Symmetry, Stereochemistry and Applications

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Lecture - 09
Molecular Point Groups - Part II

In the last class, we were discussing about molecular point groups of various organic and organometallic complexes. So, in today's lecture, we will continue our understanding with different molecules and how to derive their point groups.

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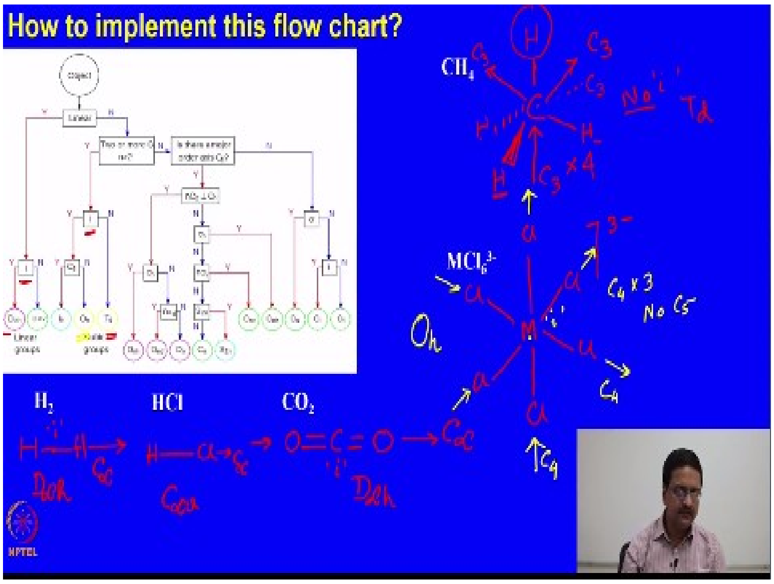

So, in the previous class, if you remember, we had discussed about this flowchart which we need to follow for various organic compounds to find out their point groups. So, let us first discuss the point groups of these 3 very simple linear molecules. So, in case of hydrogen, the molecule as we all know is linear and what are the symmetry elements that are present in this molecule?

This molecule has the bond axis as C infinity axis. So, this molecule being linear, it has infinite degree of rotation so, which means if you rotate hydrogen molecule by infinitesimal small amount it remains the same. So, the next question that one should ask for it being a linear that whether it has inversion center i or not as you can see here in the flow chart. So, the answer is yes.

This molecule has an inversion center i. Therefore, the point group of this should be D infinity h. In our previous class, we have learnt how this D comes here. If you have a C infinity axis like this, you have infinite number of perpendicular C2's about this C infinity axis. So, those infinite number of perpendicular C2's makes it D infinity and the C infinity being the principal axis,

The plane which is perpendicular to the principal axis is your sigma h and that sigma h makes it D infinity h. You see, this molecule has an inversion center. This is true with carbon dioxide as well. Carbon dioxide is a linear molecule. The axis of this 2 bonds that is O double bond C and C double bond O, this axis is a C infinity axis. The molecule has an inversion center located at the carbon.

So, this also should have been the D infinity h point group. But, in between we have HCl which is although linear and although, it contains the C infinity axis like other 2 molecule, it does not have the inversion center. What does it mean? It means that the i is missing and once the i is missing, what we consider is that then if this is a C infinity axis. The next point, we consider whether it has infinite number of sigma v's which are containing the axis of symmetry, which this molecule has.

The point group of this molecule is C infinity v. Let us then see the other molecules. It is a very simple molecule as we all know is methane and the geometry of methane is tetrahedral. So, if we consider these 3 bonds to be on the plane of the projection, then the other 2 bonds are above and below the plane of projection. The way I am writing the fat bond is above the plane of projection and the dashed bond is below the plane of the projection.

So, for this particular molecule, it is non-linear, then we ask, do we have 2 or more Cn with n greater than 2? Yes, this molecule has C3 and how many such C3's? Four such C3's because if you consider this as the vertex, the other 3 hydrogens form a triangular base. So, you have a C3 like that. Similarly, containing this hydrogen and the carbon, there would be another C3 like that. That should be third C3 like this and there should be fourth C3 like that.

So, there are 4 C3's in this molecule. So, the next question that one should ask is, does it have inversion center? The answer is no. The molecule does not have inversion center. No i. Therefore, the point group of this molecule should turn out to be tetrahedral or T_d. Hope, this is clear to all of you. The next molecule rather an ion is MCl_6^{3-}. What are the symmetry elements that one can see here? One can very easily see that this molecule has a C4 passing through this bond.

And as a matter of fact through all the axis, all the Cl M Cl direction, this has C4. So, this molecule has 3 C4 axis present. The next question to be asked is, does the molecule have an inversion center? So, what we see is that the metal has the inversion center located at it. Unlike the molecule methane which did not have inversion center, this MCl_6^{3-} has an inversion center.

So, next question that one should ask is whether the molecule has a C5 axis and the answer is no C5. So, when the molecule has three 4-fold axis, inversion center is present and no C5. Then the point group would turn out to be octahedral or O_h. Remember that this is one of the very high symmetry point groups.

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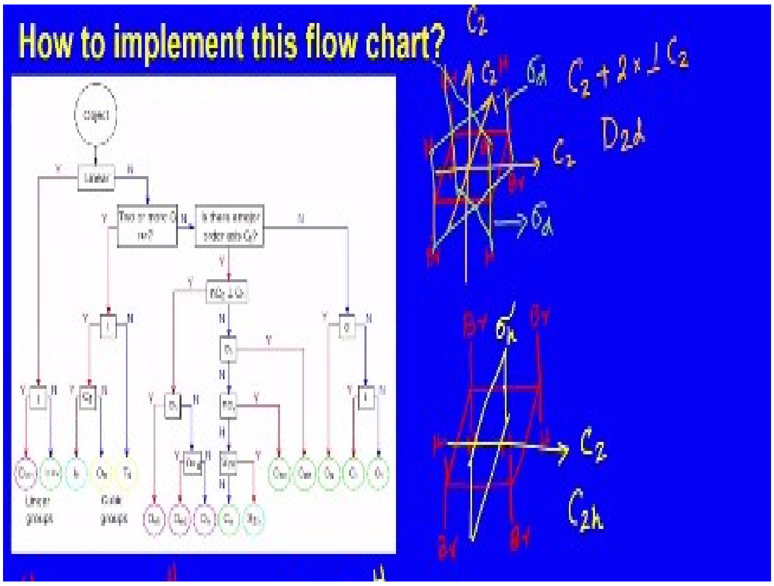

Now, let us try to draw a few small organic molecules and try to find out their respective point groups. Here, what we should try to understand is that we are trying to draw the molecule in the plane but of course, it is not a planar molecule and these bonds are not in the same plane. What I am drawing is a tetrabromo cyclobutane and we are assuming that the 4 carbon atoms of cyclobutane are in the same plane.

So, if we have this tetrabromo cyclobutane where the bromines are all trans, which symmetry element do we see in the molecule? There is a C2 axis passing through the center of the molecule. Right. So, then the question is, do we have more C2's perpendicular to this original C2? The answer is yes. There is one more C2 here. There is a third C2 going like that.

So, you have one C2 plus 2 into perpendicular C2's. This makes the molecule to be D_2 whether it is D_{2h}, D_{2d} or simple D_2. We should go for the next step. Now, the question is, does it have a sigma h? The answer is no because you take any C2 and apply a mirror plane perpendicular to that. There is no symmetry in the molecule. So, there is no sigma plane present in this molecule.

So, the next question that one is asking is that if there is no sigma h, does it have a sigma d? The answer is yes. The molecule has sigma d. If you consider the mirror plane passing through the molecule like this which is bisecting 2 C2's, you have a mirror plane like that which is bisecting again 2 C2's. So, this one is a sigma d and that plane is also a sigma d. So, this molecule has 2 sigma d's. So, the point group of this molecule should be D_{2d}.

Let us try to draw the other isomer of this molecule. Here, the adjacent bromines are up. The on the other side the adjacent bromines are down. So, now, what are the symmetry elements present in this molecule? What do we see? Here, you can see that if I draw a C2 bisecting that bond, this hydrogen goes down and that bromine goes up and they interchange.

So, this has a C2 axis and no other C2 is present in the molecule because if you have a C2 like that then the hydrogen comes down, bromine goes up, although that bromine and this hydrogen interchange their places. So, there is no other C2 present in the molecule. So, what we have here is then a mirror plane which bisects these 2 bonds like that and that mirror plane is nothing but sigma h because that is perpendicular to the C2 that we have considered.

So, the point group of this molecule will is it turns out to be C_{2h}. Now, let us try to draw another molecule which is a derivative of allene, which we have done already. We have done allene before. So, we should do some derivatives of allene. So, while doing this point group for allene, what we did is we had drawn the molecule inside the cube. So, we will do the same once again.

We will try to draw the molecule inside a cube. For your easy understanding, I will use different color for drawing the molecule. So, if I have, if I put chlorine and hydrogen at this 2 corners, I can put chlorine and hydrogen at those 2 corners and the carbon atoms are like that. So, now, what are the symmetry elements that we see in this molecule? There is a C2 axis passing through this centre of the face to that center of the face through the central carbon atom.

Now, does it have any other symmetry element that one can see? You see here because of this C2, those 2 chlorines interchange their place; these two hydrogens interchange their place. That particular symmetry of the 2 corners is not there in any other pair of corners. So, there is no other C2 present here. In case of allene, when we had 4 hydrogens at the corners then we had 3 perpendicular C2's bisecting or passing through the center of the faces.

But here, since it is substituted and the corner atoms are not same. It has only one C2 present and no other symmetry element that is present in this molecule. So, the point group of this molecule is C_2.

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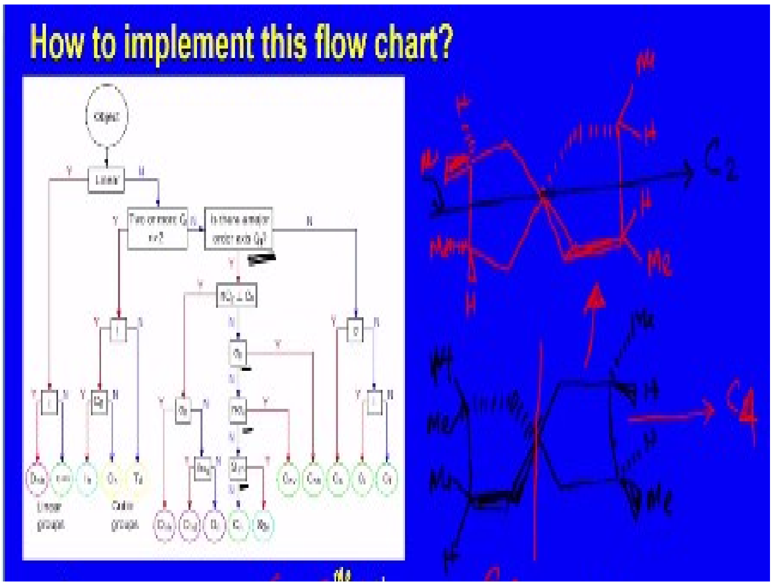

Let us try to draw a slightly complicated molecule. We all have seen this type of molecule while learning our IUPAC nomenclature. This molecules are called the spiro-molecules and in this spiro-compound, we have substitutions like methyl group and here also methyl group that one hydrogen, one methyl is here, one hydrogen, this carbon bond has hydrogen and a methyl group.

So, if we try to carefully look at this molecule has a C2 axis which is passing through the midpoint of these 2 bonds. So, if you see that this methyl which is down comes up and the hydrogen which is down it comes up. So, this makes it a C2. This molecule does not have n number of perpendicular C2's. This molecule does not have a sigma h. It does not have sigma v as well.

So, the next question is, does it have S4? Because when we see that it does not have sigma h, does not have sigma v. The question asked is whether it has a S4. S4 means, we should rotate the molecule by 90 degree and take a reflection. So, if you rotate the molecule by 90 degree, what happens is you get the molecule like this. So, whatever was down becomes up and whatever was up becomes down.

So, these hydrogens are trans to each other. Methyls are trans to each other and here the hydrogen and methyl are like that. And the methyl and hydrogen is like that. So, on doing a S4, we have actually rotated the molecule by 90 degree and then if we apply a mirror plane perpendicular to, see this one we applied as C_4 and then we apply a mirror like that. So, when we apply a mirror like this, what we end up is the molecule similar to the one from where we started.

So, that means, when we have rotated the molecule by 90 degree and take a mirror image of the molecule, then we go back to the original molecule. So, this particular molecule has an S_4 axis and the point group of this molecule is S_4. Let us try to draw 2 more molecules. The first molecule is a cyclopropane derivative, dimethyl cyclopropane. So, let us try to find out what symmetry element this molecule has.

If you look at it very carefully, if we assume that the 3 carbon atoms of propane are in the plane of the board and then you have the 2 hydrogens here above and below the plane; 2 methyls above the plane; 2 hydrogens below the plane on 2 other carbon atoms. Then the plane which is perpendicular to the plane of projection that is this plane, which is perpendicular to the plane of projection is a sigma plane and that is the only symmetry that is present in this molecule.

So, we identify this molecule to be as C_S point group. Now, let us draw a bicyclic compound which is this one. So, in this molecule, what symmetry do you find? We look very carefully at this molecule and what we see is if we join a line, if you join these 2 points with a line like that, this particular axis that we have drawn is a C3 axis. As a result, this methyl which is down here goes up.

This methyl which is on the right hand side of the bond goes to the left hand side of the bond like that and that methyl which is there comes down and meets here. So, these 3 carbon atoms are placed at 3 corners of a triangle. Similarly, the other 3 carbon atoms on the other side are placed at the corner of another triangle and that makes this molecule as to have a C3 axis. So, the point group of this molecule is nothing but C_3.

So, our last molecule today is this one. The conformation of this molecule is the opposite conformation, like we have same substitutions on 2 sides but they are oriented in a different direction. So, if I draw the molecule like this where the 4 carbon atoms are on the plane of the board, then this bromine and hydrogen are above the plane and below the plane and the 2 bromine and hydrogen are in opposite way that is here.

So, here the bromine is below the plane and this hydrogen is above the plane of the board and this particular molecule has inversion symmetry present here at the center of this bond. So, the point group of this molecule is C_i. So, in this particular case, there is no other symmetry that is present in this molecule. So, hope you have got an idea about how to identify; how to generate the molecular point groups of various organic molecules.

You should try this identification of point groups from a standard textbook. There would be a lot of examples. So, from there, you should practice these point groups for yourself. So, we will continue this course in the next lecture. Thank you