

# Effects of Polyene Chain Length and Acceptor Substituents on the Stability of Carotenoid Radical Cations

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Received: December 20, 1999; In Final Form: March 24, 2000

The stability of radical cations of three series of carotenoids substituted with terminal ester, aldehyde, and cyano groups and with different numbers of backbone double bonds was studied by electrochemical and optical methods. The ethyl esters are 8'-apo- $\beta$ -caroten-8'-oate (**I**), 6'-apo- $\beta$ -caroten-6'-oate (**II**), and 4'-apo- $\beta$ -caroten-4'-oate (**III**); the aldehydes are 8'-apo- $\beta$ -caroten-8'-al (**IV**), 6'-apo- $\beta$ -caroten-6'-al (**V**), and 4'-apo- $\beta$ -caroten-4'-al (**VI**); and the cyano compounds are 8'-apo- $\beta$ -caroten-8'-nitrile (**VII**), 6'-apo- $\beta$ -caroten-6'-nitrile (**VIII**), and 4'-apo- $\beta$ -caroten-4'-nitrile (**IX**). Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) results indicate that the stability of carotenoid radical cations depends on the number of conjugated chain double bonds. For the esters, the longer the olefin chain, the more unstable the radical cations. In contrast, for the aldehydes and the nitriles, the stability of the radical cations is similar or varies slightly with backbone chain length. The half-lives, determined by stop-flow, and the decay rate of optical absorption of the radical cations generated by reaction with ferric chloride are: **I**, 202; **II**, 125; **III**, 2.35; **IV**, 149; **V**, 167; **VI**, 257; **VII**, 227; **VIII**, 158; and **IX**, 133 (s). AM1 molecular orbital calculations predict a large decrease in the dipole moments between radical cations and the neutral aldehydes and nitriles, but an increase for the esters as the number of chain double bonds increases. Radical cations with larger dipole moments have shorter lifetimes. It is likely that stronger interactions of the radical cation dipoles with the solvent dipoles result in enhanced decay of the radical cations. For esters, aldehydes, and nitriles, the shorter the olefin chain, the more difficult is the oxidation. The UV-vis optical absorption spectra of the carotenoids containing aldehyde groups in solvents of different polarity exhibit intramolecular charge transfer (ICT) phenomena, and their optical spectra are sensitive to the polarity of the solvents. In contrast, the esters do not show this behavior.

## Introduction

It is well established that carotenoids play important roles in photosynthetic systems because they serve as photoprotecting agents and light-harvesting antenna pigments.<sup>1–3</sup> Certain carotenoids have important biochemical and biological functions, such as providing the essential provitamin A compounds.<sup>4</sup> Carotenoids are also good antioxidants<sup>5</sup> and have been implicated in cancer prevention and treatment,<sup>6</sup> the efficacy of which may be due to their free-radical-quenching activity,<sup>7</sup> their immune enhancement effect,<sup>8</sup> and their in vivo function as antioxidants.<sup>7,9</sup> Other research has shown that carotenoid radical cations can play an active role in photodriven electron transport processes,<sup>10–12</sup> and that they are present in the photosystem II reaction center.<sup>13</sup> It is therefore of fundamental interest to study the formation and decomposition of carotenoid radical cations as well as their stability and the factors that influence it. Methods of generating carotenoid radical cations include chemical,<sup>14–18</sup> photochemical,<sup>19</sup> acid-induced,<sup>20</sup> and electrochemical oxidation.<sup>21,22</sup> Modification of carotenoids by substitution with electron-accepting and -donating terminal groups provides interesting molecules for this purpose. Studies by electrochemical oxidation in dichloromethane solution<sup>22,23</sup> of more than 10 carotenoids containing various donor/acceptor substituents but the same number of chain double bonds indicate that, in general, the stronger the electron-accepting nature of the substituent, the

more difficult it is to oxidize the compound, and the more stable is the radical cation. In addition to the electrochemical properties, the photophysical properties of donor/acceptor-substituted polyenes and carotenoids (push-pull polyenes) have been studied.<sup>24–28</sup> However, studies of the effect of the conjugated backbone length on the electrochemical properties of carotenoids containing donor/acceptor substituents are scarce, although the electronic structures and photophysical properties of polyenes and carotenoids with 3–19 conjugated double bonds have been investigated.<sup>29–31</sup> In this study, the properties of three series of carotenoids substituted with terminal ester, aldehyde, and cyano groups with 8–10 conjugated polyene double bonds were investigated by voltammetry and optical spectroscopy. The effect of the olefin chain length on the radical cation stability was ascertained. AM1 calculations of the dipole moments of the neutral species and radical cations were carried out, and the dependence of the radical cation stability on its (gas-phase) dipole was explored.

## Experimental Section

All-*trans* ethyl 8'-apo- $\beta$ -caroten-8'-oate (**I**) and 8'-apo- $\beta$ -caroten-8'-al (**IV**) were generously provided by Hoffmann-La Roche (Basel) and Roche Vitamins and Fine Chemicals (Nutley, NJ), respectively (for structures, see Table 1). Ethyl 6'-apo- $\beta$ -caroten-6'-oate (**II**) was prepared by Wittig reaction of **IV** with  $(\text{Ph}_3\text{PCH}_2\text{CO}_2\text{Et})^+\text{Cl}^-$  ( $\text{CH}_2\text{Cl}_2$ , aq 10%  $\text{K}_2\text{CO}_3$ , 3 d, rt); 6'-apo- $\beta$ -caroten-6'-nitrile (**VIII**) was formed from **IV** and diethyl

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**TABLE 1: Data Derived from Simulation of Cyclic Voltammograms<sup>a</sup>**

compounds	E <sub>1</sub> (mV)	E <sub>2</sub> (mV)	ΔE (mV)	E <sub>3</sub> (mV)
Ethyl 8'-apo-β-caroten-8'-oate (I)	722±2	875±5	153	205±15
Ethyl 6'-apo-β-caroten-6'-oate (II)	692±32	795±25	103	130±20
Ethyl 4'-apo-β-caroten-4'-oate (III)	600±15	630±9	30	70±25
8'-apo-β-caroten-8'-al (IV)	720±10	865±25	145	75±25
6'-apo-β-caroten-6'-al (V)	653±23	778±22	125	230±20
4'-apo-β-caroten-4'-al (VI)	625±10	695±15	70	235±10
8'-apo-β-carotene-8'-nitrile (VII)	722±20	864±25	142	272±20
6'-apo-β-carotene-6'-nitrile (VIII)	672±15	785±20	113	245±15
4'-apo-β-carotene-4'-nitrile (IX)	660±15	700±20	100	250±15

<sup>a</sup> E<sub>1</sub>, E<sub>2</sub>, and E<sub>3</sub> are the redox potentials for the first, second, and third waves, respectively. ΔE is the difference between E<sub>2</sub> and E<sub>1</sub>.

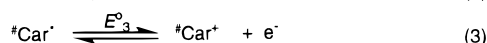
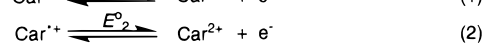
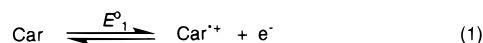
cyanomethyl phosphonate (THF, NaH, 10 min, rt); 6'-apo-β-caroten-6'-al (V) was obtained by Wittig reaction of IV with Ph<sub>3</sub>P=CHC(O)N(OCH<sub>3</sub>)CH<sub>3</sub> (PhH, 3 d, 65 °C) followed by reductive cleavage with DIBAL-H (THF, -78 °C, 1 h). Ethyl 4'-apo-β-caroten-4'-oate (III), 4'-apo-β-caroten-4'-al (VI), and 4'-apo-β-caroten-4'-nitrile (IX) were similarly prepared from V. 8'-Apo-β-caroten-8'-nitrile (VII) was obtained by dehydration of the 8'-aldoxime with (CF<sub>3</sub>CO)<sub>2</sub>O (THF, Et<sub>3</sub>N, rt, 10 min; then 60 °C, 3 h). According to NMR analysis, purification of the crude products by treatment with MeOH and/or column chromatography (silica gel) of the insolubles gave pure all-*E* isomers of II, III, V, and VIII. Compounds VI and IX were mixtures of the all-*E* and the 5'-*Z* isomers: VI, 85% all-*E*; IX, two fractions: 85% all-*E* and 85% 5'-*Z*.<sup>32</sup> Tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) of polarographic grade was purchased from Fluka. Anhydrous dichloromethane (99+%), cyclohexane, acetonitrile, ethanol, and ferric chloride were obtained from Aldrich.

Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) were carried out using the Bio Analytical Systems BAS-100W electrochemical analyzer. A platinum disk electrode (diameter: 1.6 mm) was used as the working electrode, the auxiliary electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE).

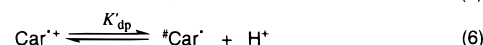
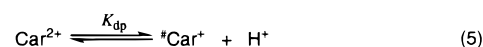
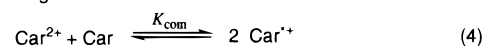
Optical absorption spectra in the range of 190 to 1100 nm were measured using a Shimadzu UV-1601 spectrophotometer. Quartz cuvettes (1-cm optical path length) were used for spectral measurements. Optical absorbance decrease of the carotenoid radical cations, generated by oxidation with ferric chloride, was measured using a flow cell (Shimadzu, 1-cm optical path length and 3-mm diameter) by stop-flow. A carotenoid solution (2 mL, 15 μM) and a ferric chloride solution (2 mL, 15 μM), contained in two separate syringes, were simultaneously injected into the flow cell through a tee, and the optical absorbance change of the carotenoid radical cation was recorded.

**SCHEME 1**

Electrode reactions



Homogeneous reactions



\*Car represents the carotenoid with one less proton

All measurements were carried out at room temperature (ca. 23 °C). For CV and OSWV measurements, dichloromethane solutions of 0.1 M TBAHFP and 1.0 mM carotenoids were used. Dichloromethane solutions of 15 μM carotenoids were used for optical spectral measurements. Saturated stock solutions of ferric chloride in dichloromethane (≈45 μM) were diluted to 15 μM. All solutions were prepared in a drybox under a nitrogen atmosphere at room temperature.

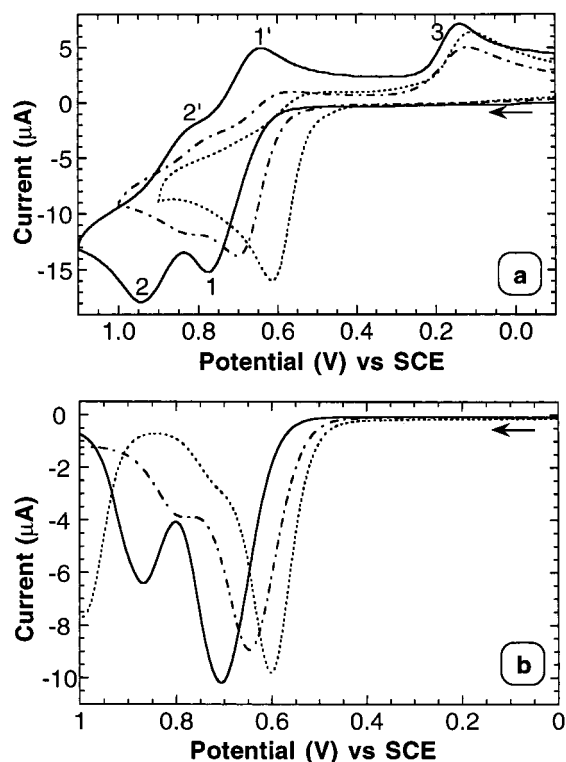
AM1 (Austin Model 1) semiempirical molecular orbital calculations<sup>33</sup> were carried out using HyperChem software<sup>34</sup> on a Gateway 2000 P5-60 (Pentium) personal computer. Digital simulations of the CVs were performed using the DigiSim program<sup>35</sup> on the same PC.

**Results**

**Cyclic and Square Wave Voltammetry.** Earlier studies of carotenoids revealed that during an electrochemical oxidation–reduction cycle, not only radical cations, but also dications, cations (loss of one H<sup>+</sup> from dications), and neutral radicals can be formed, and the electrode and homogeneous reactions shown in Scheme 1 have been established.<sup>17,21–23,36–38</sup>

The electrochemical oxidation–reduction reactions of many carotenoids are quasi-reversible or reversible, so that the CVs display comparable, symmetrical anodic and cathodic waves. For example, the cyclic voltammogram in dichloromethane of canthaxanthin consists of two pairs of separate anodic and cathodic waves (ΔE° = E°<sub>2</sub> – E°<sub>1</sub> ≈ 200 mV). As the stability of the radical cation decreases, the CV displays only a small or no second anodic wave (wave 2); the same is true for the reversal cathodic waves (waves 1' and 2').

The CVs of the esters, compounds I–III, are shown in Figure 1a. The CV of I, Figure 1a (solid line), exhibits two separate waves (waves 1 and 2) during the anodic scan, which correspond to the oxidation of the neutral species and the resulting radical cations, respectively. During the cathodic scan, in addition to the two reverse waves (waves 2' and 1') which correspond to the reduction of the dications and the radical cations, an additional reduction wave (wave 3) near 0.1 V is present, and this is attributed to the reduction of <sup>\*</sup>Car<sup>+</sup> (eq 3, Scheme 1). The CV of II (Figure 1a, chained line) shows that the relative magnitude of wave 2, as well as those of waves 2' and 1', decreases. Decreases in wave 2 and its reverse wave 2' indicate that these radical cations are more unstable. The decrease in wave 2 is even more pronounced in the CV of III (Figure 1a, dotted line) in which waves 2, 2', and 1' are absent, i.e., an irreversible CV occurs. The decrease of wave 2 of I–III can be more clearly observed in OSWVs (Figure 1b). The voltammetry results show that the stability of the radical cations of



**Figure 1.** (a) Cyclic voltammograms of compounds **I** (solid line), **II** (chained line), and **III** (dotted line). Dichloromethane solutions of 0.1 M TBAHFP and 1.0 mM carotenoids. Scan rate: 100 mV/s. (b) Osteryoung square wave voltammograms of compounds **I** (solid line), **II** (chained line), and **III** (dotted line). The arrows indicate the potential scanning direction.

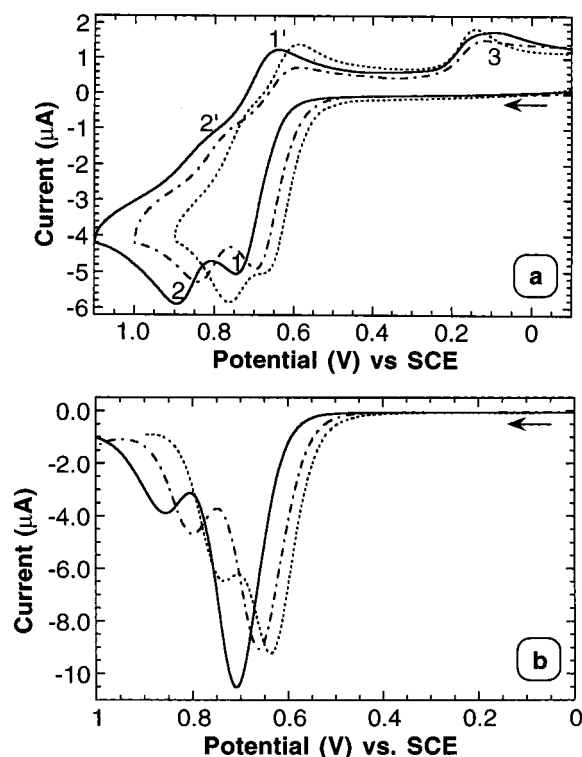
**I–III** decreases in the sequence of **I**, **II**, and **III**; i.e., the longer the conjugated backbone, the less stable the radical cations.

The CVs of the aldehydes, **IV–VI**, are shown in Figure 2a. In contrast to those of the esters, the CVs of these aldehydes show similar magnitudes of waves 2. OSWVs of **IV–VI** (Figure 2b) show the same behavior. These results indicate that there is little difference or only a small increase in the stabilities of radical cations of **IV–VI** (see Discussion). Therefore, the stability of the carotenoid radical cations depends on both the length of the conjugated backbone and the type of terminal substituent.

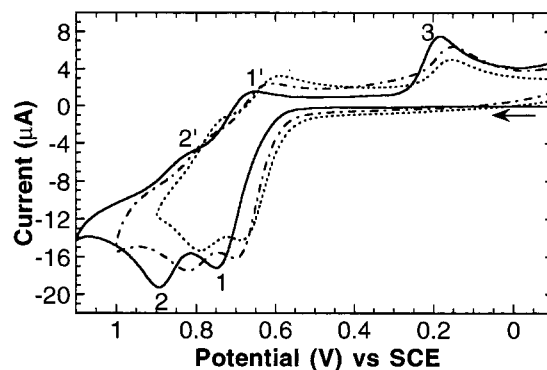
CVs of another series of carotenoids, **VII–IX**, are shown in Figure 3. The CVs of nitriles **VII–IX** display features very similar to those of aldehydes **IV–VI**, (see Figure 2a), indicating that the stabilities of radical cations of **VII–IX** are similar to those of aldehydes.

Digital simulations of the CVs using the DigiSim program<sup>35</sup> resulted in the redox potentials and other relevant data listed in Table 1. Note that the oxidation potentials for the first and second waves increase as the length of the conjugated chain decreases; in other words, the shorter the olefin chain, the more difficult the oxidation.

**Optical Absorption Spectra in Solvents of Different Polarity.** Optical absorption spectra of compounds **I–VI** in three solvents of increasing polarity—cyclohexane (relative polarity 0.04), acetonitrile (0.65), and ethanol (0.88)—are shown in Figures 4 and 5. For **I–III**, the spectra show no large variation except that considerable fine structures occur only in the least polar solvent, cyclohexane; the absorption maxima are red shifted by about 16 nm with each additional double bond. It is evident that the spectra of the esters, which are substituted with weakly electron accepting groups, are not sensitive to



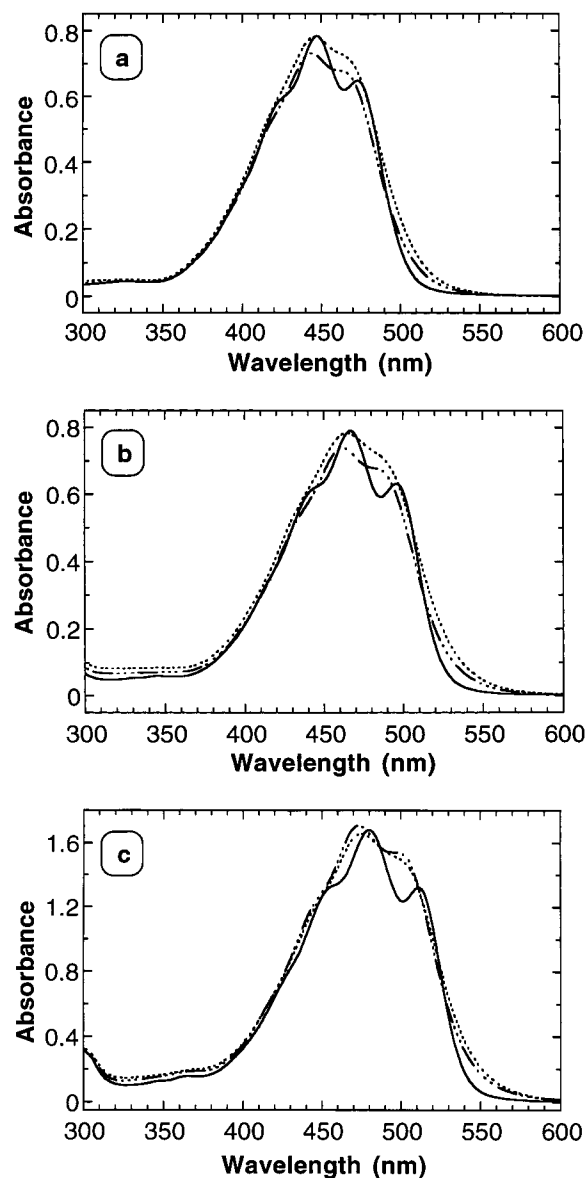
**Figure 2.** (a) Cyclic voltammograms of compounds **IV** (solid line), **V** (chained line), and **VI** (dotted line). Dichloromethane solutions of 0.1 M TBAHFP and 1.0 mM carotenoids. Scan rate: 100 mV/s. (b) Osteryoung square wave voltammograms of compounds **IV** (solid line), **V** (chained line), and **VI** (dotted line). The arrows indicate the potential scanning direction.



**Figure 3.** Cyclic voltammograms of compounds **VII** (solid line), **VIII** (chained line), and **IX** (dotted line). Dichloromethane solutions of 0.1 M TBAHFP and 1.0 mM carotenoids. Scan rate: 100 mV/s. The arrow indicates the potential scanning direction.

solvents. In contrast, the spectra of the aldehydes **IV–VI** (Figure 5) show considerable broadening of the bands with increasing solvent polarity. The presence of a conjugated, strongly electron-accepting terminal substituent greatly increases the sensitivity of carotenoid photophysical parameters to solvent polarity.

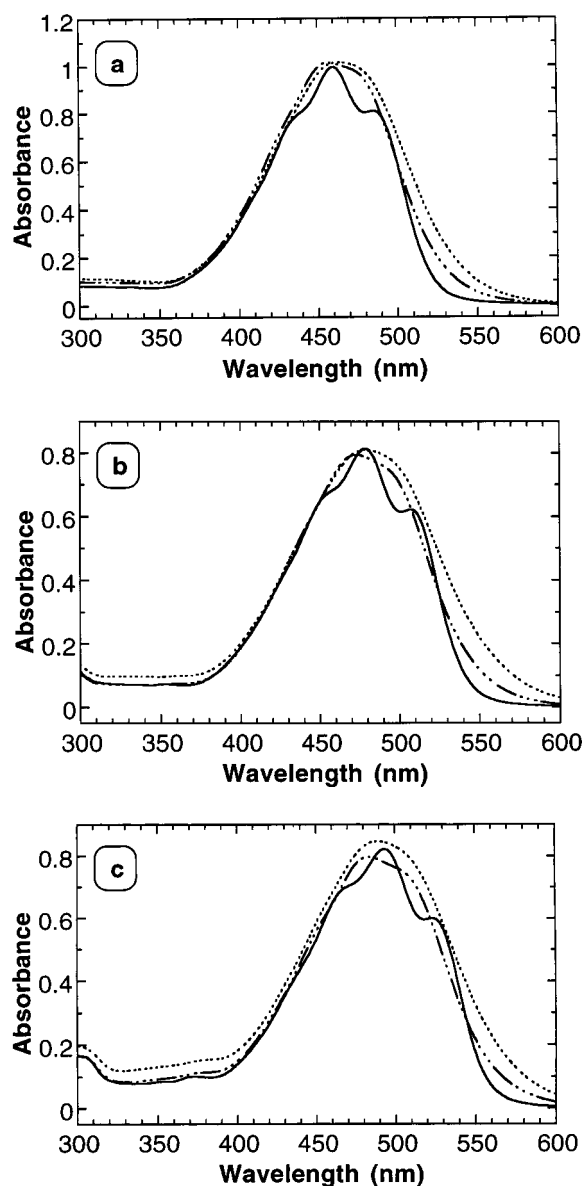
**Lifetimes of Carotenoid Radical Cations Measured by the Stop-Flow Method.** It is known that carotenoid radical cations can be generated by oxidation with ferric chloride and detected by optical absorption in the near-infrared region.<sup>17,18</sup> Examples of the spectra of the neutral species of **II** (solid line) and its radical cation generated by oxidation with ferric chloride (chained line) are shown in Figure 6. The neutral compound **II** does not absorb above 600 nm. Upon addition of ferric chloride, the absorption of the radical cation centered at 902 nm appears immediately and then rapidly decreases to about one-half of its



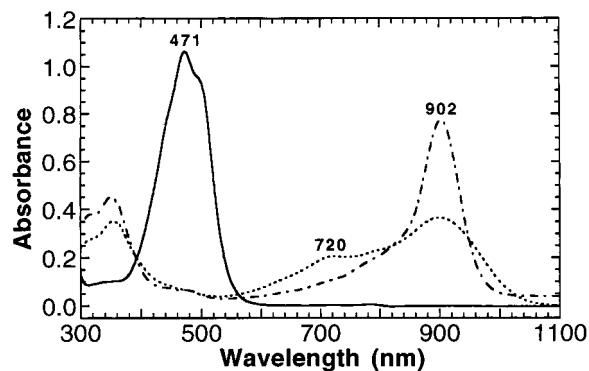
**Figure 4.** Optical absorption spectra of neutral carotenoids (a) **I**, (b) **II**, and (c) **III** in cyclohexane (solid line), acetonitrile (chained line), and ethanol (dotted line).

intensity. The spectrum measured 10 min after addition of ferric chloride is also shown in Figure 6 (dotted line). In addition to the residual absorption at 902 nm, a new band appears near 720 nm. The lifetimes of different carotenoid radical cations, which vary from a few seconds to a few minutes, were evaluated by measurements of the initial decreases of the optical absorbances. The time courses of the reactions of radical cations of **I**–**III** are shown in Figure 7a–c, respectively. Relevant data, listed in Table 2, show that the stability of the radical cations of the esters decreases considerably with increasing number of conjugated double bonds. In contrast, the results obtained for the aldehydes and nitriles **IV**–**IX** (Table 2) indicate much less variation in lifetimes of the radical cations: small increases for the aldehydes and small decreases for the nitriles with increasing number of conjugated double bonds. The optical results obtained by the stop-flow method are consistent with the voltammetry results discussed above.

A possible reason for the observation that the absorbances of radical cations do not go to zero is that radical cations rapidly convert to other species which are much more stable and have a similar absorption band to those of their parent molecules (see



**Figure 5.** Optical absorption spectra of neutral carotenoids (a) **IV**, (b) **V**, and (c) **VI** in cyclohexane (solid line), acetonitrile (chained line), and ethanol (dotted line).

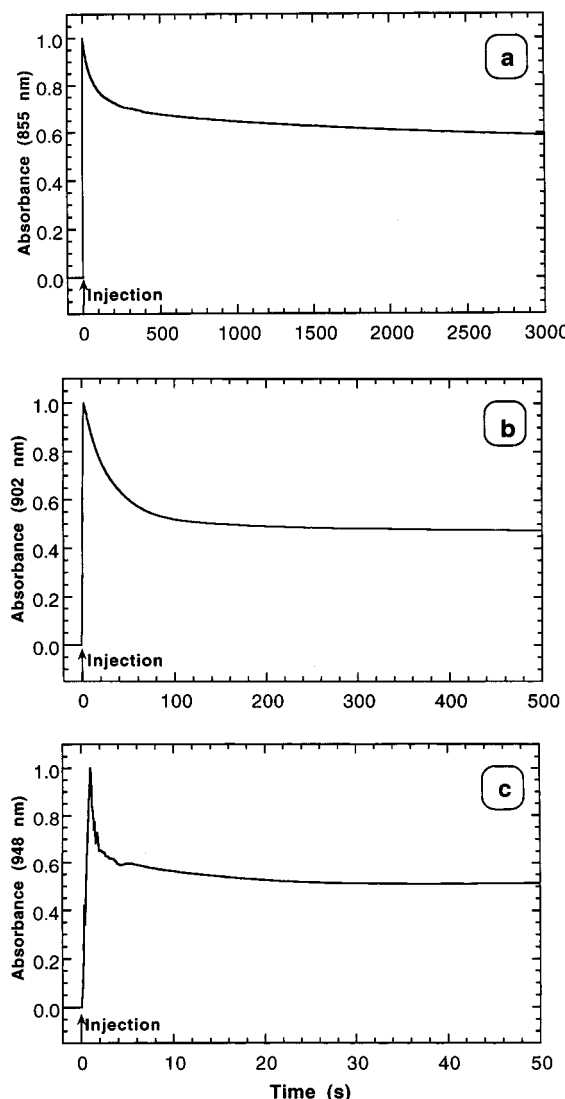


**Figure 6.** Optical absorption spectrum of 8  $\mu$ M compound **II** in CH<sub>2</sub>Cl<sub>2</sub> (solid line), spectrum measured immediately after mixing with same amount of 8  $\mu$ M FeCl<sub>3</sub> (chained line), and spectrum measured 10 min later (dotted line).

Figure 6). The decay kinetics of the radical cations do show an initial fast step and a second slow step.

**AM1 Molecular Orbital Calculations.** AM1 semiempirical molecular orbital calculations of the gas-phase dipole moments





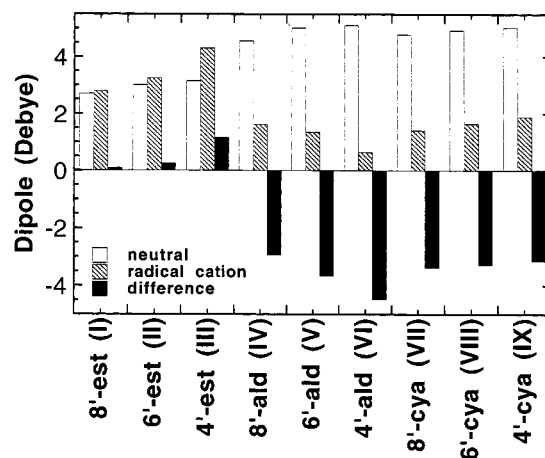
**Figure 7.** The change with time of optical absorbance of radical cations generated by rapidly mixing equal amounts of 8  $\mu$ M FeCl<sub>3</sub> and 8  $\mu$ M compounds (a) **I**, (b) **II**, and (c) **III**, by stop-flow method. Note that the time scales differ.

**TABLE 2: Optical Absorption Maxima and Half-lifetimes of Radical Cations for Nine Carotenoids**

compounds	$\lambda_1$ (nm) <sup>a</sup> $\pm 2$	$\Delta\lambda_1$ <sup>a</sup> (nm)	$\lambda_2$ (nm) <sup>a</sup> $\pm 2$	$\Delta\lambda_2$ <sup>a</sup> (nm)	$t_{1/2}$ <sup>b</sup> (s)
8'-CO <sub>2</sub> Et ( <b>I</b> )	453		855		202 $\pm$ 6
6'-CO <sub>2</sub> Et ( <b>II</b> )	471	18	902	47	125 $\pm$ 1
4'-CO <sub>2</sub> Et ( <b>III</b> )	485	14	948	46	2.35 $\pm$ 0.18
8'-CHO ( <b>IV</b> )	468	18	848	47	149 $\pm$ 1
6'-CHO ( <b>V</b> )	486	10	895	49	167 $\pm$ 3
4'-CHO ( <b>VI</b> )	496		944		257 $\pm$ 5
8'-CN ( <b>VII</b> )	456	18	841	49	227 $\pm$ 5
6'-CN ( <b>VIII</b> )	474	14	890	49	158 $\pm$ 2
4'-CN ( <b>IX</b> )	488		939		133 $\pm$ 1

<sup>a</sup>  $\lambda_1$  and  $\lambda_2$  are the wavelengths of the optical absorption maxima of the neutral and radical cation species, respectively. <sup>b</sup>  $t_{1/2}$  is the half-lifetime of radical cations generated by ferric chloride determined by the stop-flow method.

of the neutral species and radical cations of carotenoids **I–IX** were carried out. The structures of the species were optimized by the AM1–RHF method prior to a single-point calculation. As illustrated in Figure 8, the open, shaded, and solid columns represent the magnitudes of the calculated dipole moments of the neutral species, those of the radical cations, and the



**Figure 8.** AM1-calculated dipole moments of neutral species and radical cations of nine carotenoids. Open columns are for neutral species, shaded columns are for radical cations, and solid columns are the differences between dipoles of radical cations and neutral species.

differences between the magnitudes of radical cations and neutral species. It is interesting to note the following: (1) For the esters, positive changes between the dipoles of radical cations and neutral species occur; in contrast, for the aldehydes and nitriles, large negative changes between the dipoles of the radical cations and the neutral species occur. (2) For the neutral species, the dipole moments of the aldehydes and nitriles are greater than those of the esters; however, the dipole moments of the radical cations of the aldehydes and nitriles are smaller than those of the esters. (3) For the radical cations, an increase in the backbone length results in an increase in the dipole moments for the esters and a decrease for the aldehydes, but only a small increase for the nitriles.

## Discussion

Some effects of electron-donating and -accepting substituents on the stability of carotenoid radical cations have been discussed.<sup>22,23</sup> From a study of a series of carotenoids terminally substituted by electron-donating and -accepting groups, it was concluded that the stronger the electron-accepting nature of the substituent, the more stable the radical cations in dichloromethane solutions. The magnitudes of the EPR parameters,  $\Delta H_{pp}$  and  $g$ , for the carotenoid radical cations suggest a polyene  $\pi$ -radical cation structure, with little unpaired electron density present on the donor or acceptor substituent.<sup>22,39</sup> However, the influence of the conjugated double-bond chain length on the stability of carotenoid radical cations has not been studied before.

In solution, radical cations undergo decomposition via deprotonation (eq 6, Scheme 1) and other reactions.<sup>23,38</sup> Stronger interaction of the solvent dipoles with the radical cation dipoles appears to result in enhanced decay of the radical cations; evidently, the larger the dipoles of the radical cations, the less stable the radical cations. The voltammetric and kinetic results for radical cation stability parallel the AM1 calculated dipole moments in that (1) for ester radical cations, the species with the shortest backbone chain has the longest lifetime and the smallest dipole moment; (2) for aldehyde radical cations, an extra double bond in the backbone results in a decrease in the dipole moment, and therefore the lifetime increases slightly; radical cations of **IV–VI**, which show smaller dipole moments, are relative more stable than those of the esters; and (3) for the nitrile radical cations, AM1-calculated dipole moments increase slightly with increasing number of chain double bonds, so the stability also decreases slightly.

It is relevant to mention that the dependence of the lifetimes of the carotenoid lowest excited singlet states on solvent polarity has been investigated.<sup>40</sup> As the dielectric constant of the solvent increases from 1.9 to 36, the lifetime of the lowest excited singlet state of all-*trans* 7'-apo-7',7'-dicyano- $\beta$ -carotene decreases from 11.7 to 1.9 ps. AM1 molecular orbital calculations predict a large change in dipole moments between the lowest excited singlet and the ground states (a 5.1 D increase); interaction of the excited-state dipole with solvent dipoles results in enhanced charge-transfer character within the excited state, which in turn enhances nonradiative decay of the excited state.

The photophysical properties of donor-acceptor molecules, "push-pull" polyenes, and carotenoids bearing various acceptor and donor groups and linked together by chains of different length and structure have been studied by absorption and fluorescence spectroscopy.<sup>25</sup> The position of the absorption and fluorescence maxima and their variation in solvents of increasing polarity are in agreement with an intramolecular charge transfer (ICT) nature, which will greatly enhance the sensitivity of the polyene photophysical parameters to solvent polarity. In this study, the aldehydes **IV**–**VI**, which are substituted with a strongly electron-accepting group, display ICT properties because their absorption spectra exhibit solvent-sensitive behavior as shown in Figure 5. In contrast, the esters **I**–**III**, substituted with a weaker electron-accepting group, do not show ICT properties because their spectra are not sensitive to solvents (Figure 4). This behavior is also in agreement with the magnitudes of the dipole moments of these carotenoids. As shown in Figure 8, the dipoles of the neutral species of the aldehydes **IV**–**VI** are much larger than those of the esters **I**–**III**. The larger the dipole of a species, the more intense the interaction between the species and the solvent, resulting in enhancement of the sensitivity of the polyene photophysical parameters to solvent polarity.

## Conclusions

From voltammetry and optical spectroscopic studies of three series of carotenoids substituted with terminal ester, aldehyde, and cyano groups with different lengths of the backbone chain, we have drawn the following conclusions: (1) For carotenoids substituted with weak terminal electron acceptors (ester groups), the stability of the radical cations is relatively low, and the radical cations with shorter length are more stable than those with longer length. (2) In contrast, for carotenoids substituted with a strong terminal electron acceptor (aldehyde group), the stability of the radical cations is relatively high, and the stability of radical cations increases slightly with increasing conjugated backbone length. (3) For carotenoids substituted with cyano terminal groups, the stability of the radical cations is relatively high, and the stability of the radical cations decreases slightly with increasing conjugated backbone length. (4) For all esters, aldehydes, and nitriles, the shorter the olefin chain, the more difficult the oxidation. (5) The aldehydes display intramolecular charge transfer (ICT) properties because their absorption spectra exhibit solvent-sensitive behavior; in contrast, the esters do not. (6) It is evident that the radical cation stability is related to the change in dipole moment between radical cations and the neutral species; AM1 calculations predict large decreases in dipole moment between radical cations and neutral species for the aldehydes and nitriles, but increases for the esters. (7) Interaction of the radical cation dipoles with the solvent dipoles results in enhanced decay of the radical cations.

**Acknowledgment.** We thank Dr. Elli Hand for synthesizing the carotenoids. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy under Grant No. DE-FG02-86-ER13465.

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