Concepts of Chemistry for Engineering
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Lecture 71
Configurations, Symmetry and Chirality

Hello, everyone. Welcome the module on stereochemistry. We are still trying to discuss the arrangement of atoms in space, and look at how does that give rise to different properties.

In this lecture, we will go into a bit in detail about what are the symmetry elements of a molecule, and how that dictates the chirality or the lack of it in a molecule. Before we get there, let us just quickly recap what we learned in the last lecture.

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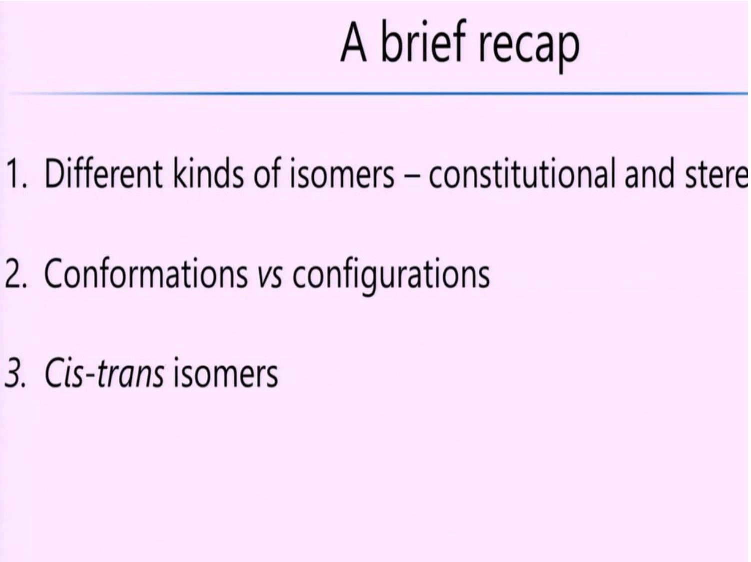

A brief recap

1. Different kinds of isomers – constitutional and stere
2. Conformations *vs* configurations
3. *Cis-trans* isomers

In the last lecture, we had seen different kinds of isomers that is constitutional and stereoisomers. By constitutional, we learned that here, to go from one form of isomer to another one has to break a bond and rearrange the atoms and that would give rise to constitutional isomers. That is, the connectivity for constitutional isomers are completely different. A classic example we had seen was between a cyclohexane and a few forms of hexene, 1-hexene, 3-hexene or others.

On the other hand, if you come to the stereoisomers, here, the main distinction is the connectivity remains the same, but the way they are arranged in the space is what distinguishes the two isomers. And for this, we had looked at two classes. One is called as cis-trans isomers, and we had looked at few examples of those and another is what are called as isomers based on a chiral center or an asymmetric center. So in this lecture, we are going to go into a bit more detail on that and see what how, what are the different properties of that system.

We had also learned that there are two different kinds called as conformations and configurations. In conformations, the, you have different isomers which actually can rapidly or can be easily inter-converted between one among, one, between the two without actually breaking the bond. However, in case of configurations, one has to break a bond to go from one confirm, one configuration to the other configuration.

And an example we saw, where the two chiral forms of a particular molecule called 2-methyl butanol. And, we had also discussed in a bit detail about cis-trans isomers. So with this background, let us now get into looking at a bit more closely on stereoisomers which have a chiral center or an asymmetric center.

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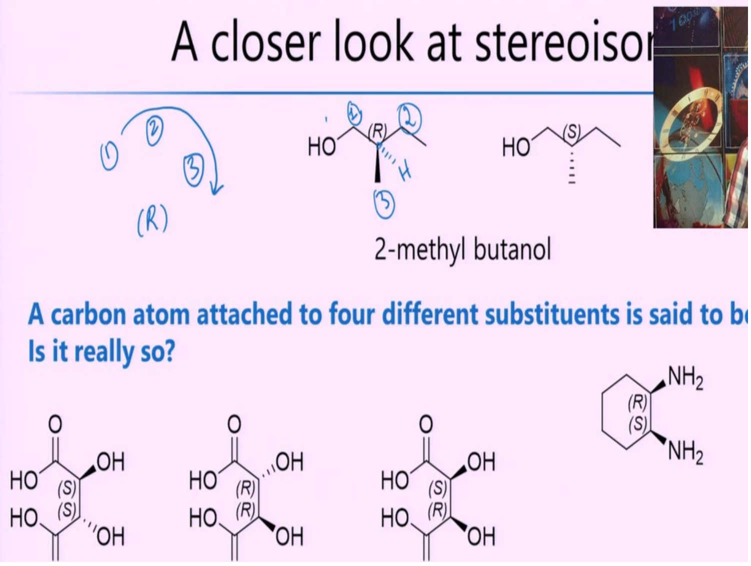

A closer look at stereoiso

2-methyl butanol

A carbon atom attached to four different substituents is said to b

Is it really so?

So, these are the two examples which we had looked at in the previous class. On the left hand side you have a 2-methyl butanol derivative in which the methyl group is protruding out of the plane of the screen. On the right, you have the methyl actually going back. And I am sure you, you are all aware of what is called as a Cahn–Ingold–Prelog method of naming this, or giving them the absolute configuration, that is the R and S.

So just to refresh your memories, let us just look at that. If you go by the Cahn–Ingold–Prelog method, so then if you know, we are looking at this particular carbon atom here, and so then what you have is you are going to try and look at the priority of the carbon atoms.

So, we have one, this is, this would be the first priority because that has the oxygen attached to it. Then you have the second priority is this which is having two carbon atoms. And then the third priority would be to the methyl. And you would also have something which is going back, which is the hydrogen.

So, if I put it here like this, so in the Cahn–Ingold–Prelog we have the hydrogen always pointing away from us and that is indeed the case in this particular isomer. So if you now put it like this, we have 1, we have 2, and 3, arranged in space. So then this would actually go as a clockwise, and this would give rise to R enantiomer or R form, and that is what we have here.

Similarly, one can elucidate for the one on the right hand side. And this we would call it a S enantiomer or the S configuration. And this is what we typically saw as, in a molecular model we saw as this, where a central carbon atom is attached with four different units. And this was also the definition or the proposition given by van't Hoff, to begin with.

Now, let us look at one particular statement and see if this particular definition that a carbon attached to four different substituents is chiral, is this true or is this universal, or are there any limitations on this particular statement?

To understand that, let us go back and look at a very classic example of a system which contains two centers or two chiral centers. Here is an example of what is called as a tartaric acid. This was some, this was the first derivative which was studied by Pasteur in 1850s, around 1850s, and what he observed is that there are two forms, one is called as the, one, one form which rotates the plane of polarized light along one direction. And that is why we call it as optically active, because it rotates the plane of polarized light.

And similarly, there is another form which actually rotates in the opposite direction. So these were the two forms which Pasteur understood or Pasteur isolated. However, there was also another form which was later realized that this was actually optically inactive.

That means, if you shine a polarized light on it, it would not absorb or it would not change the direction of the plane polarized light. So this was a bit puzzling.

If you now look at this particular molecule which is shown here, in the light of what we just discussed above, what you indeed see is that it has what we call as a chiral centers, it has 1 and 2 chiral centers, but still, it is actually optically inactive. So how do we go about rationalizing or understanding this?

And this is not just one particular molecule, there are actually many, many such systems where you could have chiral centers in the 1, 2 positions, which would be optically inactive. And there are also different kinds of molecules called alenes, which do not even contain a chiral center and they are still optically active. So how does one rationalize or understand this. So we need a much more broader perspective on this.

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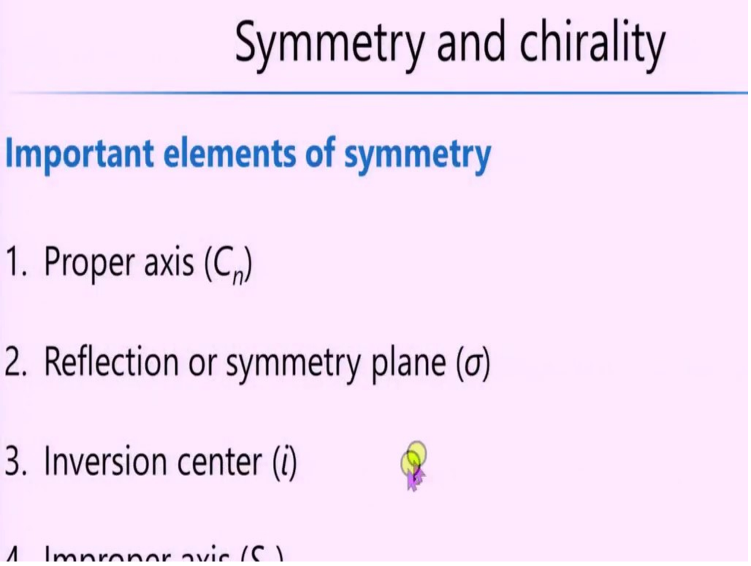

Symmetry and chirality

Important elements of symmetry

1. Proper axis (C_n)
2. Reflection or symmetry plane (σ)
3. Inversion center (i)
4. Improper axis (S)

In order to evolve a broader perspective, what we need to do is we need to go back and look at symmetry and chirality in relationship with each other. So far, what we said was, we just said that if you have a carbon atom attached to four different centers, then we call it as a chiral center or a molecule as chiral.

However, when one has more than one carbon atoms or more than one chiral centers, then the whole system has to be in considered in totality. So for that, we have to actually understand what are the symmetry elements or a symmetry operations which are applicable in a molecule and how that leads to chirality or the lack of it.

There are four major or four classes of symmetry operations which are possible on a molecule. One is called as a proper axis, and, proper axis of symmetry. And other one is called a reflection or a symmetry plane. And third is called the inversion center. And the fourth is called as an improper access.

So now, what we will do is we shall look at each one of them in a little more detail, and try to understand them with a few examples. And finally, we will come back to what is the relationship between these elements and chirality of a given molecule or a system.

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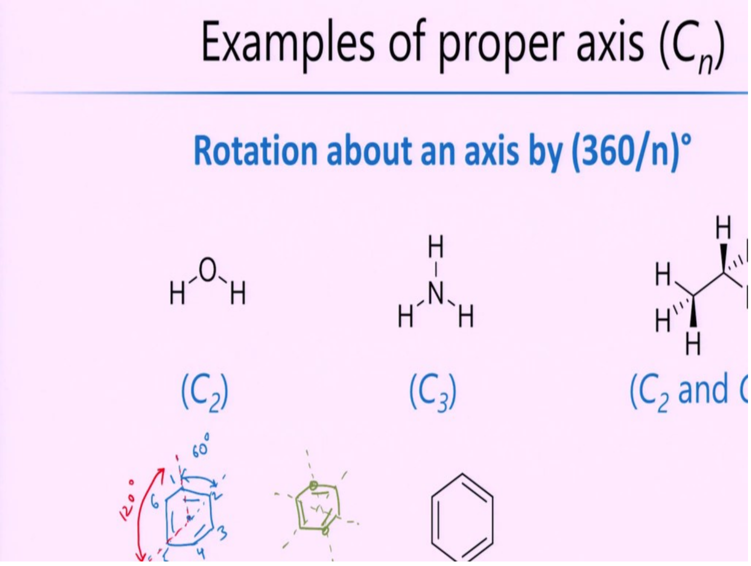

Examples of proper axis (C_n)

Rotation about an axis by (360/n)°

(C_2) (C_3) (C_2 and

Let us look in by looking at what is called as a proper axis of symmetry, which is denoted by this C with an underscore n. And this is simply nothing but the axis along which if I rotate the molecule, it should come back to the same position. And the number of the turns which it would take is what is denoted as n here. It would become clear if I take you, a simple example of a molecule of water.

If I take a molecule of water, which is shown here with the red oxygen and the two white as the hydrogens, and if in order to get back to the same molecule, or an indistinguishable molecule, what I have to do is, along this direction, along the direction perpendicular to the oxygen, I would rotate it by 180 degrees. I would go and rotating the 180 degrees. That would lead to the same molecule again.

And here, the, what n stands for is 2, because I need to rotate the molecule along this axis by 180 degrees to get back the same molecule. So if you put n is equal to 2 in the formula, you will see that I need a 180 degree rotation. And that is indeed what we did here. We went from a molecule like this, we just rotated by 180 degrees to get the same molecule back. I hope this is, gives you an idea of what I mean by proper axis of symmetry.

To give you another simpler example. So I have taken here an ammonia molecule NH 3, where the black ball represents the nitrogen and the green ones represent the hydrogen, in this case. If I have to get back this molecule, I need to do a 120 degree rotation. That is, this is the angle by which I need to rotate, which is the 120 degrees. So if I rotate, then I would get back the same molecule. And I can keep on doing this to get the same, same molecule.

And if we now have, divide the 360 degrees by 120 degrees, that is, angle needed to get back to an indistinguishable molecule, you will now see that we have a C 3 symmetry. That is what is written here.

Now let us go ahead and take a look at a slightly, slightly difficult but still a simple molecule, which is called as an ethane, which is something which we looked at in the first two lectures. So here, I am showing you a staggered configuration of an ethane molecule, where you see the three hydrogens which are actually coming towards you, and the carbon. And at the back, we have one carbon and the three hydrogens.

So, I guess this will be again, very apparent, if you want to look at what are the symmetry elements present. So the one, the one way to do is to hold this carbon and rotate the entire molecule by 120 degrees and see if I get a similar molecule back. So let us do that, I am going to hold this carbon, and I shall just rotate it till I get the, get it back onto this version. That is 120.

So, you see that I have got exactly the same molecule back. If I hold any one of them, and rotate, I would get back the same molecule. This is actually very similar to what you saw for the ammonia case, that you, because we these three are in a dispersion along the tetrahedral of a carbon, you will have a C 3 symmetry in this case, which is, I guess, is a little more obvious.

However, what is not obvious is the C 2 axis. So to understand the C 2 axis, let us do one thing, let us now hold the molecule like this, where what you see is that, I hope you all can see that there is one particular plane which is going through this hydrogen, the carbon, the carbon and the hydrogen. So the plane which is actually going through these four atoms is one plane.

And if I have this particular plane, what I can do is, I am just going to hold this, and I can come up with an axis which is perpendicular to this. And I will try to do a 180 degree rotation here. So I will, around this if I do a 180 degree rotation, I actually end up on the same molecule. I hope you see that. And I can just do that again. So the hydrogen is, on the bottom is coming towards you and hydrogen at the back is going, is coming towards me.

And if I do again a 120 degree rotation, or a 180 degree rotation or a C 2, you will see that the same molecule is retained, that is, the bottom hydrogen is again coming out of the plane and towards you, and the one here at the top carbon is coming towards me. So this is what would give rise to a C 2 symmetry.

And since I have, I can create one plane, I have one C 2 symmetry, which I am showing you currently, but I can, since there are, I can actually similarly make three total planes where two hydrogens and two carbons are present, like for example, this is one, one plane, which I have currently now, and what I can also do is, I can also take these atoms, which is again another plane, and similarly you can also come up with another, which is this.

So, it may not be very apparent now because all the substituents are exactly the same. So it will be hard to see all the three planes and the consequent C 2, but I hope you at least can see one of the planes and the C 2 axis which is perpendicular to it or the, orthogonal to it.

Now let us go ahead and look at a slightly more symmetric or a complicated system. So here, what we have is, we have a benzene as a particular system. And I guess you, this is a little more easy to look at because the molecule is planar. So you can actually just look at it in the plane of the board itself.

And here, what you have is you have different elements of symmetry. One is, you can do what is called, if you actually go orthogonal to the board, that is, perpendicular to the board, I have a, I will just try and, so if I draw the benzene again, here, assume it is symmetrical, or the bond lengths are the same, I can actually come up with an axis which is, or the axis is perpendicular to the plane of the screen.

So, if I come up with this, then what I can do is, so if I rotate it by 60 degrees, that is, one carbon to two. So then I would end up in the same molecule again. So the degree of rotation I am doing is 60 degrees. So that means 360 by 60, that I have a C 6 axis of symmetry in this case. So that is one of the elements which is shown here, that is the C six.

Similarly, I can also do a 120 degrees. That is if I, if I draw this, and, so then I would do 120 degree rotation. So if I now do a 120 degree rotation with the axis perpendicular to the plane of the benzene, then I would again get the same molecule. And if you now divide 360 by 120, you would get a C 3 symmetry because you, now n is 3. So that is what we are looking at here is, C 3. So we understood hopefully, C 6, as well as C 3.

And now coming to the, so these were actually where the axis was perpendicular to the screen of the, or the plane of the benzene. So now let us come back and look at what is called as a C 2. So in this particular case, you can, so you can try and do one thing, which is now you are going to try and look at within the plane of the benzene. So for that I will draw again, once again, so that it is a bit more clear.

So now what you can do is you can actually have a plane which is passing through this, so if you now, along this plane, which is within the plane of the benzene, if you now flip it, you get back the same molecule, because the molecule is symmetric. So now you get one C 2.

Similarly, I guess you can easily understand that I can get this C 2, and I can also get this C 2. So I already have three C 2s now. And, so this is when you go from one atom to the other atom, that is, this to this, or similarly to the other atoms. Now what happens if I go between the atoms. So let us look at that.

So, since the, the bond lengths are same, although I am drawing double bonds here, but this is actually alternating double bond, so the bond lengths are exactly the same. So given that, what I can do is I can actually go in between the two bonds as well. So this is where I am actually going through the, not going through atoms, but I am going through bonds. And this would also give me one C 2 axis. Similarly, I can have two more C 2 accesses.

So, what this tells you is that you can have symmetry elements or the symmetry operations going through not just bonds, you can also have them going through atoms as well as through the bonds. Now we looked at what is called as a proper axis of symmetry. And now let us go ahead and look at something what is called as a plane of symmetry or a reflection plane.

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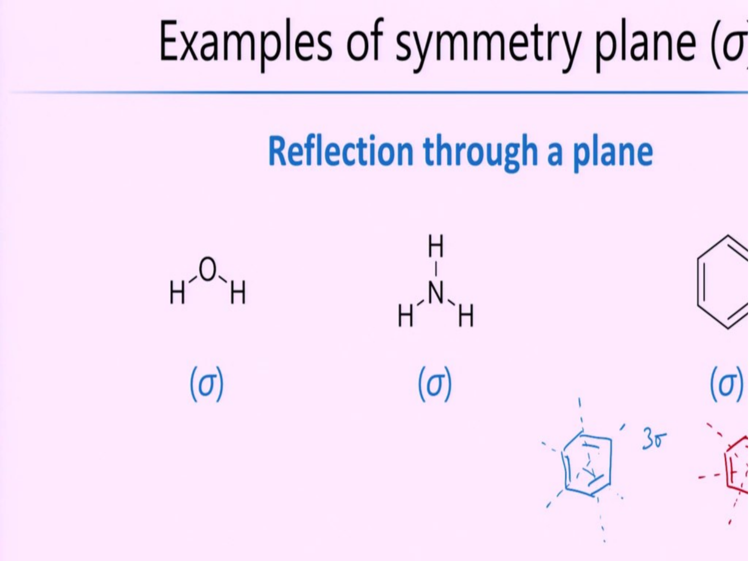

Examples of symmetry plane (σ

Reflection through a plane

So, in this, what we will do is we will actually take the molecule and look at the reflection, if there is any reflection in the molecule, and on reflection, does it give a same molecule or a different molecule.

So, I understand that these symmetry operations, which I am trying to show now are actually not that easy to understand if you do not have these kinds of molecular models with you. But what you can certainly do is you can go to this very nice website, which is given here, Symmetry at the rate Otterbein.

So, this has a very visual ways of looking at symmetry elements and symmetry operations in these simple molecules, and even in some of the more complicated systems.

I think that would give you much more better feel of what the symmetry elements are. So I would encourage you to go back and play around on this website.

Coming back to symmetry plane. So now let us again go back to a simple case, which we looked at, that is, the molecule of water. So if I take this molecule, so is there any reflection plane or a plane which is, which cuts the molecule equally, equally? So there are actually two symmetric planes here.

One, if I take this molecule, and if I cut it in this, or if I put a plane across this, I see that the atoms on either side are exactly the same. That is, I put a plane here, I have a hydrogen here, and I have hydrogen on the other side. So that means I have one plane of symmetry, or one sigma plain here.

And what could be the other sigma plane here? Because this is a little obvious, the one which I showed you is obvious. So the other one is, actually I could even cut through the atoms. I can actually, in the plane of the molecule itself, in the plane of water molecule if I cut, or if I have a plane which is going through the atoms, then that would also give me a sigma plane. And so in totality, I have two sigma planes for a simple water molecule. I hope that's understandable.

And now let us look at the case of the ammonia which we had previously seen. So if you now take this molecule, again, I am viewing it from this, from the front-on view, I could have one sigma plane, which is actually going through the carbon and one of the hydrogens.

And here, what you see is that if I have a sigma plane going through, it has both hydrogens on, on the other side. So that means it is a symmetric system. So this would be one sigma plane. And similarly, I can have it going through the other two as well. So in total, in ammonia, I would have three sigma planes.

And now coming to over more symmetric benzene molecule, so you go, you would have imagined that, you would have already guessed that here also similar thing is possible. So let us just look at that briefly.

So, if I draw again, one more benzene for the, to make it clear, so I could have a plane which is actually, we could have a sigma plane, which is going through this and perpendicular to the, perpendicular to the plane of the benzene, and that would be one sigma plane. And similarly, I could draw two more here, one, and another one. So I have now three sigma planes which are actually going perpendicular and through the atoms.

And similarly, as we did for the proper axis, we can also do for the, for the sigma plane, that I can draw now between the atoms and through the bonds. So yeah, I can actually have one which is going through this. And similarly, between these two opposite bonds, I can have another going through. And here again, I have one more going through this. So this is three sigmas, through the bonds, and, three sigma, we have through the atoms.

And these are little more sort of intuitive. Whereas another one which people typically miss is that if I have a benzene, I can also have it, I can also slice through it, or I can also have a plane going across the atoms. And that would also give me a sigma. So in total, I will have seven, that is, one is the horizontal, and other six are vertical. Among the six, three are going through the atoms, and three are going through the bonds.

So, you could actually play around with this, you can draw the molecule on a sheet of paper or go through this website and play around. And I am sure that will become a little more clearer to you as you go through that website.

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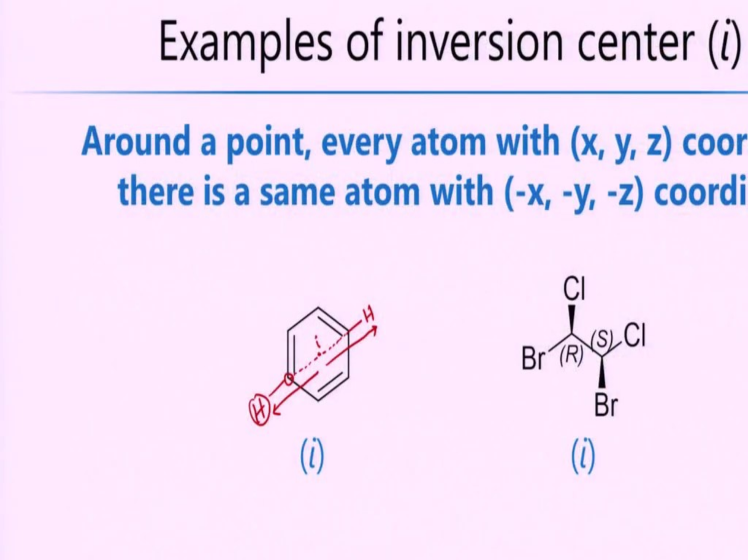

Examples of inversion center (*i*)

Around a point, every atom with (x, y, z) coor
there is a same atom with (-x, -y, -z) coordi

Now let us go ahead and try to look at what is called as an, an inversion symmetry. So an inversion symmetry is one in which every atom should have a corresponding atom at exactly the opposite distance on the, in the molecule. So this might look a bit mathematical and abstract. So to clarify that, let us look at a case of the benzene.

Again, if we take the benzene, and what we have here is that we have a center of inversion here, and here I will draw the hydrogens, just to be, point out. And now if I want to go from here to this carbon, I am going to draw here, in this, in this direction. And to find, to see whether this is indeed the center of inversion I, I need to come back equal distance, and I indeed find another carbon.

Similarly, if I want to go towards an hydrogen, I can go towards this hydrogen. And to find out whether it is again a center of inversion, I need to come back and find out, find another hydrogen here. And I have an hydrogen here as well.

So, you can do the same exercise for all different kinds of atoms present in a molecule. And that would lead you to an, in, center of inversion in benzene, which is at the centeroid of this, of this hexagon.

And another, let us look at another example, which is this 1, 2-dichloro dibromo ethane. So here, I have a model of this 1, 2-dichloro dibromo ethane for you. So what I have is, the black ones are the carbons, and the green ones are the chlorines, and orange ones are the bromines, and the white ones are the hydrogens. So what I am trying to do is, I am going to hold it like this, let us, I am going to hold it like this.

And let us say I have a center of inversion in the middle of this bond. And if I have that, then let us go from here to the carbon atom, or to the hydrogen atom. I see that there is an, I can find a hydrogen atom. And if I actually go back from here to the, on the other, on the reverse direction, I indeed see hydrogen atom here. So I have both the hydrogens on this positive as well as the negative side.

Similarly, if you want to do for the chlorine, you do see that from here going from center, I can go and find that chlorine atom here. And if I come back, I do find a chlorine atom. And the same thing holds for the bromine atom as well. So this would tell you that the molecule is, has a center of inversion, which is again another important symmetry element.

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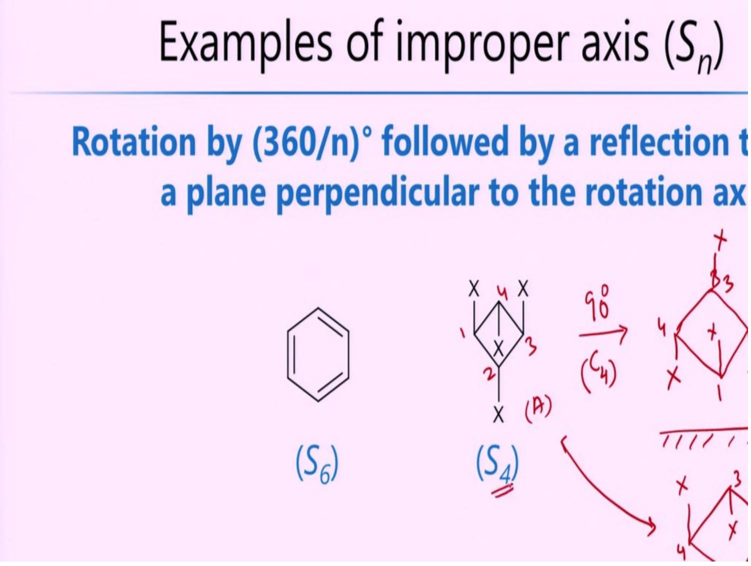

Examples of improper axis (S_n)

Rotation by (360/n)° followed by a reflection t
a plane perpendicular to the rotation ax

And finally, we will come to an important thing which is called as improper axis of symmetry, which is nothing but a rotation by 360 degrees by n, which is the proper axis of symmetry which we saw previously, followed by a reflection or a sigma plane which is perpendicular to the rotation axis. Let us say if this is my rotation axis in a molecule, the sigma plane should be perpendicular to it. That would define you an improper axis which is denoted by S n.

Let us look at a simple molecule which is the benzene, again. So here we know that we have a C 6, that is, I have a plane of benzene here, and I know that I have a C 6 which is perpendicular to this. But I once I have the C 6, in order to see whether I have an S n or not, I should put up a reflection plane or I should put a sigma plane here.

And if I put a sigma plane which is cutting through the atoms of the benzene, I indeed find that there is a sigma plane. So that means I have a C 6 followed by sigma plane which is orthogonal to it. So in the end, I will have an S 6 for benzene.

And similarly, if you want to convince yourself of a slightly different atom, what we can do is we can take this cyclohexane derivative with X being a substituent. And what I will try and show you is that if I have this particular molecule, I am going to rotate by 90 degrees. So for sake of convenience, let us number the atoms as 1, 2, 3, 4.

And I am going to write down similar, so I have my 1 here, so the substitute X will be here, 2, 3, and 4. So if I go to 2, the substituent is down, and if I go to 3, the substituent is again, up. So I write 3 here, And if I come to 4, the substituent is down. So now I've done a 90 degree rotation here. So now what I will do is I will put a mirror plane here. So if you put a mirror plane what you would end up then, is something like this. So now this would become, and this will come here.

So, I hope you can see that the one which I have drawn here initially, let us call this A and the one which we have got by operating a 90 degree C, a 90 degree proper rotation, followed by a mirror plane, mirror plane or sigma, And this is C 4, I hope you can all see that, and followed by sigma, I have ended up with exactly the same molecule here. That is, on C 1, I have the X which is pointing up and C 2 the X is coming down, and so on and so forth. So in essence, what I have is an S 4 elements of symmetry for this particular molecule.

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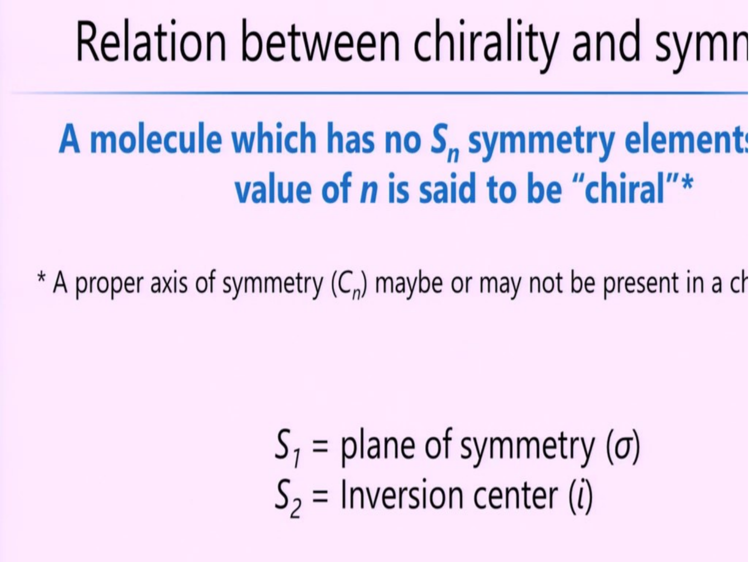

Relation between chirality and symn

A molecule which has no S_n symmetry element
value of n is said to be "chiral"*

* A proper axis of symmetry (C_n) maybe or may not be present in a ch

S_1 = plane of symmetry (σ)
S_2 = Inversion center (i)

So, you must be wondering, what is this got to do with chirality, or why is he trying to tell us about symmetry rather than about chirality? So, the reason why I am trying to talk to you about chirality and the symmetry is that a molecule is said to be chiral, not only when it has four different substituents, but a molecule is said to be chiral in a more rigorous stir, if it has no S n or improper axes or improper elements of symmetry. So only and only then a molecule is set to be chiral.

But please do note that a chiral molecule can have a proper axis of symmetry. That does not forbid it from having any C ns. But that is not a necessary condition. It may or may not have.

So, if you just want to convince yourself, what I would encourage you to do is to actually go back and try to test out these two hypotheses which I have shown you, that S 1, or improper axes with, or, with S 1, improper axis of the first symmetry has it, actually equal to plane of symmetry. And S 2 is nothing but an inversion symmetry.

So, you can take a very simple molecule like ethane or the, the dichloro dibromo ethane I showed you in the previous slide, to convince yourself of these two, these two aspects which actually embed both the plane of symmetry as well as inversion into the improper axes, improper symmetry element.

As a result, only one symmetry element, that is, improper is good enough to define whether a given molecule is chiral or not. With this, we shall stop here. In the next lecture we shall go ahead and look at what are called is an enantiomers and diastereomers. Thank you.