



Functional interpretation of the role of cyclic carotenoids in photosynthetic antennas via quantum chemical calculations



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ARTICLE INFO

Article history:

Received 1 June 2015

Received in revised form 12 July 2015

Accepted 13 July 2015

Available online 29 July 2015

Keywords:

Carotenoids

Excited electronic states

Excited energy migration

ABSTRACT

In the paper positions of the energy levels of the first three excited states of cyclic carotenoids are calculated. The pigments studied include the representatives of β -carotene homologous series containing 5, 7, 9 and 11 conjugated bonds, as well as xanthophylls: zeaxanthin, violaxanthin, lutein, canthaxanthin, astaxanthin and auroxanthin. The results are obtained using quantum chemistry computational methods. The data obtained are discussed in relation to biological functions of carotenoids and their role in the processes related to electronic excitation energy migration involving chlorophyll and oxygen molecules.

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1. Introduction

Carotenoids and chlorophyll are the most widespread organic pigments in nature. They exist in a majority of organisms, including human beings, but they are synthesized only in plants and bacterial cells. Free carotenoids can be found in lipid membranes and liposomes, or in a specific protein-bound form. Structurally these substances are included into the class of terpenoids, which may contain various amounts of π -conjugated bonds and substituents. At the moment more than 799 various carotenoids have been extracted from biological objects [1], and this number is persistently growing every year. An extended class of carotenoids, for convenience, is divided into subclasses in accordance with their structure. Carotenoids, containing only hydrocarbon substituents are called *carotenes*, and those containing oxygen atoms – *xanthophylls*. Oxygen in xanthophyll in most cases is included into hydroxyl, ketone and epoxide groups. With respect to the molecular terminal groups carotenoids are divided into acyclic and cyclic classes. The cyclic carotenoids include structures containing at least one cyclized group, and are more often represented by β -ionone ring. A general structure of a cyclic carotenoid is given in Fig. 1.

Carotenoid structures directly related to their biological functions are listed below:

1. *Structural function* – non-specific for Carotenoids. Since carotenoids comprise lipophilic or amphiphilic rigid linear molecules, they are able to reinforce proteins and membranes they are bound to [2,3].

2. *Antioxidant function* – is another non-specific function of carotenoids. Carotenoids are able to quench effectively active radical forms of oxygen as well as singlet oxygen [4]. As a result of free oxygen radical quenching an inert carotenoid-radical forms, with an unshared electron stabilized by a π -conjugated system. Such carotenoid-radical is chemically inactive that is why an interaction of radicals with carotenoids results in the break of free radical reaction chains. With respect to singlet oxygen carotenoids play the role of spin-catalysts, by transferring oxygen from the excited singlet state into its ground triplet state. The low triplet electron level of carotenoids accepts excitation energy of singlet oxygen [5]. In the quenching process excitation energy transfer occurs coupled to simultaneous change of multiplicity of carotenoid and oxygen, and generation of an inert pair of triplet oxygen – triplet carotenoid.
3. *Light-harvesting function* – is a specific function of carotenoids in a photosynthetic unit. Carotenoids bound to the light-harvesting proteins operate as additional light-harvesting antennas providing light absorption within a wider spectral wave length range [6,7]. Carotenoid molecules excited by blue light, give rise to electronic excitation migration to antenna chlorophyll molecules, and further to the photoactive chlorophyll dimer (special pair), which in the excited state acts as an electron donor to the photosynthetic chain. The presence of carotenoids in light-harvesting antenna allows extending the spectral range of its light excitation up to 350 nm.
4. *Photoprotective function* – another specific function of carotenoids in photosynthesis. Under excessive electronic excitation certain carotenoids can serve as energy acceptor from the excited chlorophyll molecules resulting [6]. This protective

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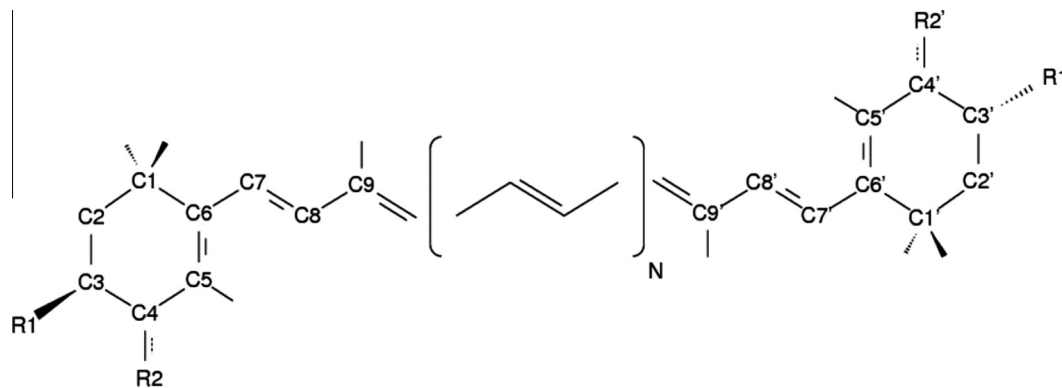


Fig. 1. A general structure of a cyclic carotenoid with β -ionone ring. Carbon atoms are marked by typical labels.

mechanism preventing chlorophyll degradation through photo-oxidation is very important under excessive light illumination and depends on the composition of the quenching carotenoids [8].

Carotenoids are long rigid linear π -conjugated molecules, similar to linear polyenes in their properties. In carotenoids double bonds are mainly in the trans-configuration. However the structure may include from one to three cis-bonds and their number may vary as a result of photoisomerization or interaction with a protein [9,10]. Extracted carotenoids acquire almost always one definite stereoisomeric form, suggesting that definite conformation is important for their biological activity. Thus, for example, typical carotene- β -carotene has conformation with two cis-bonds in C6 positions. In addition to cis-trans isomerism the geometry of carotenoids is strongly affected by various substituents which repel from each other or affect the distribution of electron density in the system of conjugated bonds of carotenoid. Related changes in the equilibrium geometry play an important role in the process of interaction of carotenoids with each other as well as with proteins [2,11].

After carotenoid absorb a light quantum or receive energy from an excited chlorophyll or oxygen molecule, it can transfer into one of the three available excited electronic states: S2, S1 and T [12] (Fig. 2). The higher electronic state S2 corresponds to the blue

quantum absorption and determines the intensive band in the carotenoid absorption spectrum. Through the rapid vibrational relaxation S2 state transfers to S1 state, which is also deactivated as a result of vibrational relaxation to the ground S0 state (Fig. 2B1). S1 level actively interacts with the excited singlet state of chlorophyll (Q_y). Relative position of these levels determines the direction of excitation energy transfer between carotenoids and chlorophylls. If the S1 level position of carotenoids lies above the Q_y level of chlorophyll (as in violaxanthin) the S1 state becomes an excitation energy donor to chlorophyll, and such carotenoid acts as a light-harvesting agent. If the level S1 lies below the level of Q_y chlorophyll (as in zeaxanthin) such pigment accepts chlorophyll's excitation energy and quenches it (Fig. 2B2 and B3). The T state may arise from the ground S0 state as a result of spin-spin exchange with spin-catalysts which are represented in biological systems by singlet oxygen and triplet chlorophyll (Fig. 2B4 and B5). Almost all carotenoids extracted from biological objects act as quenchers of oxygen singlet $^1\Delta_g$ state. This fact shows that their energy T state levels lie below 0.98 eV, which is the excitation energy of $^1\Delta_g$ state of oxygen. T state is a long-lived state and since in our discussion it is not deactivated spontaneously, it can be considered as a ground T state.

The system of electronic excited states of carotenoids, chlorophyll and oxygen form a dynamic interacting system [13–15].

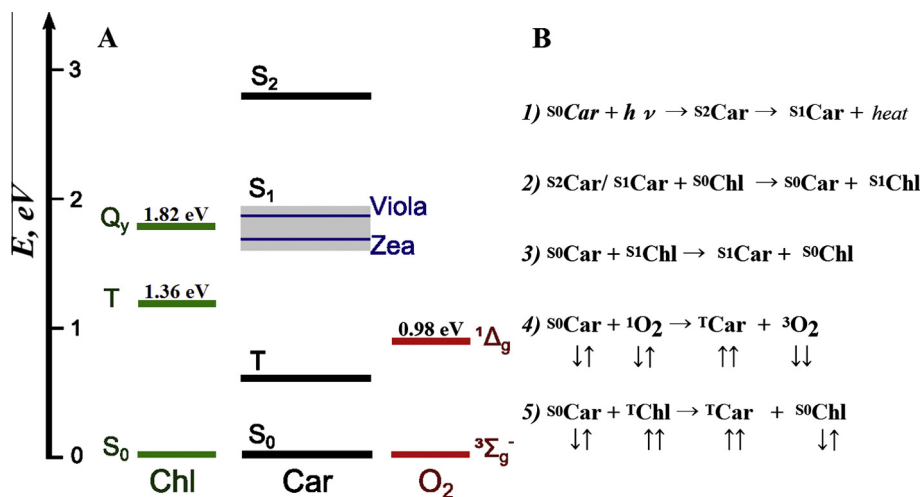


Fig. 2. (A) The scheme of the mutual arrangement of the excited electronic state energies for carotenoids, oxygen and chlorophyll – denoted as Car, O2 and Chl, respectively. Energy of the carotenoids S1 excited state is represented as a continuum of values (light blue box) that it takes for the various carotenoids. In the area of the possible values continuum (light blue box) the position of S1 state energy for viola- and zeaxanthin are marked (deep blue stripes). Any energy state that has higher energy position in the scheme act as a donor of a excitation energy по отношению to any state that has a lower energy position, if that transition is not forbidden by the selection rules. (B) The reactions of an excited energy migration involving carotenoids (see explanation in the text). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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