Symmetry, Stereochemistry and Applications
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Lecture - 06
Molecular Symmetry in Small Organic Molecules

Welcome to the course on Symmetry, Stereochemistry and Applications. In the first week of this course, we have discussed about the IUPAC nomenclature of organic compounds. So, in the second week today, we are going to start talking about the symmetry elements that we should learn about the organic molecules. So, today we will start discussing about molecular symmetry and point groups in small organic molecules.

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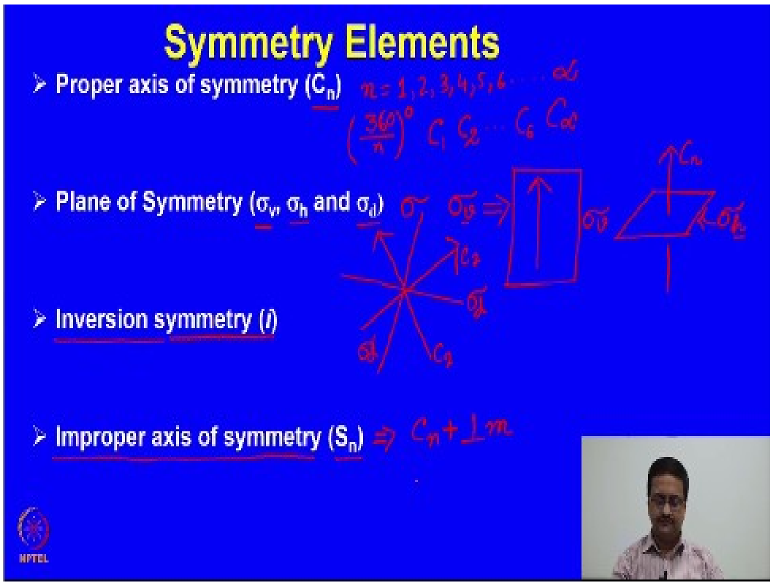

So, when we try to identify the symmetry elements that may be present in a molecule, we need to really study the molecule in 3 dimension. So, in that case, we need to try to find out what are the possible elements of symmetry that are present in the molecule. When we try to do that we need to understand a few different types of symmetry elements that are known to be present in the molecules.

So, for example, the first symmetry element that one should look for is the proper axis of symmetry, which is written as Cn. Here, the value of n can be anything from 1, 2, 3, 4, 5, 6, etcetera, up to infinity that means it can be any integral value from 1 to infinity and it means that if you apply this n-fold rotational axis of symmetry in the molecule, the molecule remains unaltered.

That means if you rotate the molecule about this access by 360 divided by n degree, then you will get the same molecule back. So, that means when you have C_1, it means you only get back the same molecule when you rotate the molecule by 360 degree. When we write C_2, it means the same molecule is regenerated when we rotate the molecule by 180 degree about that particular axis.

So, like that if we continue and write C_6, it means 60 degree rotation brings the molecule to be same as the first molecule that you started with. And when we write C infinity that means if we rotate the molecule by infinitesimally small amount, the molecule does not change its orientation. So, that is why the C_n or the proper axis of symmetry that one should look for at the very beginning.

Then the next point of symmetry that one should look for is the mirror plane or the plane of symmetry. The plane of symmetry can be of 3 different types; sigma v, sigma h and sigma d. The plane of symmetry is always designated by the greek letter sigma and the suffix v, h and d are used to identify those planes with respect to some principal axis or the proper axis of symmetry.

So, when we talk about sigma v, then we should understand that if the axis of symmetry is on the plane of this projection and the mirror plane that we are talking about is in the same plane of projection, then we call it as sigma v. But, if we are talking about a plane which is perpendicular to this plane of this board and is actually perpendicular to this axis, which is a C n axis.

So, this particular mirror plane which is perpendicular to C n axis is called the sigma h, and sigma d is the diagonal plane or the mirror plane passing through the point of intersection of two 2-fold axes. So, if you have a 2 fold axis passing like that and you have a 2 fold axis passing through the molecule like this, both are C 2s, then the mirror plane that is generated in between, these mirror planes are called sigma d or sigma diagonal.

The terminology v and h comes from the concept of vertical and horizontal. So, when we consider the principal axis of a molecule, we consider the principal axis of the molecule to be perpendicular with earth, so, it is vertical. So, the mirror plane that is passing through the principal axis like this is a vertical plane. So, we call this vertical plane as sigma v and any plane that is perpendicular to this axis which is like that is the horizontal plane. So, we call this plane as sigma h.

So, sigma h is a plane which is perpendicular to the principal axis and horizontal to the earth surface and sigma v is a plane which is perpendicular to the earth surface that is sigma v. The next point of symmetry that one should worry about is the inversion symmetry, which means, if you apply the symmetry, the molecule gets inverted and remains unaltered. The last point of symmetry that one should understand is the improper axis of symmetry, which is written as a S_n.

What is a S_n? Sn is not a single symmetry element, it means it is actually Cn plus a perpendicular mirror plane. That means if you have a C2 and a sigma h in the molecule then you should have the S axis, S2 axis. So, like that if you rotate the molecule by 120 degree and do a mirror plane you get the mirror image. So, by doing that if you get the same molecule, then you say that it has Sn axis.

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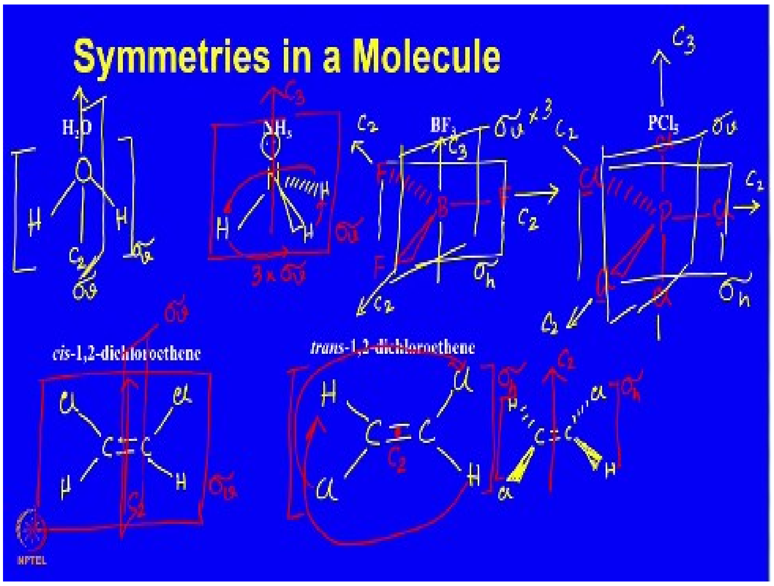

So, now, let us try to understand the symmetries in some very simple molecules. The first molecule that I would like you to understand or see is water. So, as I said what we need to know is the 3 dimensional geometry of a molecule to find out the corresponding symmetry elements present in it. So, when you write water molecule, how do we write water? Water is a molecule which is bent and we write it like this.

What are the symmetry elements that one can see in this molecule? If I assume that I have drawn this water molecule on the plane of this board, then this axis which is on the plane of the board is a 2 fold axis which when we apply the molecule rotates like this. So, you had water molecule which is like that it rotates like that. So, the hydrogen atoms interchange their place. So, we call these as C_2 axis by 180 degree rotation one hydrogen falls on the other.

What else? What other symmetry elements are present in this molecule? The other symmetry element that is present in the molecule is the mirror plane, which is the plane of this board and that mirror plane contains the C_2 axis. So, this mirror plane is nothing but a sigma v and there is another mirror plane which is perpendicular to the plane of the board, but still contains the 2 fold axis or C_2 axis, which I am drawing like that is another sigma v.

So, this molecule has one C_2 and 2 sigma v plane present in this. The next molecule that we would like to understand or discuss is ammonia. What is the geometry of ammonia? Ammonia is a pyramidal molecule. So, we write nitrogen, we write one hydrogen on the plane of the board. So, this nitrogen and hydrogen both are on the plane of the board and 2 hydrogens are above and below the plane of the board. And what else we have?

We have a lone pair which is here. So, this molecule if we will look at it very carefully, I will use a different colours So, that you can understand the presence of the axis, this vertical line which I am drawing is a C3 axis that means if you rotate the molecule about this axis by 120 degree, then the hydrogen atoms would interchange its position. So, that ensures the presence of a C3 axis. What else?

You see the molecule is like this and the 3 fold axis has gone from the middle of the triangular phase like that. And then if we construct a mirror plane, which contains this nitrogen and the hydrogen and bisects the molecule, this hydrogen and that hydrogen and then mirror image related. Therefore, this one N-H bond contains this C 3 axis and forms a mirror plane. So, that mirror plane here is the mirror plane passing through the plane of the projection is one of the 3 sigma v's.

So, you can understand that if this one is on the plane of the board, we have drawn this mirror plane then similarly, there is one mirror plane like that and one mirror plane like this. So, this molecule has 3 sigma v's. Is that clear? Let us see the third molecule. Third molecule is BF3.

What is the geometry of this molecule? We all know that it is a planar trigonal molecule. See how I am drawing this molecule.

So, I have drawn the molecule in such a way that the 2 fluorines are above and below the plane and the third fluorine is on the plane of the projection. So, now, if you try to find out what symmetry element is present, it is very easy to see that there is a 3 fold axis of symmetry which is C3. What else it has? It has 3 C2's, as you may be able to find out. Then the plane of the molecule which is that plane which contains the molecule is perpendicular to C3.

So, this plane which is like the plane of the molecule is perpendicular to the C3 axis. So, that mirror plane is nothing but sigma h and this compound has 3 other mirror planes which are passing like that, like this and like that. So, it has 3 sigma v's; into 3 numbers. Such a simple molecule like BF3 has a C3, 3 2-fold axis of symmetry, 3 sigma v's and one sigma h.

Now, let us see the next molecule which is PCl5. What is the geometry of PCl5? We should draw it appropriately. We have phosphorus, one chlorine in the plane of the board, then 2 chlorines above the plane and below the plane of the board and then 2 chlorines on the plane of the board, but above and below the plane containing the other three. So, that means these 3 chlorines which I have drawn in the beginning, those chlorines are forming a plane, a triangular plane.

And these 2 chlorines are up and down. So, this is a trigonal bipyramidal geometry. So, in this now, we need to see what are the symmetry elements that are present. If we see it carefully that it has very similar condition like BF3 and it will have all the symmetry elements that BF3 molecule has, the PCl5 molecule also will have the same symmetry. Of course, there is a C_3.

The plane of the molecule is the sigma h. These axes are all C2's and there are 3 sigma v's just like the BF3 molecule. Now, let us see a different molecule, a slightly complicated organic molecule cis-1,2-dichloroethene. By now, we know that ethene means C double bond C and when I say cis, I have chlorine on the same side and hydrogens on the same side. So, what are the symmetry elements that one can find out in this?

See the way that I have drawn it that the entire molecule is on the plane of the board. So, if I draw the symmetry elements in red, a 2 fold axis which bisects the bond, It is my C2, then the plane of the board or the plane of the molecule is a sigma v and a plane which is perpendicular to the plane of the board, but contains the C2 axis is another sigma v. What does it mean? It means in terms of symmetry, both water and cis-1,2-dichloroethene has the same set of symmetry elements.

Now, let us see the other isomer of this compound, the trans-1,2-dichloroethene. So, in case of this trans-1,2-dichloroethene, what do we see? We see that the 2 fold is passing through the centre of the bond but perpendicular to the plane of projection and that rotates this chlorine to that place and this hydrogen to that place and so on. And what else? The plane of this molecule is a sigma plane.

But this plane of the molecule that is the plane of the projection is perpendicular to that C2 which is passing through the centre of the bond and perpendicular to the plane of the projection. So, this sigma is nothing but sigma h. What one can do is to understand this in a different way that one can draw the molecule, perpendicular to the plane of projection, which I am trying to draw here, slightly small.

And you see I am drawing it in a projection formula, which indicates that the bonds which are thick are above the plane, the bonds which are dashed, those are below the plane and let us draw it properly. So, the chlorine and hydrogen are above the plane of the projection and that chlorine and hydrogen are below the plane of the projection. So, now here this 2 fold axis is in the plane of the projection, in the plane of those C-C bond.

And the plane which is perpendicular to this plane of projection, perpendicular to the plane of this C-C bond and perpendicular to that C2, this is my sigma h. Therefore, this molecule has C2 and sigma h and no other symmetric element. So, therefore, by symmetry cis-1,2-dichloroethene is different from trans-1,2-dichloroethene.

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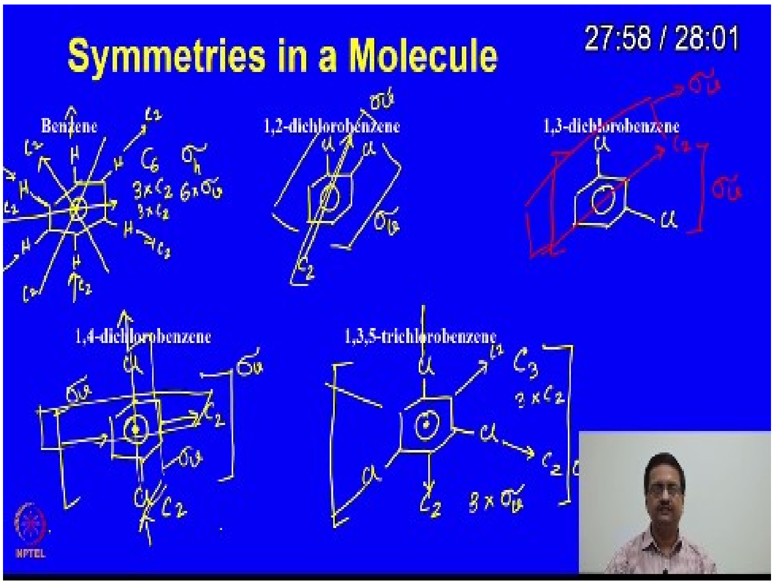

Now, let us try to see a very simple molecule, benzene. We all know that benzene is hexagonal, having 6 carbon atoms and 6 hydrogen atoms and they are at 120 degree. Very quickly if you can think of what are the symmetry elements that are present, you can quickly say that it has C6. It has 3 into C2's because C6 is passing through the centre of the ring and perpendicular to the plane of projection.

C2's are going from one hydrogen to another hydrogen across the molecule. Those are C2's. There are other 3 C2's that means 6 C2's, which are bisecting the molecule like that. What else? The plane of the molecule is sigma h because that plane is perpendicular to the C6. C6 is the principal axis because that has highest number of n that is the highest value of n. So, it has sigma h and of course, there are 6 numbers of sigma v which are passing through each of those C2 axis.

So, next molecule is 1,2-dichlorobenzene. So, now, you see by adding these 2 chlorine atoms in this molecule, what we have got is we have lost the privilege of C6. What we have is just one C2 axis bisecting the molecule like that, the plane of the molecule is the sigma v and the plane which contains the C2 axis and perpendicular to the molecule is another sigma v. So, this molecule is very similar in symmetry with water.

Let us see 1,3-dichlorobenzene. So, here also if you look at it very carefully, we have lost the privilege of C6, but then it also is very similar to 1,2-dichlorobenzene because it has a C2 axis. The plane of the molecule is a sigma v and a plane which is perpendicular to the plane of the molecule but containing this C2 axis is another sigma v. So, I am trying to show that different molecules may look very different, but they may have very same symmetry elements.

And some other molecules, which may look similar, but have totally different symmetry elements. Let us see the case with 1,4-dichlorobenzene. So, what we have in this case? We have a C2 axis passing through the midpoint of the ring. We have a C2 axis in the plane of the molecule. We have a C2 axis bisecting the molecule like that, then the plane of the molecule is a sigma plane that is sigma v.

Then the molecule can be divided by this mirror plane which is another sigma v and the molecule can also be divided into 2 parts by that plane which is another sigma v. So, this molecule has 3 perpendicular C2's and 3 different sigma v's which are perpendicular to each other. And let us see the third molecule of this class, last molecule of this class 1,3,5-trichlorobenzene.

So, what we have here passing through the centre of the molecule is a C3 axis then you have C2 axis passing through the C-Cl bonds. So, it has 3 numbers of C2 axis. And what else? The plane of the molecule is sigma h because this plane is perpendicular to the C3 axis and C3 is a principal axis. So, when this is perpendicular, so, this is sigma h and there are 3 numbers of sigma v planes which are passing through the individual C2 axis.

So, here in this particular case, you have C3 plus 3 perpendicular C2's and 3 sigma v's just like 1,4-dichlorobenzene. So, in the next lecture we will continue from here.