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An Article Review: Charge-Transfer of Polyenes and Carotenes

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Abstract

When an electron moves from one atom or molecule to another, a charge-transfer complex is formed. The other objects must be able to accept these electrons, and one entity must have free electrons or a tendency to donate them. This resembles an internal oxidation-reduction reaction more. This research aims to shed light on charge transfer complexes formed by polyenes and carotenes, which act as electron-donating molecules due to their alternating double and single bonds. This allows them to create such complexes when interacting with organic molecules that lack electrons. These complexes exhibited distinctive optical and physicochemical properties, enabling them to be adapted for a wide range of applications. In addition, the researchers demonstrated significant interest in the study of the ability of some of these compounds to form self-internal charge-transfer complexes, also known as intramolecular charge-transfer complexes, and their precise electronic and dynamic states.

Keywords: Carotenes, Charge-Transfer complex, Physicochemical properties, Polyenes.

1. Introduction

A complex made from the union of two or more molecules is known as a charge-transfer complex (CT complex) or an electron donor-acceptor complex (EDA complex). For this kind of complicated situation, the electrostatic attractiveness equipment balances the force. A photoelectric shift into an inspired photoelectric state is capable of occurring in several distinct aggregates. The visible electromagnetic frequency domain is where this change's excitation strength occurs quite frequently, giving these aggregates their distinctively passionate color. The fact that the absorption spectra of CCT complexes often differ from those of the donor and acceptor is one of their properties (1). For the spectrophotometric determination of drugs (2-9), pesticides, herbicides (10,11), dyes (12), and organic particles, including polyenes and carotenes, an elementary CT is a standard response. A polyunsaturated chemical called polyene has at least three conjugated double bonds that alternate between double (C=C) and single (C-C) bonds. This conjugation produces specific, peculiar optical characteristics. Human antibiotics made from polyenes include trichomycin, candidin, nystatin, pimaricin, methylpartricin, and amphotericin B (13). Plants can create the unsaturated hydrocarbon compound known as carotene. In contrast, animals cannot (except for a few aphids and spider mites, which acquired the carotene-producing genes from fungi).

Carotene has the chemical formula $C_{40}Hx$. Significant pigments for photosynthesis include carotenoids. Their structures do not contain oxygen (14).

2.Materials and Methods

2.1. Charge-transfer of polyenes with chloranil

A report demonstrating the potential for producing a CT from the interaction of polyenes with chloranil was published in 1971 by Iida *et al*.

2.2. Adsorption of some charge-transfer complexes of polyenes on the solid films

It was investigated whether various electron-acceptor complexes could adsorb on solid films. All of the trans forms of Provitamin A, trans-beta-apo-8'-carotenal, astatine, and methylbixin were employed as polyenes in the current study. These polyenes were carefully layered onto the quartz surface as polycrystalline thin films.

2.3. Semi conduction effects of some polyenes charge-transfer complexes and their applications

The semiconducting characteristics of certain polyene-iodine (CT) compounds and their uses in solid-state batteries were the subject of a study by Sen *et al*., published in 1993.

3. Results

In charge-transfer complexes of polyenes with chloranil, the absorption spectrum, which provided the maximum absorption wavelength, the equilibrium constant, the molar absorptivity coefficient, as well as thermodynamic parameters, showed the difference in concentration between chloranil, as the acceptor, and polyenes, as the donor. According to the most recent research on the polyene CT complex, natural polyenes may be affected by the electron transfer relationship *in vivo* (15). Some solid films of some charge-transfer complexes of polyenes were subjected to I_2, Br_2, HNO_3, and ICl fumes. After the solid film was exposed to the vapors, the absorption spectra were captured at 28 °C. For [trans-carotene, -Apo-8'-carotenal, Astacene, and Methylbixin], the observed peak with λmax was at approximately 11550 cm^{-1}, 12000 cm^{-1},13150 cm^{-1}, and 13200 cm^{-1}, respectively, in the case of I_2. Unquestionably, the solution's observable charge-transfer absorption peak typically occurs at a shorter wavelength than it does in the solid state (16). The outcomes of semi conduction effects of some polyenes charge-transfer complexes and their applications showed that while the energy required to activate the charge-transfer complex reduces, conductivity increases by orders of magnitude. Because of this, batteries with the configuration Mg/ (polyene-iodine CT complex)/graphite were created, taking advantage of these complexes as cathodic electrodes (17).

4. Discussion

There is a possibility of producing Intramolecular CT complexes of polyenes**.** This issue was addressed in numerous papers. To analyze two sequels of donor-acceptor polyenes with increasing length, Blanchard-Desce *et al*. (1995) provided electro-optical absorption data.

The empirical results show that the redshift of the intramolecular charge-transfer complex absorption peak is guided by the lengthening of the polyene chain connecting the donor and acceptor terminal groups, which also increases the excited and transition state dipoles. At the same time, the ground state's dipole is mostly unaltered. Due to this, reported photoinduced dipole moment changes (up to 33 D) were obtained with a corresponding increase in molecule elongation (up to 27°), leading to highly excited state polarization (18). Wagner *et* *al*. (2013) published a study that effectively combines theoretical concepts and experimental findings to understand the ICT complex state of peridinin, as shown in **Figure (1)**.

The study shows that bond-order reversal caused by the interaction of the more highly polar excited singlet states with the more polar solvent is what creates the developed state. Time-resolved pump-probe spectroscopy experiments on these distinct states, as a function of the solvent nature, are introduced to start the investigation (19).

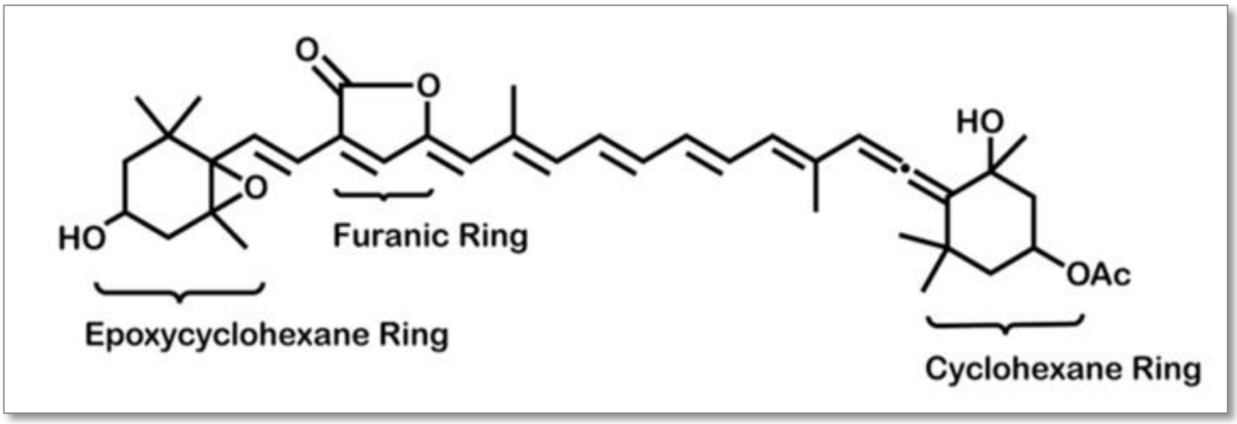

Figure 1. The molecular structure of peridinin (19).

To fully comprehend the electronic structure and dynamics of the intramolecular CT state, an article was published in 2014. In this article, different donor-acceptor substituted compounds from the diphenyl polyene series and ethenyl indoles are discussed in terms of excited-state intramolecular CT, photoisomerization, and fluorescence probe features. The research demonstrated that the ground state of linear polyenes is covalent, non-polar, and particularly unaffected by solvent polarity or substituents. The following low-lying states often represent the photodynamic retinal polyenes singlet excited state:

1(n-π*), ^{1}Ag* (π-π*a dipole forbidden transition), and ^{1}Bu* (π-π*, a allowed transition). The following factors have impacted these electronic states:

(i) the medium, such as polar, non-polar, or solvents for hydrogen bonds.

(ii) the geometrical structure of the polyene chain.

(iii) a functional group that is located at the polyene chain's end.

The protein-bound, photoactive retina was observed to absorb light at wavelengths between 380 and 780 nm. The all-trans-retinal ethanoic solution exhibits maximum absorbance at 380 nm. Retinal absorbs most effectively in ethanol when covalently linked to n-butyl amine at 440 nm (20). Femtosecond time-resolved optical spectroscopy was also used to study carotenoids and polyenes that participate in intramolecular CT. This study demonstrated that as the polarity of the solvent employed increases, the lifespan of the low-lying S1 excited state diminishes. As the number of double bonds in the conjugate system rises, this influence becomes stronger. The state characteristics of three substituted polyenes (CT) were studied:

Crocetin dialdehyde, the first, is a polyene having two terminals that are replaced with carbonyl groups that form a conjugate bond with the -electrons.

The first polyene
(Crocetin dialdehyde)

The second polyene
(is (8,8'-Diapocarotenedioic acid)

The third polyene
(2,6,11,15-tetramethyl-hexadeca-2,4,6,8,10,12,14-heptaene-1,16-diol).

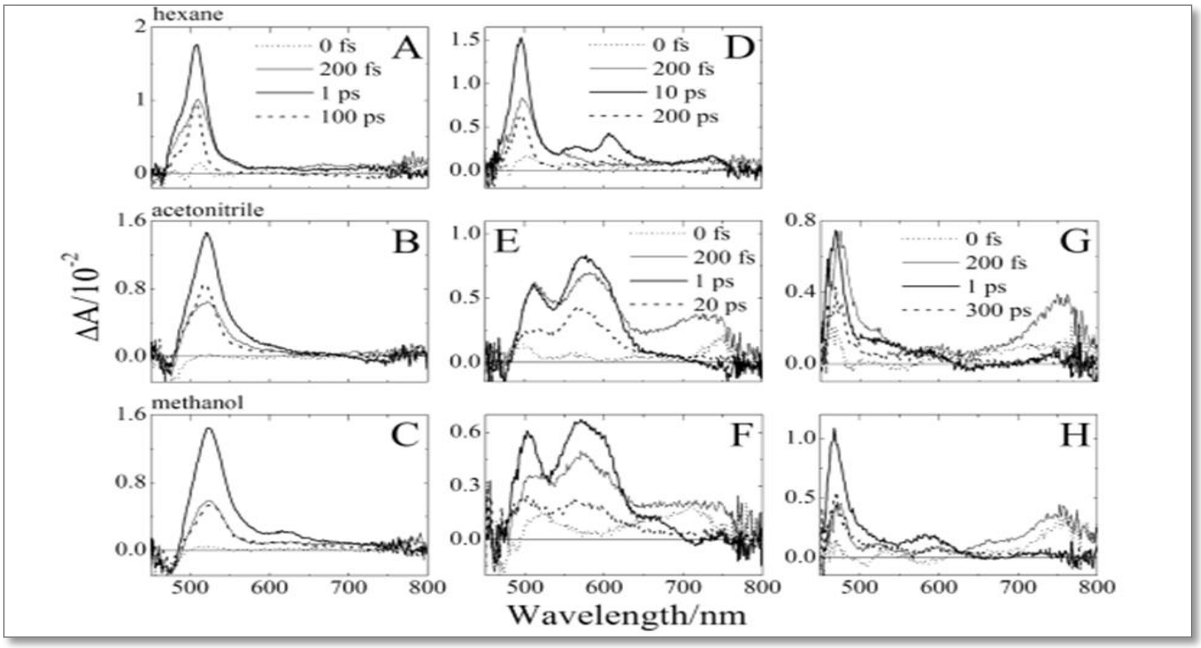

Figure 2. Femtosecond time-resolved transient absorption spectra of different carbonyl-containing polyenes and carotenoids taken at different time delays after excitation at 406 nm in different solvents at room temperature (21).

The second is (8,8'-Diapocarotenedioic acid), which has one hydroxyl group and one terminal conjugated carbonyl.

The third one has two terminals, symmetrically positioned hydroxyls (2, 6, 11, 15-tetramethyl-hexadeca-2, 4, 6, 8, 10, 12, 14-heptaene-1,16-diol), using the molecular orbital theory, the results are interpreted.

Only the first polyene exhibits the solvent impact on the wavelength at which it absorbs the most light. From hexane to acetonitrile to methanol, the Crocetin dialdehyde absorption spectra displayed a bathochromic impact (21, 22).

5. Conclusion

This article discusses CT complexes of polyenes and carotenes with various substituted functional groups, their physical and chemical characteristics, which are discovered using multiple techniques, including UV-VIS Spectrophotometry, FTIR, electro-absorption modulation, a femtosecond spectrometer system based on an amplified Ti: Sapphire laser, and their applications.

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Conflict of Interest

The authors declare that they have no conflicts of interest.

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Ethical Clearance

The study has been approved by the Committee of the University of Baghdad/ College of Education for Pure Science (Ibn Al-Haitham).

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