

hello we are discussing some fundamental concepts and basic principles in organic chemistry in the last lecture we touched upon the concept of isomers organic compounds are capable of exhibiting isomerism isomers are essentially compounds having the same molecular composition but different structures

So one can define isomers same composition but different structures just to illustrate an example if you consider C_2H_6O as a molecular formula see how many different types of structures one can write for this molecular formula keeping in mind the tetravalency of oxygen and the tetravalency of carbon and the divalency of oxygen one of the structures one can write would correspond to ethyl alcohol and the other structure one can write would correspond to dimethyl ether ethyl alcohol and dimethyl ethers are isomers in terms of functional isomers this is an alcohol whereas this is an ether now isomers there are different types of isomers we broadly classify them into structural isomer and stereoisomers in the case of structural isomer we have different types of structural isomer one is chain isomer chain isomerism for example then you have functional group isomerism then you have positional isomerism then finally you have what is known as metamerism now chain isomerism is normally exhibited by alkane kind of substance substances you take a simple example of C_4H_{10} which is a saturated hydrocarbon molecular formula let us say butane now butane can exist in several forms this is the linear chain butane and this is called the n butane or normal butane you can also have branching in the butane and this is called isobutane now these are the two isomers of butane one can have and these are called chain isomers because the chain is different in these two structures that are drawn here if you have longer hydrocarbons there are several isomers possible for example one can write for pentane the linear pentane one can write this would be normal pentane or n pentane then you can write isopentane which is a branched pentane one can also have what is known as neopentane which is a completely branched pentane of this kind

So longer the higher the molecular formula the more number of isomers in terms of the chain isomers that you can have for a given organic compound now in case of functional group isomers if you consider for example this example this is acetone the functional group here is ketone which is the $C=O$ functional group in this molecule one can also have an aldehyde which has the same molecular formula propanal for example in this particular case the two structures have the same identical molecular formula or the elemental composition but the functional group is different in this particular case the functional group is aldehyde whereas in this case the functional group is a ketone So they constitute the functional group isomerism by this example one can illustrate it one can also have as I mentioned earlier alcohol versus ether let us say for example this is the normal propyl alcohol or propanol one can have a corresponding functional group isomer which is ether also for example in this particular case this will be methyl ethyl ether is the ether that we are referring to as an isomer functional group isomer of the ethyl alcohol one more example I can give this is nitro ethane this functional group is called the nitro functional group NO_2 functional group and the structure that is written is the nitro ethane is the structure that is written nitro ethane can have an isomer where the connectivity is different between the functional group and the carbon to which the functional group is connected in this particular case the connectivity is between carbon and nitrogen

So the functional group actually is represented by the nitro functional group represented by this particular structure which clearly shows that the connectivity is between carbon and nitrogen

So this is a nitro compound whereas this is a nitrite compound the connectivity between carbon and oxygen is being present here the functional group is connected through oxygen here whereas the functional group is connected through the nitrogen here

So such isomers are called the functional group isomers then you can have positional isomers this can be easily illustrated by taking a compound having a functional group in different positions let us take the example of butanol this is one butanol or butane vernal is the IUPAC name that one can write the functional group can also be present anywhere in the carbon chain in this particular case the functional group is shifted to the interior carbon

So this would correspond to two butanol

So one can have for example in a pentane chain this is corresponding to hexane n hexane this would correspond to hexane one all how many positional isomers can hexane one all have can have you can write the basic skeleton of hexane once again you can put the

hydroxy functional group in the two position

So this would be hexane to all then you can have the hexane chain to be written like this have the functional group in the third position this would be hexane three all if you move it once more that again becomes hexane three all only because the numbering would start from this side

So that would correspond to the hexane three all

So all of this example constitute the positional isomers positional isomers are isomers wherein the functional group position changes from one carbon to another carbon in a carbon chain and that would correspond to the positional isomers metamerism is essentially when two groups are attached to let us say an oxygen in this example it could be sulfur also or it could be nitrogen also this is diethyl ether the metamer is where the the two functional group that are attached are different across the heteroatom in this particular case the oxygen atom here you can see with the oxygen atom two ethyl groups are attached whereas in this particular case one methyl group and one n propyl group is attached to the oxygen such isomers are called metamers in this particular instance now isomers have independent existence they are physical and chemical properties will be different in all aspects for example in terms of the structural isomers that we are referring to now let us move on to the stereoisomers stereo essentially means space in other words isomers where the groups are spatially having different orientation are called the stereoisomers in other words you have a structure where certain functional groups are attached the three dimensional orientation of the functional groups is different in the stereoisomers there are two types of stereo isomers that are possible one is geometrical isomers the second one is optical isomers geometrical isomers are also known as cis trans isomers now let us take the example of geometrical isomers and explain the term geometrical isomer essentially implies the geometry is different with respect to a double bond for example now if you consider one two dichloro ethene this is an alkene and it has a one two dichloro substituent now let us say for example ethylene is this molecule this is the structure of ethylene if you remove two hydrogens and put two chlorines then you get one two dichloroethylene or one two dichloro ethane now the question arises whether you would replace these two hydrogens or these two hydrogens because that matters in terms of the structure that is obtained let us for example replace these two hydrogens by two chlorines what one gets is a structure wherein the two chlorine atoms are on the same side of the double bond

So is the two hydrogen atoms they are also in the same side of the double bond on the other hand let us replace these two hydrogens and see what happens now the two chlorines are on the opposite side of the double bond similarly the two hydrogens are also on the opposite side of the double bond now this is what is known as the cis isomer and this is called the trans isomer and this is an example of a geometrical isomerism now the geometrical isomers have independent existence they are not interconvertible with respect to each other they do not interconvert under normal conditions under some special conditions they do undergo inner conversion but under normal condition during heating and all they do not undergo isomerization from one to the other

So they are stable independently the reason for that is the the bond rotation energy of the carbon carbon double bond is much higher than the carbon carbon single bond

So this molecule does not undergo this kind of a rotational motion imagine if it were to undergo a rotational motion along the carbon carbon double bond these two structures would be indistinguishable from each other or they will be in rapid equilibrium with respect to each other in the absence of such a rapid equilibrium the absence of the carbon carbon double bond rotation these two molecules are independently existing

So this is a system where you have a no rotation of c double bond c and that is the reason you have these geometrical isomers existing in this particular example one can also give geometrical isomer example of any compound which has for example x and y group in this particular manner let us say for example x x equal to chlorine and y is equal to methyl group you can have two isomers possible this is one isomer you can call this as a trans isomer because the two functional group namely methyl group and the chlorine group are trans with respect to each other they are on either side of the double bond you can have another structure where the methyl group and the chlorine group are on the same side of the double bond this would be cis this would be trans you can also have stereoisomers of simple alkenes like for example this molecule is known as is called two butene or buty twin how many isomers are possible in this molecule is very similar to the one two dichloro ethylene or one two dichloro ethene there are two possible isomers the first

isomer one can write with the two methyl groups which are on the same side of the double bond this would be the cis two butane one can also have what is known as the trans tubulin by putting the two methyl groups on opposite side of the double bond that would correspond to the trans to butane molecule in this particular case

So geometrical isomers arise out of the restricted or the absence of any rotation of the carbon carbon double bond when they are either symmetrically substituted as in the case of dichloroethylene or unsymmetrically substituted and as in this particular case for example you have isomers of this kind there are several examples of the cis trans isomers that are known in the organic chemistry realm i will give you some examples of the cis trans isomers of the this is butano nitrile is the compound that i have written here this is the trans isomer it can also exist in the form of the cis isomer which is this particular isomer this is the cis isomer of still being stillbean is a colloquial name or non-systematic name for example if you have to write the systematic name this would be 1,2 diphenyl ethene is the name of this particular compound trivial name is known as the stillbin in this particular case one can also have the trans till bean which is this particular molecule one more example i will give this is called the cinnamaldehyde this is cis cinema aldehyde and can also have the corresponding trans isomer of the cinema alligator all these are examples of cis trans isomerism or simply geometrical isomerism among the stereoisomers that you have here they have physical and chemical properties are different since the structure is different the physical and chemical properties are entirely different for this class of isomers which are shown as cis trans isomers in this particular case let us now move on to the other stereoisomerism namely optical isomerism the term optical isomerism comes because of the fact that the optical activity property of these molecules are different in other words when these molecules are kept in a tube and plane polarized light is sent through this tube the plane of the plane polarized light rotates in opposite direction because of the kind of molecule that we are dealing with these are called optical isomers

So the optical rotation is different for these isomers let us illustrate this with an example now optical isomerism arises because of the nature of the carbon atom which is chiral in nature what is chirality let us start with optical isomerism let us take the example of this particular acid this is alpha hydroxy or two hydroxy propanoic acid simply known as lactic acid this particular acid if you look at the carbon in the middle this carbon has a hydrogen a methyl group a hydroxy group and a carboxylic acid group there are four different functional groups that are attached to this particular carbon So as a result of that you call this as a chiral carbon or you can also call this as an asymmetric carbon because there is no symmetry element present in this particular carbon the molecule is not a symmetrical molecule because of the fact there are four different groups attached to this how do we know it is not symmetrical with respect to the four groups attached to this now let us say for example this perspective that is drawn in this particular manner is indicating that this hydrogen is in the front projecting out of the plane of the black board and this c o o h functional group is inside the plane of the black board and these three these two groups namely the o h group and the c h three group are on the plane of the black board this is how one represents a tetrahedral carbon on the plane of the black board by indicating projections by indicating this wedge as well as the dashed wedge that is shown in this particular manner now how many isomers are possible in terms of this molecule to have an isomerism let us say for example i put a mirror in this place and look at the reflection of this molecule on the mirror in this manner these two groups which are on the plane of the blackboard will essentially show up in the opposite direction in this particular manner this functional group which is inside the plane of the blackboard also will remain in the inside of the plane of the blackboard whereas this is projecting in this manner

So this will essentially project in the front

So what you are looking at is essentially the mirror image of these two structures and these two mirror images because of the devoid of any kind of a symmetry that is present in the molecule they are non super impossible what is meant by non super impossible let us take for example i lift this molecule up and i want to match the this is a hydroxy functional group i am sorry let us say for example i want to lift up this molecule and put it on top of the molecule such that the like functional groups namely the c o h will overlap with the c o h of this the o h will overlap with o h of this the methyl will overlap with the methyl of this and the hydrogen will overlap the hydrogen of this this is not possible because of the asymmetry and that is why it is called the non super

impossible structure i can take it up i can rotate it and bring the o h carbon and c h three and overlap these three groups namely the c h three carbon and o h i can overlap on top of each other however when i do that the c o h will be in the front and the hydrogen will be in the back

So these two functional group will not overlap with respect to each other now let me illustrate this with a slightly a different way of drawing the structure let us say for example i view the molecule along the carbon hydrogen bond let us say i am standing in the back side of the black board and looking at the carbon hydrogen bond

So i will be looking at this carbon and this through three groups that are attached to the this is how i would look at the molecule in other words let me draw it once again here let us say for example i am standing here i am looking at it along the axis of carbon and hydrogen

So what i will see in front of me is the carbon the hydrogen will be exactly behind the carbon i wont be able to see the hydrogen in other words the carbon is going to eclipse the hydrogen

So if i am viewing the molecule from here along the carbon hydrogen bond the hydrogen will not be seen only the carbon will be seen now if you look at the other three groups they will essentially form an apparent angle of 120° with respect to the view because the perspective view that is shown here is what is known as the newman projection formula So the hydrogen is behind the carbon and these three groups are essentially looking like they are in the trigonal arrangement like this

So what you would see is the methyl group on the left hand side carboxylic acid group on the right hand side and the hydroxy group on the top like this one suppose if i draw the mirror image structure of this the mirror image structure would be corresponding to this particular structure let us say i am standing here now and looking at the molecule along the carbon hydrogen axis now what are you going to see is the carbon the hydroxyl group on the top on the left hand side i am going to see the sievo h group on the right hand side i am going to see the methyl group in this particular manner

So this is the way you view the molecule looking along the carbon hydrogen axis from here looking along the carbon hydrogen axis from there this is the perspective that one going to see in looking at this molecule now if you look at the orientation of the hydroxy carboxylic acid and methyl let me just number it for the sake of sequence the hydroxy carboxy and methyl in that particular sequence this is appearing in the clockwise direction if you look at the same molecule in the same sequence you take hydroxy carboxy and the methyl group it appears in the anticlockwise manner and this is one of the reasons the two structures are non superimposable let us lift this molecule up and bring it over here the hydrogen is still in the back side of the carbon the hydroxy is still on the vertical line here

So they will match up the hydroxy the hydrogen and the carbon they will overlap with each other but then it is a cooh which is going to overlap with the methyl and this eo is going to overlap with the methyl

So if i put these two molecules on top of each other this is going to how it is going to look like let us for the sake of identity color code it with the red color

So initially i am going to have the molecule which is this one on the left hand side is going to be like this and then if i superimpose this structure on top of this particular structure the o h is going to superimpose whereas the c o h is going to superimpose here and the methyl is going to superimpose over here

So this is how the molecule becomes non super impossible when you have an asymmetric carbon a carbon which is divided of any kind of a symmetry element

So such isomers are known as optical isomers the non super impossible structures these two isomers are also known as enantiomers term chiral essentially means handedness you have a left handedness here and you have a right handedness here of the three groups that are attached to the particular carbon the c h being a constant in both the cases the o h c o h and the methyl group is in the left handed direction in the sequence that is written this is in the same sequence if you take it is in the right handed direction So the such a handedness is what is responsible for the chirality of the carbon or the carbon which is chiral is supposed to have the handedness in other words this is as if you have the left hand here and the right hand here left hand and right hand are non super impossible with respect to each other when you bring it like this for example the two thumbs and the fingers do not overlap with respect to each other

So that is what constitutes the optical isomerism this is a brief introduction to the

concept of optical isomerism that we are seeing

So any compound which has a carbon which is a chiral carbon which is an asymmetric carbon is likely to exhibit the optical isomerism the term optical comes because the optical rotation will be different for the two types of compounds that you have

So these enantiomers definition is optical isomers that are not super impossible that are mirror images of each other and non super impossible

So any molecule which has this molecular formula four different groups attached for example or different groups attached to this molecule they would constitute a set of isomers which are known as the optical isomers or the enantiomers this particular example illustrated is the lactic acid example that is illustrated I hope the illustration with respect to the various types of isomers is easy to follow namely the structural isomer and the stereoisomers particularly in the stereoisomers one needs to have a good three dimensional perspective of the molecule

So that one can appreciate the kind of isomers that are exhibited by this class of molecule now let us look at some electronic effects in organic chemistry in order to describe the property of a molecule or the reactivity of the molecule the reaction mechanism of a particular reaction it is important to understand the electronic effects in an organic molecule electronic effects can be classified as follows first let us start with inductive effect inductive effect is a permanent feature of a molecule is always present in the system in the molecule this can be easily illustrated by a simple example let us say for example you have a carbon carbon bond as in the case of ethane for example the electron density on each of these carbon in ethane is going to be essentially same because it is a symmetrical molecule there is no electronegativity difference between these two carbon

So if one were to map the electron density around these two carbon is essentially going to look like this indicating equal electron density around each of the carbon I am just representing a sigma bond in terms of electron density by showing this particular diagram indicating that the electron density around the carbon and hydrogen are essentially same suppose if you have a carbon halogen bond the \bar{x} group is now either chlorine fluorine bromine or iodine as the case may be let us consider C-F bond for example the electronegativity difference between carbon and fluorine is fairly high they do not have the same electronegativity fluorine is more electronegative than carbon atom So as a result of that the fluorine molecule would tend to polarize the electron density towards itself because it is higher electronegativity nature is going to pull the electron towards itself

So if one were to draw the electron density map of a carbon fluorine bond it will be something like this the electron density around the carbon is going to be depleted whereas the electron density around the fluorine is going to be more for the simple reason that the fluorine is a higher electronegative element compared to the carbon and this is what is known as the inductive effect in this particular case the inductive effect is normally represented by means of arrows drawn on the bond itself for example if you consider ethyl chloride the ethyl chloride inductive effect can be represented by drawing the structure of ethyl chloride like this and showing that the inductive effect is in this particular manner inductive effect is represented by the symbol I and if it is an electron withdrawing type of a group then the inductive effect is known as minus I effect what is the consequence of this inductive effect essentially this bond between carbon and chlorine gets polarized and the chlorine accumulates more electron density So one can write the structure as if you have a δ^+ here and δ^- in terms of the electronic charges of the carbon chlorine bond in this case now what happens to this carbon carbon bond here now this carbon and this carbon are having no longer having the same electronegativity or electron density by virtue of having a positive partial positive charge on this carbon that becomes slightly more electronegative than this one

So again the inductive effect is felt in this particular carbon

So as you move away from the atom that is causing the inductive effect the effect inductive effect falls off quite rapidly beyond two or three carbons the inductive effect will not be felt now what is the consequence of the inductive effect the consequence is that the bond is polarized and as a result of that you have the charges being developed or the dipole being developed in this molecule what is the consequence of the inductive effect let us take the example of this is acetic acid molecule acetic acid ionizes to give the acetate ion and that is the reason it is an acid now the question is if you take

trichloroacetic acid and compare it with acetic acid itself what would be the comparison in terms of the acidity of the hydrogen both are carboxylic acid functional group but then here the electronegativity difference between carbon and hydrogen is not very large moreover the methyl group will have a positive inductive effect like this for example So this will have a plus i effect whereas the chlorine is going to have the opposite effect the chlorine being more electronegative in nature this has minus i effect So as a result of that the carbon here becomes more and more electron deficient and that in terms of the inductive effect that is felt it is going to be propagated in this manner So the ionization of this hydrogen as a proton becomes much easier

So because of the minus i effect of the three chlorine atoms this carbon becomes delta positive this carbon in turn feels the effect of the delta positive character of this particular carbon whereas here in this particular case this becomes because it is pushing the electron towards the carboxylic acid the ionization of the carboxylic acid is not going to be as much as the ionization of the carboxylic acid in the case of trifluoroacetic acid

So one can compare the acidity of the acids chloroacetic acid dichloroacetic acid trichloroacetic acid as we put more and more of electronegative c l two c h c l c o h as you put more and more of electronegative chlorine on this particular carbon because of the inductive effect of the chlorine the acidity goes up in this particular direction this will be the strong guest acid in the series compared to this will be the weakest acid in this particular series you can also compare for example c f three c o o h and c c l three c o o h and c h three c o h for example the fluorine is the most electronegative all of them are having tri substitution this is three chloro and three fluoro three hydrogen in this particular case

So as a result of the number of chlorine atoms being more in this particular case and the electronegativity of fluorine being more than the electronegativity of chlorine this is the strongest acid and this will be the weakest acid this particular case the inductive effect also helps to understand the reaction mechanism of certain reactions let us say for example methyl chloride is treated with sodium hydroxide

So this is methyl chloride and sodium hydroxide o h minus is reacting let us say for example how do we know where to react the hydroxy functional group on this molecule will it react with the chlorine or will it react with hydrogen or will it react with the carbon is the question that one needs to address this can be understood by invoking this particular structure where the inductive because of the inductive effect you have a delta positive and delta negative a dipole being set up this is a permanent dipole that is why the inductive effect is a permanent effect as long as the chlorine is there in that molecule it is going to have that particular effect

So now it is clear that this positively charged or partially positively charged carbon is the one that is going to attract this negative charge

So it is going to react in this particular fashion with the chlorine leaving as a chloride ion

So the reaction is facilitated by this polarization which is because of the inductive effect of the chlorine

So c h three o h is going to be formed and c l minus is going to go away in this reaction So this is a substitution reaction and this is a nucleophilic substitution reaction this is a nucleophile seeking the electron deficient center in this molecule which is this particular molecule and chlorine being most electronegative it is going to withdraw the electron in this particular manner leading to the formation of methyl alcohol as the product

So the inductive effect or the electronic effects that we are going to deal with essentially helps you to understand the reaction mechanism how the reaction would have proceeded in a particular manner where the attacking reagent is going to attack the molecule whether it is going to attack the chlorine or the carbon is decided essentially by the dipole that is being set up in the molecule because of the inductive effect please remember that inductive effect is a permanent effect it essentially polarizes the molecule permanently and the reactivity is dictated by the kind of polarization the molecule feels because of that one can also have plus i effect which is the let us say for example acetic acid propanoic acid next homolog series isobutyric acid and finally tertiary butyl carboxylic acid which is this particular carboxylic acid just like chlorine was showing the minus i effect the alkyl groups namely the c the common quality is c o h what is attached to the c o o h is methyl ethyl isopropyl and tertiary butyl

these groups are considered to have the plus i effect in other words they donate electron towards the carbon to which they are attached in other words the alkyl group that is present in the system they donate an electron or they polarize the electron towards the carbon center to which they are attached

So as a result of that these are examples of the

So called plus i effect that we see in this cases the next electronic effect is known as the electromeric effect the electromeric effect is usually felt in unsaturated systems either in aryl systems or in vinyl systems or unsaturated c double bond c or c triple bond c kind of a system is what one

So the second effect is known as electromeric effect this can be illustrated by the following example this is a temporary effect this effect is felt only when a reagent approaches a particular reaction center let us take the example of again a carbon carbon double bond remember the sigma electrons are fairly fixed whereas the pi electrons are little more mobile than the sigma electron in other words this pi electrons can be delocalized whereas the sigma electrons are seldom delocalized let us say for example the electron density map if you were to draw for the ethylene molecule this would be the electron density there will be a pi cloud above and below the plane containing the four hydrogens and the two carbons suppose a proton is approaching this molecule in other words ethylene is put in an acid which is sulfuric acid let us say as the proton approaches closer and closer to the carbon either carbon is ok does not matter which carbon it is approaching because both the carbons are identical there will be a polarization of the pi electron that is shown here towards the proton because proton is positively charged

So the electron attraction will be there

So as a result of that you are going to have an effect because of the presence of h plus approaching this molecule you will have an effect such that a positive charge is created temporarily because of the presence of the hydrogen that is going closer to the one of the carbons when the hydrogen permanently gets attached then you produce a carbonium ion So this would be the overall reaction

So during the course of the reaction as the hydrogen approaches when it reaches a distance there you can feel the electrostatic interaction between the pi electrons and the h plus which is what is known as the electromeric effect you get a polarization the polarization is complete in terms of developing a fully positive charge on the carbon because of the proton is being attached to this particular CH_2

So this is what is known as the electromeric effect this is a temporary effect it is felt only in the presence of an atom that is a reagent that is being approaching the carbon atom instead of having the proton one can also think of a chloronium ion or a bromonium ion approaching during the bromination of the molecule let us say with the bromine we are going to brominate the molecule what is the overall reaction the overall reaction is a bromine is added to this molecule to give one two dibromoethane

So what will happen if the bromine were to approach this molecule initially the bromine does not have any kind of a charges associated with this because it is a homonuclear diatomic molecule

So is the ethylene which is devoid of any kind of charges because this is identical carbon there is no polarization that is possible but then now imagine the bromine is approaching closer and closer there will be an electrostatic interaction between the two atoms which are approaching closer together it does not matter whether you approach the bromine on this carbon or this carbon because it is a symmetrical molecule as the approach becomes closer and closer there will be a development of a delta positive and a delta negative delta negative on the because this electron is a mobile electron and bromine is a electronegative element it is going to attract towards itself the electron density

So that will deplete the electron density at this position temporarily during the course of the approach of the bromine originally the electron density is equal here similarly the electron density is equal here but because of the approach of the bromine closer to the delocalizable pi electron of the pi bond there is a partial positive charge developed here and a partial negative charge developed here when the bromine is completely attached to the a fully developed carbonium ion will be formed this bromide ion will be formed for example

So this would be a sort of an intermediate structure that you have then the bromide ion and the positive charge will collapse this is ionic interaction inter ionic interaction

leading to the formation of the product which is the dibromos

So the electromagnetic effect is a temporary effect let me illustrate one more example if you consider a carbonyl functional group carbonyl follicle already has a dipole moment because of the electronegativity difference between the carbon and the oxygen suppose if a cyanide functional group is approaching here this will essentially form a cyanohydrin like this but during the course of the approach of the cyano functional group this polarization becomes more and more and that is what is known as the electromeric effect that we are referring to let us move on to now two other effects that we need to discuss one is the resonance effect the other one is hyper conjugation effect we will discuss these two effects in the next lecture i thank you very much for your kind attention you

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