Structure, Sterochemistry and Reactivity of Organic Compound and Intermediates: A Problem-solving Approach

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Lecture 5

Conformational analysis of perhydrophenanthrene

Hello everyone, welcome back to this course on Organic Chemistry involving molecules, reactive intermediates and the role of structure stereochemistry and their reactivity of a molecule. That is in essence what is the underline objective of this course. So far, we have covered the we have introduced you the course, the course elements and we started with the structure and steel chemistry aspect of organic molecules and we have seen the role of symmetry elements in imparting the chirality to a molecule.

Then we have seen how the point group notations can be framed to describe the symmetry elements of a molecule. And we also have gone through symmetry number, what is mean by symmetry number how to calculate it. And then the order of the point group and then we went to some of the absolute configuration notation to molecules which lack the conventional chiral center or the SP3 stereo genic center.

For them how to assign the absolute configuration namely chiral axis molecules possessing chiral axis or chiral plane or helical having helical chirality. Then we went on to discuss the conformational analysis of bicyclic cycloalkanes, that means the bicyclic fuse cycloalkanes so which are we took (())(2:17) taken as our point of discussion and then we have seen the different conformations different stereo isomers that are possible and the related confirmations.

And then we went on to describe the more complicated system mainly the perhydrophenanthrene and the perhydroanthracene systems. After that, we are today we take a pause and then do again revisit the contents what had been described and in the process we will solve certain problems. The problems are mainly related to the point group symmetry number and order of symmetry, that is why we start.

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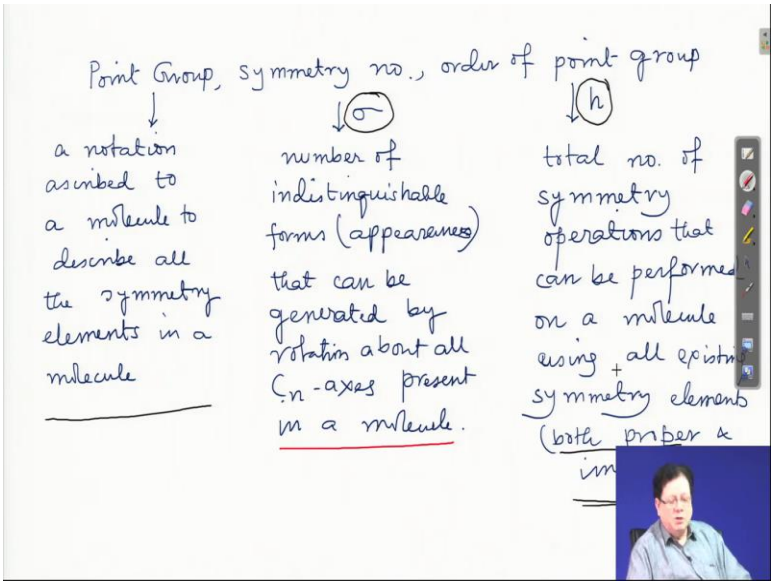

Now, again I just remind you, what is a point group? Point group is a notation ascribed to a molecule to describe all the symmetry elements in a molecule. So basically, it this notation tells you about all the symmetry elements that are possible to be present in a molecule. That is what is point group and there are different notations as you have the seen which and then in addition to that we have something what is call symmetry number, what is symmetry number?

Which is denoted by sigma the number of indistinguishable forms that is written here, the number of indistinguishable forms basically number of indistinguishable appearances that can be generated by rotation about all the Cn axis that are present in a molecule.

So, it is basically involving only the proper element of symmetry namely the simple axis of symmetry. And rotational around all possible simple axis of symmetry give you the number as the symmetry number, basically the number of indistinguishable forms that you can generate out of these rotations around Cn axis and then we have another parameter which is called h that is the order, sorry the symmetry order h this is the total number of symmetry operations that can be performed on a molecule using all existing symmetry elements.

So, there is a difference between sigma, sigma is basically the number of indistinguishable forms that you get by rotation around Cn axis, whereas symmetry order, order or you can call the order of the point group is the total number of symmetry operations that can be performed on a

molecule using all possible symmetry elements that are present in the molecule. That means the symmetry element both proper and improper.

Now, so obviously h is basically tells you about all the symmetry elements, however sigma, sigma tells you only about the operations about the Cn axis. So, there is a difference h gives a complete picture of the symmetry operations possible in a molecule.

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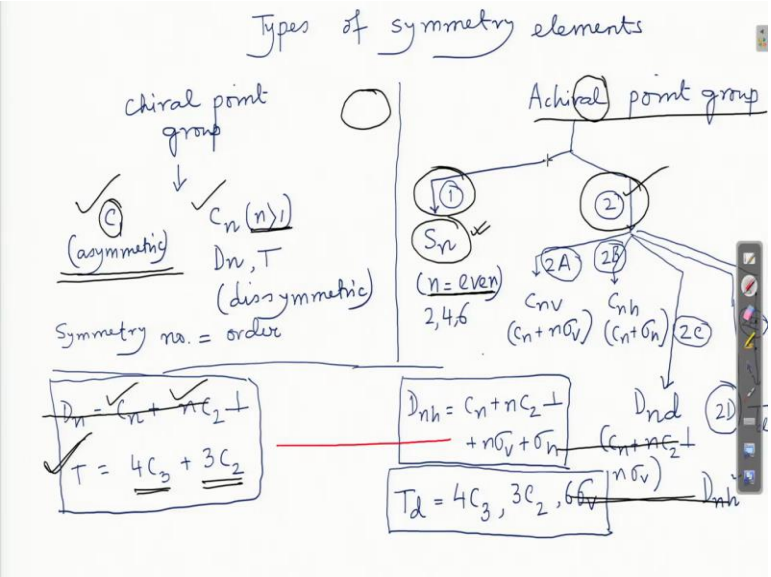

So, let us see how this symmetry the point group, so let us now go to different types of point groups, that have been described to molecules or assign to molecules different types of molecules. Now, the molecules can be broadly classified into chiral and achiral molecules. For chiral molecules you have a chiral plant group system, whereas for achiral point group you have achiral point group system. Let us talk about the chiral point group which is actually little bit simpler because you know the chiral molecules can have only at the best Cn axis and in some molecules Cn, where n is greater than 1, may also be absent.

So, it is basically all involving C-axis the whatever point group one has to assign to chiral molecules. So, the chiral point group starts with C1, C1 means molecules which have got only the identity operation, C1 means you rotate by 360, that means you come back to the original that will always happen. So, molecules which only have C1, remember all molecules have this C1 every molecule have this C1 and molecules which only pauses C1 and none of the other

elements of symmetry is definitely chiral because for chirality you need the absence of sigma i and sn.

So here, no sigma no sn no i, so these are all chiral the first set is C1 point group, it is basically a dividing of we say it is dividing of all types of symmetry elements, so that is what is called a asymmetric, so this is the basically the molecules having C1 point group belongs to the asymmetric molecules.

And then you have other chiral molecules with different point groups like Cn, where is greater than 1, so now there are a chiral molecules where C is 2 or C3 etcetera they may be present, they are still chiral because they lack the improper element of symmetry, so that is Cn and then you can have Dn, Dn is the head of symmetry Dn is basically you have Cn plus nc2.

So, Dn is whenever you have (())(8:08) symmetry you have this Dn means Cn class n number of C2 which will be perpendicular to the Cn axis, perpendicular to the Cn axis. So, Cn axis is the principal axis. So, that is what is Dn and then you have tetrahedral point group and tetrahedral point group is T only T no subscript and that means that it has got 4C3 and 3 C2 axis.

So basically, whatever we have written is that all chiral molecules are only having C axis stars from C1, then Cn then Dn and finally T. And whereas the achiral point group, the achiral point group can be of many types, I think when I took the class, it was described but today I want to clarify any doubt or I want to systematically do the classification and try to elaborate it in such a way very simple way, so that you can understand this achiral point, if it is specially the achiral point group and then how to calculate the symmetry number and the order.

Now, achiral point group what I have done is I divided it into two groups, one is a Sn only having alternating axis of symmetry only and that is only possible when n is even, molecules which have only sn axis only sn axis where n is equal to n will be even. So, that means it will be 2, 4, 6 etc. On the other hand, so that is one point group, if you have other elements of symmetry apart from sn or if at all sn is present in the form of sigma or i then accordingly you have different types of point groups.

So, one as I said first I divided into two molecules which have got only sn and the others having other proper and improper elements of symmetry. So, in this case, we have term this as class 1

type molecules and this is class 2 molecules. In class 2 molecules, you have different types of point groups and that is, let me see I want to, we have different.

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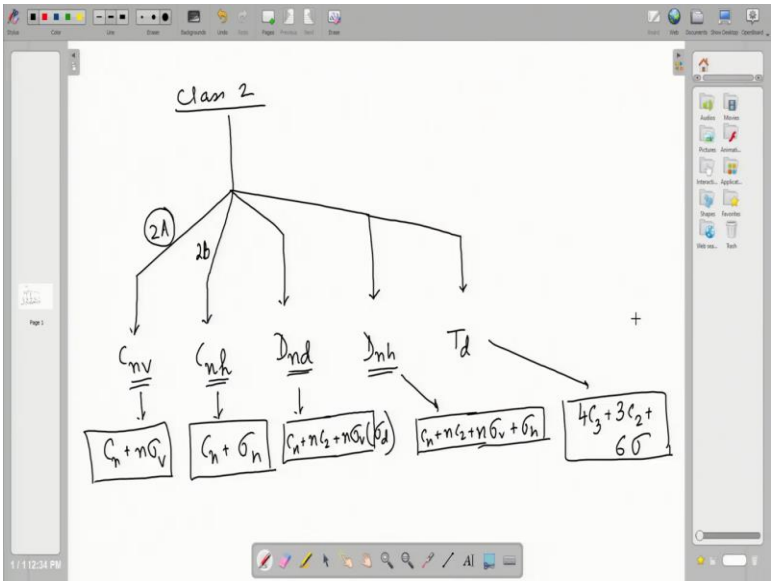

So, we are talking about the class 2, class 2 type of achiral molecules. So, one group is, it is divided into subgroups 2A, 2A is basically you have Cnv, I will come back to that you have already know what is Cnv but then again clarify that Cnh, Cnv, Cnh, now this is 2b, then you have Dnd, Dnd and then you have Dnh.

So basically, Cnv and then nh this is nd because the sigma planes are basically the diagonal planes of symmetry which bisects the angle between two C2 axis. And then Dnh you have and finally you have Td, that is the tetrahedral Td is the tetrahedral achiral point group. So, let us elaborate this, what is Cn? Cn means you have Cn plus n sigma v n number of sigma v and then you have Cnh that is the difference between v and h, in this case Cn plus only sigma h because horizontal plane sigma h can be only one plane but vertical planes vertical to the horizontal can be many.

So, this is n sigma v but this is Cn sigma h then Dnd you have Cn nC2 because it is a dihedral symmetry these are perpendicular to the Cn axis plus, sorry plus you have n sigma v, actually sigma this can be called as sigma d. And then Dnh is basically nothing but Dnd plus 1 sigma h,

that means you have Cn, you have nC2 which are perpendicular to the Cn plus n sigma v n plus sigma h, sorry.

So, n sigma v plus sigma h and then Td is 4c3 3c2 and 6 sigma, so this for tetrahedral symmetry. Now, let us take one by one that how to because the major problem which is encountered by students is the existence of whether or not there is a sn axis present in this point group. So, there are certain mnemonic you can you can follow which I will tell or if you can have your own way of understanding, you can do that, the way I do it is basically.

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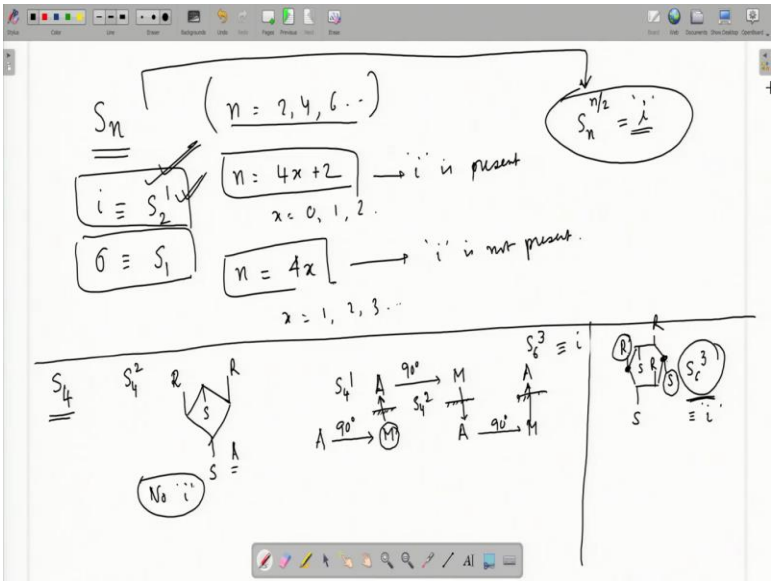

Let us take the subgroup which is again let us come back to the first category which is sn only having sn, so sn we are talking about only having the improper elements of symmetry sn, n is even. Now, you know that n when a sequel n equals to 2, then there is this presence of i because we know that i is equated to remember i is equated to s21, that means the first operation involving s2 and then the sigma is equated to is equated to your s1, that means you give a turn by 360 and then take the mirror image.

So, these things you have to remember especially that one, when you are considering sn because here n is even that means it starts from 2, 4, 6 etc. Now, the question is, molecules with sn whether they will have center of symmetry or not, there will be center of symmetric or not, that

depends on the type of the n, if n is equal to 4 x if you can express it in the form of 4x plus 2 x equal to your 0, 1, 2 etc then you have a center of symmetry, then i is present.

And if n can be expressed in the in the form 4x, then x is same 0, 1, 2 then not 0 basically n a cannot be this cannot be 0, so this is 1, sorry this is 1 x equal to 1, 2, 3 etc then so that i is not present. Let us take, let us first take this that some examples where this is valid. So, let us take a molecule which has got, say s4 which has got s4, the question is whether it has got whether it has got a center of symmetry or not.

Now, when there is center of symmetry present in a sn axis, so you know the successive operations there is sn1, sn2, sn3 so the first rotation then mirror image, then again another rotation, then mirror image, so you have to do continuously do it, these are called successive operations. So, when you do this operation sn n by 2 that is basically the question mark that whether it leads to i whether there is it is equivalent to i like you if you put 2, so that will be s21 that is we already know that is equal to i but there are other possibilities like the question is what is s42 or what is s63.

So, at the super script or the power is half of the half of the sub script. So, we have to see that whether this is equivalent to i or this is equivalent to i or both are equivalent to i but our rule says that if n can be expressed in 4x plus 2, then you have i present where s in this case, when you have sn n by 2 that is equal to equivalent to i. So, let us take a molecule that will take you that will be that will clear the whole thing.

So, if you take a cyclobutene and it is attached to 4 groups, suppose this is R, a group which has got stereogenic center, so that suppose that is the absolute configuration of the substituent, then you have S, so this is S, so alternate R and S and the other alternating thing is that up and down, so one is up another is down.

So, if you take this molecule, obviously you see that there is no i because in order to have i you should have s at this side. So, no i because i is the very easy to detect, so no i and, so how the operations successive operations are done? Suppose this molecule I call A molecule, so A basically what, in S operation first you give a because it is s4 so 90-degree operation gives you a

form which is basically the mirror image, otherwise if it is not mirror image, then the another you place a mirror and the image that will be formed will be identical to A.

So, that means this is basically is the mirror image of A, M can be expressed in a form which is mirror image of A. So that is your first is s41, then you have to now successive operations means whatever you have you continue the process, so 90 degree and then you again come back to a mirror image situation and then that will so that will be A again because mirror image of a mirror image is the original one.

And this way, so that means this is your this completes your s42 and then s42 and then is s43 will be another 90 degree, so that will go to M and then another mirror image and that goes to A, actually that finishes up because s44 is nothing but an identity operation. So, this is the situation for s4 system, the s4 point group.

So, if you have s6 point group, you can see a 6-point group I write a very similar molecule only it is a cyclohexane but the same type of story that RS alternates and up and down also alternates R and then S. So, here you can see that there is a center of symmetry and this is only achievable when you have the third operation, that means the third successive operations, we are performing successive operations, as the third one is basically A63, so that will be your that will be equivalent to i because at that point this replaces that one these goes at that point and this comes here with opposite configuration I can show it if you do that step-by-step, let me see I will do that next one.

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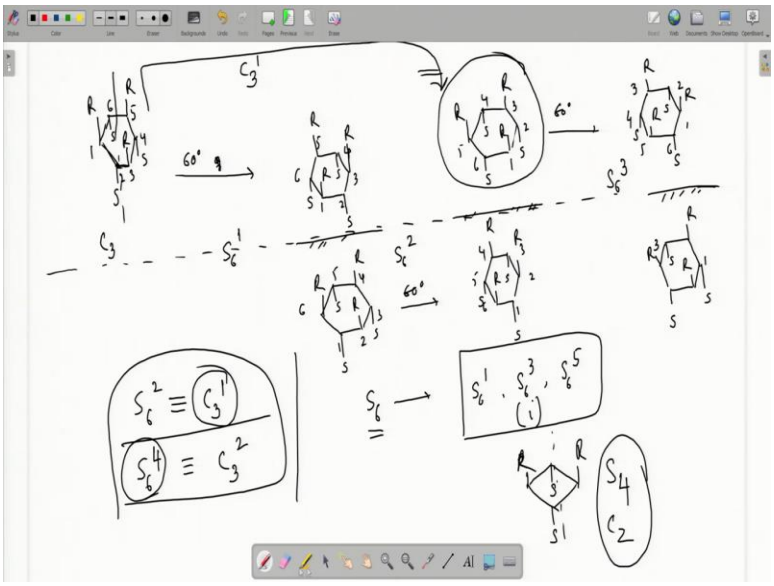

So, take this molecule again the type of analysis I was doing is basically, sorry this was the so here it is R this is S, this is R S this is R and that is S, so 1, 2, 3, 4, 5, 6. So, if you give a rotation of 90 degree, sorry now this is s6 so that will be 60 degree, 60 degree means the it will look like this hexagon and then your R 1 will be here 2, 3, 4, 5, 6. So R is here, that means this is up and then S then R, then S, then R and then S.

So, now you take the mirror image of this, so place the mirror and your 1, 2, 3, 4, 5, 6 so that will be now R up and this will be S down, so now you can complete the whole thing, S, R, S. Now, look at this molecule, this molecule is basically similar to this one, so that is what it is, that means this is as S61 operation. Then you continue this operation, now another 60-degree rotation will make it that 1 will be here, 2, 3, 4, 5, 6.

So, 1 now 1 having down S so down S and then 60 degree, so 2 will be having R, 3S 4R 5S and 6R so that is a situation. Now, you take again the mirror image of this, so if you take the mirror image of this, so you come back to the same level, same level means this is your line which divides this different forms of the molecule, so on one side it is the original level the original level and on the other side it is the mirror image the side of the mirror image.

And the, so it again comes back to your original level and then it goes to this will become R and that will become S so that is R, that it S, that is R, that is S. So, this is the situation, now you

write 1, 2, 3, 4, 1, 2, 3, 4, 5, 6. So, that completes the, so this is basically S61 this is your S62 and S61 is this, this is S62 and now you have S63. So S63 means you give another 60 degree we will stop at S63 then you see that here now 1 is here, 2 is there, 3, 4, 5, 6.

So, what is the status of 1? This is R and this is your S so that will be S that will be R that will be, sorry not here, that will be R and this will be S, I think let me so this is a situation this is your, sorry 1, 2, 3, 4, 1, 2, 3, 4, 5 this is 6, so this is your 5 this is your 4 that is written here 4, this is your 3, this is 2, this is 1 maybe I write it in a better fashion.

So, this is 1, 2, 3, 4, 5, 6 so at 1 you have the you have R, then 2 you have S then 3 R then 4S 5R up and this is down. So, now you take the mirror image, so what you when you take the mirror image this is 1 and that is S now, this is 2, that is R now, this is 3 that is S now, this is 4 that is R, this is 5 that is S and this is 6 that is R.

Now, you see as I said for center of symmetry what will happen 1 will come to 4, 4 will come to 1 and in fact 2 will also exchange positions with 5 and 3 and 6 will also interchange positions, the other thing that happens is that the groups change their configuration, not only configuration if that was up earlier that goes to the points to the down points down like earlier here R was up, now it is S down.

So, that is the perfect condition for having the i symmetry, that means the insertion point. So, now some interesting other observation is that when you have this, this is actually basically the form you are obtained by S62 operation, the second S6 operation and you see that the molecule has come back to the original level not on the mirror image side and you can actually convert go to from this to this anyway by having A C31 operation.

If you do a C31 operation, that means 1 will come to 3, 1 will come to the position of 3 and then and 3 will go to the position of 5 and 5 will come to the position of 1. So, that is what is happening and but you see the it appearance is same as that one, so that means this is nothing but that means we have got a very good important conclusion that S62 is equivalent to C31. Similarly, if you continue this way you will see that S64 is also equal to C3 the second one the second successive operation of C3, that means C32 which is equivalent to S64.

So, that means whenever something has S6 the unique or distinct operations that are possible for S6 is S61, S63 and a S65, S63 by the way this is S63 by the way is the center of symmetry. So, these are the unique operations that you can have, otherwise because why that S62 is now nothing but C31 and S64 is nothing but C32.

Remember whenever I talk about sn point group, that does not exclude the proper element of symmetry, the proper element of symmetry could be present. So, like this in S6 you can tell that there is a C3 axis there is a C3 axis going through this and there is C3 and then that is why you have C31 and C32.

If you have a cyclobutene, the earlier example cyclobutene which is very similar molecule R, S, R, S you have here you have S4 but also what you have is a C2. So, in addition to so what you are seeing that for S4 you have a C2 for S6 you have a C3, similarly for S8 you will have Sc4 so that is the case and then some of this S operations basically are becoming equivalent to some of the operations about the C axis.

So, that is all about the sn, now we will go to the others part which is the other achiral point group and that is the Cnv, Cnh then Dnd, then Dnh and Td we are not looking at the octahedral systems. So, I think that will be done in the next lecture, so thank you.