Pericyclic Reactions and Organic Photochemistry
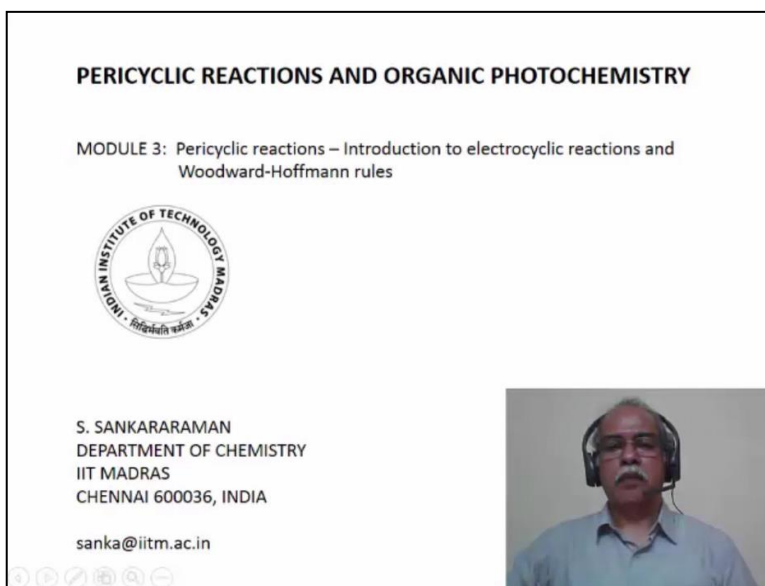**S. Sankararaman**
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Module No. #01
Lecture No. #03
Pericyclic reactions – Introduction to Electrocyclic reactions and Woodward-Hoffmann Rules

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Hello, welcome to the course on, pericyclic reactions and organic photochemistry. This is module three. We will consider in this particular module, the introduction to electrocyclic reactions, and the derivation of Woodward-Hoffmann rules, using various methodologies.

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ELECTROCYCLIC REACTIONS

➢ Cyclization of an acyclic conjugated polyene system.
➢ The terminal carbons interact to form a sigma bond with simultaneous reorganization of the pi bonds.
➢ Cyclic transition state involving either 4n electrons or 4n+2 electrons.

Now, what are electrocyclic reaction. Electrocyclic reactions are either cyclisation of an acyclic conjugated polyene system, or ring opening up a cyclic conjugated polyene system. The ring closing reaction, if we consider for an acyclic conjugated system, the terminal carbon interacts to form the sigma bond, with the simultaneous reorganization of the PI bonds. It involves a cyclic transition state with, either 4N electrons or 4N +2 electrons.

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Electrocyclization of butadiene (4n) and hexatriene (4n+2)
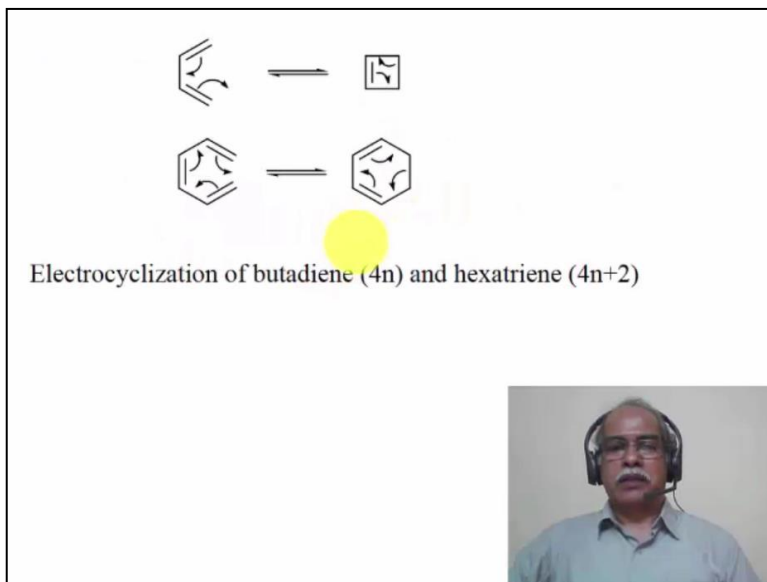
Let us consider, these two generic examples of electrocyclic reaction. The first example is the ring closing of butadiene to cyclobutene. This is what, i meant by saying, the terminal carbons are interacting with each other. The carbon number one and the carbon number four has to come. They have to come close together, to form this particular sigma bond. So, this is a reaction
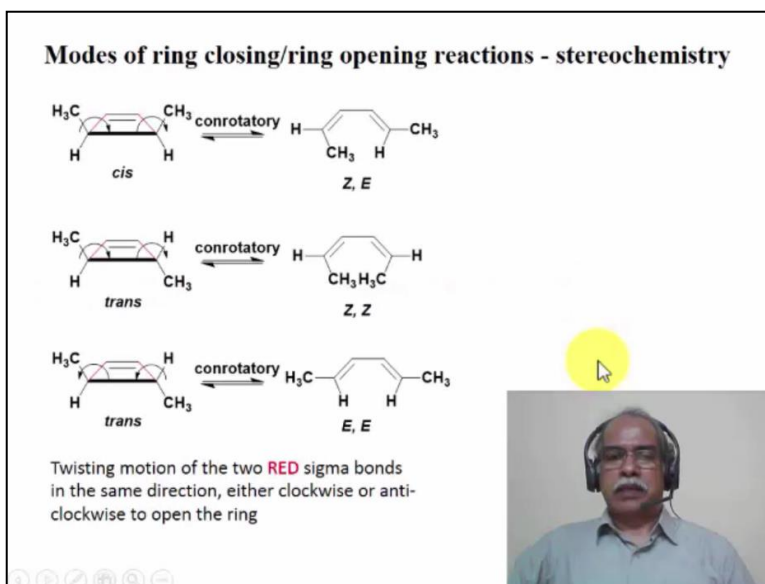
involving four PI electrons in the forward direction, or in the reverse direction, if we consider, considers two PI electrons and two sigma electrons.

So, overall the reaction can be represented, by the curved arrows, that is shown here. That is, this orbital is going to interact with this particular carbon. This carbon number one is going to interact with carbon number four, in closing the ring, with the simultaneous migration of this particular bond, to give this PI bond over here. On the other hand, if you consider the reverse reaction, which is electrocyclic ring opening reaction, this carbon-carbon sigma bond is breaking, and it gives to the rearrangement of this PI bond, to give the two PI system, that are shown in the left-hand side.

Similarly, in the case of a cyclohexatriene, carbon number one and carbon number six, they have to interact with each other forming the sigma bond, with the simultaneous reorganization of the PI bond, to give cyclohexa-1,3-diene, as the product. In the reverse direction, if you want to go, you break this carbon-carbon sigma bond, with the reorganization of the PI bond, to give the hexatriene molecule. So, electrocyclic reactions involving the butadiene going to cyclobutene, would be considered as a 4N electron system, because 4N is equal to 1.

There are four electrons, involved in the forward direction, as well as in the reverse direction. In the forward direction, it is four PI electrons. In the reverse direction, it is two PI and two sigma electrons. If you consider the hexatriene unit, the cyclisation involves six PI electrons. That is, 4N plus 2N is equal to one. In the reverse direction, it will be two sigma electrons and four PI electrons. (4 +2) 6, totally 6 electrons are involved in the system. So, one can classify, the electrocyclic reaction as reactions involving, either a 4N electrons system, or a 4N +2 electrons system, as the case may be.

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Modes of ring closing/ring opening reactions - stereochemistry

cis → conrotatory → Z, E

trans → conrotatory → Z, Z

trans → conrotatory → E, E

Twisting motion of the two RED sigma bonds in the same direction, either clockwise or anti-clockwise to open the ring

Now, before we go into the Woodward-Hoffmann rules and derivations for the electrocyclic reaction, let us consider the different modes of ring closing and ring opening reaction, and the consequence of the mode on the stereochemistry of the product, that is being formed. Now, let us consider the ring opening of the cyclobutene, as the case. If you want to break this carbon-carbon bond, which is indicated by this thick line, what one really needs to do is, to twist this carbon-carbon bond, that are indicated in the red color. In other words, twisting of this bond, and twisting of this bond, will essentially break this carbon-carbon bond, resulting in the formation of the butadiene molecule.

Now, if you want to twist this carbon-carbon bond, which are indicated in the red arrow, there are two modes by which, one can do this. One mode is, twist them in the same direction, like the arrow shows. This carbon-carbon bond is twisted in the clockwise direction. Similarly, this carbon-carbon bond is also twisted in the clockwise direction. So, this type of twisting, where the twisting motion takes place in the same direction, is called the conrotatory mode of ring opening reaction.

Now, see the consequence of the conrotatory mode of ring opening reaction, on the stereochemistry of the product. This is a 3,4-cis dimethyl cyclobutene, is the starting material. The two methyl groups are cis with respect to each other. And, so are the two hydrogen. The twisting motion of this two carbon-carbon bonds, in this particular direction will bring the methyl group, inside the PI framework. And, this methyl group will be outside the PI framework. Simultaneously, this hydrogen will go out, and this hydrogen will come inside.
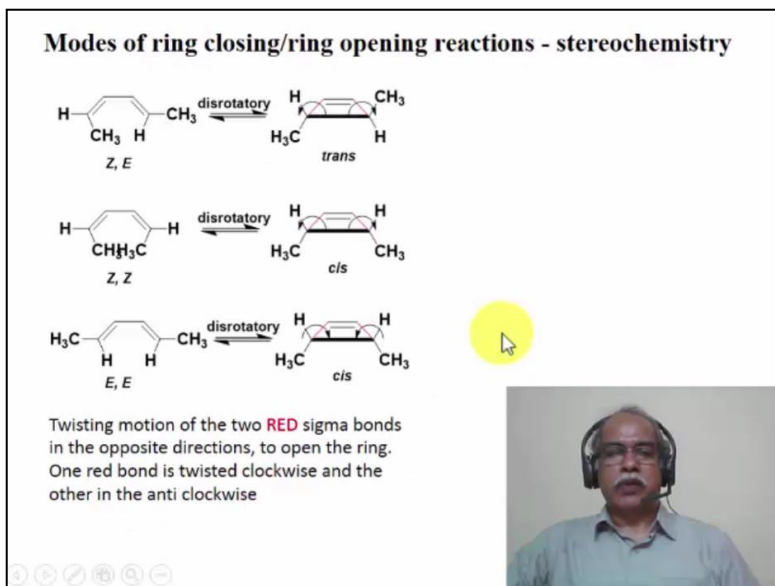
So, that will result in the formation of the Z, E. This is the Z isomer of the stereochemistry of this double bond is Z, whereas the stereochemistry of this double bond is E. So, we get Z, E isomer of the dimethyl butadiene, as the product. If you take the trans isomer, and do the same conrotatory mode of ring opening reaction, the twisting motion will bring the methyl group, inside here. Similarly, the twisting motion will also bring the methyl group, over here. And, this particular conrotatory mode of ring opening in the clockwise direction, essentially brings this two methyl groups, close to each other in the Z, Z form.

It can also happen that, twisting motion can take place in the anticlockwise direction. All that is necessary for the conrotatory motion to take places is, the twisting motion has to be in the same direction. It can be either in the clockwise direction, as in the top case, or in the anticlockwise direction, as in the case of the bottom case, here. So, in this particular case, the conrotatory motion will bring, this methyl outside, and this hydrogen inside, and this methyl outside, and this hydrogen inside.

So, we end up with a E, E isomer of the products. So, you can see here, these reactions are highly stereospecific. The stereochemistry of the product that is formed, is dependent on the mechanism, whether it is disrotatory or conrotatory mode. And, in this particular case, the stereo isomer, that is responsible for the Z, Z isomer formation is trans.

And, in the conrotatory motion in the clockwise direction, or in the anticlockwise direction, depending upon the mode of the rotation, you can either end up with a Z, Z isomer, or the E, E isomer. So, what is important in this particular slide is, the fact that, the twisting motion can happen in the conrotatory manner, either in the clockwise direction, or in the anticlockwise direction. That will have a consequence in the stereochemistry of the product, that is being formed, depending upon the stereochemistry of the starting material.

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Modes of ring closing/ring opening reactions - stereochemistry

Twisting motion of the two RED sigma bonds in the opposite directions, to open the ring. One red bond is twisted clockwise and the other in the anti clockwise

Now, what if these two bonds are twisted in opposite direction. You take the example of the, again, the dimethyl isomer, trans isomer of the cyclobutene itself. One can twist this bond in the anticlockwise direction. Twist this bind in the clockwise direction. So, they are actually twisted in opposite direction. And, such a rotation is called the disrotatory motion of ring opening reaction. So, this will bring essentially the hydrogen out, and the methyl inside, hydrogen out, and methyl inside. In this case, the methyl will go out, and the hydrogen will come inside.

You can see here, the hydrogen is inside, the methyl is outside, here. So, the trans isomer gives the Z, E isomer of the product, in the disrotatory motion. The disrotatory motion can be, either inward or outward. You can see here, this is outward disrotatory motion. And, this is inward disrotatory motion, essentially. So, that will again have a consequence of, whether to get the Z, Z stereochemistry, or the E, E stereochemistry.

The twisting motion of the two red bonds of the sigma bonds, the two-red sigma bond in the opposite direction, to open the ring. The one bond is twisted in clockwise direction. The other bond is twisted in the anticlockwise direction. Such a rotatory motion is, what is known as the disrotatory motion. As in the case of conrotatory motion, the reactions are highly stereospecific in nature. Depending upon the stereochemistry of the starting material, and the kind of rotation that takes place, the stereochemistry of the product can be dictated or predicted, in this particular case.

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Frontier orbital method for electrocyclic reactions
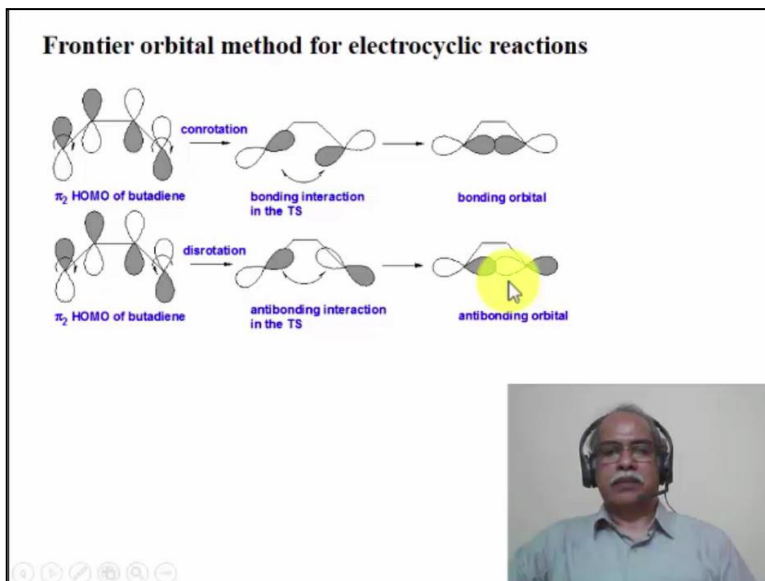
Now, let us start using the three methodologies, for the analysis of the pericyclic reaction, namely the frontier molecular orbital method, the orbital symmetry correlation method, and the transition state aromaticity method. We will start with, the frontier orbital method for electrocyclic reaction. Now, if you consider the frontier orbital of butadiene, undergoing a ring closing reaction to the cyclobutene.

The frontier orbital of butadiene is essentially, the SI 2 or the PI 2 of the second molecular orbital with one node, which is at the center of the molecule. This is the nodal point, for example. In the conrotatory process, the two lobes are essentially brought close together, namely this particular lobe on the top, and this particular lobe at the bottom. And, the interacting lobes during the conrotatory motion, twisting in this direction inwardly, and twisting in this direction inwardly, in both the clockwise direction. So, it is conrotatory process.

The orbital lobe, the top lobe, and carbon one, and the bottom lobe, and carbon four, will come closer together, in forming a bond. And, this is in the transition state, there is a bonding type of an interaction. So, as a result of the bonding type of an interaction, the bond formation actually takes place to form the cyclobutene. So, this will be a lower energy transition state pathway. Because, in the transition state, you have an orbital interaction, leading to the bonding type of an interaction.

As opposed to the same molecule, the butadiene molecule homo is, what is represented here. And, if you do that disrotatory motion, this will be the clockwise rotation, and this will be the anticlockwise rotation, in the opposite direction. So, this will bring the top lobe of the carbon number one, and the top lobe of a carbon number four, closer together.
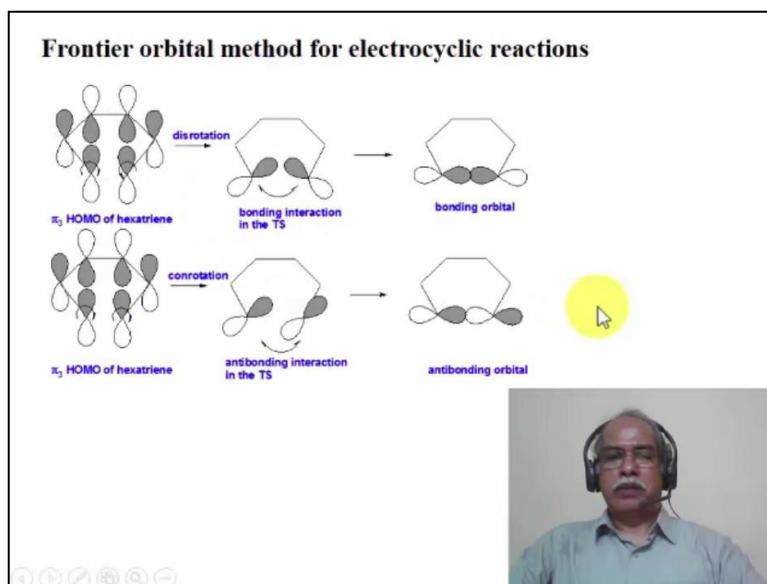
So, in the transition state, you can see, these two are the orbital lobes, that are going to interact. This is clearly an anti-bonding type of an interaction, in the transition state. And, that will essentially result in the anti-bonding formation. Anti-bonding orbital is, what is being formed. So, the transition state, if you consider the one, which is going through the bonding type of an interaction, and the one, that is going through the anti-bonding type of interaction, clearly the one, that is going through the bonding type of an interaction, will the favorable. It will be lower energy path way.

So, as a result of that, we say, this particular process namely butadiene, undergoing conrotatory process to ring close, to give the cyclobutene, is an allowed process under thermal condition. Why are we considering, thermal condition? Because, we are considering the ground state molecular orbitals of the butadiene, and not the excited state molecular orbital of the butadiene. So, under thermal condition, according to the frontier orbital methodology, it is evident that, butadiene can undergo a conrotatory process.

And, such a process will lead to a transition state, involving bonding type of an interaction. And, because the bonding type of interaction will have a lower energy, compared to the anti-bonding type of an interaction. This is an allowed process. So, a 4N electron system in general, under thermal condition, will undergo a conrotatory process of ring closing, as well as ring opening. You can analyze the same thing, in the reverse direction also.

And, you can come to the same conclusion that, the ring closing and ring opening will have essentially, the same kind of a Woodward-Hoffmann rule, associated with this. So, under thermal condition, the disrotatory process for a 4N electron, electrocyclization is a forbidden process, or a disallowed process.

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Frontier orbital method for electrocyclic reactions

π_3 HOMO of hexatriene — disrotation — bonding interaction in the TS — bonding orbital

π_3 HOMO of hexatriene — conrotation — antibonding interaction in the TS — antibonding orbital

Now, let us consider a six-electron system. This will be the SI 3 of the homo, which is a SI 3 of the hexatriene, the ground state electronic configuration. This will be the highest occupied molecular orbital of hexatriene. Now, if you consider the disrotatory process, that will bring this two-loop close together, in terms of bond formation in the transition state. So, that will be a bonding type of a transition state.

As opposed to, if you do a conrotatory process, this lobe will essentially interact with the bottom lobe, in the carbon number six. So, in the transition state, these two orbitals will interact, leading to the formation of an anti-bonding interaction. So, in the transition state itself, the anti-bonding character will develop, for example. So, naturally the transition state with the bonding character, will have a lower energy, compared to the transition state with the anti-bonding type of a character.

So, as a result of that, the top process, where the 4N +2 electron system, this is now a six-electron system. 2 +2+2 6 electron system is undergoing electrocyclization in a disrotatory mode, is a thermally allowed process. We are here considering, the thermal electronic configuration, in the ground state. So, it is a thermal process, that we are considering. Now, if you want to consider the excited state, we have to go to the excited state electronic configuration of butadiene.

In the ground state, there are two electrons in SI 1, and two electrons in SI 2. In the excited state, there will be two electrons in SI 1, one electron in SI 2, and one electron in SI 3. So, SI 3 is the homo or the highest occupied molecular orbital of the excited state of butadiene. And, that figure

is representing, the essentially, the highest occupied molecular orbital of the excited state of butadiene. The same is represented here.

First, we will consider the dis-rotation, that leads to the bonding type of an interaction, in the transition state. And, if you consider the conrotatory process, that leads to an anti-bonding type of an interaction. This transition state is a more favorable transition state, compared to the anti-bonding interacting transition state. So, in the excited state, the disrotatory process is allowed process, for an 4N electron system.

So, this is essentially applied to the hexatriene system also. In the case of hexatriene system, the SI 4 will be the highest occupied molecular orbital hexatriene. So, the SI 4 should have three nodes. You can observe the three nodes, one node here. One node between carbon number three and four. And, one node between carbon number five and six. So, one, two, three, four, and five, six. These bonds have the nodal points, associated with this particular molecular orbital.

And, the conrotatory process essentially leads to, bonding type of a transition state. And, the disrotatory process leads to, the anti-bonding type of a transition state.

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Woodward – Hoffmann rules for electrocyclic reactions

| System (no of electrons)	Mode of reaction	Allowedness of reaction	
		Thermal	Photochemical
4n	Conrotatory	Allowed	Forbidden
4n	Disrotatory	Forbidden	Allowed
4n+2	Conrotatory	Forbidden	Allowed
4n+2	Disrotatory	Allowed	Forbidden

So, from all this, we come to the conclusion, based on the frontier molecular orbital methodology. For a 4N electron system, if it is a conrotatory process, it is thermally allowed. If it is a conrotatory process, then it is photochemically allowed. Whatever is allowed or disallowed for the thermal process, will be complementary to the photochemical process, for example. And,

whatever is allowed or disallowed for the 4N system, will be complementary to the 4N +2 system, for the given mode of reaction

If it is a 4N conrotatory thermally allowed, then it will be 4N + 2 conrotatory thermally it will be forbidden. So, if you understand this Woodward-Hoffmann rule in its entirety, you will be able to apply this to the electrocyclic reaction, and analyze the electrocyclic reaction, in terms of the stereo-chemical processes, that are predictable using the Woodward-Hoffmann rules.

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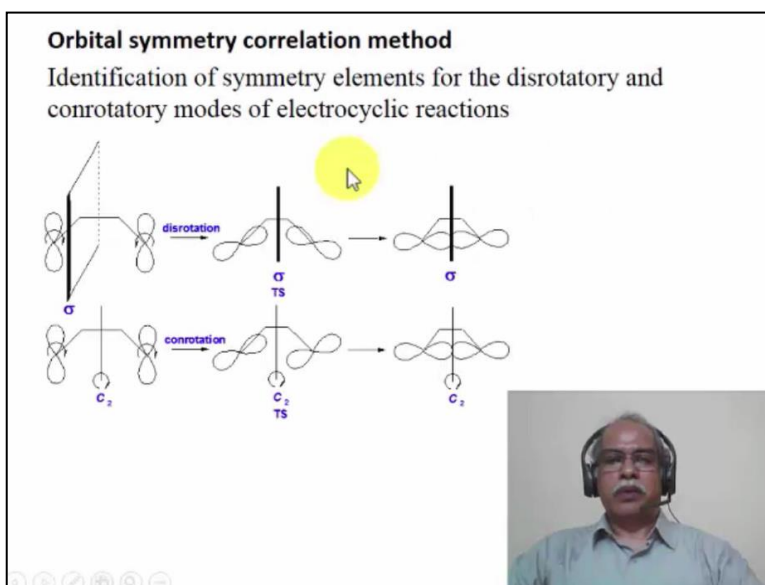
Now, let us turn to the orbital symmetry correlation methodology. First of all, we will need to identify, what symmetry element needs to be used, for the disrotatory and conrotatory modes of electrocyclic ring closing reaction. Now, in the disrotatory process, this orbital is pushed towards inside. this orbital is also pushed towards inside. So, around the transition state, this will be the orientation of the two molecular orbitals, or the lobes of the molecular orbitals, in the disrotatory process.

In the conrotatory process, because a rotation is taking place in the same direction, this would be the orientation, in the transition state of the two molecular orbital lobes, for example, in the transition state. So, if you apply, for example, the symmetry operator, sigma here. Sigma is present in the starting point. Sigma is also present in the transition state type of a structure, where this is reflected over here.

And, this is reflected over here. And, sigma is also present in the end point of the product, which is a sigma orbital, that is being performed in this particular case. Whereas, in the conrotatory

process, it is a C2 symmetry that is being present. This is C2 symmetry. This is also C2 symmetry. This lobe will come here. And, this lobe will come here, for example, on C2 rotation. You will produce an identical picture, if you allow a C2 rotation, to operate in this particular picture. And, essentially in the product state also, there is a C2 symmetry, that is being present.

So, if you want to analyze a electrocyclic reaction, under disrotatory condition, one should use the sigma as the symmetry operator. And, if one wants to analyze the conrotatory process of the electrocyclic reaction, one should use the C2 operation, as the symmetry operation for the analysis.

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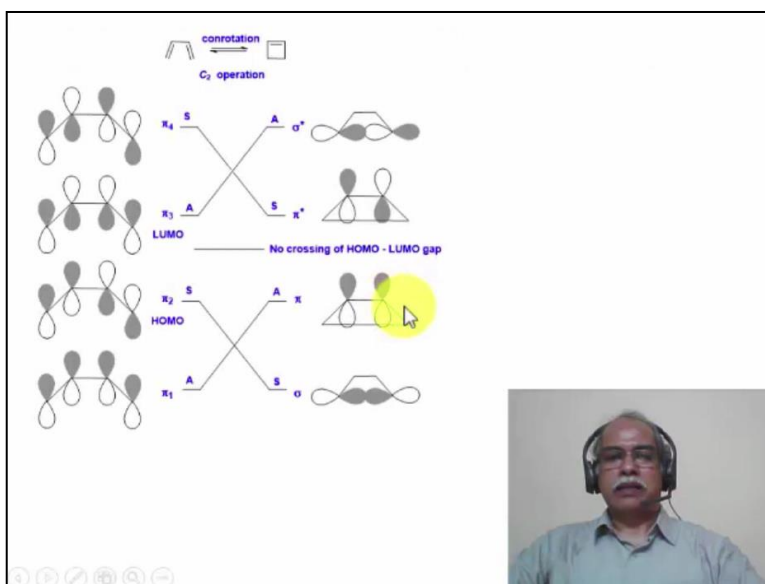
Now, let us consider first, the butadiene go in to cyclo-butane. And, i am defining this process as a conrotatory process. So naturally, i will take the C2 axis of symmetry, as the symmetry element, that is being present here. Now, the starting molecular orbitals of butadiene are written on the left-hand side, SI 1, SI 2, SI 3, and SI 4, of the butadiene molecule. It is represented as PI 1, PI 2, PI 3, and PI 4.

This is the highest occupied molecular orbital. This is the lowest unoccupied molecular orbital. If you consider the products, the two bonds that are formed are, one is a sigma bond. So, we will consider sigma and sigma star. Other one is a PI bond, which is a newly formed PI bond. So, we will consider PI and PI star. In doing the orbital correlation, symmetry correlation method, one needs to arrange the orbital with increasing energy.

This is SI 1, and this is SI 4. So, the increasing energy level, SI 1, SI 2, SI 3, and SI 4 is the increasing energy level. Similarly, if we consider the right-hand side, it is a sigma molecular orbital, which is the lowest energy. Then comes, the PI, the PI star, and, finally the sigma star, of the molecular orbital.

Now, let us start doing the C2 operation, on this left-hand side molecular orbital. this molecular orbital, clearly anti-symmetric, with respect to C2 axis of rotation. Because, if you do, the C2 axis is passing through the center of the molecule, which is a pointer, that is showing now, for example. And, this is the portion, where, we have the nodal point. So, essentially the C2 axis is pointing, passing through the midpoint of the C2 and C3 carbons. So, if you do a symmetry operation, C2 operation, all the shaded lobe will come to the bottom.

And, all the unshaded lobe will come to the top. So, that is not reproducing itself. So, it is anti-symmetric with C2 operation. If you do a C2 operation, SI 2 of the molecular orbital of the butadiene, the two shaded portions will essentially change place, with respect to each other. So, that result, it will reproduce itself. The picture will be reproduced. So, it is symmetric, with respect to the C2 operation. SI 3 will be anti-symmetric. And, SI 4 will be again symmetric, with respect to the symmetry operation.

Now, if you consider the C2 operation on the sigma molecular orbital, it is symmetric. If it is a PI molecular orbital, it is anti-symmetric. PI star molecular orbital, it is symmetric. And, it is the sigma star molecular orbital, which is anti-symmetric, with respect to the C2 operation. All you have do is, rotate the molecule by 180 degree, and see whether, you reproduce the same molecule, molecular orbital picture, or not.

This particular case, for example, if i do a C2 operation, along this direction, the shaded lobe will come to the bottom, and the unshaded lobe will come to the top. So, it will not reproduce itself, it will have an inversion. So, as a result of that, it is anti-symmetric with respect to that particular operation, that is being performed.

So, we have identified, this molecular orbital to be anti-symmetric, with respect to C2, symmetric with respect to C2, anti-symmetric with respect to C2, and symmetric with respect to C2, on the left-hand side. And, symmetric with respect to C2, anti-symmetric with respect to the C2, symmetric with respect to the C2, anti-symmetric with respect to the C2. And, on the right-hand side, which is the product side of this molecule.

Now, if you look at the symmetry correlation, we have to correlate orbitals of the same symmetry first, starting from the lowest energy. So, let us start from this orbital, which is anti-symmetric. It is a symmetric correlated. The PI 1 of the molecular orbital of the starting point, is symmetric correlated, to the pie molecular orbital of the cyclobutene. So, these two have the same symmetry. So, they are correlated.

Similarly, starting from this molecular orbital, the closest one that has the same symmetry, which is a symmetric molecular orbital is the SI 2. So, the sigma is correlated to the SI 2. And then, you have the non-bonding HOMO-LUMO gap. Then, this molecular orbital symmetry correlated to this one. And, this molecular orbital is symmetric correlated to SI 4, for example. So, what you see is, the transformation of the starting molecular orbital, to the product molecular orbital, in the ground state itself, where the symmetry conservation is taking place.

So, this is the orbital symmetry conservation method, is what, we are talking about. So, this symmetry is conserved here. And, this symmetry is conserved over here. Similarly, this anti-symmetric is conserved over here, as an anti-symmetric molecular orbital. And, this anti-symmetric is conserved.

In other words, all the molecular orbitals in the ground state, are essentially symmetric correlated. And, all the molecular orbitals in the antibonding levels, are also symmetric correlated, with respect to each other. There is no symmetric correlation between, the filled molecular orbital, and the unfilled molecular orbital, of the product. In other words, there is no crossing of the HOMO-LUMO gap.

So, essentially under the thermal condition, this is an allowed process. So, conrotatory process for a 4N electron system, because the symmetry correlation takes place within the ground state electronic configuration, all the filled molecular orbital of the starting material, to the filled molecular orbital of the product. You would say that, this is a conrotatory process, is a thermally allowed process.

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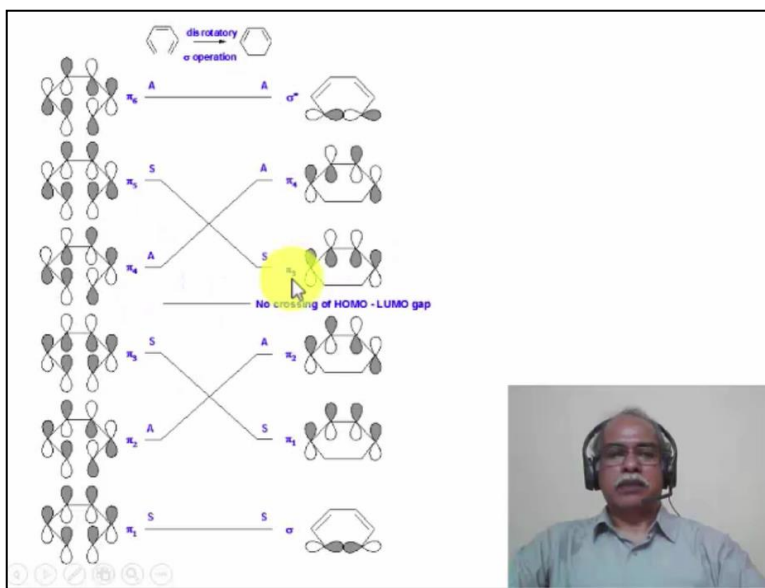
The same analysis can be done, for example, with respect to the symmetry operation, which is the disrotatory symmetry operation. Here, we consider the C2 operation, which is a conrotatory C2 operation. If you want to do the disrotatory process, then it is a sigma. Now, let us consider the cyclohexatriene, undergoing cyclisation, to give cyclohexadiene, for example. In other words, 1,3,5-hexatriene undergoing cyclisation, to give a cyclohexa-1,3-diene as the product. These are the six molecular orbitals of the starting material, namely the hexatriene.

In the product, if you see, there is one sigma bond, that is formed. And, the re-organization results in two PI bonds, as a butadiene system. So, this is sigma and the sigma star, which has the highest energy. In between, essentially you have a butadiene molecular orbital picture drawn, corresponding to the hexadiene-1,3-diene, which is essentially same as butadiene. So, you correlate, those pictures of the butadiene to the hexa-1,3-triene molecule, in this particular case. Now, with respect to the sigma operation, if we consider, this is symmetric with respect to this.

Sigma is a plane, that is bisecting, the space between the carbon number one and six, and passing through, the midpoint of the carbon number three and four. This midpoint between, these two carbon. And, the midpoint between these two carbon. That is a symmetry plain, that we are considering. A mirror plane, that we are considering. With respect to that mirror plane, it is symmetric. Similarly, the sigma orbital is also symmetric, with respect to the mirror plane.

So, they are correlated in the ground state itself, with respect to each other. Now, this molecular orbital is anti-symmetric, with respect to the sigma plane. And so, it is written in the symbol, A for anti-symmetric, S for symmetric. This particular molecular orbital is symmetric, with respect

to the sigma plane. This is anti-symmetric, with respect to sigma plane. SI 5 is symmetric, with respect to the sigma plane. And, SI 6 is finally anti-symmetric, with respect to sigma plane.

If you consider the PI star molecular orbitals, sorry, the sigma star molecular orbital, which is the highest energy molecular orbital. The sigma is anti-symmetric. The next one, which is SI 4 is anti-symmetric. SI 3 is anti-symmetric. SI 2 is anti-symmetric. SI 1 is symmetric in nature. Finally, we already saw the sigma being symmetric, with respect to each other.

In this case also, you will see, all the filled molecular orbitals of the starting point, has orbital transformation taking place with the same symmetry, which is again the filled molecular orbital of the product. So, these two are symmetric correlated. The two anti-symmetric groups are symmetric correlated. In other words, there is no symmetry correlation between, the filled molecular orbital, with the antibonding molecular orbital. There is no crossing of the HOMO-LUMO gap, between the two-product stage, and the starting materials stage. So, this reaction is thermally allowed process under the disrotatory process.
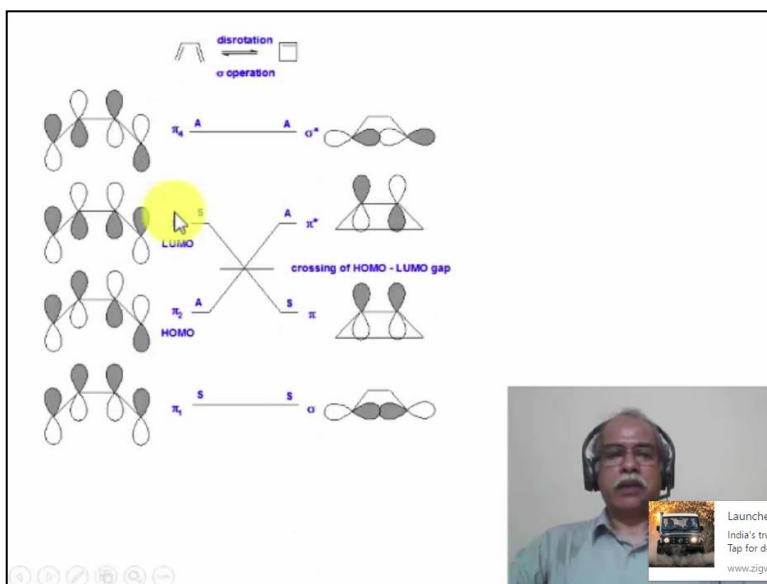
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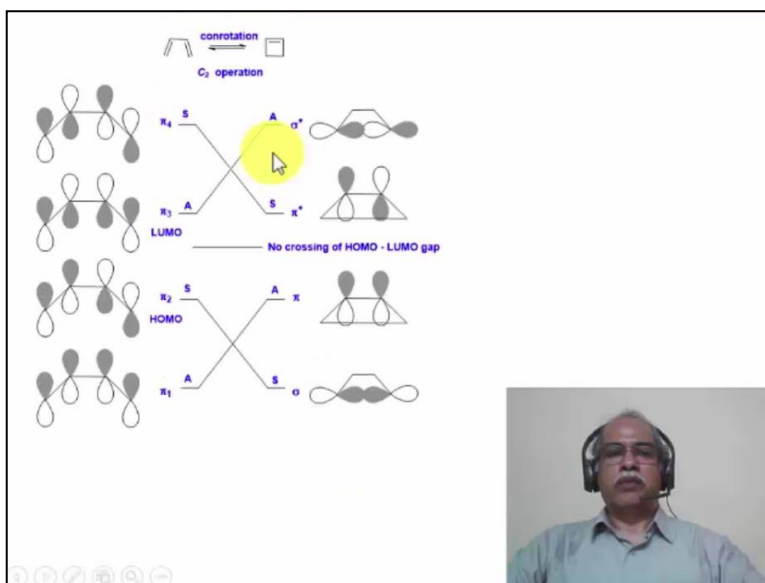
So, a 4N system is thermally allowed, under a conrotatory process.

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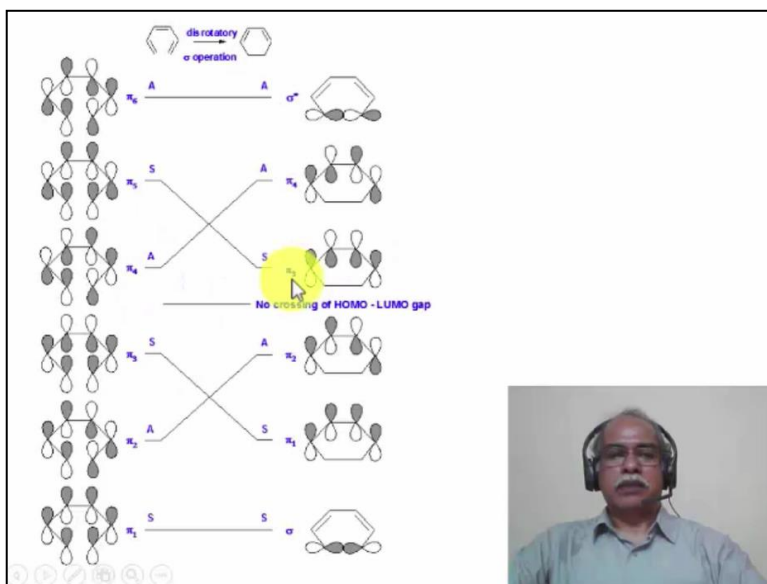
A 4N +2 system is allowed under disrotatory process under thermal condition, is the conclusion, that we are arriving at.

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If you want to do the photochemical condition, we need to see the crossing of the barrier between the HOMO-LUMO gap. In other words, the symmetry correlation takes place between, the ground state electronic configuration, to the excited state electronic configuration. This, to be a filled molecular orbital, for it to be correlated, it has to be an excited state molecule. So, the ground state molecular orbital, essentially there is a crossing of the HOMO-LUMO gap, in this particular case.

This is, what is called the violation of the non-crossing rule, sorry, not violation of the non-crossing rule, this is essentially the crossing the HOMO-LUMO gap, between the two systems.

And, that is essentially crossing the orbital, to correlate with a filled molecular orbital, to an empty molecular orbital, or antibonding molecular orbital. But, if it is a photo chemically excited state, this would be a filled molecular orbital.

So, the correlation can take place, only under photo chemical condition. So, the sigma operation essentially identifies, the symmetry properties of the molecular orbitals. And, the symmetry correlation method tells you that, this reaction can occur, only under the photochemical condition.

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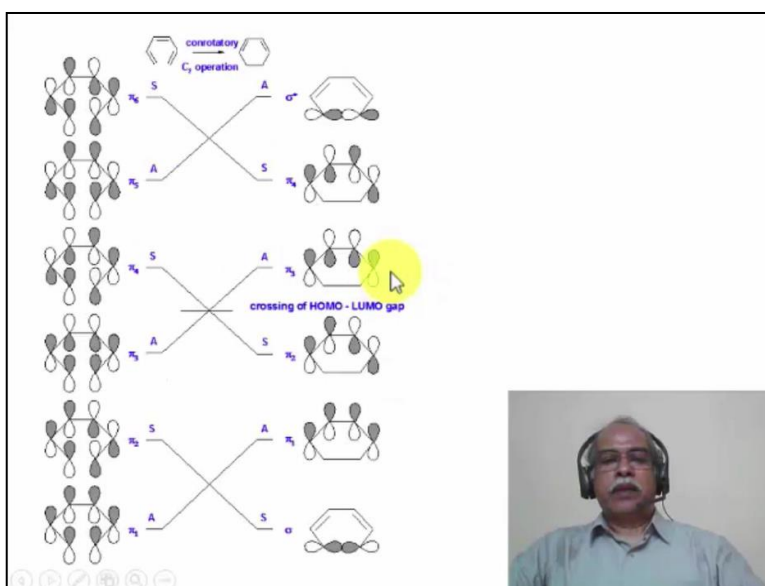
The same observation is made again, for the case of the hexatriene system. You can see here, there is a crossing of the symmetry correlation, with respect to the HOMO-LUMO gap, or the non-bonded level. So, this crossing is essentially, what tells you that, the electronic configuration in the ground state is correlated, to the excited state molecule, in this particular case. Therefore, this reaction can take place, only under the photochemical condition.

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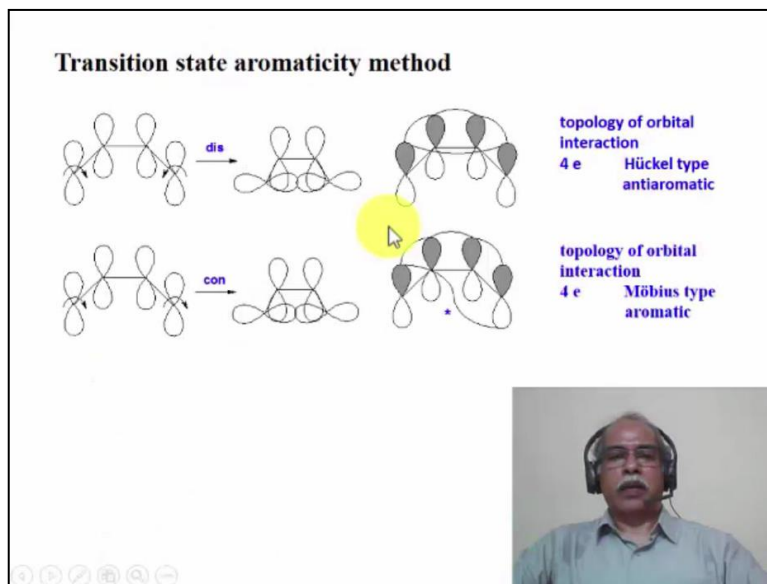
Now, finally, let us analyze this reaction, by means of the transition state aromaticity method. If it is a disrotatory process, you are going to have a continuous loop of electrons of this kind, which is a 4N electron system, or 4 electron system. This is a huckel type, four electron system, which has an antiaromatic character, as far as the transition state is concern. If you consider the conrotatory process, it is a top lobe, that is going to interact with the bottom lobe, with a nodal point being clearly visible, in this particular case.

Here, it is a continuous loop of electrons, four electron system. So, it is a huckel type of a loop. Whereas, this is with an inversion. So, it is mobius type of a loop, four electron system. So, topology of interaction is such that, it is a 4-electron system, with the mobius. Hence, it is an aromatic system. So, this would be an allowed process, under thermal condition. Whereas, this will be a disallowed process, under the thermal condition, is what we are arriving at in this case.

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Chemical systems that undergo electrocyclic reaction

Number of electrons	Chemical system
2 electrons	cyclopropyl cation – allyl cation
4 electrons	cyclopropyl anion – allyl anion cyclobutene – butadiene cyclopentenyl cation – pentadienyl cation
6 electrons	cyclopentenyl anion – pentadienyl anion cyclohexadiene – hexatriene cycloheptadienyl cation – heptatrienyl cation
8 electrons	cycloheptadienyl anion – heptatrienyl anion cyclooctatriene – octatetraene cyclononatrienyl cation – nonatetraenyl cation

So, what we have seen in this particular module, is the definition of a electrocyclic reaction, introduction to electrocyclic reaction, and looking at the various modes of electrocyclic reaction, and the resulting stereochemistry aspect, in terms of conrotatory process, and disrotatory process. Defining the stereo specificity of the electro cyclic processes. And then, we consider the butadiene system and hexatriene system, by three different methods namely, frontier molecular orbital method, symmetry correlation method, as well as by transition state aromaticity method.

And, came to the conclusion that, 4N electron system under thermal condition, will be allowed under conrotatory process. And, vice versa will be the 4N+2 electron system, that will be undergoing thermal electrocyclic reaction and disrotatory mode. Now, we have to count the number of electrons, that is allowed, that is taking place in the electrocyclic reaction, and the chemical system, that is capable of undergoing the electrocyclic reaction.

So, this is a chemical system, that undergoes electrocyclic reaction table, that is, what is given here. If we consider a cyclopropyl cation rearranging into allyl cation, that is an electro cyclic ring opening reaction involving two electrons, which are the two PI electrons of the cyclopropyl cation. If you consider, for example, the cyclopropyl anion going to allyl anion ring opening, that will be a 4-electron system. The anion will have two electrons, extra. So, it will be 2+2, 4-electron system.

If we consider cyclopentadienyl anion, for example, that is a 6-electron system, going to pentadienyl anion. On the other hand, cyclopentadienyl cation will be a 4-electron system, undergoing a pentadienyl cation ring opening. So, you will see specific examples of each one of

these type of chemical system, undergoing the electrocyclic ring closing or ring opening, in the next module. Thank you very much, for your kind attention.