Symmetry, Stereochemistry and Applications

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Lecture - 07
Symmetry Elements in Organic Molecules

Welcome back to the course on Symmetry, Stereochemistry and Applications. In the previous class, we were discussing about symmetry elements of small organic molecules and we have learnt how to identify different symmetry elements in a series of molecules.

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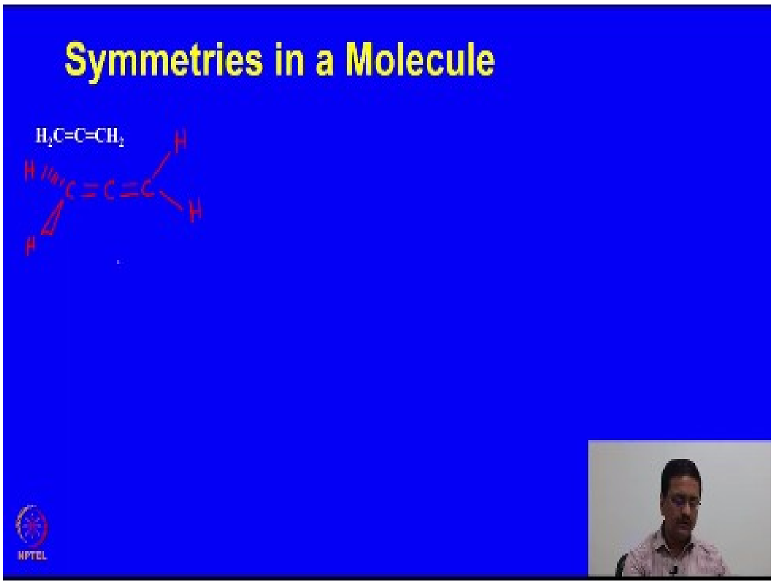

So, we will continue our discussion in the same line and we will see a few complicated molecules for which we would like to understand the symmetry elements that are present in these molecules. The first molecule that I would like to discuss now in this session, is a very simple molecule called Allene. And many of you are aware that this molecule is a very peculiar molecule where you have 3 carbon atoms in a row and they are bonded by double bonds.

And if we draw the 2 hydrogen atoms on this carbon in the plane of the projection, the other 2 hydrogen atoms on the other carbon are above and below the plane of the projection. So, when you have such a molecule like that one should actually try to draw it in a slightly different way. So, that one can find out the symmetry elements that are present in this particular molecule.

So, I would like to draw this molecule inside the cube. So, let us remove this drawing and try to draw this molecule inside a cube.

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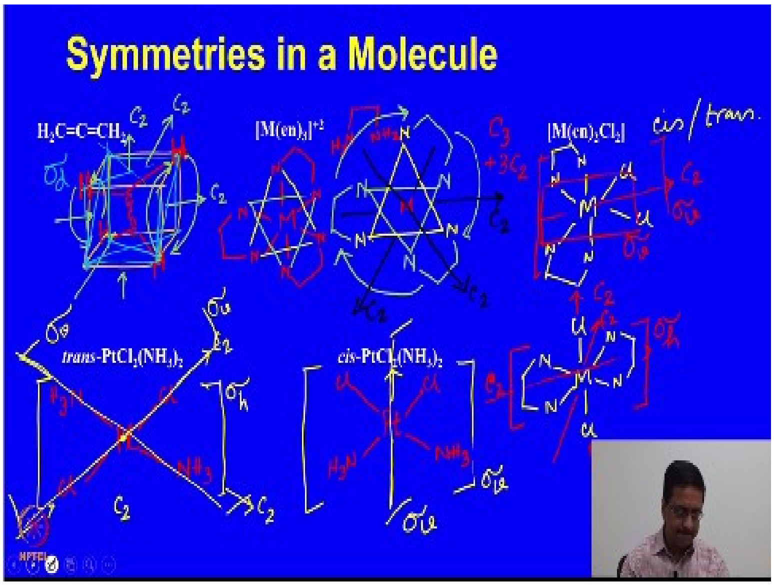

I am drawing a cube and then I will draw the molecule inside it in a different color. I am adding the hydrogens first. These 2 hydrogens are in the upper surface of the cube. Those 2 hydrogens are on the lower surface of the cube and these hydrogens are connected to carbon atoms. These hydrogens are connected to carbon atom and there is a middle carbon in between which is bonded like that.

So, if you see this molecule now, it may be easy to identify the presence of different symmetry elements in this molecule. You see, if I have a 2-fold axis passing through the center of this phase which actually is passing through the C C C linear chain. So, that is a 2-fold axis which converts 1 hydrogen to the other and rotates. There is another 2-fold axis passing through the midpoint of these 2 parallel phases which brings that hydrogen down here and this hydrogen goes there.

Similarly, that hydrogen comes here and this hydrogen goes back there. Similarly, there is a 2-fold axis passing through the front and back surface, center of the front and back surface that is the third C2 that you have. So, here what we have is 3 C2 axis and then what we have are a set of mirror planes which contain these individual C2 axis. So, if we divide the cube like that, that is a mirror plane. If we divide the cube like that, this is a mirror plane.

And if we divide the cube like this, is another mirror plane. So, this has 3 mirror planes which are technically sigma d because every individual sigma plane that we have drawn here is dividing or bisecting 2 perpendicular C2's. Now, let us try to draw some metal complexes $[M(en)_3]^{+2}$. So, when I write en, en means ethylene diamine which is like this. So, this is, all of us know that this is a chelating ligand.

So, if I have the metal ion which is octahedral and we have the nitrogens connecting the ligands and as you know, the ligand, this ethylene diamine; ligand cannot connect from top to bottom. The connectivities are like that. So, now, it becomes very difficult to identify what symmetry element is present there. So, how do we identify the symmetry elements in this molecule that we need to see here.

What I am trying to draw is a triangle containing the nitrogen at the top and 2 nitrogens present in the equatorial plane and then another triangle containing the other 2 nitrogen in the equatorial plane and the nitrogen at the bottom. So, if we redraw this molecule considering these 2 triangles, here, this triangle has 3 nitrogens at corners. The other triangle has 3 nitrogens like that.

So, a very nice star shaped geometry is formed and the metal that we have is sitting at the center of this star and the bond that we have between the 2 nitrogen atoms are like that. Clear? So, now, what we have here it is very easily seen that there is a 3 fold axis which is passing through the metal perpendicular to these 2 triangles which are actually opposite to one another.

So, the 2 triangles are opposite and the 3 fold is passing through the center of the 2 triangles and intersecting the metal ion. So, that 3 fold converts this ethylene diamine groups from there to here, here to there and they are back to this point. In addition to this 3 fold, what we have? You can easily see that passing through the metal in between the 2 triangles, there is a C2. Similarly, there is a C2 like that and there is a third C2 going like this.

So, when you do this C2's, the position of the ethylene diamine part that is the C single bond C portion does not change its position. So, the nitrogens get interchanged. The nitrogen which is above the plane of the board goes to below the plane of the board and the one which is below the plane of the board comes to above the plane of the board. So, this particular molecule has a C3 plus 3 numbers of perpendicular C2's.

Now, let us see 2 very similar molecules which are all very well known molecules. So, if we write platinum at the center, when I say that it is trans. We write it as trans in this way. So, what are the symmetry elements that you can see in this molecule. This molecule has a C2 which is passing through the center of this molecule. This molecule has a plane of symmetry which is perpendicular to this C2. So, it is sigma h.

What else you have? It has 2 more C2's which are going like that and this. What else? This is a mirror plane. That is also a mirror plane and these contain the C2's, so it is sigma v. Let us see the other molecule. Here, it is cis-platin; NH_3, NH_3. Let me write it better. So, now, what we have here is a C2 but in a different orientation. In the previous case, the molecule that I had drawn was drawn in the plane of the projection.

Here, the molecule that I have drawn is in the plane of projection but the C2 in the previous case was perpendicular to the plane of projection and in this case the C2 is in the plane of projection then the molecular plane that we have here is a sigma v and the plane which is perpendicular to the plane of projection but contains this C2 axis is another sigma v which essentially means that this particular molecule also has a very similar symmetry or same symmetry like water molecule.

So, when we try to draw these symmetry elements, let us finish with one more molecule which is $[M(en)_2Cl_2]$. As you know, this can have 2 different configurations. It can be cis or trans. So, if we write M Cl Cl and then en can be like that. So, this is cis and the other is trans where you write M Cl and Cl above and below and the ethylene diamine is in the equatorial plane.

So, what are the symmetry elements that are present here? What you can see in case of the cis compound? You have a C2 axis passing through the molecule and a mirror plane which is containing the C2 axis and a mirror plane which contains the 4 equatorial atoms with the metal and both of them are sigma v's as both of them contain the C2 axis.

In this particular case, when it is trans it has a C2 axis bisecting the equatorial plane and it has a mirror plane which is the plane of the molecule, equatorial plane of the molecule which is sigma h. It has other C2 axis which is like that which divides the molecule into 2 parts. It has 2 more C2's like this. So, it has actually 3 C2's and several sigma planes.

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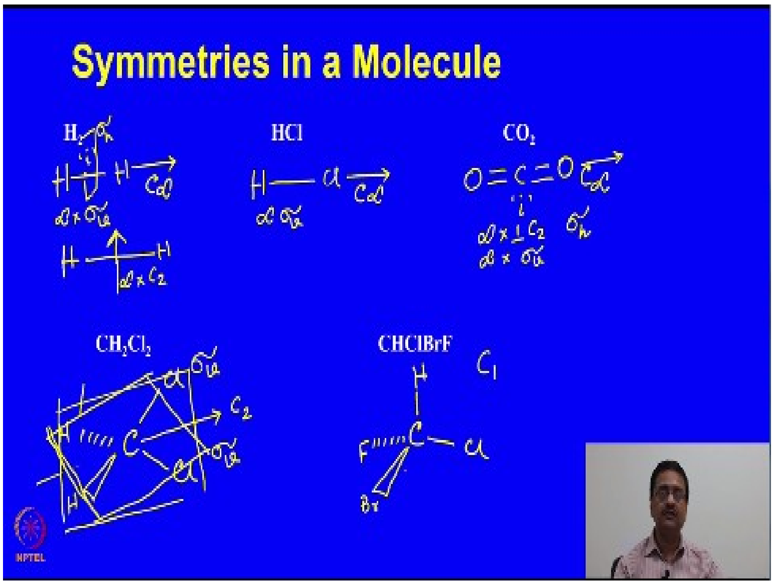

So, when we now go and try to find out the symmetry elements present in much simpler molecules, we will see that these molecules have very different symmetry compared to the previous ones. So, here in case of hydrogen molecule, the molecule is nothing but linear. So, in this molecule the axis of the bond is a C infinity axis. What does it mean? This molecule which is a linear molecule like that you rotate the molecule infinitesimally small about its bond. It does not change its orientation.

This molecule has a C infinity axis. What else this molecule has? Because of this molecule being linear the plane which bisects the molecule like that every plane that is bisecting the molecule like this are infinite number of sigma v's and this molecule has i which is the inversion center present at the middle of the bond and also it has a mirror plane passing through the midpoint of the bond.

Now, how is HCl different from hydrogen? In case of HCl, we have the C infinity axis as usual and then we also have infinite number of sigma v's but the inversion center is not present and also the sigma h is not present. We should also remember that hydrogen molecule has a C2 passing through the midpoint of the bond and there are, infinite number of such C2. So, this is hydrogen molecule.

The C2 can be here; can be there; can be here; can be here; anywhere perpendicular to the bond. There may be infinite number of C2 axis in case of hydrogen. So, hydrogen has a large number of different symmetry elements. Now, if we go to CO2, you see it is very similar to hydrogen because it is having a center of inversion or i. This molecule has C infinity axis. This molecule has infinite number of perpendicular C2's.

And this molecule has infinite number of sigma v's and by virtue of this being centro-symmetric here in the linear molecule it has a sigma h as well. So, CO2 has all the symmetries that are present in hydrogen molecule. Now, we go to another very simple molecule dichloromethane, if we draw dichloromethane like this, 2 chlorine atoms and the carbon atom on the plane of the board.

The other 2 hydrogens are above and below the plane of the board. What are the symmetry elements that we can see here? What we see easily is a C2 axis and a plane which is containing the C2 axis as the sigma v, bisecting the H C H angle and another C2 axis which contains the H C H angle but bisects the Cl C Cl angle as another sigma v. So, this dichloromethane is again by symmetry exactly same like water molecule.

So, both of them have the same set of symmetry elements. Now, let us see a molecule which looks very simple. Carbon. We have 4 bonds hydrogen, chlorine, bromine and fluorine. Do we see any symmetry elements in this? It does not have any other symmetry other than C1 because this molecule does not have any symmetry. Only by rotating about 360 degree about any axis, we only get that molecule back and that is why this molecule does not have any symmetry.

So, this is how we should try to identify the symmetry elements present in various molecules and look at them and compare them with other molecules having similar symmetry to understand the role of symmetry in molecules.

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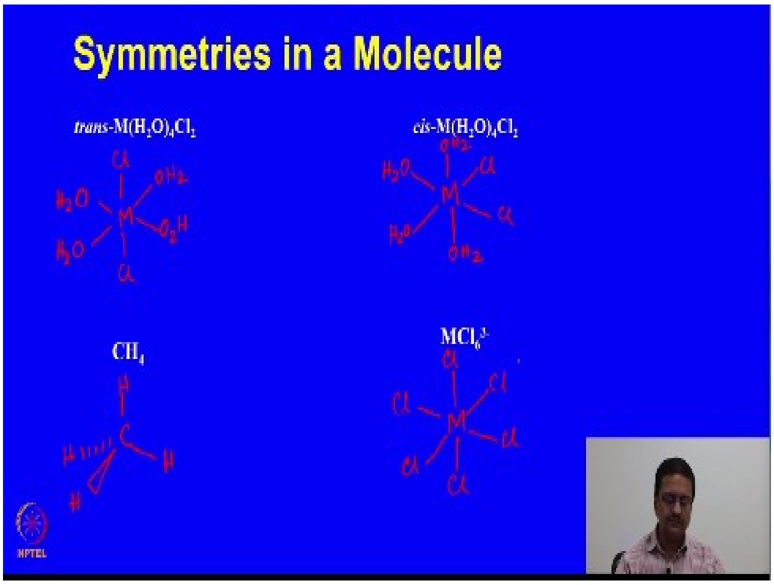

So, when we try to do that we have a few other molecules which I would like you to do it yourself. I am going to only draw the molecules for you to try to find out the symmetry elements present in those, trans dichlorotetraaqua complex. So, like metal, Cl and Cl above and below and then you can have water molecules. You may be wondering why I am writing water molecule as OH2,

And on the other side as H2O, it is a convention to write like this to identify that the bond is through oxygen and this is the trans $M(H2O)_4Cl_2$ and the corresponding cis we should write here. You all know that methane is tetrahedral, try to find out the symmetry elements present in tetrahedral methane and in octahedral complex M Cl 6.

So, once you try to find out the symmetry elements present in that I hope you will be able to understand how to derive these symmetry operations in any given molecule. We will discuss some more molecules during a tutorial but till then you should practice these identification of symmetry elements by taking any molecule that you may think of. So, we will continue in the next class from this point.