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How Does the Conjugated Structure in Organic Compounds Affect Its Color

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Abstract: Conjugation effect is a manifestation of electronic effect, which has great influence on the properties of organic compounds, especially on the stability of active intermediates formed in the reaction process. These influences make some abnormal phenomena of organic compounds and products and yields of organic reactions fully and thoroughly explained. Based on the color of matter and its influencing factors, the essence of color of matter is discussed by using chromogenic theory, and the relationship between the color of organic compounds and its molecular structure is emphasized. The microcosmic mechanism of organic compounds' coloration is discussed by using molecular orbital theory, and the relationship between conjugated transition types of organic molecules and color is expounded. It is concluded that conjugated transition types in organic molecules are the main reason for organic compounds' coloration.

1. Introduction

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The essence of color rendering of compounds is that the transition energy of valence electrons between different molecular energy levels falls within the visible light range. Because the distribution and combination of valence electrons in different compounds are different, the transition energy required for transition is also different [1]. It is also related to the properties of adjacent bonds and the interaction between atoms that are not directly connected. This interaction between atoms in a molecule through the polar transmission of bonds is the result of the movement of shared electron pairs along covalent bonds, which is generally called electronic effect [2-3]. It can be summarized as induced effect and conjugate effect.

When the electrons in organic compounds make a transition, the absorbed light wave and wavelength fall in the visible light wave region, and the substance shows color. Because different substances can absorb different light waves and wavelengths, the substance has different colors. The longer the light wave is absorbed by the substance, the darker the substance is. This deepening is called “reddening effect” [4]. In an organic compound, when the energies of bonded orbit or non-bonded orbit and anti-bonded orbit (hereinafter referred to as π^*) are not much different, the π electron or n electron can be transferred to . without strong light, and then the organic matter will emit color. Actually, the energy required for the transition of n electrons is often lower than that required for the transition of π electrons.

2. Color of Substance and Its Influencing Factors

2.1 Color of Matter

Up to now, there is no exact statement about the color of matter. According to the actual situation, a part of absorbed, reflected (supplementary light of absorbed light) or transmitted light is a comprehensive visual reflection after it acts on human eyes [5].

The above statement can be simply understood as shown in Figure 1:

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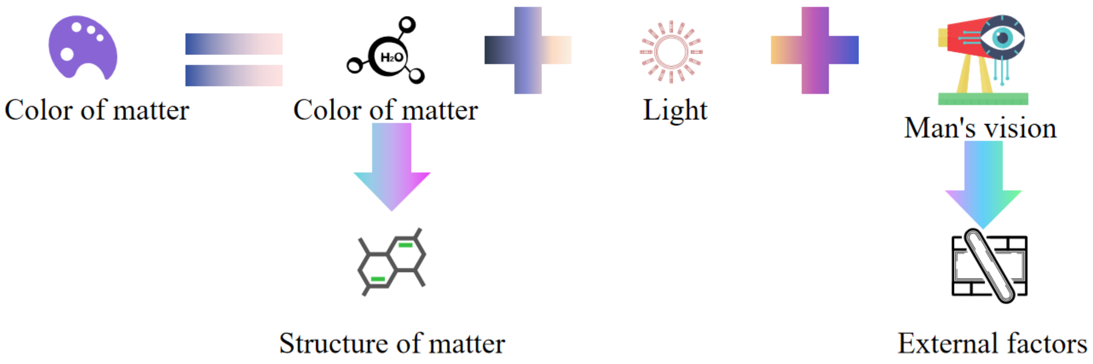


Fig.1 Color Diagram of Substance

The above factors are the elements that make matter show color. All three are indispensable.

2.2 Influencing Factors of Color

(1)The nature of matter itself

The molecular structure of matter is the internal cause that affects the color development of matter. The molecular structure of matter determines the absorption characteristics of light. The change of molecular structure of matter will directly affect the absorption, reflection or transmission of light, so the color of matter will change accordingly.

When a substance totally absorbs visible light, it appears absolutely black, while totally reflects visible light, while when it absorbs visible light of various wavelengths, it appears gray, and when it selectively absorbs light of a certain wavelength, it appears its complementary color.

(2)Light

Light is the external factor of material color development. For substances that do not emit light, if there is no light, the human eye will not feel the color of the substance (people will not see or even feel the existence of objects when they are placed in an absolutely black environment); If the light illuminating an object changes, the color of the object will also change [6].

(3)Man's vision

People's color judgment of matter is a comprehensive reflection of light acting on people's visual system. People with visual system defects can't judge the color of materials, such as blind people and patients with color blindness and color weakness.

3. Conjugate Effect

3.1 Conjugated System

The so-called conjugated system generally refers to the system composed of unsaturated bonds and single bonds, which can be summarized into the following three main types:

(1) $\pi-\pi$ conjugate system;
(2) $p-\pi$ conjugate system;
(3) σ-π conjugate system.

3.2 Static Conjugation Effect

(1)Origin of conjugate effect

In conjugate system, the overlapping of adjacent π electrons or the mutual influence of p electrons in π bonds make the electron cloud density of each bond in conjugate system average, and the difference between adjacent single bonds and heavy bonds disappears partially or completely. This effect is called conjugate effect. The conjugate effect originally existing in molecules is also called static conjugate effect.

Conjugation effect exists only in conjugate system, unlike induction effect on all bonds. It is generally considered that the atoms (clusters) giving two electrons show $+\mathrm{C}$ effect, and the atoms or clusters attracting π electrons show $-\mathrm{C}$ effect [7].

(2)Conduction mode

Conjugation effect is due to the transfer of π electrons along conjugate bonds, and as a result, the cloud density of π electrons in conjugate bonds is averaged.

(3)Distance of conduction

In conjugate system, the influence can be easily transmitted to a considerable distance along the conjugate bond, and there is no obvious fading away.

(4)Intensity of conjugate effect

The intensity of conjugation effect depends on the structural characteristics of atoms, covalent states, properties of bonds between atoms and their spatial arrangement, which can be calculated from the measurement of changes in electric dipole moment and bond length, or deduced from the periodic table of elements.

The direction and conjugation degree of electron transfer in conjugation system can be judged according to the position of elements in the periodic table. $+\mathrm{C}$ effect:

In the same period, it decreases with the increase of atomic number: $\mathrm{NR_2} > \mathrm{OR} > \mathrm{F}$;

In the same family, it decreases with increasing atomic number: $\mathrm{F} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I}$.

$-\mathrm{C}$ effect:

In a conjugated system with a heavy bond atomic group, the element at the end of the atomic group has the greater ability to attract electrons, such as $\mathrm{C=O} > \mathrm{C=NH}$.

The conjugation effect of an atom (group) is not eternal, because the intensity of conjugation effect depends not only on the condition of an atom (group), but also on the structure of other atoms (groups) and the whole molecule.

3.3 Dynamic Conjugation Effect

Dynamic conjugation effect is that the density of p electron cloud is deformed and redistributed at the moment of reaction due to the action of offensive reagent or the influence of external conditions when chemical reaction occurs in conjugated system [8].

Dynamic conjugation effect is often the expansion of static conjugation effect and tends to polarization, which has great influence on the reaction performance of this organic compound. Generally speaking, the dynamic conjugation effect is only beneficial to the reaction, while the static conjugation effect may sometimes hinder the reaction.

4. Influence of Valence Electron Transition on Color

4.1 Electronic Transition Types of Molecular Species of Organic Compounds

Organic compounds are mainly composed of $\mathrm{C, H, O, S, N, X}$ and other elements. According to the molecular orbital theory, the valence electrons in the ground state molecules are distributed on the bonded σ orbitals and bonded π orbitals with lower energy, and the unbonded unbonded orbitals (n). When different types of ground state valence electrons are excited by light, they transition from occupied orbitals to the unoccupied orbitals with higher energy-anti-bond σ orbitals and anti-bond π orbitals, which will produce absorption peaks [9].

Different types of electronic transitions in organic molecules are shown in Figure 2.

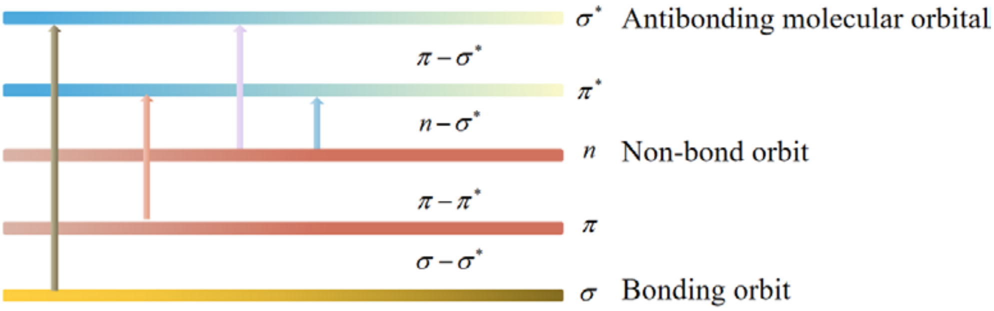


Fig.2 Types of Electronic Leaps in Organic Molecules

The $\sigma \to \sigma^*$ transition requires high energy, and the absorption peak is often in the far ultraviolet region below 150nm. Saturated hydrocarbons-C- C- are colorless because they only have σ electrons with lower energy and can only produce $\sigma \to \sigma^*$ transition.

The transition energy of $n \to \sigma^*$ transition is lower than that of $\sigma \to \sigma^*$ transition, and the absorption peak is generally in the near ultraviolet region near 200 nm. Saturated hydrocarbon derivatives containing -OH,-NH,-X,-S- and other groups can form $n \to \sigma^*$ transition because the heteroatoms contain unbonded lone pair. Such as the absorption spectrum of $CH_3NH_2, CH_3OH, CH_3I, CH_3SH$ these compounds are generally colorless.

The transition energy of $n \to \pi^*$ transition is small, and the absorption peak has a longer wavelength, generally in the range of 200~ 400 nm. But the probability of this kind of transition is very small, $\varepsilon < 100$. In organic compounds containing heteroatom double bonds, the unbonded p electrons on heteroatoms can transition to the anti-bond π orbit, so there is $n \to \pi^*$ transition.

$n \to \pi^*$ transition, such as π electron on double bond of unsaturated olefin compound, can transition to $\pi \to \pi^*$ orbit after absorbing energy, forming $\pi \to \pi^*$ transition. Transition energy is generally similar to $n \to \sigma^*$ transition energy.

From the above discussion, it can be seen that the order of transition energies ΔE of different types of electrons in organic molecules is $\sigma \to \sigma^* > n \to \sigma^* \geq \pi \to \pi^* > n \to \pi^*$. And the existence of a single organic chromophore is not enough to color organic compounds.

4.2 Influence of Electronic Transition on Color

When a molecule absorbs light quantum and obtains certain energy, the change of motion state is called transition. The energy needed in the transition process is called excitation energy. Molecules only choose to absorb the light quantum with the same energy level difference, instead of absorbing the light quantum with various energies generally, which is the reason why colored molecules have selectivity in light absorption.

The energy of a photon is proportional to its frequency v and inversely proportional to its wavelength:

$$E = hv = \frac{hc}{\lambda} \quad (1)$$

If the excitation energy of a molecule is small, the wavelength λ of light absorbed by the molecule will be long, and the color will become darker, for example, from red to green to blue. On the contrary, if the excitation energy of a molecule is larger, the maximum absorption wavelength shifts to short wave, and the color becomes lighter, for example, from red to orange to yellow. The energy level difference between the ground state and excited state of colored matter is generally in the $150 \sim 300\text{KJ/mol}$ energy range, so it can selectively absorb visible light and present the complementary color of visible light [10].

Obviously, 100% reflection does not exist, and 100% absorption is impossible unless it is “absolutely blackbody”. Colorless organic matter does not mean that it has no absorption of light energy, but the wavelength of light absorbed by them is not in the visible light range (such as infrared spectrum, ultraviolet spectrum, etc.).

Generally speaking, organic compounds absorb light waves to a certain extent, and the selectivity of absorbing light waves is closely related to the structure of compounds. Only when the energy of visible light with a certain wavelength is equal to the excitation energy of substance molecules can it be absorbed. Therefore, the color of any substance is due to its selective absorption of visible light.

5. Effect of Conjugated System in Organic Compounds on Color

5.1 Effect of Conjugation on the Activity of Organic Compounds

Conjugate effect can be divided into power supply conjugate effect and power absorption conjugate effect. Because of their different effects, the structure of the compound has changed, and the difficulty of some reactions of the compound has also changed. This is particularly evident in electrophilic and nucleophilic addition and substitution reactions. However, when benzene is substituted by some groups, the electron cloud density of benzene ring and groups will change due to electronic effects (including induction effect and conjugation effect). The power supply group increases the activity of benzene ring and accelerates the reaction speed; Electricity-absorbing groups reduce the activity of benzene ring and slow down the reaction speed. Table 1 below gives the relative rates of nitration of some substituted benzenes:

Table 1 Relative Speed Of Nitration of Substituted Benzene

Substituent	Relative velocity	Substituent	Relative velocity
$-N(CH_3)_2$	$\sim 2\times10^{11}$	$-Cl$	0.033
$-OCH_3$	$\sim 2\times10^{5}$	$-Br$	0.03
$-CH_3$	24.5	$-CH_2Cl$	0.0302
$-C(CH_3)_3$	15.5	$-NO_2$	6×10^{-3}
$-H$	1	$-N^+(CH_3)_3$	1.2×10^{-3}

It can be seen from Table 1 above that the conjugate effect is quite significant. Another example is:

$C_6H_5CH = CH_2$ (2)

$p\text{-}CH_3C_6H_4CH = CH_2$ (3)

$p\text{-}O_2NC_6H_4CH = CH_2$ (4)

Compared with the reaction rate of addition of HBr. Their intermediate carbocations are:

$C_6H_5CH + CH_3$

$p\text{-}CH_3C_6H_4CH + CH_3$

$\text{-}O_2NC_6H_4CH + CH_3$

The latter two are equivalent to adding a substituent to the benzene ring of the former, but the methyl group in the middle has the power supply conjugation effect of $\sigma\text{-}\pi$, which can strengthen the stability of carbocation, while the $\pi\text{-}\pi$ conjugation effect of the latter is electricity absorption, which makes carbocation more unstable. The stronger the stability, the faster the conversion speed, so the reaction speed is:

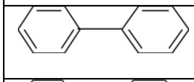
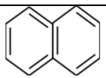
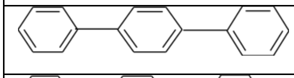
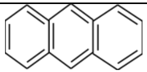
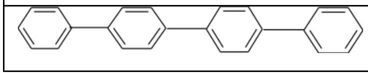
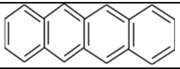
$p\text{-}CH_3C_6H_4CH = CH_2$□ $C_6H_5CH = CH_2$□ $p\text{-}O_2NC_6H_4CH = CH_2$ (5)

5.2 Influence of Spatial Effect on Color

According to the molecular orbital theory, the conjugated atoms must be in the same plane, so that the parallel p orbitals of each atom can overlap the maximum program, effectively combine the conjugated π molecular orbitals, and produce the maximum conjugation effect.

If the coplanarity of atoms in conjugated molecules is damaged to varying degrees, the molecular orbital of conjugated π will be affected, and the transition energy of conjugated $\pi \rightarrow \pi^*$ will increase, resulting in purple shift of the maximum absorption peak and light color. Table 2 compares $\lambda_{\max}$ of para-biphenyl series with that of benzo series:

Table 2 the $\lambda_{\max}$ Of P-Biphenyl Series is Compared with That of Benzo Series

Parabiphenyl series	$\lambda_{\max}/nm$	Benzo series	$\lambda_{\max}/nm$
	251.5		275
	280		370
	300		460

It can be seen from the table that the $\lambda_{\max}$ of biphenyl is similar to $\lambda_{\max}$ (255nm) of benzene. From para-terphenyl, $\lambda_{\max}$ has a little red shift with the increase of benzene ring number, which reflects that para-biphenyl has a certain degree of conjugation. However, compared with the corresponding fused ring system, the redshift effect is much smaller. This is enough to show that the rotatability of σ bond connection in para-biphenyl destroys the conjugation of the plane of molecule to a great extent, which makes the color of para-biphenyl lighter than that of the corresponding condensed ring aromatic monster.

Therefore, the spatial effect is a factor that makes conjugate $\pi \rightarrow \pi^*$ transition increase, $\lambda_{\max}$ purple shift and color become lighter.

5.3 Influence of Coplanarity and Symmetry of Molecules on Color

When the molecule and all groups are in the same plane and symmetry, the conjugation effect can be brought into full play. The mobility of the electron cloud in the whole molecule is enhanced, the activation energy is reduced, and the dark color effect is produced. Conjugated double bonds in molecules are beneficial to the coplanarity of molecules, while free rotation of single bonds is not conducive to the coplanarity of molecules.

From the comparison of the two molecular structures in Figure 3 below, the molecular weight of the lower one is reduced by half compared with that of the upper one, but the color is not obviously lighter. The reason is that the single bond in the upper molecule can rotate freely, which makes it difficult for the molecules to be in the same plane.

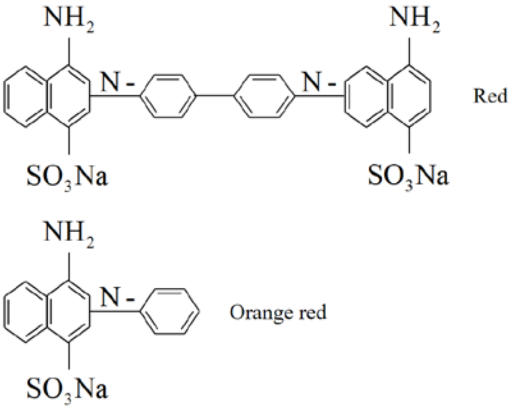


Fig.3 Comparison of Two Molecular Structures

5.4 Relationship between Valence Electrons in Molecules and Color of Substances

Electrons of atoms in a substance molecule rotate in different orbits around protons at different speeds, and the energy levels of each orbit are different. When a molecule is in a stable state, valence electrons participating in bonding (valence electrons are electrons that atoms can use to bond when participating in chemical reactions. Most of them are unpaired single electrons participating in bonding.) in the lowest energy orbit as much as possible. Different substances have different internal structures, that is, different valence electrons in the molecule, so the energy level difference of the transition of electrons is different, and the selective absorption of light is different, thus absorbing light in different frequency ranges, while the compound color of the unabsorbed visible light is the color presented by the substance.

When there are several chromophores in the compound and they are conjugated, the π electrons are easily excited due to the delocalization of electrons in the conjugated system, and this kind of organic matter can absorb the light in visible light and develop color. For example, quinones: naphthoquinone, anthraquinone and azo compounds ($R - N = N - R$) are all colored substances.

In addition to chromophores, organic compounds as dyes also contain chromophores containing unshared electrons, such as $NH_2, - NR_2, - OH, - OR, -SR, - Cl, - Br$. When these groups are connected with conjugated bonds or chromophores, p- π conjugation can occur (forming a multi-electron conjugated system), which can make the absorbed light waves of conjugated chains or chromophores move to low frequency areas, and often deepen the color of compounds. Commonly used indicators, such as phenolphthalein, litmus and methyl orange, are organic weak acids or weak bases, which show different colors due to structural changes in different PH media.

6. Summary

To sum up, chromophores and chromophores in organic compounds, ionization and space effect of organic molecules can change the conjugated $\pi \rightarrow \pi^*$ transition energy, which affects the color of organic compounds. When the conjugated system in organic molecules increases to a certain extent, its conjugated $\pi \rightarrow \pi^*$ transition energy falls in the visible light region, which makes organic compounds color. With the increase of conjugated chains, the conjugated $\pi \rightarrow \pi^*$ transition energy decreases, the absorption peak shifts red and the color deepens. Besides its own structure, the external factors that affect the color of compounds can not be ignored. For example, solvent, medium, concentration, temperature, light intensity, etc. have influence on the color of substances. If the concentration of the solution is too high, because the structural characteristics of the compound determine that its molecules are aggregated in the solution, it can not absorb the spectrum selectively, and the color will change deeply or shallowly.

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