

Carotenoid Radical Cations, Dications and Radical Tricationst

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The radical cation, dication and radical trication of the long chain polyenes known as carotenoids have been characterized by a combination of diverse techniques such as CV, EPR, ENDOR and simultaneous applications of electroanalysis and EPR, optical and resonance Raman spectroscopy, and by AM1, RHF-INDO/SP and INDO/S molecular orbital calculations. In this paper, the AM1 calculated structure and charge density distribution of the radical trication is reported and its optical spectrum is estimated based on INDO/S calculations. An iterative fit to the CV of the radical trication indicates that its acid strength ($pK_a \sim 2$) is similar to that of the dication ($pK_a \sim 1$), and that it deprotonates rapidly and is less stable than the dication.

Carotenoids are naturally occurring, intensely colored pigments formed in numerous photosynthetic bacteria, algae and plants.¹ About 600 naturally occurring carotenoids have been isolated and identified.² Carotenoids have important biochemical and biological functions such as light harvesting and photoprotection in photosynthesis in plants.^{3,4} They are also good antioxidants⁵ and as a result carotenoid radical cations, dications and possibly radical trications are formed. In addition carotenoids possess free radical quenching properties.⁶ Different isomeric forms of carotenoids appear to have different physiological or metabolic roles and play different roles in plant photosynthesis. Structurally, carotenoids are long chain polyenes containing a series of conjugated double bonds that constitute the chromophoric group of the carotenoid which may be red, orange or yellow. For example, the structure of β -carotene (**1**) consists of nine conjugated chain double bonds terminated by cyclohexene groups. Because of the increased awareness of the involvement of carotenoids in many biochemical and biological processes, characterization of the oxidation intermediates and their mode of formation and reactions is of considerable importance.

Among the numerous physicochemical techniques that have been employed in the studies of oxidation/reduction reactions of carotenoids (Car) are the following:† CV,

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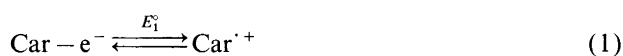
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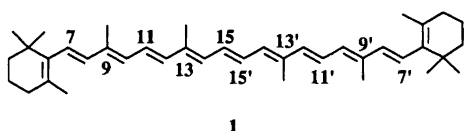
‡ CV, cyclic voltammetry; OSWV, Osteryoung square wave voltammetry; EPR, electron paramagnetic resonance; ENDOR, electron nuclear double resonance; HPLC, high performance liquid chromatography; FIA, flow injection analysis.

OSWV, CV simulation, chronocoulometry, optical spectroscopy (UV, VIS, near IR), EPR spectroscopy, simultaneous electrochemical oxidation/reduction and EPR and optical spectroscopy, ENDOR, and optical spectroscopy of carotenoid solutions treated with chemical oxidants, e.g., $FeCl_3$, I_2 . While the results of some methods simply confirm those of others, in general, each method addresses different aspects of the redox behavior of carotenoids or of the physical properties of the transient, positively charged ($Car^{\cdot+}$, Car^{2+} , $*Car^+$) and neutral ($*Car^{\cdot}$) intermediates, where * indicates loss of one proton. Such studies are essential if the complex functions of the ubiquitous natural carotenoids are to be understood. It should be recalled that the survival of photosynthetic plants depends on these compounds, and that these are also essential nutrients for higher animals which can obtain them only from the food they ingest.

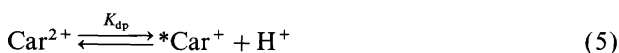
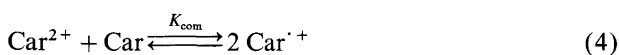
The original formulation in 1975 of the reactions occurring during the electrochemical oxidation of β -carotene⁷ was simultaneous loss of two electrons from the neutral species to give dications (Car^{2+}), which can again be reduced to the neutral species, but which can also deprotonate⁷ to give cations ($*Car^+$). On the basis of more recent data,^{8,9} this mechanism has now been expanded to include the series of reactions given in eqns. (1)–(10).

Electrode reactions:

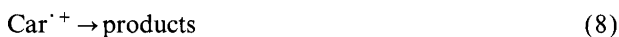




Solution reactions:



Side reactions:



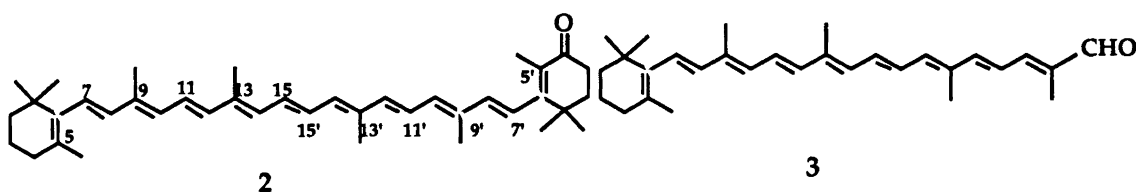
In contrast to β -carotene (**1**), other carotenoids, e.g., canthaxanthin (**2**) and 8'-*apo*- β -caroten-8'-al (**3**) exhibit two sequential one-electron oxidations [eqns. (1) and (2)]. A study of a series of structurally similar synthetic¹⁰ 7'-*apo*-7'-phenyl- β -carotenes (**4**) in which the phenyl ring bears various substituents, showed that the difference in oxidation potentials ($\Delta E = E_2^\circ - E_1^\circ$) depends on the electron-withdrawing strength of the substituents;¹¹ the stronger the electron withdrawal, the larger is ΔE . This behavior is also observed for carotenoids of more diverse structures.⁹ For example, ΔE values for 7'-substituted 7'-*apo*- β -carotenes are (7'*E*)-CO₂Et (**5**), 147 mV; (7'*E*)-CN (**6**), 155 mV; (7'*E*)-CO₂Et, (7'*Z*)-CN (**7**), 159 mV; 7',7'-di-CN (**8**), 177 mV. With decreasing electron-acceptor strength of terminal substituents, the difference in the two oxidation potentials decreases, i.e., the anodic peaks move closer together, and finally merge into a single peak, as for example in the CV of 7'-*apo*-7'-phenyl- β -carotene¹¹ (**4**, X=H), 7'-*apo*-7',7'-dimethyl- β -carotene (**9**)⁹ and β -carotene itself. With the exception of 7,7'-*diapo*-7,7'-diphenylcarotene (**10**) ($\Delta E \sim 80$ mV), all other hydrocarbon carotenoids investigated so far, including lycopene (**11**),¹² 15,15'-didehydro- β -carotene (**12**) (cent-

ral triple bond)⁸ and its 7,7'-*diapo*-7,7'-diphenyl analogue (**13**), have shown only a single anodic CV peak for the two-electron oxidation ($\Delta E < 15$ mV). However, the values of the oxidation potentials differ considerably ($E^0 = 545$ mV for **1**, 880 mV for **13**).⁸ It thus seems likely that this is one of the reasons for the considerable diversity in the structures of naturally occurring carotenoids (at least the hydrocarbons).

While chronocoulometry has shown that two electrons are transferred, i.e., dicationic species are formed, EPR measurements of CH₂Cl₂ solutions of bulk-electrolyzed β -carotene containing excess, unreacted **1** showed the presence of carotenoid radicals.¹⁴ The solution comproportionation reaction [eqn. (4)] was therefore postulated. Confirmation was obtained from, e.g., SEEPR experiments¹⁴ of canthaxanthin in which no EPR signal was observed during bulk electrolysis at high potential (1.0 V) when only dicationic species are generated, but an EPR signal, which intensified during the course of several minutes and then gradually decayed [eqns. (6) and (8)], arose after application of the potential was stopped.^{14,15} Clearly, EPR measurements were essential in unraveling this aspect of the reactions occurring during the oxidation of carotenoids.

Formation of the uncharged radical [eqn. (3)] was postulated to account for the low cathodic potential peak in the CV of **1**;⁷ it is present in the cathodic CV scan of all carotenoids examined so far.^{8,9,11-18} This species rapidly decays [eqn. (10)] so that its reoxidation to $*\text{Car}^+$ [eqn. (3)] upon reversing the CV scan can be observed only under certain conditions. It has been possible to demonstrate by SEEPR experiments that low concentrations of carotenoid radicals ($*\text{Car}^\cdot$) are present at low potential (0.2 V) during the cathodic scan. Results of CV studies of perdeuterated β -carotene¹⁴ definitively established that formation of this electrochemically active species ($*\text{Car}^\cdot$) involves the cleavage of a CH (CD) bond. Further, the precursor must be Car^{2+} since the CV cathodic peak due to the reduction of $*\text{Car}^+$ is observed only if the scan is reversed¹⁴ at high positive potential (E_2° of canthaxanthin, for example), where Car^{2+} is formed, and not if the reverse CV scan is started near the first oxidation potential (E_1°).

While the transient species decay relatively rapidly in solution, radical cations are remarkably stable when immobilized on Nafion, silica,¹⁹ or on activated silica-alumina solid support.²⁰ It was therefore possible to



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assess the distribution of the unpaired electron density by ENDOR measurements.^{20–22} The results are essential for determining the structure of these radical cations. The multiple-signal resolved spectra show large coupling constants with the protons of the four chain methyl groups as well as smaller couplings with other protons, indicative of an extended conjugated π -radical structure. Assignments were based on RHF-INDO/SP calculations.²¹ The width at half height (ΔH_{pp}) for EPR spectra of all $\text{CAR}^{\cdot+}$ are nearly the same in the solid as in solution and equal to 13 ± 2 G. Further, coupling constants of the methyl protons are the same in these media. These data confirm that the same species is present under the different conditions.²⁰

Deprotonation of $\text{Car}^{\cdot+}$ [eqn. (6)] was first postulated when it was found that the decay rate of the perdeuteriated β -carotene radical cation is ten times slower than that of the non-deuteriated species.¹⁴ Further, greatly improved agreement between the experimental and simulated CVs was achieved^{8,9,18} when this reaction was included in the overall reaction scheme.

Highlights of our recent results

Optical absorption. Optical spectroscopic studies have now confirmed that the same Car^{2+} and $\text{Car}^{\cdot+}$ species are formed by electrochemical or chemical oxidation and photochemical excitation. It has been possible to selectively form either species under appropriate conditions and to determine their quantitative optical absorption spectra. While spectra of carotenoid radical cations have been known for some time,^{23,24} those of the dications have only recently been obtained.²⁵ The spectra of several carotenoids, two of which contain electron-withdrawing terminal groups [**2** and 7'-cyano-7'-ethoxycarbonyl-7'-*apo*- β -carotene (**7**)] and two others have electron-donating substituents [**1** and 7',7'-dimethyl-7'-*apo*- β -carotene (**9**)], show that in each case the dication absorption maximum falls between the maxima of the neutral (VIS) and radical cation (near-IR) species. Relative intensities of the maxima of the three species are different for each carotenoid and show the same trend as the oscillator strengths and absorption maxima obtained by INDO/S calculations.²⁵ Molar extinction coefficients of the transient species, generated by treating CH_2Cl_2 solutions of the carotenoid with appropriate amounts of FeCl_3 , were evaluated from the absorbance determined immediately after mixing the reactants (< 1 min). Our current investigations using FIA yielded similar extinction coefficients for canthaxanthin radical cation and dication and the radical cation of **1** and **3**. The advantages of FIA include facile repetition of the measurements, no potential loss of the volatile solvent CH_2Cl_2 (b.p. 40°C) and automated control of the delay time between mixing and the absorption measurement. Error estimates in the ϵ values can be deduced from the data given in Table 1.

Resonance raman spectra. Another method of detecting and characterizing the neutral and oxidized species is

Table 1. Extinction coefficient of carotenoids measured by FIA (flow injection analysis) in dichloromethane at room temperature.

	Species	log(ϵ) (FIA results)	log(ϵ) ^a
β -Carotene	Radical cation (1000 nm)	4.89	4.8 ²⁵
Canthaxanthin	Radical cation (889 nm)	5.23	5.4 ²⁵
	Dication (708 nm)	5.15	5.2 ²⁵
8'- <i>apo</i> - β -Caroten-8'-al	Radical cation (850 nm)	5.66	5.6

^a Calculated from known amounts of ferric chloride added manually to a stirred solution.

resonance Raman spectroscopy. Raman spectra of the radical cations of three carotenoids [**1**, **2**, 7',7'-dicyano-7'-*apo*- β -carotene (**8**)], which were generated electrochemically, have now been determined.²⁶ The results show that the stretching frequencies of bonds near the center of the polyene chain differ considerably from those in the neutral species. The frequencies of C=C double bonds decreased (by $30\text{--}40\text{ cm}^{-1}$), while those of C-C single bonds increased (by $15\text{--}30\text{ cm}^{-1}$), indicating changes in the bond orders; double bonds in the neutral species have a smaller bond order in the radical cation and the opposite is true for C-C single bonds. These changes are consistent with delocalization of the unpaired electron throughout the carbon backbone as has been deduced from resolved ENDOR spectra.^{20–22}

k_s^{ap} determinations. Apparent heterogeneous electron transfer rate constants (k_s^{ap}) (apparent rate constant uncorrected for double layer effects) have been determined by rotating disk experiments at different potentials.¹⁵ The values of the order of 10^{-2} cm s^{-1} are similar to those recently deduced from CV simulation.^{8,9,18} We are currently investigating the combination of fast-scan CV and use of ultramicroelectrodes, a technique that also provides (k_s^{ap}) and depends on the characteristic scan rate²⁷ at which the difference between the anodic and cathodic peak potentials becomes greater than the 59 mV observed for a reversible one-electron transfer at slower scan rates. The parameters are related by the equation $k_s^{\text{ap}} = 0.74 (Dv^*F/RT)^{1/2}$. To date, only canthaxanthin (**2**) has been subjected to these conditions. A lower limit of $k_s \geq 0.1\text{ cm s}^{-1}$ (one and two electron oxidation, Pt-electrode, CH_2Cl_2), an order of magnitude larger than evaluated by other techniques, was obtained. Such a high heterogeneous rate constant agrees well with predictions based on very little solution reorganization energy for large organic molecules.

Isomerization. Another type of reaction that Car^{2+} and $\text{Car}^{\cdot+}$ undergo is geometrical isomerization as shown by the following. After bulk electrolysis of **1** and **2** in

dichloromethane, up to ca. 40% of the products are various *cis*-isomers which were separated by reversed-phase HPLC and identified by ^1H NMR and/or optical absorption spectroscopy. The major isomers have the 9- and 13-*cis* configuration.²⁸ Such changes can be viewed as a 180° twist about the corresponding *trans*-double bond. AM1 calculations of the total energy as a function of the dihedral angle described by adjacent carbon atoms and their substituents show that much lower energy barriers to *trans/cis* isomerization exist in the $\text{Car}^{\cdot+}$ and Car^{2+} species than in the neutral compounds. The first step in the isomerization is therefore a configurational change in the charged species which are then converted into the neutral isomers by the comproportionation of Car^{2+} and Car [eqn. (4)] and subsequent electron exchange of $\text{Car}^{\cdot+}$ and Car .²⁸

Photolysis. Spin-polarized 35 GHz time-resolved EPR (TREPR) spectra were obtained for the first time of the radical cations of **1**, 15,15'-didehydro- β -carotene (**12**), **7** and **8** and the radical anion of the solvent, which were formed by 308 nm photoexcitation of the carotenoids in carbon tetrachloride solution.²⁹ Although the EPR spectra are weak in intensity due to the small dimensions of the 35 GHz quartz flat cell and have very broad linewidths, it was possible to unambiguously determine from the polarization pattern that the electron transfer to the solvent occurs from the excited singlet state of the carotenoids. The 35 GHz EPR spectra consist of two resolved EPR lines (one absorption and one emission) from which it has been possible to measure the *g* factor and ΔH_{pp} of the solvent-separated radical ion pair that was formed; such measurements were not possible at 9 GHz.³⁰

This study

Evidence was recently uncovered that another oxidation product of carotenoids is formed in addition to the radical cation [eqn. (1)] and the dication [eqn. (2)]. This is the radical trication, formed by loss of three electrons from a carotenoid. This section presents the structure and stability for such a species as deduced from CV data and AM1 and INDO/S calculations.

Experimental

β -Carotene and tetrabutylammonium hexafluorophosphate (TBAHFP) were purchased from Fluka. Anhydrous dichloromethane was obtained from Aldrich.

Cyclic voltammetry was carried out using a Bio Analytical Systems BAS-100W electrochemical analyzer. For CV measurements, a platinum disk (diameter = 1.6 mm) was used as the working electrode, the auxiliary electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. For bulk electrolysis, a platinum coil was used as the working electrode, a silver wire was the pseudo reference electrode, and a platinum wire was the auxiliary electrode. All solutions were

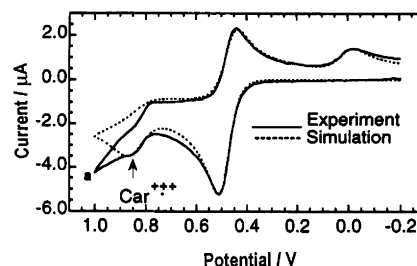


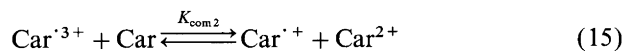
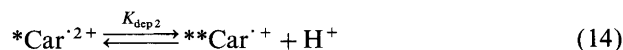
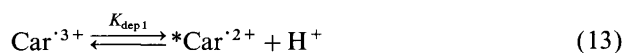
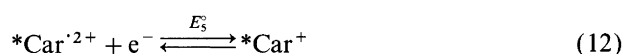
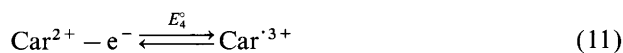
Fig. 1. Experimental and simulated CVs of **1** including formation of the radical trication at a scan rate of 100 mV s^{-1} versus SCE.

prepared in a dry box under a nitrogen atmosphere. Except as specifically noted, solutions of β -carotene (1 mM) and TBAHFP (0.1 M) in dichloromethane were used.

AM1 (Austin Model 1) and INDO/S (ZINDO/S) semiempirical molecular orbital calculations³¹ were carried out using HyperChem software³² running on a Gateway 2000 P5-60 (Pentium) personal computer.

Results and discussion

Radical trication. The CVs of **1** and the 'dimethyl' compound **9**, which exhibit only one peak for the two-electron oxidations and have relatively low half-wave potentials (near 0.5 V), show another small peak at higher potential (Fig. 1). A possible source of this peak is the formation of radical trications. Preliminary chronocoulometric studies show that three electrons are involved. Improved CV simulation was obtained when formation of the radical trication and its (rapid) deprotonation and decay were included in the reaction scheme¹⁸ [eqns. (11)–(18)].



The redox potential of the interconversion of the dication to the radical trication [eqn. (11)] is $0.882 \pm 0.0005 \text{ V}$ versus SCE. The deprotonation of the

radical trication [eqn. (13)] equilibrium constant is 0.01, which is an order of magnitude smaller than that for the deprotonation of the dication. The k_f value for reaction (13) is 20 s^{-1} . This value for the deprotonation of the radical trication is even larger than that for the dication and provides evidence for the low stability of this radical. The amplitude of the forward and reverse wave obtained for the oxidation of dication to the radical trication and *vice versa* is very small compared with that of the first two electron transfers. Since the dication precursor undergoes many side reactions, for example, deprotonation and comproportionation, only a low concentration of dication is available for further oxidation to the trication radical.

The product obtained from the deprotonation of the radical trication is $^*\text{Car}^{2+}$, and this can undergo reduction in the low potential region. The value of α for both electron transfer steps [eqns. (11) and (12)] was set equal to 0.5. The species $^*\text{Car}^{2+}$ can also deprotonate [eqn. (14)] to form $^{**}\text{Car}^+$ (where ** denotes a species containing two protons less than the parent carotenoid). The $K_{\text{dp}2}$ value for this deprotonation reaction is 0.0008 and its k_f is 20 s^{-1} . The comproportionation equilibrium [eqn. (15)] constant given by $K_{\text{com}2}$ is 7.6×10^5 which is more than five orders of magnitude greater than that for the comproportionation equilibrium that exists between the dication, neutral and radical cation species. The very large value of $K_{\text{com}2}$ shows that the product radical cations and dications are much more stable than the radical trication. Eqns. (16)–(18) give the decay reactions for the Car^{3+} , $^*\text{Car}^{2+}$ and $^{**}\text{Car}^+$ that are formed as intermediates in the overall oxidation process. Although these reactions do not influence the CV simulation in any significant manner, they were included since the decay of all other intermediates had been taken into account for the CV simulations. Radical cations are formed in various equilibria and the predicted decomposition rate of the radical trication will make it very difficult to convincingly identify the radical trication by simultaneous electrochemistry and EPR techniques.

AM1 calculations of radical trication. Fig. 2 shows the calculated bond lengths of β -carotene and the species formed by loss of one, two and three electrons. In the radical cation (Fig. 2A), the major changes occur in the central portion of the polyene chain where the bonds become equal in length. In the dication (Fig. 2B), compared with the neutral molecule, the bond orders are inverted. Although all bond lengths are affected, the greatest changes also occur near the center of the chain. In the radical trication (Fig. 2C), however, the terminal bonds, especially $\text{C}_8\text{--C}_9$, $\text{C}_9\text{--C}_{10}$ and $\text{C}_{10}\text{--C}_{11}$, show the most dramatic variation. Further, all C–C bonds are longer than the shortest bonds (1.34 Å) of the neutral, radical cation and dication species; similarly, all bonds in the radical trication are shorter than the longest bonds (1.46 Å) in the other species. Complementary information is found in Fig. 3 where the charge distribution in

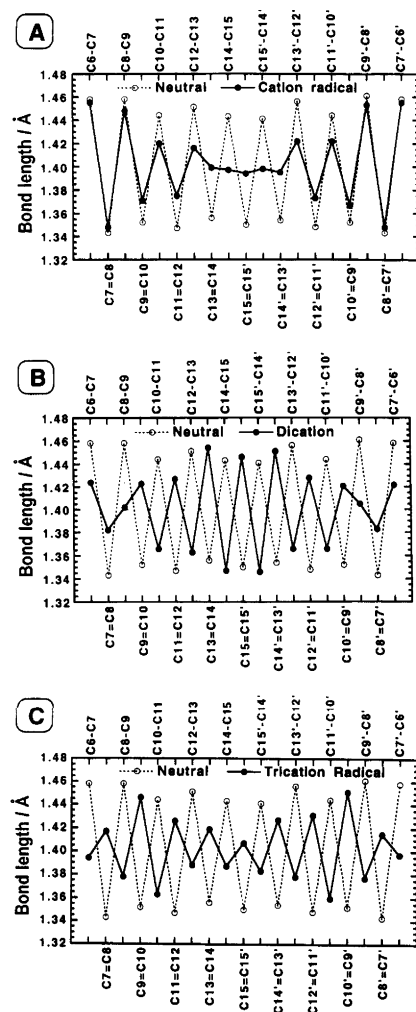


Fig. 2. AM1 calculated bond lengths of β -carotene for (A) $-\text{O}-\text{O}-$ neutral versus the $-\bullet-$ radical cation; (B) $-\text{O}-\text{O}-$ neutral versus the $-\bullet-$ dication; (C) $-\text{O}-\text{O}-$ neutral versus $-\bullet-$ radical trication.

the polyene carbon atoms is plotted. In the neutral species, all chain carbon atoms bear an excess (negative) charge. This excess is reduced at most carbons in the radical trication (Fig. 3C) and even becomes a deficiency (i.e., positive excess charge) at C_7 , C_9 , $\text{C}_{9'}$, and $\text{C}_{7'}$. The distribution of the three positive charges can thus be approximated by one plus charge near each end of the chain centered about C_8 and $\text{C}_{8'}$ and one-half of the remaining plus one charge centered at C_{13} and $\text{C}_{13'}$. In contrast, the dication has a plus one charge centered around C_{10} and $\text{C}_{10'}$ while the cation radical has approximately one-half of a positive charge centered at C_{10} and $\text{C}_{10'}$. It is noteworthy that the carbon atoms (9, 13, 13', 9') to which the methyl groups are attached bear a sizeable positive charge in all three cationic species so that the C–H methyl bonds are weakened and loss of a proton from these methyl groups is facilitated.

In Fig. 4, the positive excess charge density per chain proton and the average density per proton on the methyl groups for the neutral species, the radical cation, the

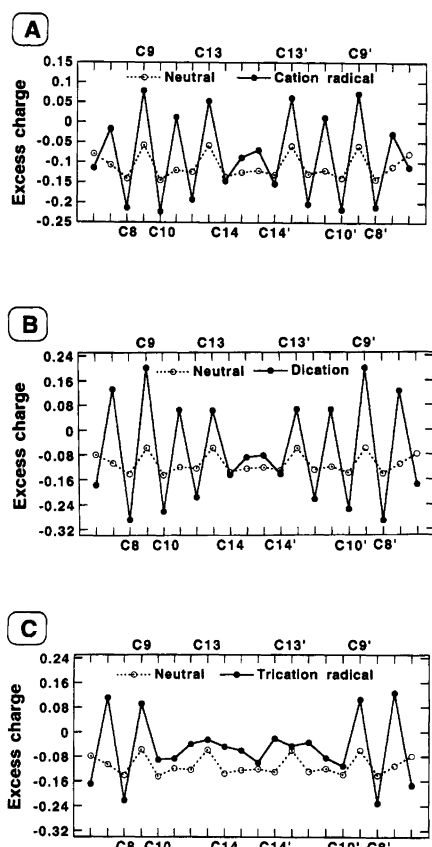


Fig. 3. AM1 calculation of charge distribution on the chain carbon atoms of all-*trans*- β -carotene for (A) $\text{---}\circ\text{---}$ neutral versus $\text{---}\bullet\text{---}$ radical cation; (B) neutral versus dication; (C) neutral versus radical trication.

dication and the radical trication is given. For most protons, there is an increase in positive density with increasing electron loss. In all species the positive charge density on the methyl protons is much lower than the density on the neighboring chain protons. For instance for the C_9 -methyl proton it is 0.11, 0.13, 0.13, respectively, for the radical cation, dication and the radical trication, while the C_8 or C_{10} protons have a charge density of ca. 0.145, 0.16, and 0.15, respectively. This is consistent with the mechanism usually considered for the loss of an H^+ species from a methyl group where C_9 (13) is more positive and the methyl protons are more negative than the respective neighboring carbons or chain protons.

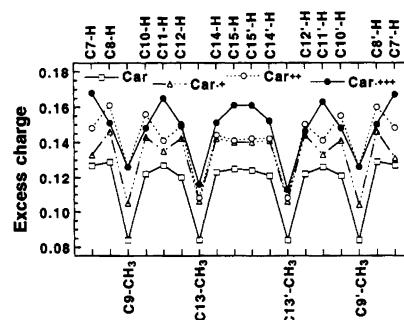


Fig. 4. AM1 calculation of charge distribution on the chain hydrogen atoms and the average value on the CH_3 protons for β -carotene.

The charge distribution and bond length variation upon loss of three electrons is also consistent with the calculated barrier to rotation about $\text{C}_7\text{--C}_8$ ($6.3 \text{ kcal mol}^{-1}$), $\text{C}_9\text{--C}_{10}$ ($2.5 \text{ kcal mol}^{-1}$), $\text{C}_{13}\text{--C}_{14}$ ($10.5 \text{ kcal mol}^{-1}$) and $\text{C}_{15}\text{--C}_{15'}$ ($44.8 \text{ kcal mol}^{-1}$). This is in marked contrast to the barrier for isomerization about these same bonds in the dication of β -carotene ($22.6, 9.2, 3.3$ and $3.9 \text{ kcal mol}^{-1}$).

INDO/S calculation. Optical spectra for the β -carotene species were predicted (Table 2) to occur at 627 ($\log \epsilon = 4.0$) and 1366 nm ($\log \epsilon = 2.3$) for the radical trication, at 528 nm ($\log \epsilon = 4.1$) for the dication, 652 ($\log \epsilon = 2.3$) and 1035 ($\log \epsilon = 0.05$) nm for the radical cation and at 414 ($\log \epsilon = 3.8$) nm for the neutral compound. Experimental spectra in dichloromethane showed maxima at 817 ($\log \epsilon = 5.1$) for Car^{2+} , 970 ($\log \epsilon = 4.8$) and 1425 ($\log \epsilon = 3.3$) for $\text{Car}^{\cdot+}$ and 461 nm ($\log \epsilon = 5.05$) for Car. Although the INDO/S calculations do not match the optical absorption maxima or the experimental extinction coefficients, the INDO/S calculations do predict the correct trend for both. Unfortunately, the more intense optical maximum for the radical trication (627 nm) is predicted to occur close to that for the radical cation (652 nm). The difficulties of optical detection of the radical trication expected on the basis of its instability are thus compounded and may present a formidable challenge to successful measurements.

Acknowledgments. We express our gratitude to Hoffmann-La Roche Ltd., Basel, Switzerland for a generous gift of the dialdehyde precursor of the 7,7'-diphenyl

Table 2. Calculated oscillator strengths at λ_{max} (nm, in parentheses) of transitions for neutral, radical cation, dication and radical trication species of β -carotene using the INDO/S semiempirical method.^a

Neutral $\text{S}_0 \rightarrow \text{S}_2$	Radical cation		Dication $\text{S}'_0 \rightarrow \text{S}'_1$	Radical trication	
	$\text{D}_0 \rightarrow \text{D}_2$	$\text{D}_0 \rightarrow \text{D}_1$		$\text{D}_0 \rightarrow \text{D}_2$	$\text{D}_0 \rightarrow \text{D}_1$
3.8 (414)	2.3 (652)	0.05 (1035)	4.1 (528)	4.0 (627)	0.23 (1366)

^aThe geometries were optimized using the AM1 method and as input to a single point INDO/S calculation. A single excitation configuration interaction involving about 50–125 configurations was used to calculate the optical spectrum. The weight factors for $\sigma\text{--}\sigma$ and $\pi\text{--}\pi$ overlap are 1.267 and 0.64, respectively.

analogue and 15,15'-didehydro- β -carotene. Roche Vitamins and Fine Chemicals of Nutley, New Jersey is thanked for a gift of the oil suspension of 8'-apo- β -caroten-8'-al, a precursor of a number of our donor-acceptor substituted carotenoids. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research of the US Department of Energy under grant No. DE-FG05-86ER 13465.

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