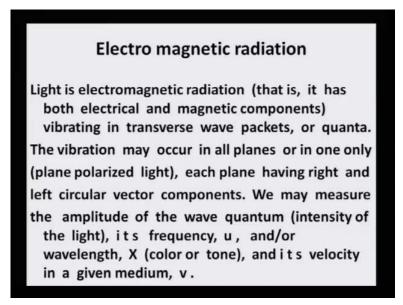
Natural Dyes Prof. Padma Vankar Department of Chemistry Indian Institute of Technology, Kanpur

Lecture No. # 04

Now, let us look at the fourth lecture understanding the relationship between color and constitution. So far, we have dealt with the history and then the light and its interaction with the color. Then thirdly we looked at the classification of the dyes both synthetic and natural in terms of their structural details. And now we will see how color and structure is related in this present lecture.

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Electromagnetic radiation - that is light is electromagnetic radiation that is, it has both electrical and magnetic components vibrating in transverse wave packets, or quanta. The vibration may occur in all planes or in one only plane polarized light, each plane having right and left circular vector components. We may measure the amplitude of the wave quantum that is the intensity of the light, it is frequency and or it is wavelength.

And then, look at the color tone and its velocity in a given medium. So, all this will be now related to what color will be observed or seen. We also show that the complementary color is generated from the transmitted light, because the absorbed light is taken up by the material.

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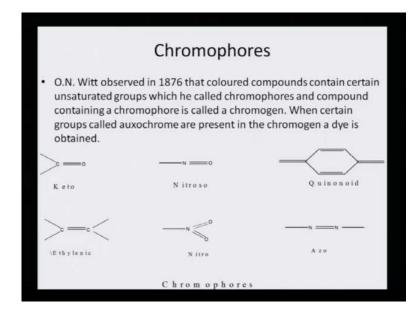
Color, Chromophore and Auxochromes

The carbonyl and ethylene (vinyl) groups have chromophoric properties only when they are present in the molecule in multiple conjugated order. Thus, acetone is colorless, while diacetyl is yellow, as is benzil which is deeper yellow, and triketopentane is yelloworange. Since it is the delocalization of pi-electrons that is related to the production of color, it is evident from these examples that such delocalization accompanies multiple conjugated unsaturation.

Now, if we try to have a recap of Color, Chromophore and Auxochromes. The carbonyl and the ethylene or vinyl groups have Chromophoric properties only when they are present in the molecule in multiple conjugated order. Also, now you understand, what is a Chromophore? Thus, acetone is the colorless molecule, while diacetyl is yellow, and benzil is deep yellow, while triketopentane is yellow-orange.

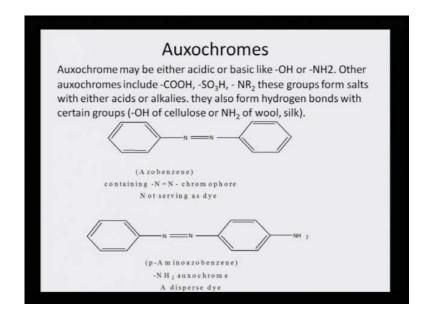
Since it is the delocalization of the pi-electrons that is related to the production of color, it is evident from this these examples that such delocalization accompanies multiple conjugated unsaturation. So far, molecule to be a colored molecule, it has to have Chromophore and Auxochromes and the two put together if they are in a conjugated system will create color. So, that is the relationship between color Chromophore and Auxochrome.

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Now, if we try to look at various types of chromophores Witt observed in 1876 that coloured compounds contains certain unsaturated groups which are called chromophores and the compound containing chromophore is called chromogen. When certain groups called auxochrome are present in the chromogen a dye is obtained. So, combination of chromophore and auxochrome creates a dye. The various different types of chromophores are Keto group, Nitroso group, Quinonoid group, Ethylenic group, Nitro group, azo group. These are some of the common chromophores that we saw that we see in the case of dyes.

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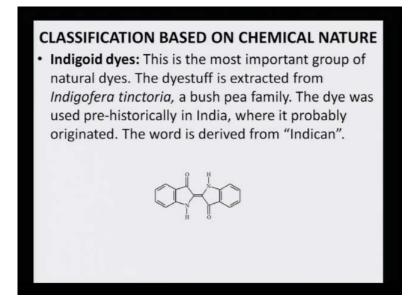


The common auxochromes chromes that are observed may be either, acidic or basic like -OH or –NH2. Other auxochromes include carboxylic acid that is -COOH, -SO 3 H, N H, NR 2 these groups forms salts or either acids and alkalies. So, with either they will be forming a salt with an acids or an alkalies. They also form hydrogen bonds with certain groups like - OH of cellulose or NH 2 of the wool and silk. So, a basic Azobenzene has N double bond N with aromatic rings on the side.

Whereas this contains the auxochromophore and not serving truly as a dye, because it is not having in our conjugation and there is no auxochrome, but simply by adding an -NH 2 which is an auxochrome, you see that the conjugation extends. The loan pair of the nitrogen of the amino group at the end is in conjugation with the first ring which is in conjugation with the azo linkage, and which is in conjugation with the benzene ring.

So, you see that there is an extension, and this is very well-known disperse dye, and example of a disperse dye. So, azobenzene is not a dye, but the phara aminoazobenzene becomes a dye. So, you understand now how the role of an auxochrome enhances. The coloring property of are material or or compound chemical compound and from a colorless compound it becomes color compound, because of the extended conjugation.

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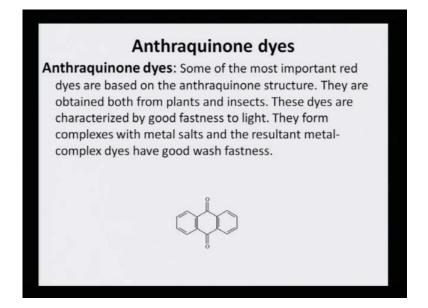


Classification which is based on their chemical nature, now let us try to I told you several names, but I will still repeat so that you get a good idea about the relationship between color, and the structure. That time we were taking classification only in terms of the

structure. This indigoid dye indigoid dye is most common group of natural dyes. That dyestuff is extracted from indigofera tinctoria, a bush pea family member.

The dye was used pre-historically in India, where it probably originated. The word is derived from Indican. You see it has benzene ring, it has carbonyl group, it has an NH 2, NH and they are now connected with the C double bond C. So, that makes it blue color dye, because it has all the requisites of chromophore and auxochrome.

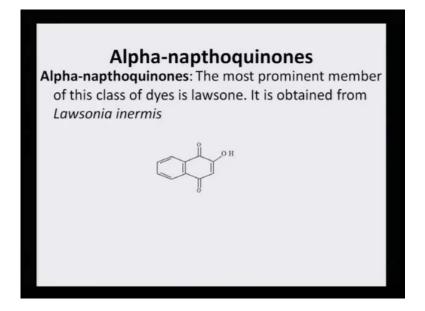
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Now let us look at the Anthraquinone dyes, we just look that the various structures of anthaquinone examples of madder or mangiest, and we saw that how alizarin and the other dyes are all having this basic skeleton. Now this is called an anthraquinone or quninone basic skeleton. Now different types of auxochromes when attached at different positions on either of these rings can produce more and more color, and the intensity of color goes up and as much as delocalization of the electrons happen, and that is related to the various functional or auxochromes that are connected to these aromatic rings.

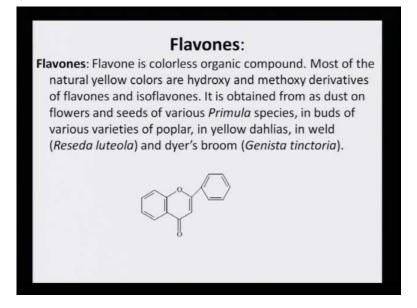
Some of the most important red dyes are based on anthraquinone structure. They are obtained both from plants and insects. These dyes are characterized by good fastness to light. They from complexes with metal salts and the resultant metal complex dyes have good wash fastness. Now when these aromatic ring have the OH. The OH at the auto position calculate the metal very easily, we will learn all this at in new course of time right now it is important for you to simply understand what the basic structure is...

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Similarly we have another category of structurally different dye which is called alphanapthoquinones. Alpha-napthoquinones the best example is the henna dye which has lawsone. Lawsone is a compound which has the very simple structure as shown on the slide. It has just one benzenering and this double carbonyl and an alpha beta unsaturated you say double bond carbon carbon double bond having an auxochrome OH attached to it. So, you see it is from henna which is lawsonia inermis that is the botanical name of mehndi plant and the mehndi plant consists of this lawsone dye, which is orange in color, and it stains the palm protein skin protein very redly.

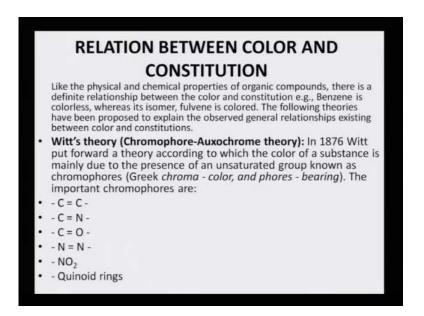
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The next category of structurally different compound is flavones. Flavone is a colorless organic compound to begin with most of the natural yellow colors are hydroxy or methoxy derivatives of flavones and isoflavones. It is obtained from as dust on the flowers and seeds of various Primula species, in buds of various varieties of poplar, in yellow dahlias, in weld that is Reseda luteola and dyer's broom that is Genista tinctoria.

So, these are the various sources of yellow dyes, but the basic flavones ring does is the colorless compound. So, what does it make you understand? I am trying to draw your tension to the simple fact that auxochromes are rarely rarely required to make a conjugated molecule in to a colored molecule or a dye molecule.

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Relation between color and constitution: Now if one has to understand this, like the physical and chemical properties of organic compounds, there is a definite relation between in the color and constitution. Benzene is colorless, whereas it isomer, fulvene is colored. The following theories have been proposed to explain the observed general relationships existing between color and constitution. So, there are various theories postulated from time to time in order to explain.

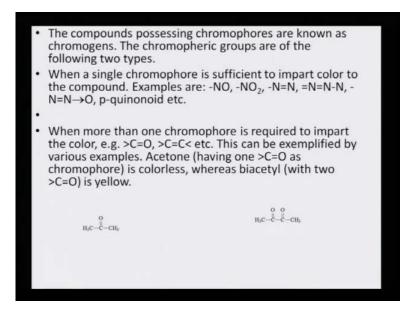
What is the relationship between the structure and the color of a compound? So, we try to learn and understand one one theory after another theory to be able to understand, how we came to modern theory of color explanation. With theory which is the most important

and the earliest theory that was postulated is based on the Chromophore and Auxochrome theory, the one which I have been explaining for a while in this lecture.

In 1876 Witt put forward a theory according to which the color of a substance is mainly due to the presence of an unsaturated group known as the chromophores, and it comes from the Greek word chroma which means color, and pores means bearing. The important chromophores are -C double bond C-, -C double bond N-, -C double bond O-, -N double bond N- and -NO 2, Quinoid rings and so on. So, we just looked at the various chromophores a while ago.

So, according to with it is because of these chromophore groups and the association of auxochrome that makes a chemical moiety a dye, because of extended conjugation. So, there are three criteria's that he mentioned. Presence of chromophores, presence of auxochromes, and the third thing it they must be in conjugation. To create a greater delocalization of electrons, and only when the electrons are more and more delocalized, colorless compound moves towards becoming a color colored compound.

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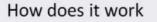
The compounds possessing chromophores are known as chromogens. The chromopheric groups are the following two types. When a single chromophore is sufficient to impart color to the compound, then these chromophores are of the category -NO, -NO 2, -N double bond N, -N double bond N double bond N and so on or -N double bond N O or

para-quinonoid structures. This if they are present only in one number, even then they can create lot of color or impart color to the compound.

When more than one chromophore is required to impart color like C O, C double bond C, this can be exemplified by the example that I took a while ago. C acetone which has just C double C sorry C double bond O is actually colorless, but when there are two such groups attached to it in by acetylene it is yellow in color. So, you see that one is not enough to impart color, but when two such chromophores are present or if there was an alpha beta unsaturated ketone.

Having C double bond O and C C bond, then it would have been pale yellow in color. So, the more conjugation it brings in the better it is so, among the two categories of chromophores. The nitrogen bearing or a quinonoid once even if they are present in one number can impart enough color, but in the case of carbon baring chromophores like C double bond O or C C bond. It they have to be more than one chromophoric group to create the color relation.

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Since the auxochromes are capable of forming salts either with a basic or acidic groups their presence also convert a colored compound (devoid of salt forming groups) into a dye which must fix permanently to the fiber, i.e., it must be fast to water, light, soap and laundering, when fixed to the fiber. The permanent fixing of dye to the fiber is generally due to the formation of chemical bond between the fiber and the auxochrome. This can best be exemplified by the following examples.

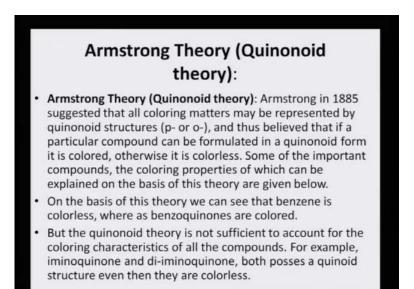
How does it work? Since the auxochromes are capable of forming salts either with a basic or acidic groups their presence also convert a colored compound, devoid of salt forming groups into a dye which must fix permanently to the fiber, it must be fast to water, light soap, and laundering, when fixed to the fiber. The permanent fixing of dye to

the fiber is generally due to the formation of chemical bond between the fiber and the auxochrome.

This can exemplified by the following examples. Now auxochrome; that means, have two roles to play: one role is that they enhance the conjugation effect, and or at least they participate in the conjugation effect, and the second role that they play when they participate in making a compound into a dye is in the adjuration of the dye to the fabric. So, auxochromes are very important integral part of a dye molecule.

Now when we try to look at these molecules you see benzene is colorless. Dye azobenzene is also color colorless, but the moment and amino group or a dyezonium salt is made. Dyezonium chloride it makes a kind of a colored dark yellow compound, and that is what makes that the more and more presence of auxochrome makes it a better dye material.

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The next theory that was proposed for explaining the relationship between color and constitution was the theory proposed by armstrong, which is based on the Quinonoid theory: Armstrong or Quinonoid theory in 1885 suggested that all coloring matters may be represented by quinonoid structures that is para or ortho, and thus believe that if a particular compound can be formulated in quinonoid form it is colored, otherwise it is colorless. Some of the important compounds, the coloring properties of which can be explained on the basis of this theory are given below.

So, you see he suggested Armstrong's theory says that all structures which can form quinonoid structure; that means, all chemical compounds can become a dye, if they fall in the category of writing their quinonoid structures, and if that is not possible there then they are colorless. On the basis of this theory we can see that benzene is colorless, where as benzoquinones are colored.

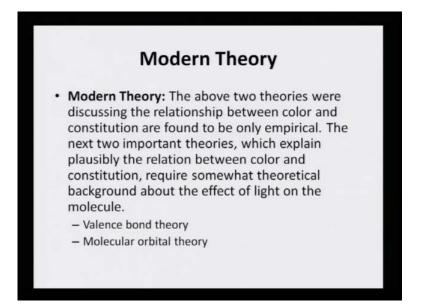
So, that is how he proved that you know benzene because it has it does not have a quinonoid structure it is just a benzenoid structure, but the quinonoid theory is not sufficient to account for the coloring characteristics of many compounds. For example, the iminoquinone and di-iminoquinone, both possess a quinoid structure even then they are colorless.

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So, if we try to look at these four structures now, Benzene is colorless that Benzoquinones means this kind of ring with double bonds and carbonyl is a colored situation, but when we look at Imnoquinone. That is carbonyl with NH or NH with NH Di-iminoquinone then these two are not colored. So, how does one explain the that this quinonoid structure is valid? So, there it is it is kind of feeling to explain many structures, which cannot be written up in their quinonoid form.

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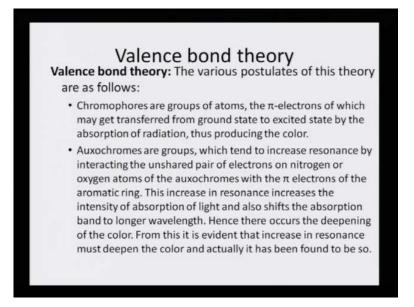


So, therefore, the Modern Theory came in to existence, and the Modern Theory then talks about great detail has how these is structures can be correlated, to the various explanation of the previously explained which theory and the second Armstrong theory. It has to offer something better, and more convincing explanation for the relationship between color and constitution. And that is what actually has come into being and it has been practice.

The above two theories were discussing the relationship between color and constitution are found to be only empirical; that means, it was valid in certain cases, but not valid in many cases. The next two important theories, which explain the possibly the relationship the plausibly relationship between color and constitution, require somewhat theoretical background about the effect of light on the molecule. So, this modern theory is now based on of very different concept.

It is not based on what is present on the structure, but it is based on how light is reacting on that structure and therefore, it is the effect of light on the molecule, which is the basis of the modern theory. To explain the difference between a chemical and a dye to explain the deference between its color and it is constitution, and two theories that were postulated, were Valence bond theory and Molecular orbital theory. So, from time to time with advancement first came the valence bond theory and then subsequently the most acceptable molecular orbital theory came into existence.

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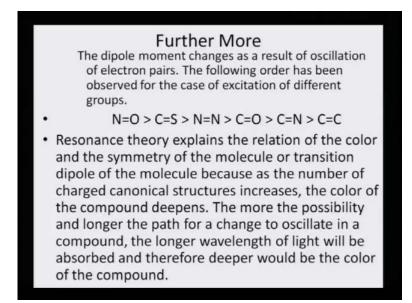
The Valence bond theory valance bond theory: The various postulates of this theory are as follows: Chromophores are groups of atoms, the pi-electrons of which may get transferred from ground state to excited state by the absorption of radiation, thus producing the color. So, this is what we actually were trying to refer to the fact that is has so many conjugation. Each pi bond has pi electrons and it is the delocalization of these pi electrons which are getting transferred from ground state.

Once they absorb light they are so fissile that they can get excited to the exited state by the absorption of the radiation and so, the more number of pi electrons the more light will be absorbed by them or exiting the pi electrons from ground state to exited state, and auxochromes are groups, which tend to increases the resonance by interacting the unshared pair of electrons on nitrogen or oxygen of auxochromes with the pi electrons of the aromatic ring. This increase in resonance increases the intensity of absorption of the light and also shifts the absorption band to longer wavelength.

Hence there occurs the deepening of color. From this it is evidence that increase in resonance must deepen the color and actually it has been found to be so. Now, this also is based on the presence of auxochrome and chromophore, but auxochrome how they are participating is being explained on the basis of lone one pair of electron that are present on the nitrogen or oxygen containing auxochromes and their participation with the pi electrons.

So, when the pi electrons have an influx of electrons from the loan pair of the nitrogen and oxygen, what happens is that their excitation by the absorption of light it facilitated, and that also causes deepening of color, because the more fissile the excitation the longer will be the wave length and shorter will be the energy requirement for such transitions.

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Further More: The dipole moment changes as a result of oscillation of electron pairs. The following order has been observed for the case of excitation of different groups, if we try to look at the various roles of auxochrome. It is N double bond O which is greatest which is less than which is greatest and less then that is C double bond S which is greater than N double bond N which is subsequently less than C double bond O N double bond N C double bond C.

So, this is the order of there you know dipole movements and the dipole movements then is a creating this excitation of these different groups. Resonance theory explains the relationship of color and symmetry of the molecule or transition dipole of the molecule, because as the number of charged canonical structures increases, the color of the compound deepens.

The more the possibility the longer the path for a change to oscillate in a compound, the longer wavelength of light will be absorbed and therefore deeper would be the color of the compound. So, it all depends on how many canonical structures can be written and the canonical structures are occurring due to the resonance that is accruing between the different participation of the loan pair with the pi electrons.

So, it is all classical organic chemistry based fundamentals, which need to be revived when we are trying to look at the valence bond theory of understanding the color and the constitution, because everything is very systematic. If there is nitrogen or amino group attached to aromatic ring. The loan pair on the nitrogen will participate with the pi electrons of the ring as a result it will have an enhancing effect. Now if we try to look at various structures.

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We will also appreciate I just took an example. I will go back to that example that Benzene Diazobenzene and this amino substituted compound. You see that benzene had only the pi electrons. Diazobenzene had the pi electrons of the ring, and the N double bond N as chromophore, but still it was only light yellow in color, but the movement was this amino at the substitution of one of the aromatic ring.

This amino then started the loan pair started conjugating with this ring electrons and this electrons were participating with the azo linkage and the azo linkage was then participating with the second aromatic ring. So, you see how beautifully this conjugation system can be explained and the various resonance structures that can be written for this purpose.

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Molecular orbital theory Molecular orbital theory: According to this theory the excitation of a molecule means the transference of one electron from an orbital of lower energy to that of higher energy. These electrons may be σ , π or n (non-bonding) electrons. The higher energy states are commonly known as anti-bonding orbitals. The anti-bonding orbitals associated with σ and π bonds are called σ * and π * orbitals respectively. However, there are no anti-bonding orbitals associated with n (non-bonding) electrons because they do not form bonds. Chart of the simplest form, the essential types of energy are givenin the next slide:

Now then came the most advance theory of Molecular orbital the Molecular orbital theory: According to this theory the excitation of a molecule means the transference of one electron from an orbital of lower energy to that of higher energy. These electrons may be sigma, pi or n that is non-bonding electrons. The higher energy states are commonly known as anti-bonding orbitals.

The anti-bonding orbitals associated with sigma and pi bonds are called sigma star and pi star orbitals respectively. However, there are no anti-bonding orbitals associated with n that is the non-bonding electrons because they do not form bonds. Chart of the the next chart will show you essentially how the energy is a increasing for this various types of electrons, and how the anti bonding orbitals are placed.

Now first and the far most thing is that one should understand is that these electrons, how fissile it is to exit a sigma bond what is the kind of energy difference for a sigma electron to go to sigma star orbital or whether it is easy for a pi electron to go to pi star or is it easy for the N electron to go to either pi star or sigma star. So, these are various transformations that are possible when the light is absorbed. Now light is bringing it is an electromagnetic radiation has a certain amount of energy associated with it.

Now when that energy is actually compatible with the energy requirement of the molecule for the excitation, only then the light will be absorbed. First thing that has to be understood very clearly. The light has to have a matching wave length of the wave length

that would be actually required for the excitation, wave length of light is associated with the certain amount of energy, and these amounts of an energies are always quantize. So, when it comes with its energy that energy is what actually causes the excitation of the electron.

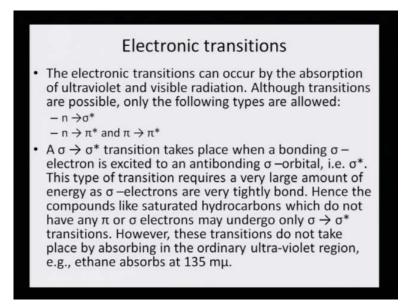
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		Chart showing molecular orbitals	
	α*	Anti-bonding	
E	π*	Anti-bonding	
+	n	Lone-pair Non-bonding	
F	π	bonding	
F	σ	bonding	

So, if we try to look at this chart, you will see that this is the order of increasing energy levels of various orbitals, you see bonding sigma is the lowest bonding pi is above that non-bonding or loan pair electrons are above that pi star is further above that and sigma star is... So, if one has to promote an electron from sigma to sigma star. It would require the highest amount of energy.

If one has to promote from pi to pi star that would require certain amount of energy, and the most fissile would be promotion of a loan pair electron to the pi star orbital instead sigma star. So, these are the kind of energy requirements and when the energy requirements are matching with the wave length that is incident on the compound. That the transaction of the of the movement of the electron can be facilitated. It is not that any electron can move to any situation.

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So, the electronic transition the electronic transition can occur by the absorption of either u v light or visible radiation, because that is what matches the range. Although transitions are possible, only the following types are allowed: although it I possible to promote sigma to sigma star or pi to sigma star, but you will see that only n to sigma star and n to pi star and pi to pi star are the allowed transitions.

Sigma to sigma star transition takes place when a bonding electron is exited to an antibonding orbital sigma star. This type of transition requires very large amount of energy as sigma electrons are very tightly bound. Hence the compounds like saturated the hydrocarbons which do not have any pi or sigma electrons may undergo only sigma to sigma star transitions. However, these transition do not take place by absorbing ordinary ultra-violet region, and therefore, ethane absorbs at 135 micro mu.

So, you see that has a wave length requirement which is even below ultra-violet region, and therefore, these transactions require very high energy, and they are colorless compounds all together. So, if one tries to look at these transformations you will also understand that what is allowed is n to pi star and pi to pi star and n to pi star. Now if you try to correlate with auxochrome and the chromophore, you will see that pi to pi star is a typical case of using the chromophoric electrons.

Chromophores are pi containing pi electron containing groups. So, it is the excitation. Now the modern theory does not completely violate the witts theory, because it is also based on the chromophore and auxochrome, but the more closable explanation in terms of electronic excitation and the electronic excitation is related to the incident light, when the incident light is matching completely with it is energy content which is required for this pi to pi star or n to pi star transition.

Then only the colored compound will absorb and will transmit the complimentary color. So, by now you may have understood that the witt's theory still holds good, and can be related to the modern theory of these pi to pi star and n to pi star transaction of electronic excitation. It is very important that you have to understand in the perspective of the structural constitution and the structural constitution containing the chromophore. And the auxochrome, how they participate in these transactions when the light is incident and the matching of the light with these transactions giving you an example of ethane, why ethane is not a colored molecule, because it is not even following it requires an energy which is much much higher than the energy content of the u v light or the visible light. Therefore, it cannot be seen as a colored molecule. So far, a molecule to be identified as the colored molecule, with the help of the incident light, it is important.

That it should have chromophore and the chromophore bares the electrons which need excitation from the pi to pi star or n to pi star. So, auxochromes chromophore light and constitution, they all play a very important role and go hand in hand. Otherwise one will not be able to explain, why certain chemical compound is colored. Why it is categorized as a dye and it is it is identification as a dye molecule comes from it is structure.

We just took at over view of various types of structures, anthraquinoid dyes, the indigoid dyes, the dye hydropine dyes, anthrax chinadin dyes. These structures all have chromophores, all have auxochromes and therefore, they are able to take up the light from the visible region and excite their electrons to from pi to pi star n to pi star there by showing that they are colored molecules.