this molecule has S4, how the 4 arises? Again I repeat, because you have rotated it by 90 degree, the fold is equal to 2 pi by N, so that means 360 divided by 90 and that gives you the 4. So this molecule has S4. So now we have completed discussion about all the elements of symmetry.

So one is simple axis of symmetry, that is CN, then the plane of symmetry, Sigma, then we have the centre of symmetry or the impression point that is called I and the 4^{th} one is alternating axis of symmetry. For a molecule to be chiral, 3 elements of symmetry have to be absent. What are these? The plane of symmetry should not be there. The centre of symmetry should not be there and the alternating axis of symmetry should not be there.

What about the the simple axis of symmetry? It may be present, it may not be present. It is not any criteria, it is not mandatory to be absent for a chiral molecule. So now, summarise a more summarise a little bit more that for a molecule to be optically active or for a molecule to be chiral, what you need is that the molecule should lack, should be devoid of plane of symmetry, should be devoid of centre of symmetry, should be devoid of alternating axis of symmetry, okay?

Then it will be chiral. If it, it does not matter whether it has got C axis or other it does not have C axis. Now, a molecule which does not have any 4 symmetry elements, those molecules are called asymmetric molecules, molecules which does not have any of these 4 symmetry elements are called asymmetric molecules. Now if I say that for chirality, the molecule has to be asymmetric, is it correct or not?

If we inspect a little bit, we say that the statement is correct but you are putting an additional constraint in the system. You are saying that the molecule should be asymmetric. That means it should be devoid of all 4 elements of symmetry. But chirality is not connected to the C axis. So unnecessarily we are putting an additional restriction. So asymmetry is not the, asymmetry means devoid of all kinds of symmetry, is not the criteria for optical activity.

Yes, all asymmetric molecules will be optically active because the other 3 elements of symmetry, that means the I, the Sigma and the SN. If these 3 are absent in the molecule, that will be optically active or that will be chiral. So we have to find a different name for this absence of these 3 elements of symmetry. And what is that different name? That is what is called disymmetric molecule.

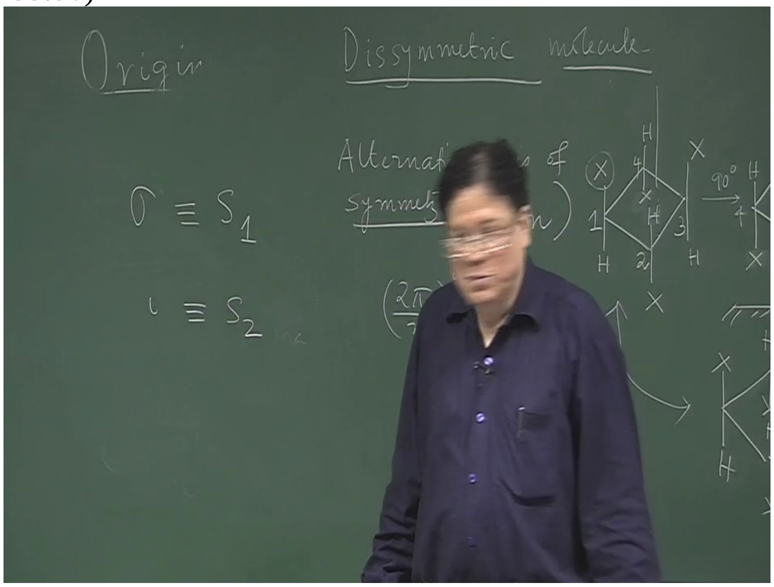
So what is disymmetry? Dissymmetry means devoid of 3 elements of symmetry, I, Sigma and SN. And the criteria, the minimum and sufficient condition for chirality is that the molecule should be disymmetric, it should be devoid of I, it should be devoid of Sigma, it should be devoid of SN okay? So you see our chiral centre never appear in this discussion.

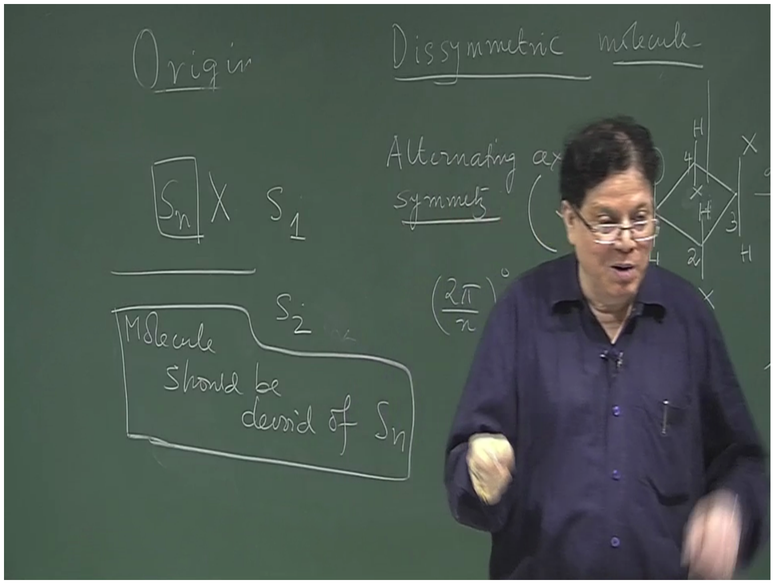
So chirality is entirely dependent on the geometric attributes of the molecule. That means the symmetry properties of the molecule okay? So if someone ask, what is the minimum condition for optical activity or chirality, the molecule has to be dissymmetric. What is dissymmetry? Dissymmetry means it has no plane of symmetry, no centre of symmetry, no alternating axis of symmetry.

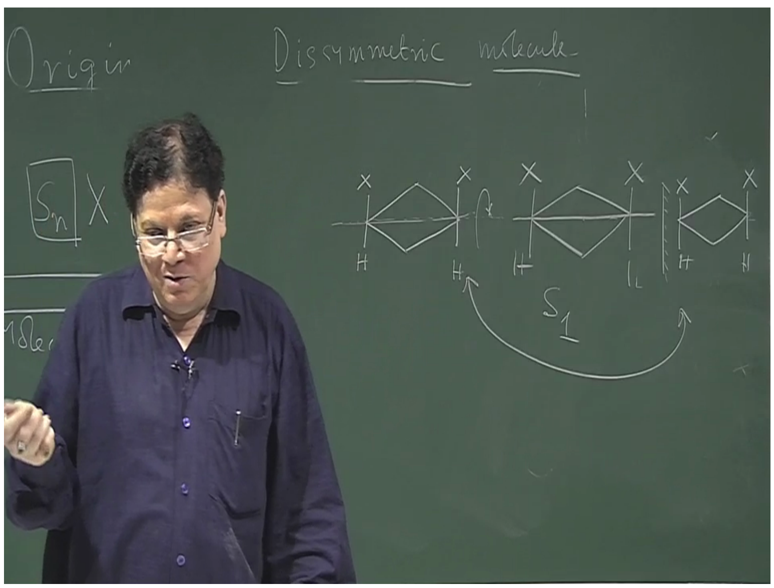
However, things do not stop here. Always, there are questions asked against and for. So again the questions were asked, can we simplify the thing even little more? And interestingly, the the present-day concept about optical activity or chirality is that you do not have to say that it lacks, it has to lack I, Sigma and SN. Just one sentence completes the whole story.

For a molecule to be chiral, it should be devoid of alternating axis of symmetry, that is the final conclusion or line but I did not explain why the molecules should be only devoid of alternating axis of symmetry because we can actually connect alternating axis of symmetry with I as well as Sigma.

(Refer Slide Time: 33:30)







Right now, before I explain that, you should know that this one, that plane of symmetry is nothing but equivalent to S1. That means one fourth. So that means if your molecule has a plane of symmetry, it must have S1 axis, one fold alternating axis of symmetry. Okay? That means Sigma is equated to S1. Similarly, I is equated to S2. Okay? So if your molecule has I that means it has got an S too, a twofold alternating axis of symmetry.

Okay? So basically now you can erase this Sigma and I because S1 means I, S1 means Sigma, and S2 means I. So if I say that if a molecule does not have SN which is not present, the molecule is optically active, the molecule is chiral. So that should be sufficient. If I say it does not have SN, that means it does not have S1 which is plane of symmetry. It does not have S2 which is centre of symmetry or it does not have any other S axis like S3 or S4 or S5, whatever it is.

So now the present-day concept or present-day basis of optical activity is that the molecule should lack or should be devoid of SN. That is the final conclusion. Now you can tell that is, how do you know that S1 is equated to Sigma and S2 is equated to I. So we have to, we have to explain that. I think then, you will accept what I am saying that molecule should be devoid of only SN because ultimately it boils down to such a simple statement.

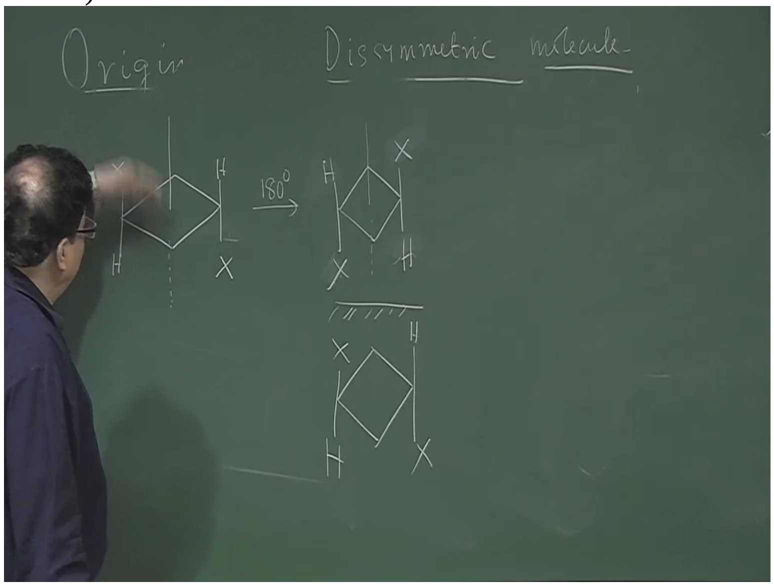
You do not have to consider any other elements of symmetry, only SN. So let us see how this Sigma is equated to S1. So we draw a molecule which has got a Sigma like this X, again we take the same molecule. So this has got S Sigma plane okay? So now if I consider an axis like this, an axis like this, that means if I take this molecule, I take an axis like this and I rotate the molecule by 180 degree.

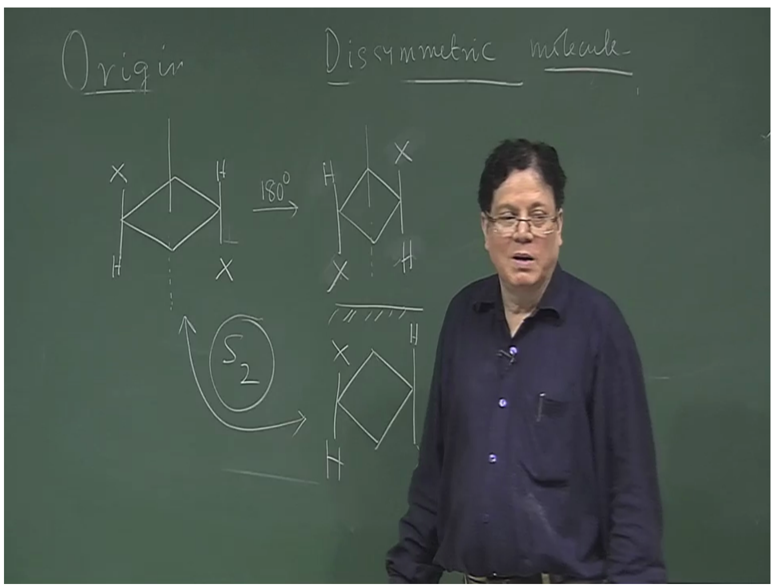
Not this molecule, this is a different one but the cyclo butane. I am just showing that the cyclo butane shown like this and it is rotated by 180 degree. so if I do that here, what happens? So I do this by 360 degrees. So if I do the rotation by 360, what happens? It remains the same because everything when rotated by 360 comes back to the original okay.

So this is, it remains X, X, H, H. This is my axis, remember, this is my axis. Now I place a mirror. What is the definition of alternating axis of symmetry? That after rotation, you place a mirror perpendicular to the axis. So I put the axis. I put the mirror perpendicular to the axis. So how does it look now? It looks the same as the original.

They are same. So that means, it has got S1 axis that if you rotate by 360 degree and then take a mirror and take the mirror image, the mirror image is same as the original. So that shows that it has got S1. Okay? So that means S1 and this is, this holds for every molecule which has got a Sigma. That whenever there is a Sigma, there must be an S1 present in the molecule. Okay? So unnecessarily, you have to bring in Sigma while describing optical activity.

(Refer Slide Time: 37:59)





Similarly, if you take a molecule which is which has got I axis. That X here and X there, okay hydrogen here and hydrogen there. And if I now have the axis like this, I rotate it by 180 degree. So how does it look? This X will come here and that X will go here. So this is hydrogen, that is hydrogen. This is after 180 degree rotation.

This is after 180 degree, sorry sorry this is after 180 degree rotation. This X will come here. That means this will be X and this X will be there. Okay? This is after 180 degree rotation. The molecule does not look like the same. Now what you do? You place a mirror. Given when your axis is this, we place a mirror and take the mirror image. This is H, that is X and this is X, that is H.

Okay? I again repeat the operation. This is my axis. This is the molecule which is having I. I rotate it by 180 degree along this axis. This is my rotated position and then I placed the mirror perpendicular to the axis, I get to this molecule. And now you see the relation between this and that. They look the exactly the same. They appear to be the same.

So that means it has got S2 because by 180 degree rotation, you are achieving this. So it has got S2. That means all molecules which has got I must have got S2. So you do not have to bring in I. When you say that a molecule is devoid of alternating axis of symmetry, that means you accept the fact that it does not have I. That is why a single line only sufficient to describe the minimum and sufficient condition for chirality. I hope this is clear to you. We can have various problems and then to show the importance of the symmetry elements in molecules in the next class, okay.