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Iodine-Catalyzed *R*/*S* Isomerization of Allenic Carotenoids

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A mechanism is proposed to explain the experimental observations in the iodine-catalyzed *R*/*S* isomerization of the allenic carotenoids peridinin, fucoxanthin, and neoxanthin. Attack of I· on C7′, suggested to be the key step, breaks (or forms a partial bond with I in a transition state) the C7′−C8′ or C7′−C6′ π bond, which allows subsequent *R*/*S* isomerization. AM1 calculations show that the charge density at C7′ of both the 6′*R*-isomer and 6′*S*-isomer is the greatest among the polyene and allenic carbons, and that the electron densities in the p_x and/or p_y orbitals of C7′ are also higher than for most other polyene and allenic carbons. Thus, I· can preferentially attack C7′, and significant R/S isomerization occurs. The calculation results can also explain the experimental observation that the ease of *R* to *S* isomerization of allenic carotenoids is peridinin > fucoxanthin > neoxanthin. Electrochemical experiments show that the radical cation and dication of fucoxanthin are unstable, which suggests that *R*/*S* isomerization of allenic carotenoids is not via their radical cations or dications. Furthermore, AM1 calculations show that *R*/*S* isomerization via the radical cations or dications is energetically unfavorable.

Introduction

About six hundred naturally occurring carotenoids have been isolated from higher plants, algae, microorganisms, and animals.[1] They play several essential roles in photosynthetic systems.[2−4] One role is to serve as photoprotection agents by quenching (bacterio)chlorophyll triplet states to prevent their reaction with molecular oxygen (which results in the formation of the damaging singlet oxygen) or directly reacting with singlet oxygen to detoxify it. Another role is to serve as light-harvesting antennae by absorbing light energy in the visible region of the spectrum, where (bacterio)chlorophylls are not efficient absorbers, and then transferring energy for use in photochemical events. It has also been suggested that carotenoids may act as anticancer agents,[5] probably because of their antioxidant and free radical quenching properties.[6,7]

In vivo, carotenoids can exist in various configurations, which affect their biochemical properties. For example, the photoprotection function of carotenoids is related to the transformation between the 15-*cis* and the all-*trans* configurations of the carotenoids bound in the photosynthetic reaction center.[8] Provitamin activity of carotenoids is also related to their configurations.[9] The geometrical isomerization (*cis*−*trans*) of carotenoids under various conditions has been extensively studied, although the mechanisms are still not clear. Photoinduced *cis*−*trans* isomerization of β-carotene and retinal was proposed to occur via their excited states (S_1 or T_1) in some studies.[10,11] However, some other studies showed that the *cis*−*trans* isomerization of β-carotene and some other polyenes does not occur via the S_1 and T_1 states.[12,13] When heating carotenoids, *cis*−*trans* isomerization can occur.[14,15] It was suggested that di-radical species are formed during the thermal isomerization. Electrochemical or chemical oxidation can also lead to *cis*−*trans* isomerization of carotenoids, which was found to occur through their radical cations or dications.[16] AM1 (Austin Model 1) semiempirical molecular orbital calculations showed that carotenoid radical cations and dications have much lower energy barriers to *cis*−*trans* isomerization than neutral species. After changing their configurations, radical cations and dications can become neutral species by electron transfer from excess neutral carotenoid and thus *cis*−*trans* isomerization may occur.[17]

For the allenic isomerization (*R*/*S*) of some allenic carotenoids (peridinin, fucoxanthin, and neoxanthin, see structures below[18]), it was found that an appropriate catalyst and strong light are necessary.[19] I_2, Ph_2Se_2, and Ph_2Te_2 have been used as catalysts.[19,20] *R*/*S* isomerizations of allenic carotenoids are always accompanied by *cis*−*trans* isomerizations of chain double bonds.

Recently, a mechanism was proposed for the Ph_2Se_2-catalyzed *R*/*S* isomerization,[19] in which a PhSe· radical attacks the central carbon (C7′) of the allene to form a C7′-SePh bond; C7′═C8′ thus becomes a single bond. Rotation around the C7′−C8′ bond allows subsequent *R*/*S* isomerization. The configuration generated after rotation can be stabilized by an intramolecular H-bond between Se and the H of the OH group on the cyclohexane ring which is linked to the allene bond. That mechanism served to explain the *R*/*S* ratio observed with a higher yield of the allenic *S*-isomers than when I_2 is used as the catalyst.[19] In the current work, a related radical mechanism is proposed to explain the I_2-catalyzed allenic *R*/*S* isomerization of peridinin, fucoxanthin, and neoxanthin. The difference of this mechanism from the previous one is that no H-bond can be formed and both C7′−C8′ and C7′−C6′ π bonds can be broken. For polyene and allenic carbon atoms in these carotenoids, the p_x orbitals are in the polyene plane and perpendicular to the chain. The p_z orbitals are also in the plane of the polyene but parallel to the

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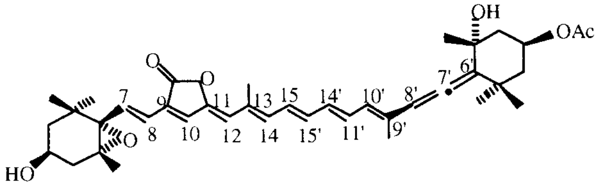
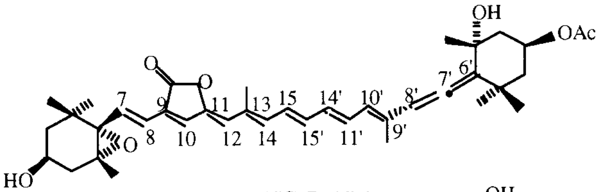
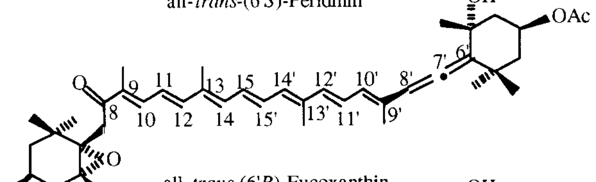
chain, whereas the p_y orbitals are perpendicular to the plane. Thus, polyene carbon atoms use their p_y orbitals to form π bonds. C8′ also uses its p_y orbital to form a π bond, while C7′ uses both p_x and p_y orbitals to form two orthogonal π bonds, and C6′ uses its p_x orbital to form a π bond. Attack of I· on the p_x orbital of C7′ will break the C7′−C6′ p bond, whereas attack on the p_y orbital of C7′ will break the C7′−C8′ p bond. Attack of I· on the p_x orbital of C7′ has less steric hindrance than attack on its p_y orbital. However, the allylic radical formed when the C7′−C8′ p bond is broken may be energetically more favorable, and I· can approach the p_y orbital of C7′ at an angle to decrease the steric hindrance. Therefore, both attacks are thought to be possible. Our AM1 calculations support the proposed mechanism. Electrochemical experiments, along with the AM1 calculations, show that *R*/*S* isomerization of allenic carotenoids is not via their radical cations or dications.



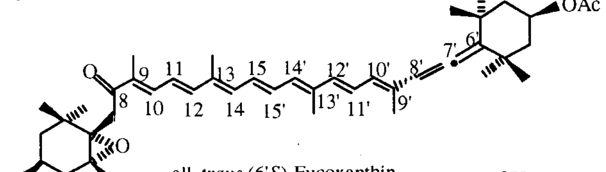
all-*trans*-(6′*R*)-Peridinin



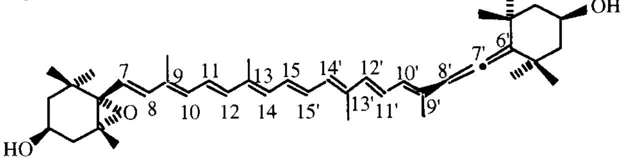
all-*trans*-(6′*S*)-Peridinin



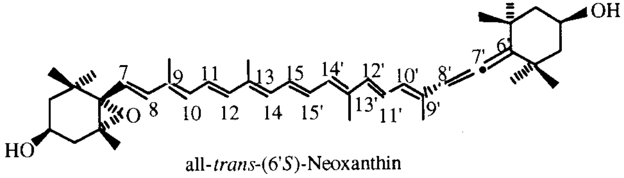
all-*trans*-(6′*R*)-Fucoxanthin



all-*trans*-(6′*S*)-Fucoxanthin



all-*trans*-(6′*R*)-Neoxanthin



all-*trans*-(6′*S*)-Neoxanthin

Experimental Section

All-*trans*-(6′*R*)-Fucoxanthin was isolated from the brown alga *Fucus serratus* by a previous procedure,[21] and has HPLC, optical absorption, MS, and ^{1}HNMR properties consistent with reported data.[21] It was stored under nitrogen over Drierite at −16 °C in a container that was wrapped with Parafilm and foil to avoid exposure to moisture and light. Prior to use, it was allowed to warm to room temperature. Anhydrous dichloromethane, purchased from Aldrich, was opened and kept in a drybox under a nitrogen atmosphere. All solutions used in electrochemical experiments were prepared in a drybox.

Cyclic voltammetry (CV) was carried out with the Bio Analytical System BAS-100W electrochemical analyzer. The working electrode was a platinum disk (diameter 1.6 mm), the counter electrode was a platinum wire, and SCE served as the reference electrode. The supporting electrolyte[17] was 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP, from Fluka). The solutions were purged with dry nitrogen to remove possible dissolved oxygen and kept under a nitrogen atmosphere.

AM1 semiempirical molecular orbital calculations were carried out using UniChem 4.0 software[22] on a Silicon Graphics computer.

Results and Discussion

Proposed R/S Isomerization Mechanism. I_2 can dissociate to I· under irradiation.[23] The generated I· then attacks C7′ to form a C−I single bond (C7′ uses its p_x or p_y orbital), so that the C7′−C8′ or C7′−C6′ bond becomes a single bond.[24] Upon rotation around this single bond and subsequent elimination of I·,[23] *R*/*S* isomerization occurs.

This mechanism accounts for the following experimental observations.

(1) At high I_2 concentration, in the dark, *R*/*S* isomerization occurs to only a very small extent during a long period of time.[19,25] For example, in benzene at room temperature, in the dark, only 8% of all-*trans*-(6′*R*)-peridinin becomes the 6′*S* isomer (all-*trans*-(6′*S*)-peridinin) in the presence of 208% (w/w) of I_2 (relative to peridinin) in 48 h.[25] In the presence of 1.8% (w/w) of I_2, also in the dark, no *R/S* isomerization occurs in 48 h.[25] However, in direct sunlight, in the presence of 1.8% (w/w) of I_2, the ratio of 6′*S* isomers to 6′*R* isomers is 46:54.[25] Strong light is essential for the *R*/*S* isomerization. This is because I· is generated to a significant extent only in the presence of light.

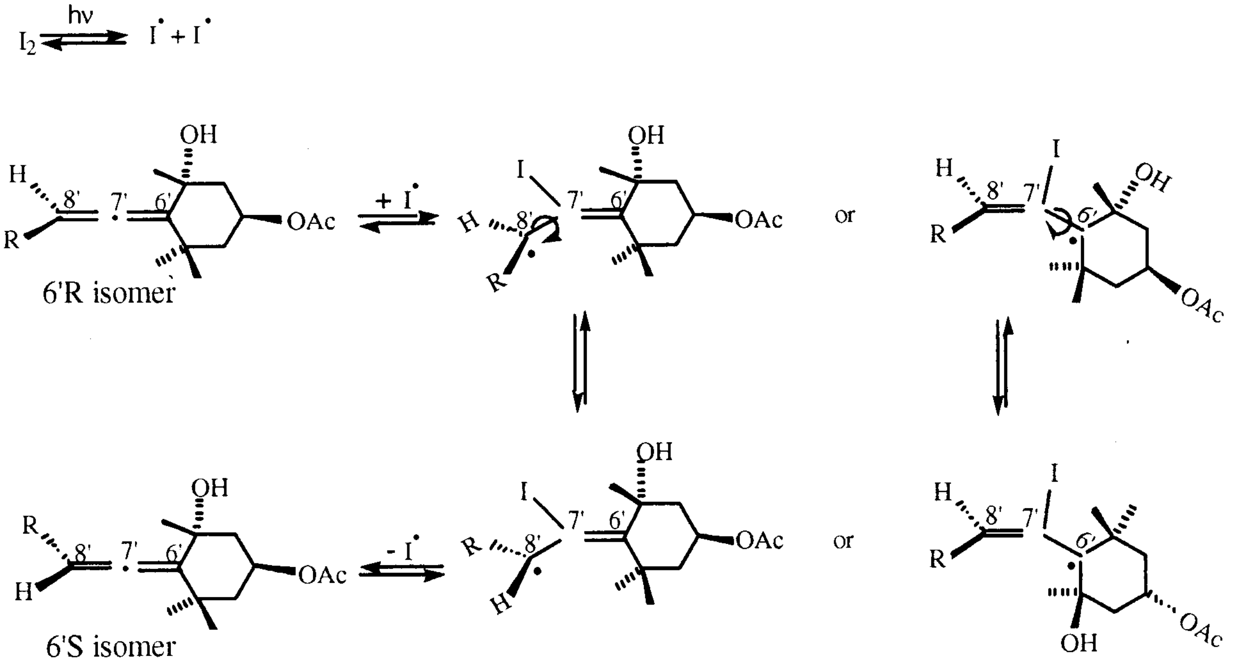
(2) I_2 is also essential for the *R*/*S* isomerization.[19,25−27] For example, in the absence of I_2, only 2% of all-*trans*-(6′*R*)-peridinin becomes the 6′S isomer (all-*trans*-(6′*S*)-peridinin) in 3 h in benzene under direct sunlight.[25] Presumably, attack of I· on C7′ causes the C7′−C8′ or C7′−C6′ π bond to break (or form a partial bond with I in a transition state), which greatly facilitates rotation around these bonds. Rotation and subsequent elimination of I· can change the configuration of allenic carotenoids from 6′*R* to 6′*S* (or from 6′*S* to 6′*R*).

(3) At high light intensity, the *R*/*S* isomerization rate is increased at higher I_2 concentrations.[19] For example, as the I_2 concentration is increased from 1.8% to 18% (w/w, relative to peridinin), the time for peridinin *R/S* isomerization to reach an equilibrium is shortened from 3 h to 1 h.[19] The higher I_2 concentration generates a larger I· concentration, which increases the subsequent isomerization rate.

(4) The most effective irradiation wavelength corresponds to light absorbed by I_2, not by carotenoids.[19,28] In hexane, the effective irradiation wavelength range is 450−600 nm, which is the I_2 absorption range.

Rationale for Two Experimental Phenomena. (1) UV light has only a small effect on the I_2-catalyzed *R*/*S* isomerization. On the other hand, Ph_2Se_2-catalyzed *R*/*S* isomerization is considerably affected.[19]

When using 18% (w/w) I_2 as the catalyst, *R/S* isomerization of peridinin reaches equilibrium in 1 h, no matter whether visible plus UV light or visible light alone is used, provided that both light sources have the same visible light intensity.[19] Furthermore, Mechanism



the ratio of 6′*S* to 6′*R* isomers is also very similar at equilibrium. However, in the case of Ph_2Se_2, the ratio of 6′*S* to 6′*R* isomers is increased four times in the presence of UV light.[19] Since I_2 has two absorption maxima at 500 nm (extinction coefficient: ca. 870 L mol^{-1} cm^{-1}) and 300 nm (extinction coefficient: ca. 7300 L mol^{-1} cm^{-1}) in benzene (Figure 1), no matter which light is used, visible light or both UV and visible light, I_2 will be excited and dissociated to initiate *R*/*S* isomerization. Thus, varying the wavelength of the light has little effect on the *R*/*S* isomerization.

Ph_2Se_2 has only one absorption maximum at 330 nm (benzene). Removing (or applying) the UV light source will reduce (or enhance) the excitation of Ph_2Se_2 and the production of PhSe·. Thus, *R*/*S* isomerization will be affected.

(2) A radical inhibitor (hydroquinone, HQ) has no obvious effect on the I_2-catalyzed *R*/*S* isomerization (using high intensity visible light irradiation). Only when high concentrations of HQ are used (10 mol equivalents relative to I_2), is there a small effect (the concentration of the 6′*S* isomer of peridinin is increased by ca. 16%).[19] This is probably because the reaction between I· and carotenoids is fast, while the reaction between I· and HQ is relatively slow.

AM1 Calculations. AM1 calculations of charge density on each carbon atom (equals 4-q_c where q_c is the sum of the atomic orbital electron density in the σ, p_x, p_y, and p_z orbitals) show that C7′ has the highest electron density among polyene and allenic carbons (Figures 2−4, except that C10′ of all-*trans*-(6′*S*)-peridinin has a charge density very similar to that of C7′), which promotes the formation of a bond between I· and C7′ in preference to I· and other carbon atoms (see below). Thus, *R*/*S* isomerization occurs to a significant extent together with the *cis*−*trans* isomerization of some chain double bonds.

Because a π bond is much easier to break than a σ bond, p_y orbital electron densities of C9−C7′ (fucoxanthin) or C7−C7′ (peridinin and neoxanthin) and p_x orbital electron densities of C7′ and C6′ may be more important for bond formation with I·. The p_y orbitals of C9′−C8′ of fucoxanthin (or C7′−C8′ of peridinin and neoxanthin) and the p_x orbital of C6′ are used to form π bonds, while C7′ uses both its p_x and p_y orbitals to form two π bonds with C6′ and C8′. The electron density in these orbitals determines the ease of the bond formation with I· and the strength of the formed bonds. Higher electron density facilitates bond formation and results in stronger C−I bonds. If these orbital electron densities are considered and taking into account the fact that C7′ has two π bonds, C7′ is still expected to react more easily with I· than other carbon atoms (Tables 1−6); thus, there is significant *R*/*S* isomerization. For all-*trans*-(6′*R*) and (6′*S*)-peridinin, the p_y orbital of C7′ has the highest electron density (Tables 1 and 2). For all-*trans*-(6′*R*)-fucoxanthin, p_x of C7′ has the highest electron density, except for p_y of C8′, and the electron density of p_y of C7′ is also among the several highest (Table 3). For all-*trans*-(6′*S*)-fucoxanthin, the electron density of p_x of C7′ is among the several highest (Table 4). For all-*trans*-(6′*R*)-neoxanthin, p_y has a medium electron density (Table 5). For all-*trans*-(6′*S*)-neoxanthin, p_y has the highest electron density (Table 6).

Considering the charge density and orbital electron density, along with the fact that C7′ has two π bonds, the most likely position for attack by I· is C7′. *R*/*S* isomerization therefore occurs to a significant extent. For peridinin, *R*/*S* isomerization is even more efficient than *cis*−*trans* isomerization in the presence of I_2 and strong light.[25,29] For example, after 2.5 h exposure of all-*trans*-(6′*R*)-peridinin in benzene to direct sunlight in the presence of 1.8% I_2 (w/w, relative to peridinin), there are 26% all-*trans*-6′*S*, 10% 9′-*cis*-6′*S*, 9% 11-*cis*-6′*S*, 4% 13-*cis*-6′*S*, 10% 9′-*cis*-6′*R*, 6% 11-*cis*-6′*R*, and 3% 13-*cis*-6′*R* isomers.[25] At equilibrium, there are 51% *R*-/49% *S*-isomers and 58% trans/42% cis isomers.

It should be clarified that I· can also attack some of the other polyene and allenic carbons, but each has a smaller probability than C7′, although the total probability of these atoms may be larger than C7′. There are other products, in addition to those from *R*/*S* isomerization. The C7′−I bond formation is preferable, but not exclusive, That is *R*/*S* isomerization of allenic carotenoids is always accompanied by *cis*−*trans* isomerizations of chain double bonds.

The orbital electron density calculations of the 6′*R*-isomers can also explain the experimental observation that the ease of *R*-to-*S* isomerization of three allenic carotenoids is peridinin > fucoxanthin > neoxanthin.[20] For example, for neoxanthin, in

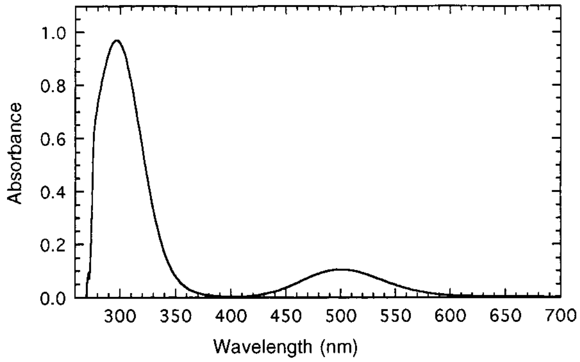


Figure 1. Optical absorption spectrum of 0.133 mM I_2 in benzene. 1 cm optical path length.

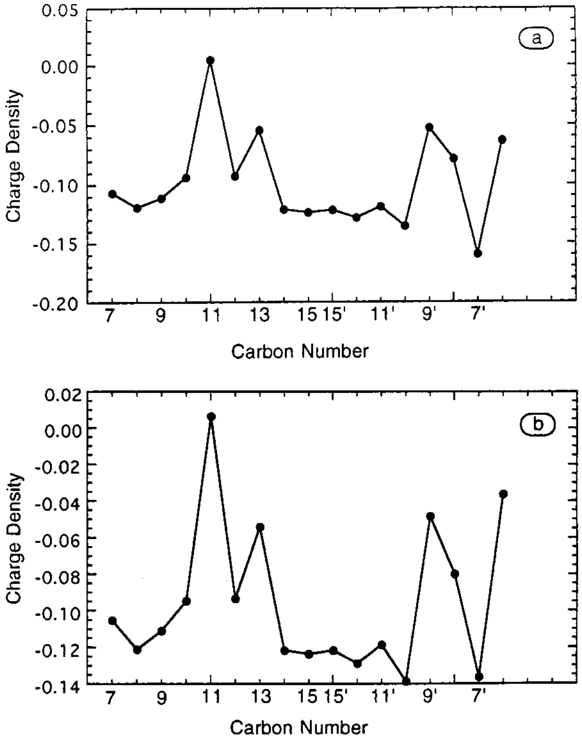


Figure 2. Charge density on carbons of (a) all-*trans*-(6′*R*)-peridinin, (b) all-*trans*-(6′*S*)-peridinin calculated by the AM1 method.

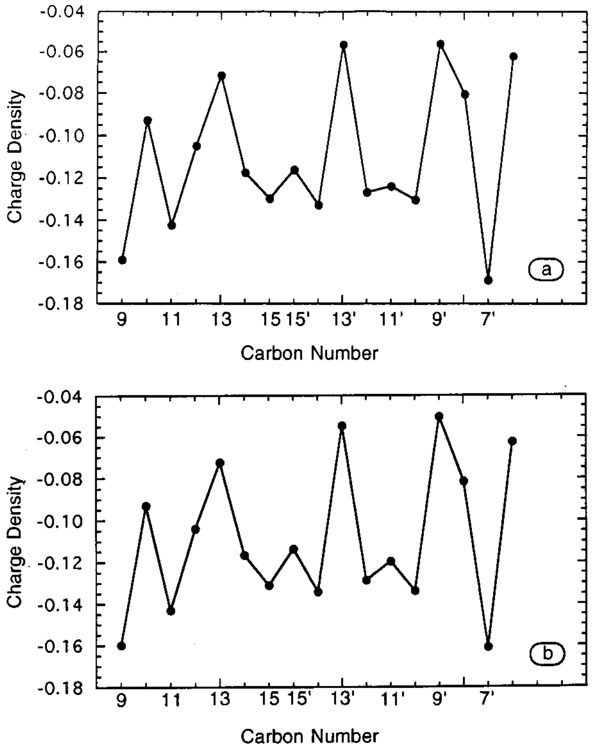


Figure 3. Charge density on carbons of (a) all-*trans*-(6′*R*)-fucoxanthin, (b) all-*trans*-(6′*S*)-fucoxanthin calculated by the AM1 method.

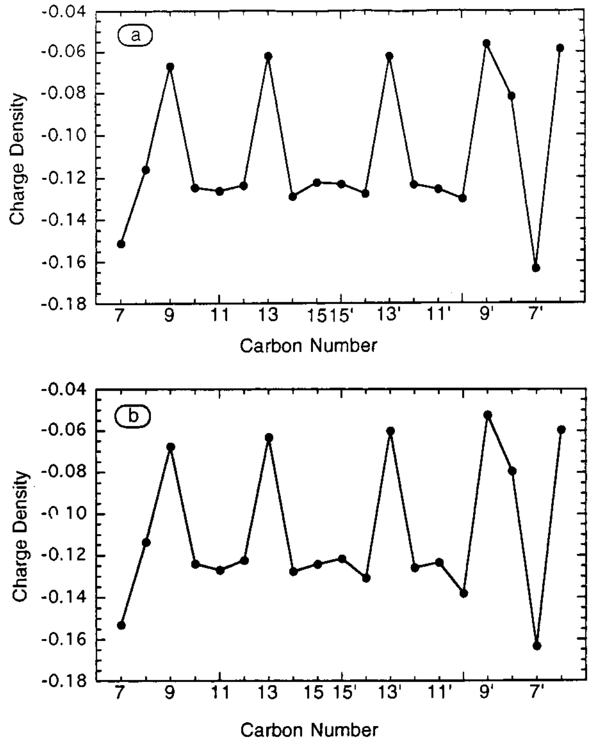


Figure 4. Charge density on carbons of (a) all-*trans*-(6′*R*)-neoxanthin, (b) all-*trans*-(6′*S*)-neoxanthin calculated by the AM1 method.

the presence of 2% (w/w) of I_2, in direct sunlight for 4 h, no *R*-to-*S* isomerization was observed; in the presence of 20% (w/w) of I_2, 40% 6′*R* isomer becomes the 6′*S* isomer.[20] For peridinin, in direct sunlight for 3 h, in the presence of 1.8% (w/w) of I_2, 46% 6′*R* isomer becomes the 6′*S* isomer.[25]

Radical Cations and Dications. Electrochemical experiments show that radical cations and dications of all-*trans*-(6′*R*)-fucoxanthin are unstable. Figure 5 shows the CV of all-*trans*-(6′*R*)-fucoxanthin in CH_2Cl_2. According to previous results from coulometry and rapid CV scan measurements for other carotenoids,[16,17] waves 1 and 2 correspond to the oxidation of the neutral species to the radical cation and the radical cation to the dication, respectively; whereas waves three and four correspond to the reduction of the dication to the radical cation and the radical cation to the neutral species, respectively. The CV shows irreversible behavior compared to that of canthaxanthin or β-carotene,[16] indicating that the radical cation and dication are not stable. At the same time, there are two reduction waves at lower potentials (waves 5 and 6), which are attributed to the reduction of decay products of the radical cation and/or the dication as shown by previous electrochemical studies of carotenoids.[16] In simultaneous bulk electrolysis and EPR experiments, only a very weak radical signal was observed (data not shown). The instability of the radical cations and dications of fucoxanthin suggests that *R*/*S* isomerization does not proceed through these species. In fact, for other carotenoids, there are few radical cations generated upon the addition of I_2.[30] Furthermore, AM1 calculations show that the energy barriers for rotation around the allenic bonds of the radical cations and

TABLE 1: Carbon Atomic Orbital Electron Densities of all-*trans*-(6′*R*)-Peridinin

	s	p_x	p_y	p_z
C7	1.228	0.937	0.982	0.960
C8	1.204	0.933	0.952	1.030
C9	1.202	0.933	0.920	1.056
C10	1.234	0.951	0.950	0.959
C11	1.210	0.862	0.879	1.043
C12	1.212	0.928	0.957	0.995
C13	1.195	0.940	0.919	1.000
C14	1.216	0.942	0.959	1.004
C15	1.215	0.949	0.958	1.001
C15′	1.218	0.949	0.959	0.996
C14′	1.217	0.950	0.958	1.003
C11′	1.216	0.948	0.959	0.995
C10′	1.216	0.942	0.959	1.019
C9′	1.198	0.935	0.924	0.996
C8′	1.193	0.921	0.944	1.021
C7′	1.222	0.939	1.005	0.994
C6′	1.203	0.905	1.001	0.955

TABLE 2: Carbon Atomic Orbital Electron Densities of all-*trans*-(6′*S*)-Peridinin

	s	p_x	p_y	p_z
C7	1.228	0.937	0.986	0.958
C8	1.204	0.933	0.952	1.032
C9	1.202	0.933	0.921	1.055
C10	1.234	0.951	0.950	0.960
C11	1.210	0.862	0.880	1.042
C12	1.212	0.928	0.957	0.996
C13	1.195	0.940	0.920	0.999
C14	1.216	0.942	0.959	1.004
C15	1.215	0.949	0.958	1.001
C15′	1.210	0.949	0.959	0.996
C14′	1.217	0.950	0.958	1.004
C11′	1.216	0.948	0.960	0.995
C10′	1.216	0.942	0.959	1.021
C9′	1.198	0.935	0.923	0.993
C8′	1.193	0.918	0.946	1.023
C7′	1.221	0.936	0.987	0.991
C6′	1.192	0.897	1.013	0.934

TABLE 3: Carbon Atomic Orbital Electron Densities of all-*trans*-(6′*R*)-Fucoxanthin

	s	p_x	p_y	p_z
C9	1.219	0.969	1.003	0.968
C10	1.214	0.974	0.969	0.936
C11	1.216	0.974	0.999	0.954
C12	1.221	0.971	0.969	0.944
C13	1.197	0.941	0.994	0.940
C14	1.215	0.984	0.984	0.934
C15	1.216	0.984	0.994	0.936
C15′	1.217	0.985	0.983	0.932
C14′	1.215	0.982	1.009	0.926
C13′	1.197	0.942	0.989	0.927
C12′	1.221	0.970	0.999	0.937
C11′	1.216	0.973	0.997	0.938
C10′	1.216	0.973	1.010	0.932
C9′	1.198	0.934	0.994	0.930
C8′	1.194	0.959	1.015	0.912
C7′	1.222	1.012	1.001	0.933
C6′	1.204	1.004	0.959	0.894

TABLE 4: Carbon Atomic Orbital Electron Densities of all-*trans*-(6′*S*)-Fucoxanthin

	s	p_x	p_y	p_z
C9	1.218	0.976	1.022	0.943
C10	1.216	0.974	0.980	0.922
C11	1.216	0.978	1.014	0.935
C12	1.222	0.970	0.980	0.931
C13	1.198	0.949	0.997	0.928
C14	1.217	0.985	0.995	0.920
C15	1.216	0.987	1.004	0.924
C15′	1.216	0.985	0.989	0.924
C14′	1.215	0.988	1.011	0.920
C13′	1.198	0.947	0.981	0.928
C12′	1.220	0.975	1.004	0.929
C11′	1.215	0.977	0.997	0.930
C10′	1.215	0.979	1.015	0.924
C9′	1.198	0.937	0.989	0.926
C8′	1.194	0.969	1.019	0.898
C7′	1.223	1.014	0.994	0.929
C6′	1.200	1.012	0.957	0.893

TABLE 5: Carbon Atomic Orbital Electron Densities of all-*trans*-(6′*R*)-Neoxanthin

	s	p_x	p_y	p_z
C7	1.223	0.931	1.020	0.976
C8	1.220	0.937	0.985	0.974
C9	1.198	0.929	1.003	0.937
C10	1.217	0.952	1.005	0.951
C11	1.215	0.953	1.003	0.955
C12	1.220	0.950	1.000	0.954
C13	1.198	0.936	0.993	0.936
C14	1.215	0.965	1.009	0.939
C15	1.215	0.964	0.998	0.945
C15′	1.216	0.965	0.998	0.945
C14′	1.215	0.962	1.004	0.946
C13′	1.196	0.940	0.983	0.943
C12′	1.220	0.947	0.998	0.960
C11′	1.215	0.950	0.999	0.961
C10′	1.215	0.949	1.004	0.963
C9′	1.197	0.931	0.975	0.953
C8′	1.194	0.932	1.002	0.954
C7′	1.221	0.987	1.000	0.955
C6′	1.202	0.968	0.972	0.916

TABLE 6: Carbon Atomic Orbital Electron Densities of all-*trans*-(6′*S*)-Neoxanthin

	s	p_x	p_y	p_z
C7	1.223	0.980	0.984	0.966
C8	1.219	0.957	0.993	0.944
C9	1.198	0.961	0.945	0.964
C10	1.216	0.957	0.992	0.958
C11	1.215	0.962	0.992	0.958
C12	1.220	0.958	0.989	0.955
C13	1.197	0.955	0.948	0.962
C14	1.216	0.953	0.992	0.966
C15	1.216	0.954	0.992	0.962
C15′	1.216	0.953	0.992	0.961
C14′	1.216	0.958	0.991	0.966
C13′	1.197	0.956	0.946	0.960
C12′	1.219	0.954	0.989	0.964
C11′	1.215	0.952	0.993	0.963
C10′	1.216	0.955	0.989	0.977
C9′	1.198	0.946	0.948	0.959
C8′	1.193	0.910	0.991	0.986
C7′	1.223	0.935	1.009	0.997
C6′	1.203	0.897	0.991	0.968

dications of fucoxanthin are high and only slightly lower than that of the neutral species (for all-*trans*-(6′*R*)-fucoxanthin, radical cation: 81.3 kcal/mol, dication: 74.2 kcal/mol, neutral species: 84.0 kcal/mol). For these reasons, we suggest that *R*/*S* isomerization does not occur via radical cations or dications.

Previous studies in our group showed that *cis*−*trans* isomerization of β-carotene and canthaxanthin can occur via their radical cations and dications,[16] which have much lower energy barriers to rotation than neutral species. For example, for β-carotene, from AM1 calculations, the relative energy barrier is 24.6 kcal/mol for the radical cation, 3.9 kcal/mol for the dication, and 56.9 kcal/mol for the neutral species[16] (experimentally 27 kcal/mol[15] for the neutral species). Furthermore, the radical cations and dications of β-carotene and canthaxanthin are relatively stable.[16]

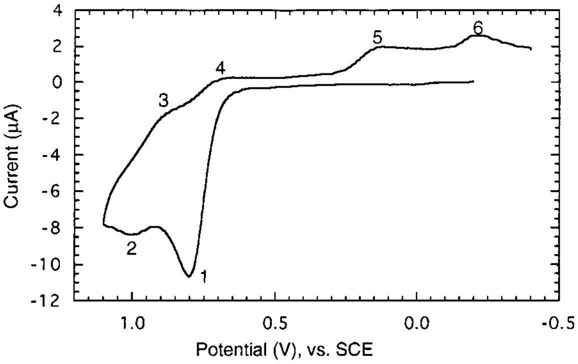


Figure 5. CV of all-*trans*-(6′*R*)-fucoxanthin in CH_2Cl_2. Working electrode: Pt disk (1.6 mm diameter); reference electrode: SCE; counter electrode: Pt wire. Supporting electrolyte: 0.1 M TBAHFP. Scan rate: 0.1 V s^{-1}.

***cis*−*trans* Isomerization of Allenic Carotenoids in the Dark.** The fact that *cis*−*trans* isomerization of allenic carotenoids can occur in the presence of I_2 in the dark[25] suggests that there is another *cis*−*trans* isomerization mechanism, besides that through attack of I· (light-induced I_2-catalyzed isomerization). This mechanism is not via a radical cation intermediate, because the amount of radical cations generated by I_2 depends primarily on the amount of I_2 used.[30] Experimental observations have shown that *cis*−*trans* isomerization of peridinin in the dark is almost independent of the amount of I_2.[25] After 48 h stereoisomerization of all-*trans*-(6′*R*)-peridinin in benzene in the dark, in the presence of 1.8% I_2 (w/w, relative to peridinin), there were 25% 9′-*cis*-6′*R*, 5% 11-*cis*-6′*R*, and 1% 13-*cis*-6*R* isomers (total of 31% 6′*R*-isomers); whereas in the presence of 208% I_2, there were 28% 9′-*cis*-6′*R*, 7% 11-*cis*-6′*R*, and 3% 13-*cis*-6′*R* isomers (total of 38% 6′*R*-isomers).[25] In addition to this, their radical cations are unstable. Further work is necessary to establish this *cis*−*trans* isomerization mechanism.

Conclusion

The *R*/*S* isomerization of allenic carotenoids does not occur via their radical cations or dications. AM1 calculations support the *R*/*S* isomerization mechanism which involves attack of I· on their C7′ to break (or weaken) the C7′−C8′ or C7′−C6′ π bond. This mechanism can explain the experimental observations.

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