Structure, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A Problem-Solving Approach Professor. Amit Basak Department of Chemistry Indian Institute of Technology, Kharagpur Lecture No. 01 Introduction on Structure and Stereochemistry of Organic Molecules: Salient Features of Symmetry Elements; Role of Principal Axis, Sigma Plane, Center of Symmetry and Alternating Axis of Symmetry in Deciding Chirality

Welcome to this course on Structures Stereochemistry and Reactivity of Organic compounds and Intermediates in Problem Solving Approach. Now, this has, this course has been floated with the view that these students who are now studying at the first year postgraduate level for them this course has been designed and this is basically an overall glimpse of the title what that reflects that means, we are going to talk about various aspects of organic chemistry.

Organic chemistry has many pillars and it is a subject which is also not which is a subject that is also creates some confusion in the minds of the students, the students feel that it is a subject of memory, there are too many reactions, too many products from a reaction too many name reactions, too many structures, too many natural products and these all these have to be memorized.

However, it is true that organic chemistry is full of structures, reactions, products, including natural products, synthetic products, all these, but there is a rationale behind knowing all these things, it is not that it is only a case of memory and memorize the structure and their products from a reaction on them. We are going to give some basic foundation on how to know the structure of a molecule and then how to know their reactivity.

Basically, this is a course on Structure Reactivity of Organic Molecules. And alongside, we are going to do several problems to clarify any doubt and still I believe that doubt will remain in your minds, queries will remain and for that we have teaching assistants for this course and there is a forum where you can put your questions and then the TS along with myself wait to answer those queries.

So, let us start the first lecture of this. As I said Organic Chemistry has many pillars, it is, it has got a foundation made up of different pillars, one pillar is Structure, structure of molecule. And

the second you could say that the second pillar is the reactivity that means, how a molecule is going to react when exposed to a particular reagent that is the reactivity or the function, you can also call the function of the molecules which depends on the groups that are present in the structure of that molecule.

Thirdly, there is a very important aspect of Organic Chemistry and that is beauty, its beauty that is the creation of new molecules and the number of new molecules is unbound. It is not limited by any structural constraint, but it is limited by one's own imagination and the difficulty level in making those compounds those structures. So, that creation which is the basic strength of organic chemistry and this is called Organic Synthesis.

Besides creation of molecules, we know that there are natural products we obtain many molecules 1000s and 1000s of molecules are being made by the natural sources, including plants, microorganisms, and mammals, bacteria everything and these molecules are made for us some of them are useful, some of them are toxic may not be useful, but anyway these are the two these are the two aspects one is creation and other is isolation of molecules, novel molecules, new molecules from natural sources.

Then it has got another big foundation that is the, it is the gateway to the polymer chemistry the reach and diverse world of polymer chemistry where the monomer is basically an organic molecule. There is a fifth foundation of the organic chemistry course, that is the how to determine the structure of a molecule because you can get a molecule you can get a compound from some source or for synthetic methods, but the next question is how to elucidate its structure. We will start with the structural aspect of organic molecules.

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Now, when we talk about structure, let us show you the show you the entire syllabus of this how it has been planned that the topic one is basically Structure and Stereochemistry of Organic Molecules. And in that we are going to give an introduction to the brief introduction to the different types of stereo stereochemistry that a molecule have can possess that is Tetrahedral, Axial, Planar, Helical etc and including the assignment of absolute configuration.

Now, remember there is another course, which is now, which is floated in 2017 that was that was called Stereo Chemistry, which is still running that course is basically a foundation course, a very basic course on Stereo Chemistry. And here the Stereo Chemistry that we will be discussing is a little advanced level, but whatever basic knowledge is required that will be that will be told in brief.

Now, the other important aspect that will be covered here in an elaborate and quite elaborately that is symmetry and point groups then you have Pseudoasymmetry that is another concept which was not much discussed in the earlier stereochemistry course, and the reflection invariance issue. And finally, we will do many problems, which is encompassing all these aspects of structure and stereochemistry.

The second topic was is the confirmations of saturated fused ring systems. The last course of foundation course, actually dealt with the stereochemistry and confirmation analysis of monocyclic systems, monocyclic systems mainly cyclohexane and the lower one cyclopentane

cyclo butane and cyclopropane. Here, we are going to discuss the confirmations of fused ring systems like decalins then we will discuss the heterocycles also how the rings packer are what is the conformation of the of the ring if there is a hetero atom present in the system.

We are made, remember we are talking about only the saturated systems because they are the flexible ones. And then this is so important that heterocycles because you have that sugar moiety and these sugars are present in the form of carbohydrates as well as in the form of nucleic acids. So, they are conformation analysis is important. Then we have more than two ring fusion that is polynuclear hydrocarbons, like on Perhydrophenanthrene, Anthracene, Perhydroanthracene and then we will go to the tetra cyclic systems like steroids and if time permits, we will also go to the penta cyclic ones, which are the triterpene systems.

And then we will also do problem solving because that will give you a basic grasp of how to write the perfect the correct conformation of a molecule and depending on the conformation, how the reactivity varies, this is the topic 2.

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The topic 3 is the as I say that structure determination is an integral part of Organic Chemistry. So, here the 3D structure determination of Chiral molecules. We are specifically dealing with chiral molecules because the structure determination of organic molecules itself is a huge course. There are different types of techniques spectroscopic techniques which are adopted to analyze or to determine the structure of an unknown organic molecule. But here we are going to only do the only we will do the optical rotator dispersion methods to determine the 3d structure of tidal molecules.

Then, in that, in that we will discuss the ORD and the CD that means the Optical Array Dispersion and Circular Dichroism. Cotton affect, Axial Haloketone, Octant rules and then utilizing these rules, how are you going to assign the structure and confirmation and configuration of an unknown organic molecule, but which is Chiral. Then we also do problem solving. So, all the topics will be backed up by solving several problems on the topics that are covered under that under the that whole lecture series.

Topic 4 is Stereo electronic control on the confirmation and reactivity, the now comes the function of an organic molecule. Now, the function of an organic molecule obviously, will depend on two aspects one is the type of functional groups that are like Carbonyl or Ester or Amide or Amines, all these functional groups or double bond, triple bond etcetera. The presence of these functional groups and the other is that how they are oriented in space that means, the conformation of the molecule itself.

So, it is basically that combination is what is called the Stereo Electronic Control that means, the how the what the electronics that is that is in the system, how it is spread in 3 dimensional space and then depending on that how the reaction goes with a an external reacting agent. Then we will have in different Intra-molecular Cyclization. So, we will show that how to make a cyclic ring because that requires that requires precise Stereo Electronic Control.

And there are certain rules, which will tell whether a 5 membered ring is going to form or a 6 membered ring is going to form when, when both possibilities are there or there may be 6 versus 7, 3 versus 4. So, all sorts of possibilities might be there in the system, when it sizes and there are certain empirical rules. One typical rule is the Baldwin's rule that we will discuss that was the topic 4.

Topic 5, now, we come to the chemistry of reactive, reactive organic compounds including the reactive intermediates because the course in title the title of the course is structures Stereo Chemistry and reactivity of organic compounds and reactive intermediates, especially organic compounds. Here, special organic compounds means we generally have reactive intermediates like Ketenes, I can write here like Allenes, Ketenes and then Alkynes Arynes.

So, these 4 we will mainly concentrate and then methods of their generation structure and reactivity that from where it will be generated and when it is generated, what is the fate of this in this reactive organic compounds or intermediates.



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Then we have this topic 6 is again we will continue with organic intermediate and one of the very important organic intermediate which has been exploited for organic synthesis is the Carbon Radicals is the carbon is the carbon based, radicals and we are not talking about the Carboketene or carbonyl chemistry, because that is well exploited and that is itself the forms one of the major areas of organic synthesis.

We will not talk about those we will talk about the carbon radicals carbon centered radicals and how they are generated, what is their structure, how what is their reactivity, and then how they have been applied for making very useful compounds. One point I forgot to mention that organic synthesis and this isolation of natural products this has a huge implication in the case of availability of drugs and pharmaceuticals, where synthetic chemistry organic chemistry is had plays the pivotal role in making those molecules.

Then Umpolung reactions, that means reversal of polarity, Barton reaction, and we will go by problem solving. Then the topic 7 and 8, what we have decided is we will take the carbonyl as our model substrate, and then we will do reactions on the carbonyl. And these reactions, that when something reacts with the carbonyl, if it reacts with the carbon in carbon, there is a

possibility of generation of an asymmetric center. And so that leads to the concept of asymmetric synthesis.

So, we will talk about different asymmetric reactions of carbonyls. One is the stereo chemistry of nucleophilic addition to carbonyl's and then we will talk about the guiding principle that which Isomer, Enantiomer or Diastereomer will predominate then alkylation asymmetric alkylation that is the alpha position of the carbonyl system where you put alkyl groups.

And finally, the topic 8 which is asymmetric mainly, Asymmetric Aldol reactions. And then how to predict which actually generates two asymmetric centers at the same time and there are models to explain all these and how to control and how to achieve high degree of asymmetry a lot of advanced advancement has taken place in asymmetric reactions of carbonyls. So, our reactivity for our reactivity topics we have selected or we will select the carbonyls as our model substrate.

So, all these 8 topics basically will cover the entire course, remember, we are not talking about the entire reactivity profile of organic molecules that is not it, it is we will just highlight some of the typical ones will not, we will not debate or elaborate the entire Stereo Chemistry high levels Stereo chemistry totally will not do that. But we will talk about certain advanced topics of stereochemistry we will talk about certain advanced topics of how the structure is determined based on optical rotatory dispersion or circular dichroism.

And we will talk about the reactivity of many organic or many organic species or they are called reactive intermediates and also the guiding principle for their reactivity, the stereo electronic namely that stereo electronic effect. So, that actually is the whole syllabus. (Refer Slide Time: 18:03)

TOPIC 1			
Structure and stereochemistry			
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A brief introduction to different types of chirality: Tetrahedral, Axial, Planar, Helical including assignment of absolute configuration.	•		× • 4 0 ×
Symmetry and point groups.			-
Pseudoasymmetry and Reflection Invariance Issue.		4	
Problem solving			
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Now, let us start with the with our first lecture which is Structure and Stereochemistry.

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In a lecture in 1893 Lord Kelvin introduced the term chirality.	
The word chiral is from the Greek name cheir (for hand or pertaining to hand).	_
Chirality means handedness (topological). It is a purely geometrical property. An	
object, for that matter, a molecule is chiral if it is not superimposable on its mirror	
image.	
Organic molecules may be conformationally mobile. A chiral molecule must be	ě
nonsuperposable on its mirror image even after operation of rotation around single	6
bond/s or translation, .i.e., it must be chiral in all conformations. Thus, in order to	
ascertain whether a flexible molecule is chiral or achiral (not chiral), all possible	-
conformers must be analyzed.	
Chirality of a particular molecular conformation of a known stereo structure may be	
decided by:	
(f) Intuition (not useful for beginners),	
(ii) Constructing the molecular models of the stereostructure of the compound and	
its mirror image and examining their probable superposability (not always	
possible)	6

Now, remember structure means, you know structure of a compound is vital to know if you want to proceed and do certain transformations on that molecule. And this structure is basically has two components that constitution which tells you how the how that different atoms are bonded to each other, that is one and for many molecules also, what you want to know in the structure is that how the groups are oriented in the 3 dimensional space.

Now, remember not all molecules that orientation in 3 dimensional space that knowledge is not required, because they are what are called symmetric molecules or Achiral molecules, molecules which are which are mainly non planar and which exhibit chirality that for them the orientation of the groups in the 3 dimensional space is important to know for other molecules a chiral molecules that is not required, because it only the connectivity of the atoms will suffice to describe completely the structure.

Again, I repeat to describe completely the structure of a chiral molecule you need to know the constitution that means the connectivity as well as the 3 dimensional orientation of the groups in space. On the other hand for achiral molecules, you do not need the second part that means the orientation in space what you need is basically the connectivity the constitution. So, let us start with the this.

Let us start with Chirality, a brief introduction to Chirality now Lord Kelvin it is interesting that it is Lord Kelvin in 1893, he introduced the term Chirality in a lecture series. This Chirality means it has come from a Greek word which is called which is cheir, cheir means for hand or pretaining, so, it is related to something to do with hand pertaining to hand that means, so, we are told that Chirality means handedness because that the two hands of a person both are chiral how do we know because one does not superimpose on the other, but one is the perfect mirror image of the of the other, but they are not same.

Their constitution is same, but they are 3 dimensional orientation of the fingers in space are not the same. Now, all now, we know that the condition for Chirality what is the minimum and sufficient condition for Chirality that we know that is the molecule should have a mirror image which should not be superimposable on it. So, the Chirality condition is that a molecule is Chiral as long as it can have a mirror image which is non superimposable with it.

Now, this how do we know looking at your molecule how do we know that whether it will be chiral that means whether a mirror image will be superimposable or non-superimposable. Now, sometimes you can do it by intuition, intuition that means with experience intuition comes you can do it by intuition or but this is not very useful for beginners very difficult. Or what you can do you can construct the model, model of the molecule like the model that I am holding you can you can make the model of the molecule and then you can make the mirror image model of this and then see whether they are super imposing on each other.

But this is also not very practical, because you may not have the models all the time in your in hand is no may not be available at that time. So, this is not the molecule may be really very big. So, to make a model a molecule using the molecular model kit, you may run out of the differential tetrahedral units. So, making the model unless the molecule is very small, I think it is difficult.

And the third is that it is based on because there must be some then some other ways looking at the molecule So, that you can tell whether this is chiral or not. You know this because that earlier stereochemistry course has elaborated on this it is the symmetry elements that are important. The symmetry elements, we know there are 4 symmetry elements the simple axis of symmetry, the plane of symmetry, the center of symmetry and the alternating axis of symmetry, just a quick brush up of things.

The simple axis of symmetry is the case called the proper symmetry element and the improper element of symmetry are the other three, the plane of symmetry the center of symmetry and the alternative axis symmetry. Now, what I will do, I will just quickly go through it I will not deal this way in detail, but I will quickly cover some of the some of the aspects which may not have been covered earlier in a industrial stereochemistry course, like simple axis of symmetry.

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Simple Axis of Symmetry we know that it is denoted by Cn. C stands for the simple axis and n stands for what is called a fold. Fold means that if you rotate the molecule along this axis by 360 degree divided by n, then you get an identical you get a molecule which is indistinguishable from the from the original one. So, you get the identical looking molecule. Remember here, if you say I get the identical molecule that is wrong because by rotation molecule remains identical all the time. It is basically it is it its appearance is exactly the same as you are seeing it from the very first place. So, that is a simple axis of symmetry.

Again I repeat that means it is an axis along which a molecule is rotated by 360 degree by n and you end up with a with a series with a form which is indistinguishable from the original or whose appearance is the same as the original one. Now, there are, we have defined this the molecule, first of all a molecule can have various kinds of simple axes of symmetry. But some are called a particular axis is called principal axis principal axis what is the Principal Axis?

Principal Axis is belongs to this class of simple axis of symmetry, but along the various axis that a molecule can have, a particular axis is called the Principal Axis. Principal axis is usually the same the axis with highest fold that means, if your molecule has both C3 and C2 axis then the principal axis will be the C3 so, that will be the principal axis.

The problem comes that when a molecule has a molecule has say the to the fold access which have similar folds like there may be there may be two C3 types of axis or there may be C2 axis

plenty of C2 axis there is no C3 axis that means, the question is if a molecule has simple axis of symmetry where the fold is same different simple axis of symmetry with same fold number same name, then which one we should consider as the principal axis?

The convention says that what do you do you take that axis out of these axis which have got same fold, you take the act that axis as the principal axis which cuts through the highest number of atoms or which passes through the highest number of atoms in the molecule like I give you an example, suppose you take Ethylene the simplest of the Alkylene. Now Ethylene has a C2 axis like this that if you if you rotate it by 180 degree this carbon will come here that carbon will go there.

So, this goes there that goes here, but it looks like the indistinguishable with the original. So, that is a C2 axis but it has got another C2 axis which is going through this and then you rotate it like this by 180 degree 180 degree that is why this is C2 and this is also C2 if you rotate by 180 degree that means it goes out of plane and then again you bring the whole height the hydrogen's in the plane. So, that is also C2.

But this will be your principal axis this will be your principal axis because it is the axis which is going through this carbon and other carbon so, two atoms it is crossing passing through whereas, this axis is not passing through any atoms that is why this is what is called a principal axis. Remember the principal axis is regarded as a vertical axis. So, whatever way you place the molecule you see the molecule, the principal axis, the direction of the principal axis is regarded as the as the as the vertical as the vertical line remember that.

Like in this case it looks like this is a horizontal line, but actually this will be regarded as the vertical line. So, anything any plane suppose which is aligned to this vertical line will be called a Vertical Plane. So, the next thing was the next thing is, so, we have done with does simple axis of symmetry and what we have what we have discussed here just we wanted to figure out which is the principal axis because that is what is required, if you want to know that if you want to go to the point groups later on.

Now, the other important the next one the Improper Elements of Symmetry you can start with the plane of symmetry. The plane of symmetry is that it is a hypothetical plane which divides the molecule into two half such that one half is the mirror image of the other half that is what is plane of Symmetry and it is denoted as sigma. Now, this sigma can be a vertical plane if you can think of a plane which is a vertical plane of symmetry. Remember that a molecule can have more than one plane of symmetry that is number one then if it has more than one plane of symmetry some planes may be aligned with the principal axis, principle simple axis of symmetry or some maybe orthogonal to it that is perpendicular to it.

So, that is why we have sigma v, sigma v is the plane of symmetry which is aligned to the principal axis which is aligned to the vertical axis what is the vertical axis the principal axis. And the other planes that means the planes which are actually orthogonal to this vertical axis or to this is vertical axis that is the principal axis they are called the horizontal the plane of symmetry, horizontal plane of symmetry.

So, we have vertical plane of symmetry, we have horizontal plane of symmetry, but we have another one which has been classified as sigma d like horizontal one is called sigma h, the vertical ones are called sigma v and there is another one which is called sigma d. Sigma d is the plane of symmetry which divides which actually bisects the angle between two C2 axis. So, some of these planes, planes of symmetry can bisect the angle that is made by two C2 axis which are present in the molecule.

Remember, this sigma d will not be will not be present in all molecules it is present it may be present in molecules where they are C2 symmetries a lot of C2 axis are present. And also remember that all molecules because we are dealing with achiral molecules, which will have these planes of symmetry, so, chiral molecules will not have any plane of symmetry that is for sure we know that. So, now, we know that there are 3 kinds of planes of symmetry sigma v sigma d sigma h and sigma d.

The third one is that comes the center of symmetry. Center of Symmetry is little different from the other symmetry elements in that center of symmetry can only be one unique a molecule can have only one center of symmetry, there cannot be more than one center of symmetry. Because center means central point that is only one and center of symmetry what is the definition that it is a, it is a point inside a molecule, if you join any substituent which is present in a molecule or any atom not substituent better it is atom, if you join any atom to this point, which is present which is a hypothetical point and then you extend it back in the other direction, the same distance you will find the same atom and this is true for all the atoms present in the molecule.

Now, you can say that I will tell that I will bring substituent or group here that it is such a point play a center of symmetry such a point that any substituent or atom or group which is joined to this molecule and extend in the reverse direction, you will find an identical substituent or identical group or identical atom at equal distance and this is true for all the substituent's all the atoms or all the groups present in the molecule.





I prefer the word atom because, so, we have just told you that plane of symmetry and these are designated as sigma v sigma h, sigma d and I have just told what are these and then I said our center of symmetry will do on various problems involving these sigma v, sigma h, and sigma d. So, we are not elaborating much at this stage, we will come back to all these when we solve various problems.

Center of symmetry which is denoted as i, i say that there can only be one center of symmetry and suppose, you have a molecule like this why I prefer the atoms and not substituent's because, suppose you have a you have a chirality in the substituent's so that this is a, this is b, this is c and on the downside you have here suppose the a and then b and c. So, if that be the case this is suppose hydrogen that is hydrogen. So, I said that you have to have a central point a central point where you if you join this hydrogen and push it backwards, you get the same hydrogen at identical distance. Here, this is a center which is a chiral center now, we know that these are called stereo generic centers specifically C3 is stereo generic center and what happens here that if you join a, a is atom and then send it back once you get a here. Similarly, c will reach this c and b will reach b passing through this central point.

So, this now, if you want to do the configuration of these assignment of this substituent because this is a, a stereo generic center and if you suppose that this a is the number 1 group gets highest priority then followed by b followed by c and this is the d is that the group of least priority that means, this one which is attached to this ring what you will see that this direction is actually this is a then going up b and then c because you have to see from this side.

So, that means this is our configuration, if you do the configuration here, you will see that if you look from this side a then b to c this is you have to look from this side, and you will see that this is also again this is the a's configuration a going to b going to c, so, that is a's configuration. So, this is a's. So, that means to have played center of symmetry you should have if it is chiral substituents, then the chiral substituent's should have opposite chirality.

But, so, that is why when you say that a center of symmetry is such a point that if you join any substituent and extend it backwards, you get the identical substituent but then you have to say that if the substituent has a stereo generic center, then the stereo generic centers should have opposite configuration. If you say atom then you do not have to say that that any atom joint to this point extended backwards, you meet the identical atom at identical distance. So, that part you should remember.

So, this molecule if you have a suppose as A is a group, AR and here AS, then this is AR AS and versus this AR AS and 3 molecules and then you have AR, AR many people might make a mistake that this is a molecule which has got a center of symmetry not this is not the center of symmetry, because it says they have the same configuration. If they have the same configuration, you will never be able to have this that all the atoms are basically spaced at equal distance from the from this inversion point and this is the other name of this center of symmetry.

So this does not have any, any center of symmetry no i this has got i and this has got this does not have i but this has got a plane of symmetry which is going through this because mirror image of R is this. So, this has got a sigma. And then we will we will ask that what type of sigma it is? Is it a sigma v? Or a or a sigma h? Sigma d is very special not always it is present. So, mostly concerned two sigma h and sigma v.

The last one is the alternating axis of symmetric. Alternating axis that is denoted by a Sn and you what is it, it is basically that if you rotate the molecule around this axis by 360 degree divided by n and then take a mirror image where the mirror is placed perpendicular to the axis of rotation the mirror image is identical with the original or mirror image is indistinguishable it takes a form which is indistinguishable from the original form.

You can actually reverse what has not been told earlier I believe is that you can reverse these two operations. So, this actually is basically have two operations, one is a rotation and another is a reflection, first you rotate the new reflect through a mirror placed perpendicular to the axis of rotation. You can actually reverse this first you can reflect, get a reflection along the axis that you want you are you have imposed or you have selected the axis and then after reflection you rotate by 360 by n. So, you get the original indistinguishable form.

So, that is also possible reflection rotation that is one point to note and the other point you already know that S2 to is equivalent to i that is inversion point or center of symmetry and a swan is equivalent to sigma. That is why you can also tell from symmetry point of view that a molecule a chiral when it lacks alternating axis of symmetry. This n is equal to either 1 or 2 etc. So, any molecule lacking alternating except symmetry is Chiral, that is the simplest condition of chirality from symmetry point of view.

So, this is the first introductory topic on Symmetry Elements. And most of it is already known, I have just pointed out a few aspects of this symmetry elements namely the Principal Axis of Symmetry, how to select that then plane of symmetry how to select a sigma v and a sigma h and a sigma d i have not given any example of sigma d maybe quickly I can give you an example if you take an allene molecule.

Allene molecules are the substituent's are orthogonal and if you have hydrogen here hydrogen here, then what will happen if you take a Newman if you take a projection formula Newman projection, then it will look like this and this is the, this is the hydrogen, hydrogen actually this that will not write there hydrogen, hydrogen and here hydrogen and hydrogen it has got a C2 axis going through this, this is one C2 that you take upside down or this has got a C2 axis here both are C2 and it has got a plane of symmetry going through these this plane of symmetry bisects the angle between the two C2 axis. So, that is what is a sigma d. So, this is an example of sigma d in just plain Allene system.

So, and then we talk about center of symmetry we have clarified this atom and this interesting point that it should be R if there is a chiral molecule substituent's then the guided substituent's should have RS type of relationship and alternative access symmetry requires two operations rotation reflection, but you can reverse that first take the reflection and then do the rotation. And finally, that well known concept that for a molecule to be chiral from symmetry point of view, it should lack alternative axis of symmetric. Thank you.