

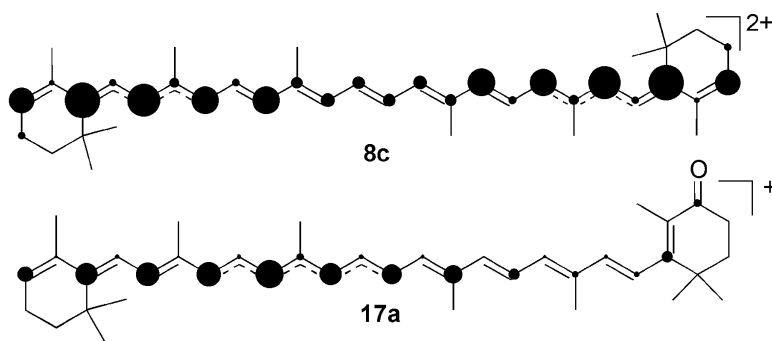
Article

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## Delocalized Carotenoid Cations in Relation to the Soliton Model

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**Abstract:** A series of charge-delocalized carotenoid mono- and dications have been prepared by treatment of selected carotenoids with Brønsted and Lewis acids. The detailed structures of the carbocations were established by NMR studies in the temperature range from  $-10$  to  $-20$  °C. The general strategy for structure elucidation by NMR of several cationic components in a mixture is outlined. Bond type and regions of bond inversion were established, as well as the charge distribution, which was determined from the difference in  $^{13}\text{C}$  chemical shift at each carbon. This method gave a more accurate estimate for the partial charges than by using the Spiesscke–Schneider relationship. The resulting charge distribution was used as models for the structure of charged solitons. These carotenoid cations have the most delocalized charge so far determined, and the monocations represent the first experimental structure determination of positively charged solitons. The soliton width determined here is in good agreement with the results of previous AM1 calculations.

### Introduction

Carotenoids are isoprenoid polyene pigments widely distributed in nature.<sup>1,2</sup> Around 800 naturally occurring carotenoids are known.<sup>3</sup> The isolation,<sup>1</sup> structure determination by spectroscopic methods,<sup>4</sup> biosynthesis and metabolism,<sup>5</sup> and total synthesis<sup>6</sup> of carotenoids are treated in recent monographs.

A general structural feature of the carotenoids is the isoprenoid polyene chain, responsible for the yellow-orange-red colors.<sup>4</sup> Carotenoproteins exhibit purple or blue colors.<sup>7</sup> Electron-deficient carotenoids, including radical cations, monocations, and dications, have received increasing attention during the past decade, theoretically and experimentally. Methods mainly employed for studies of charged carotenoid species include NIR, EPR, ENDOR, and resonance Raman spectroscopy, cyclic voltammetry, and AM1 calculations.<sup>8</sup>

Carotenoids have been encountered in both Photosystems I<sup>9–11</sup> and II<sup>12–15</sup> reaction centers. Structures of the photosynthetic

units have been determined by X-ray crystallography.<sup>9,16</sup> The carotenoids in these photosystems serve for light harvesting in the 450–570 nm region where the absorption of chlorophyll is negligible, for quenching of chlorophyll triplet states, singlet oxygen scavenging, excess energy dissipation, and structure stabilization.<sup>9,17</sup> Photosystem II (PS II), which oxidizes water to oxygen in photosynthesis, is the best studied of these photosystems, and here the functions of carotenoid cation radicals have been studied by resonance Raman, IR, EPR, ENDOR, and ESEEM spectroscopy.<sup>14,15,18–21</sup> In addition to the already mentioned roles of carotenoids in PS II, also the function as a redox intermediate in the electron-transfer pathway within PS II has been suggested.<sup>13,18</sup>

Treatment of carotenoids and other polyenes with electron acceptors, for example, iodine, in a process known as doping,

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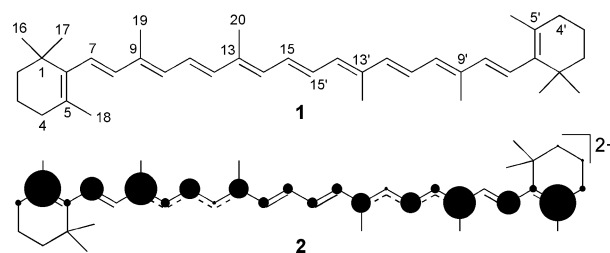
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causes an extreme increase in the electrical conductivity of the doped polyene.<sup>22–26</sup> The use of doped carotenoids in batteries has been investigated.<sup>27</sup> At present, the charge in conducting polyenes is considered to be carried in “electron holes” called positive solitons in the polyene chain, the Su–Schrieffer–Heeger (SSH) model.<sup>24,28–30</sup> This model describes the charge as a charge-density wave, with the charge located on every other carbon, and with a concentration of the charge density wave in the center of the polyene chain. This phenomenon is accompanied by a decrease in the difference between single and double bonds. The model has later been modified, showing that there might be a small negative charge on the carbons not carrying the positive charge, and that the width and position of the charge density wave and the bond-length distortions need not be the same.<sup>31–34</sup> NMR studies on dienes and polyenes, including solitons, have recently been reviewed,<sup>35</sup> but apart from NMR studies of polyene anions,<sup>36–38</sup> only short-chain ions have been examined. The studies on the structures of the solitons have otherwise been centered on electron absorption spectra and theoretical calculations.<sup>31–34,39,40</sup>

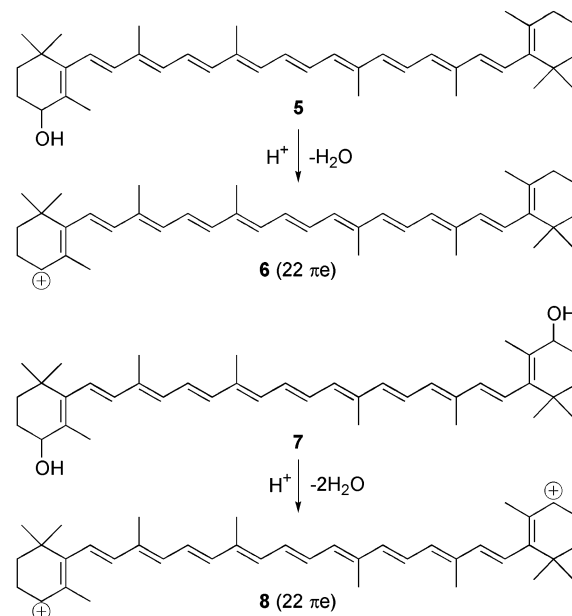
Another area receiving interest concerning the structure of charged carotenoids is in the field of molecular design.<sup>41–52</sup> This includes molecular wires<sup>41–47</sup> that are able to transport electrons across or through, for example, a lipid membrane, molecular switches,<sup>43</sup> and push–pull polyenes<sup>48–50</sup> with nonlinear optical properties. Carotenoids and structurally related compounds that have been purpose-designed, especially the caroviologens,<sup>41,44,45</sup>

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Chart 1



Scheme 1



have been extensively studied in this respect and were shown to be promising model compounds.

We have reported the first detailed studies on charged, spinless, carotenoids by NMR spectroscopy, resulting in complete structure determinations of the  $\beta,\beta$ -carotene (1) dication (2).<sup>53,54</sup> Regions of bond inversion, where the bond orders have changed from single and double to an intermediate type, are shown by dotted bonds, and distribution of the positive charge in 2 is illustrated by the diameter of the filled circles in Chart 1.

More recently, we have conducted NMR studies of protonated  $\beta,\beta$ -carotene-4,4'-dione (3, canthaxanthin) as models for electron-deficient 3,3'-dihydroxy- $\beta,\beta$ -carotene-4,4'-dione (4, astaxanthin) in the blue carotenoprotein crustacyanin,<sup>55</sup> in light of the recent X-ray structure of 4 bound in  $\beta$ -crustacyanin.<sup>56</sup>

Whereas dication 2 contains 20  $\pi$  electrons, it was considered of interest to study  $\beta,\beta$ -carotene (1) related monocations and dications containing 22  $\pi$  electrons. Removal of the hydroxy group from the allylic carotenol  $\beta,\beta$ -caroten-4-ol (5, isocryptoxanthin) provided the desired monocation 6, while  $\beta,\beta$ -carotene-4,4'-diol (7, isozeaxanthin) in principle could furnish the target dication 8, Scheme 1.

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The structure of monocation **6**, prepared by treatment of **5** with  $\text{CF}_3\text{COOH}$  in  $\text{CH}_2\text{Cl}_2$  at  $-10^\circ\text{C}$ , has been reported in a preliminary communication.<sup>57</sup> This provided experimental evidence for a cation intermediate during the elimination of allylic hydroxy groups by 0.03 N HCl in  $\text{CHCl}_3$ . This reaction, which has long been a standard reaction in the carotenoid field, has been considered to proceed via a hypothetical cation intermediate to products with prolonged chromophore.<sup>58,59</sup>

The mono- and dication species prepared in this work are the longest conjugated polyenyl cations that have been fully characterized. The studies of these carotenoid cations may be useful for the understanding of the structures of charged polyenes and solitons in general, as well as for the functions of carotenoids in the systems mentioned above.

## Materials and Methods

**Materials.** Synthetic  $\beta,\beta$ -carotene-4,4'-dione (canthaxanthin, **3**), 3,3'-dihydroxy- $\beta,\beta$ -carotene-4,4'-dione (astaxanthin, **4**),  $\beta,\beta$ -carotene-4-one (echinenone, **9**), 4',5'-didehydro-4,5'-*retro*- $\beta,\beta$ -carotene (isocarotene, **10**),  $\psi,\psi$ -carotene (lycopene, **11**), and 2,6,11,15-tetramethylhexa-decaheptaene-1,16-dial (crocetindial, **12**) were obtained from Hoffmann-La Roche, Basel. Commercially available  $\text{CF}_3\text{COOH}$  from Acros and Merck and  $\text{CF}_3\text{COOD}$  and  $\text{BF}_3$ -diethyl etherate from Acros were used.  $\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{CF}_3\text{SO}_3\text{D}$ , and  $\text{THF-}d_8$  were supplied from Aldrich.

**Instrumentation.** Visible light (VIS) and near-infrared (NIR) spectra were recorded on a Varian Cary 50 UV-vis spectrophotometer (190–1100 nm).

NMR spectra were obtained on a Bruker Avance DRX 500 instrument, equipped with a 5 mm inverse probe (TXI).  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$  was used as the solvent. Chemical shifts were cited relative to TMS with calibration against  $\text{CH}_2\text{Cl}_2$  at 5.32 and 53.8 ppm for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively, or with calibration against  $\text{CHCl}_3$  at 7.27 ppm for  $^1\text{H}$ .

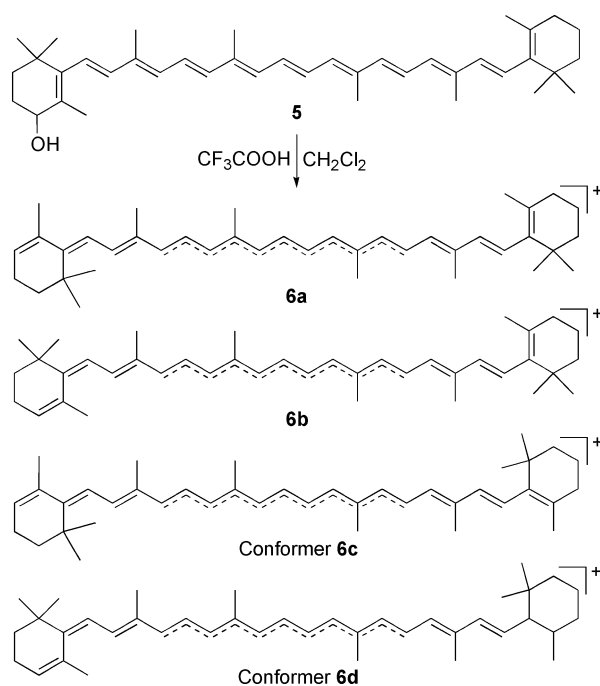
**General Method for Preparation and NMR Analysis of Carotenoid Cations.** Carotenoid substrate (1.0–1.4 mg) was dissolved in a mixture of  $\text{CD}_2\text{Cl}_2$  (0.75 mL) and Brønsted acid (in specified amounts). The mixture was transferred to a chilled NMR tube and analyzed by 500 MHz NMR (1D  $^1\text{H}$ , 2D  $^1\text{H}$ – $^1\text{H}$  gs-COSY, 2D ROESY,  $^1\text{H}$ – $^{13}\text{C}$  gs-HSQC, and  $^1\text{H}$ – $^{13}\text{C}$  gs-HMBC). Experiments with Lewis acids were performed by dissolving the carotenoid substrate (1–2 mg) in  $\text{CD}_2\text{Cl}_2$  (0.4 mL) in an NMR tube at  $-20^\circ\text{C}$  and then adding chilled  $\text{BF}_3$ -etherate (0.2 mL). The spectra were recorded as described previously.<sup>55</sup> Decomposition of the sample was observed during experiments, restricting the acquisition time. The available acquisition time, generally above 6 h, was dependent on the temperature, the substrate and acid used, and the concentration of acid.

For a detailed description of the experiments, experimental data not given in the Results, and additional carotenoid structures, see the Supporting Information.

## Results

**Analysis of NMR Spectra.** The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts and coupling constants for the carotenoid cations were established from 1D  $^1\text{H}$ , 2D  $^1\text{H}$ – $^1\text{H}$  COSY, 2D ROESY,  $^1\text{H}$ – $^{13}\text{C}$  HSQC, and  $^1\text{H}$ – $^{13}\text{C}$  HMBC experiments run at low temperatures ( $-10$  to  $-20^\circ\text{C}$ ). A common strategy was employed for analysis of all carotenoid cations. First, the different spin subsystems (2-spin, 3-spin, or 4-spin) in the polyene chain (or chains) were identified from the COSY spectrum. They then were linked to in-chain methyl groups by correlations in the

Scheme 2



ROESY spectrum. This gave the  $^1\text{H}$  chemical shifts of the entire polyene chain from H-7 to H-7'. ROESY cross-peaks between methyl group protons H-16, H-17, and H-18 and in-chain protons H-7 and H-8 connected the polyene chain to the end groups and established the bond geometry of the C-6,7 bond. The spin systems in the shielded part of the  $^1\text{H}$  spectrum, corresponding to H-2, H-3, and H-4, were correlated to the H-18 methyl protons through long-range coupling in the COSY spectrum, as well as ROESY interactions to methyl groups H-16 and H-17. Inequality of the H-16 and H-17 shifts shows that the end group is unsymmetrically substituted.

The further assignment of  $^{13}\text{C}$  chemical shifts for carbons with protons attached is available from HSQC or the direct coupling processed HMBC spectrum. By experience, HSQC and HMBC experiments on carotenoid cations in various stages of decomposition give spectra that are difficult to interpret. Quaternary carbons will in most cases be detected either by  $^2J_{\text{C,H}}$  couplings (e.g., H-16/H-17 – C-1, H-18 – C-5, H-19 – C-9 and H-20 – C-13) or by  $^3J_{\text{C,H}}$  couplings (e.g., H-16/H-17/H-18 – C-6) in the HMBC spectrum. In systems with a higher level of degeneracy, such as the symmetrical dication **8**, where the two rotamers give a theoretical total of six different  $^1\text{H}$  chemical shifts corresponding to the in-chain methyl groups H-19 and H-20, all apparently confined to a narrow window between 2.23 and 2.24 ppm, alternative approaches are needed. In this special case, the assignments of C-9 and C-13 were aided by the detection of the  $^3J_{\text{C,H}}$  couplings in the HMBC spectrum between H-7 and C-9, as well as H-11 and C-13.

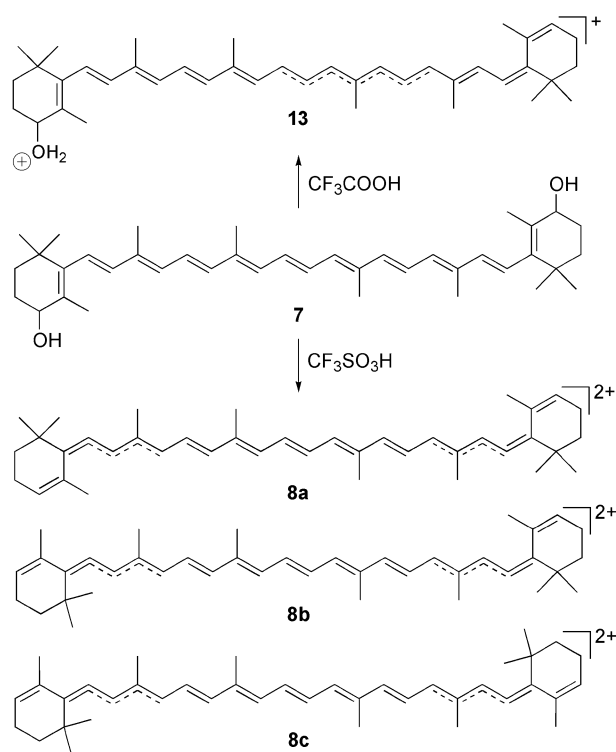
**Structure of Monocations 6, Prepared from  $\beta,\beta$ -Carotene-4-ol (5).** The above-described approach resulted in the structure elucidation of monocation **6**, prepared from  $\beta,\beta$ -carotene-4-ol (**5**), as the two diastereomers **6a** and **6b**, as reported in a preliminary communication.<sup>57</sup> Bond inversion in the central region was inferred from the coupling constants, and the distribution of the charge was demonstrated. The two isomers **6a** and **6b** differ in the stereochemistry of the C-6,7 double bond, Scheme 2. The presence of the conformers **6c** and **6d** was also

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Scheme 3



documented. Further experimental details on the monocations (**6a**, **b**, **c**, **d**), including coupling constants, are given in the present paper.

**Structures of the Dications Prepared from  $\beta,\beta$ -Carotene-4,4'-diol (7).** The first attempt to prepare the symmetrical dicarbocation **8** was performed by treatment of  $\beta,\beta$ -carotene-4,4'-diol (**7**) with  $\text{CF}_3\text{COOH}$ , by analogy to the preparation of monocation **6** from  $\beta,\beta$ -caroten-4-ol (**5**). The expected color change upon preparation of a cation was immediately noted, and VIS/NIR spectroscopy showed a  $\lambda_{\text{max}}$  of 1028 nm at  $-20$  °C.

Subsequent analysis of the cation obtained revealed the presence of a monocarbocation with the charge delocalized in the center of the polyene chain. One of the hydroxy groups was still present, as evidenced by chemical shifts and coupling pattern of the  $\beta$  end group. A more thorough investigation of the NMR data for the hydroxylated end group showed that the hydroxyl moiety had been protonated by the acid, but was still present. This was evident from the  $^1\text{H}$  chemical shift of H-4 ( $\delta_{\text{H}} = 5.43$  ppm), which, in comparison with  $\beta,\beta$ -carotene-4,4'-diol (**7**), corresponded to a downfield shift of 1.42 ppm. Comparable downfield shifts are observed for a proton in a similar neighboring position in a protonated adamantyladamantane ether ( $\Delta\delta_{\text{H}} 1.41$  ppm)<sup>60</sup> and a series of protonated alcohols,<sup>61</sup> although the effect on the  $^{13}\text{C}$  chemical shift was smaller than that for the adamantane system.<sup>60</sup>  $\text{CF}_3\text{COOH}$  is therefore not a strong enough acid to induce the elimination of both allylic hydroxy groups at  $-20$  °C. The cation prepared from  $\beta,\beta$ -carotene-4,4'-diol (**7**) by treatment with  $\text{CF}_3\text{COOH}$  was thus identified as dication **13**, Scheme 3.

A complete determination of all  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for dication **13** was not possible from the experiments performed. No further attempts were made on the complete assignments of all proton and carbon chemical shifts of **13** because of the close similarity between this cation and the monocation prepared from mono-ol **5**. Its structure would not provide new charge-distribution data.

Elevating the temperature is known to cause the elimination of protonated hydroxy groups that will not eliminate at lower temperature.<sup>61</sup> From our previous experience with carotenoid cations, increasing the temperature will result in a loss of stability, which would render the structure determination of the cation by NMR impossible. The allylic hydroxy groups were therefore acetylated in an attempt to prepare a better leaving group. However, treatment of 4,4'-diacetoxy- $\beta,\beta$ -carotene (**14**) with  $\text{CF}_3\text{COOH}$  resulted in the formation of the same dication **13**. To further enhance the leaving group, the preparation of 4,4'-di(trifluoroacetoxy)- $\beta,\beta$ -carotene (**15**) was attempted. This resulted in decomposition of the carotenoid, probably by spontaneous elimination of trifluoroacetate.

We therefore resorted to use of the stronger Brønsted acid  $\text{CF}_3\text{SO}_3\text{H}$ . Treatment of  $\beta,\beta$ -carotene-4,4'-diol (**7**) with this acid immediately caused the formation of a cation with a  $\lambda_{\text{max}}$  of 1022 nm at  $-15$  °C. Analysis by NMR as described above resulted in the structure elucidation of the target molecule, 4,4'-didehydro- $\beta,\beta$ -carotenyl dication (**8**) with 22  $\pi$  electrons. Formally, this is the dication derived from isocarotene (**10**) by removal of two electrons. Dication **8** may therefore be referred to as the isocarotene (**10**) cation.

Due to the size of the molecules, the configuration of the C-6,7 double bond does not affect the  $^{13}\text{C}$  chemical shifts beyond the central carbon atoms of the polyene chain. Therefore, the NMR spectra show two different sets of signals for the end groups of the molecule, which converge to only one set of signals when approaching the center of the polyene chain. The ratio 3:2 of the two end groups was determined from the intensities of the H-18 methyl protons, indicating a 44:45:11 ratio of the three diastereomeric dications **8c**, **8b**, and **8a**, respectively; see Scheme 3. NMR data for the two (6-*E*) and (6-*Z*) isomeric half molecules are given in Table 1.

**Structures of Cations Prepared from Echinonone (9).** A model for protonated astaxanthin (**4**) in the blue carotenoprotein crustacyanin was recently presented, based on protonated canthaxanthin (**3**).<sup>55</sup> In a recent paper, the presence of 3'-hydroxy- $\beta,\beta$ -caroten-4-one (3'-hydroxyechinenone, **16**) in another carotenoprotein has been demonstrated by X-ray crystallography.<sup>62</sup> In addition to the general interest in comparing the structure of cations of echinenone (**9**) to that of the structurally related carotenoid cations, it was therefore also of interest to see whether protonated echinenone (**9**) could be used as a model for **16** bound in this carotenoprotein.

Treatment of echinenone (**9**) in  $\text{CH}_2\text{Cl}_2$  with  $\text{CF}_3\text{COOH}$  provided the formation of cationic species, as expected, with a  $\lambda_{\text{max}}$  of 950 nm at  $-15$  °C. NMR experiments at  $-15$  °C, as described above, were used for a complete structure determination of the cations prepared. The NMR spectra revealed a complex mixture of several cations. Surprisingly, however, it

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**Table 1.** NMR Data (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -15 °C) for the Two Diastereomeric Half Molecules of Dication **8**

	(6- <i>E</i> ) half molecule ( <b>8c</b> )				(6- <i>Z</i> ) half molecule ( <b>8a</b> )			
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$^3J_{\text{H,H}}$	$^1J_{\text{C,H}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$^3J_{\text{H,H}}$	$^1J_{\text{C,H}}$
1		38.5				40.0		
2	1.71	39.0			1.75	35.2		
3	2.53	29.8			2.60	a		
4	7.05	156.7			6.91	156.6		
5		139.2				136.6		
6		185.3				188.1		
7	7.00	126.9	13.8	158	7.17	127.1	14.1	
8	8.48	166.6	14.3	157	8.39	168.9	13.8	
9		145.3				145.3		
10	7.86	169.1	12.5	157	7.83	169.3	12.3	
11	7.31	131.2		156	7.30	131.1		
12	7.59	163.2		156	7.56	163.1		
13		147.1				147.1		
14	7.26	151.4			7.25	151.4		
15	7.41	141.5			7.41	141.5		
16/17	1.48	29.6		128	1.29	28.2		125
18	2.10	21.0	H-4 <sup>b</sup>	128	2.31	25.7	H-4 <sup>b</sup>	129
19	2.23	12.1	H-8/H-10 <sup>b</sup>	129	2.23	12.3	H-8/H-10 <sup>b</sup>	129
20	2.24	13.2	H-14 <sup>b</sup>	129	2.24	13.2	H-14 <sup>b</sup>	129

<sup>a</sup> Chemical shifts could not be determined from the spectra recorded.

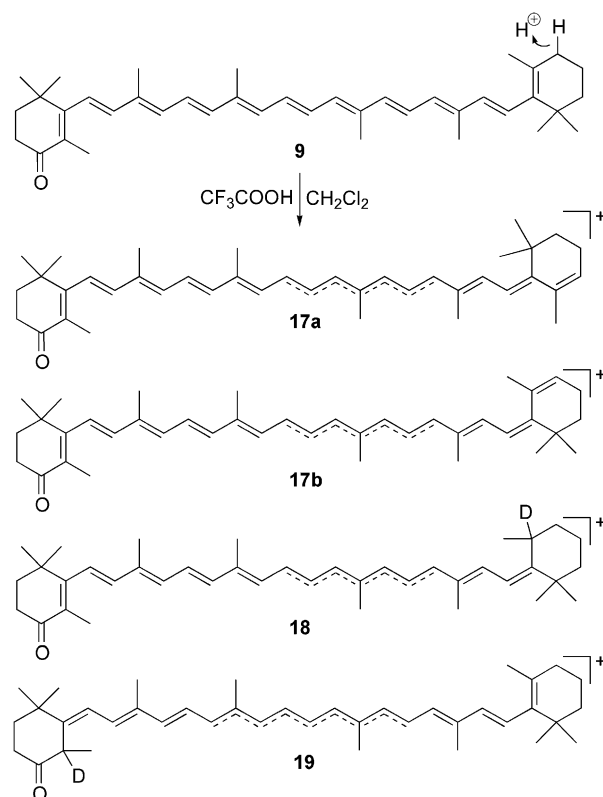
<sup>b</sup> Long-range correlations obtained from the COSY spectrum.

was found that the main carotenoid monocation had not been protonated by the acid, but that the cation was formed by elimination of a hydride from the 4'-position. The formation of hydrogen gas was not investigated. However, an analogous mechanism involving the expulsion of molecular hydrogen has been elaborated for the conversion of carotenoid furanoxides to blue oxonium ions using CF<sub>3</sub>COOH.<sup>63</sup> The monocation (**17**) obtained existed in both the (6'-*Z*) (**17a**) and the (6'-*E*) (**17b**) configurations; see Scheme 4. <sup>1</sup>H and <sup>13</sup>C chemical shifts of this cation are given in Table 2. The conformation at C-6 could not be determined because the overlap of the chemical shifts of H-7 and H-8 made it impossible to distinguish between the ROESY signals from these protons to the methyl protons on the end group.

In addition to the *E/Z* isomeric monocations **17a** and **17b**, the third major carotenoid was identified as the 5'-protonated cation **18**. For **18**, and for the minor 5-protonated cation **19**, Scheme 4, full assignment of the chemical shifts was not possible because of the strong overlap of signals and low intensity. For the same reason, the positions of the double bonds were determined only from the long-range couplings in the COSY spectrum. The three major cations **17a**, **17b**, and **18**, accounted for 75% of the total amount of carotenoid present in the reaction mixture.

**Preparation of Cations by Treatment of Carotenoids with BF<sub>3</sub>-Etherate.** Using the same approach as for the preparation of the first carotenoid dication by treatment of  $\beta,\beta$ -carotene (**1**) with BF<sub>3</sub>-etherate,<sup>54</sup> the preparation of dications from several other carotenoids was attempted to determine the effects of the end groups on the charge distribution. The carotenoids investigated include isorenieratene (**20**), lycopene (**11**), canthaxanthin (**3**), and astaxanthin (**4**). Previous problems with the NMR analyses due to the strong signals from the etherate reagent were avoided by using BF<sub>3</sub>-THF-*d*<sub>8</sub> as reagent, which could be easily distilled from a mixture of BF<sub>3</sub>-diethyl etherate and THF-*d*<sub>8</sub>.

The absorption maxima of all of these carotenoids immediately shifted from the 450 nm region to the 1000 nm region

**Scheme 4**

upon treatment with the Lewis acid, but none of them provided a stable dication whose structure could be determined by NMR analysis. Isorenieratene (**20**), however, provided monocation **21**, containing an extra hydrogen in the 7-position; see Scheme 5. Such hydrogen substituents have been observed also in other carotenoid cations, and the origin of this hydrogen atom, as a proton, a hydride, or a hydrogen radical, will be treated elsewhere. Complete <sup>1</sup>H and <sup>13</sup>C chemical shifts for monocation **21** are given in Table 2. This product only counted for a minor amount of the carotenoid species in the reaction mixture. Some signals in the COSY and ROESY spectra were also compatible with the expected dication, when compared to chemical shifts and coupling patterns of other carotenoid cations.

The special property of  $\beta,\beta$ -carotene (**1**) that the oxidation of the second electron is at a lower energy level than the first electron<sup>64,65</sup> might provide an explanation for the ease of  $\beta,\beta$ -carotene (**1**) to form a dication upon treatment with the Lewis acid BF<sub>3</sub>. Canthaxanthin (**3**), on the other hand, with a significantly higher oxidation potential for the second oxidation step in CH<sub>2</sub>Cl<sub>2</sub>, does not. Simulations in DigiSim have shown that there is a small difference in the oxidation levels for lycopene (**11**),<sup>64</sup> as for  $\beta,\beta$ -carotene (**1**), but the aliphatic **11** is known to undergo cyclizations when treated with acid. No electrochemical data are available for isorenieratene (**20**).

**NMR Assignments for Isocarotene (**10**) and Isorenieratene (**20**).** A literature survey revealed that only partial <sup>1</sup>H and <sup>13</sup>C NMR chemical shift data for isocarotene (**10**)<sup>66,67</sup> and isoreni-

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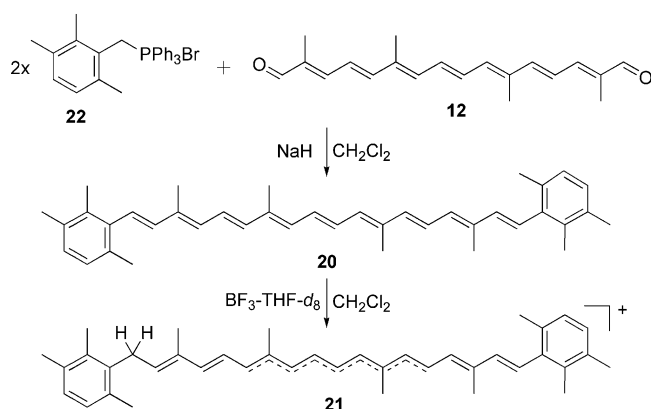
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(63) Haugan, J. A.; Liaaen-Jensen, S. *Acta Chem. Scand.* **1994**, *48*, 152.

**Table 2.** NMR Data (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -15 °C) for the C-6 *E/Z* Isomeric Monocations **17a** and **17b**, and for the 7-Protonated Isorenieratene Cation (**21**)

	17b		17a		21	
	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
1		37.1		38.4		135.8
2	1.65	39.7	1.65	35.9		134.7
3	2.35	23.7	2.4	24.6	6.92	128.4
4	6.51	144.3	6.34	144.1	6.89	127.9
5		136.5		133.5		134.3
6		169.8		172.1		136.4
7	6.77	123.2	6.86	122.8	3.66	31.0
8	7.97	155.9	7.91	157.8	6.00	147.4
9		136.6		136.2		137.2
10	7.61	165.3	7.59	166.7	7.05	156.7
11	7.15	128.1	7.15	128.1	6.85	127.9
12	7.55	163.9	7.54	164.4	7.24	159.1
13		142.3				140.9
14	7.46	161.1			7.63	166.4
15	7.06	132.8			7.10	133.2
16	1.42	29.4	1.23	27.9	2.15	15.4
17	1.42	29.4	1.23	27.9	2.21	20.5
18	2.02	21.1	2.22	25.9	2.22	20.0
19	2.15	12.4	2.16	12.4	2.08	12.2
20	2.19	12.5			2.11	12.1
1'		36.7				136.3
2'	1.91	35.9				135.4
3'	2.74	32.9			7.01	130.3
4'		206.4			6.96	128.1
5'		129.6				134.7
6'		172.2				136.4
7'	6.60	128.1			7.35	134.4
8'	6.60	143.7			6.62	139.0
9'		139.6				157.2
10'	6.56	136.3			6.72	134.7
11'	7.32	135.3			8.03	148.1
12'	6.73	140.0			6.91	138.9
13'		156.0				172.0
14'	6.77	136.3			6.99	138.5
15'	7.67	151.1			8.07	160.8
16'	1.24	27.1			2.24	17.0
17'	1.24	27.1			2.23	20.2
18'	1.92	13.7			2.28	20.8
19'	2.14	12.4			2.36	13.6
20'	2.27	13.8			2.46	14.6

**Scheme 5**

eratenes (**20**)<sup>67</sup> are available. To provide the best neutral reference data possible for determination of the charge distribution of the cations **6**, **8**, **13**, and **17**, all <sup>1</sup>H and <sup>13</sup>C chemical shifts were determined for both carotenoids. A synthetic sample of isorenieratene (**10**) was obtained, which contained both the 6-*Z* and the 6-*E* isomeric half-molecules, present in a 1:6 ratio. Isorenieratene (**20**) was prepared in a double Wittig reaction from

(2,3,6-methylbenzyl)triphenylphosphonium bromide (**22**) and crocetin dialdehyde (**12**); see Scheme 5. NMR data for isorenieratene (**10**) and isorenieratene (**20**) are given in the Supporting Information.

## Discussion

**Structures of the Carotenoid Cations.** No in-chain protonation of  $\beta,\beta$ -caroten-4-ol (**5**) or  $\beta,\beta$ -carotene-4,4'-diol (**7**) was observed by treatment with CF<sub>3</sub>COOH, or of the diol **7** treated with CF<sub>3</sub>SO<sub>3</sub>H, demonstrating that protonation of the hydroxy group is greatly favored, and that these acids are not strong enough to protonate these polyene mono- and dications. Previously, it has been shown that  $\beta,\beta$ -carotene (**1**) suffers in-chain protonation with CF<sub>3</sub>COOH<sup>68</sup> and that canthaxanthin (**3**) is protonated with CF<sub>3</sub>COOH or CF<sub>3</sub>SO<sub>3</sub>H in the polyene chain as well as on the keto groups.<sup>55</sup>

It is also interesting to note that all of the carotenoid cations, with the exception of the bond connecting the end groups to the polyene chain, seem to exist in the all-*E* configuration, as no signs of *Z* isomers have been detected in the NMR experiments. A similar observation has previously been made in studies of  $\alpha,\omega$ -diphenylpolyenyl anions.<sup>36,38</sup> For the charged carotenoids, also the 6-*E* configuration, which is not present in neutral carotenoids,<sup>4</sup> has been observed.

**4-Dehydro- $\beta,\beta$ -Carotenyl Monocation (**6**) and the Soliton Structure.** It may be concluded from basic NMR theory that the <sup>13</sup>C chemical shift is correlated to the electron density on the carbon atom. In a pioneering work, Spiess and Schneider<sup>69</sup> found that there is a linear relationship between <sup>13</sup>C chemical shift and charge ratio in charged monocyclic aromatics. O'Brien<sup>69</sup> extended this to sp<sup>2</sup>-hybridized systems, in general, however still restricted to planar, unbridged and unsubstituted hydrocarbons. The correlation between <sup>13</sup>C chemical shift,  $\delta_{\text{C}}$ , and  $\pi$ -charge density,  $\rho$ , is given in eq 1,<sup>36</sup>

$$\delta_{\text{C}} = \alpha\rho + \delta_0 \quad (1)$$

where  $\alpha$  is the total change in <sup>13</sup>C chemical shift and  $\delta_0$  is the average <sup>13</sup>C chemical shift of all sp<sup>2</sup> carbons in the uncharged molecule. O'Brien<sup>69</sup> found the best fit with  $\delta_{\text{C}} = 156.3\rho + 133.2$ . Surveying five other studies, Tolbert and Ogle<sup>36</sup> found that  $\delta_{\text{C}} = 156.2\rho + 131.9$  was the best equation to fit these data, while they in their study of a series of homologue  $\alpha,\omega$ -diphenylpolyenyl anions found somewhat higher values,  $\alpha = 187.3$  and  $\delta_0 = 133.7$ . A significantly lower change in  $\delta_{\text{C}}$  per charge has been found for aromatic di- and tetraanions. This was attributed to anisotropic ring current effects.<sup>71</sup>

In our studies of positively charged carotenoids, we have found a much higher change in chemical shifts, ca. 250 ppm per charge,<sup>54,55</sup> and this seems to be a general value for these compounds. Fitting the data obtained for monocation **6** with eq 1, we obtain eq 2.

$$\delta_{\text{C}} = 249.1\rho + 132.7 \quad (2)$$

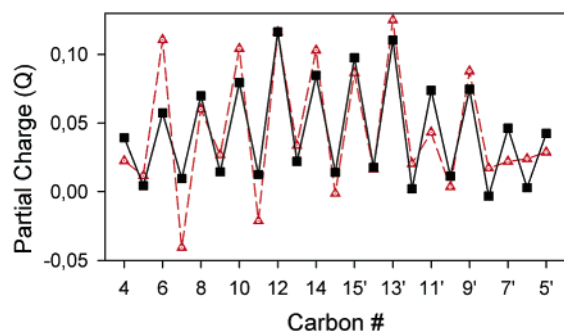
Solving this equation for  $\rho$ , the  $\pi$ -charge density at each carbon may be calculated. The result is plotted in Figure 1. The plot

(68) Mortensen, A.; Skibsted, L. H. *J. Agric. Food Chem.* **2000**, *48*, 279.

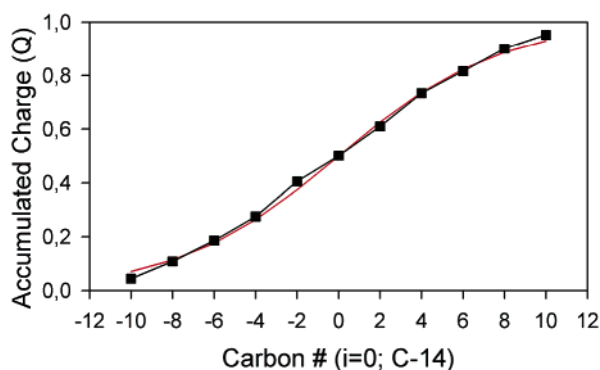
(69) Spiess, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, *3*, 468.

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**Figure 1.** Charge distribution for monocation **6**, from eq 2 (red) and eq 4 (black).



**Figure 2.** Accumulated charge ( $Q_i$ ) for monocations **6** versus carbon number  $i$  (setting middle of soliton to  $i = 0$  for C-14) (black) and regression curve for  $Q_i = 0.5 \tanh(i/7.8)$ ,  $R^2 = 0.997$  (red).

clearly shows that the resulting charge distribution does not resemble the expected distribution of a soliton, with a concentration of the charge in the center of the polyene chain, consistent with the warnings by Reimers et al.<sup>33</sup> that using O'Brien's postulate<sup>70</sup> for determining the charge on individual carbons may give quantitative errors.

A better model has been devised by employing the change in carbon chemical shift at each position,  $\Delta\delta_{C,i}$ , and correlating this to the total change in chemical shift  $\Sigma\Delta\delta_C$ . This leads to eq 3,

$$\rho_i = \Delta\delta_{C,i} / \Sigma\Delta\delta_C * Q_{\text{tot}} \quad (3)$$

where  $Q_{\text{tot}}$  is the total charge on the polyene. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift changes of **6a** and **6b** relative to the isocarotene (**10**)/ $\beta,\beta$ -carotene (**1**) neutral model described previously<sup>57</sup> are given in the Supporting Information, showing small deviations in some positions when using the new data obtained here for isocarotene (**10**), as compared to the previously published shift changes.<sup>57</sup> The total shift change of **6a** was found to be 13.8 ppm for  $^1\text{H}$  and 254.2 ppm for  $^{13}\text{C}$ . Of the  $^{13}\text{C}$  chemical shift change, 249.1 ppm, or 98%, was associated with the polyene chain. Only minor differences are seen in the results for the isomer **6b**, and the results for the major cation **6a** are therefore used for the treatment of **6** below. Inserting the values found for **6a** into eq 3 leads to eq 4 for calculation of the charge distribution of **6**.

$$\rho_i = \Delta\delta_{C,i} / 249.1 \quad (4)$$

The charge distribution calculated for **6** by using eq 4 is shown in Figure 1. It may immediately be seen from Figure 1 that

using eq 4 gives a charge distribution that is much more symmetrically located in the center of the polyene chain, as compared to eq 2, as is expected for a soliton.

From the soliton theory,<sup>28–30</sup> it may be deduced that the accumulated charge,  $Q_i$ , on a polyene chain can be expressed by eq 5.<sup>32,33</sup>

$$Q_i = Q_{\text{tot}}/2 * \tanh[(i - i_c)/l] \quad (5)$$

Here,  $l$  is the soliton charge-wave half-width, and  $i$  is the number of carbons, when the carbon number  $i_c$  gives the center of the soliton charge-wave. In Figure 2 is plotted the accumulated charge,  $Q_i$ , for **6**, against the charge-carrying carbons  $i$ , setting  $i_c = \text{C-14}$ , where  $Q_i = 0.5$ . The charge for the charge-carrying carbons has been renormalized to 1 (89% of downfield shift is located on these 10 carbons), so that  $Q_{\text{tot}}$  can be set to 1, in accordance with the charge of +1. Curve fitting with eq 5 then gives  $l = 7.8$ , in good agreement with  $l = 7–9$ , found by Reimers et al.<sup>33</sup> using AM1 calculations.

The deviations between the fitted curve and the experimental curve toward the ends of the plot, taken together with the charge localized on carbon atoms not included in the plot, may indicate that the polyene chain of monocation **6** is not long enough to avoid effects from the ends of the polyene chain, thus underestimating the half-width of the charge-wave. Nevertheless, these results indicate that the value  $l = 14$  for the soliton half-width found by Tolbert and Ogle<sup>36</sup> using O'Brien's hypothesis<sup>70</sup> is an overestimate as previously pointed out by Reimers et al.<sup>33</sup>

In a recent paper treating the protonation of carboxyl groups in canthaxanthin (**3**), we also prepared and determined the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of a monocation protonated in the C-7 position (**23**). In **23**, the charge may be delocalized over 19  $\text{sp}^2$  carbon atoms (not including the carbonyl), as compared to the 23  $\text{sp}^2$  hybridized carbon atoms available for delocalization in **6**. Applying eqs 1 and 3 for determination of the charge distribution in **23** again shows that eq 3 gives a better estimate; see Figure 3. The deviation of the alternating charge distribution to the right side of the molecule is ascribed to the carbonyl moiety. Some of the charge is being delocalized into the carbonyl moiety (including the  $\beta$ -carbon), forcing the main charge away from the carbonyl-containing end group. This also results in a compression of the soliton.

A plot of the accumulated charge for **23**, according to eq 5, is also shown in Figure 3, together with the regression curve, giving the charge-wave half-width  $l = 6.2$ , shorter than that found for **6**. This shows that the number of carbon atoms available for charge delocalization in **23** is too small to represent a free soliton.

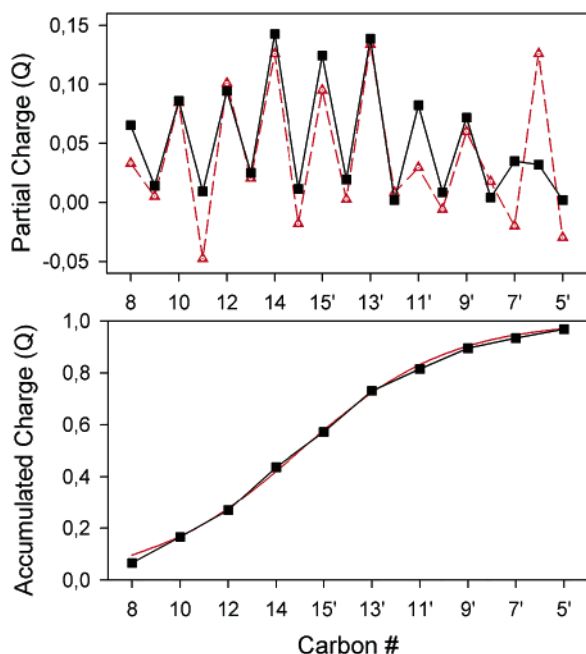
The SSH soliton model<sup>28–30</sup> also allows for the determination of the area of bond-length alternations, expressed as

$$\Delta r_i = \Delta r_{\infty} \tanh[(i - i_c)/l] \quad (6)$$

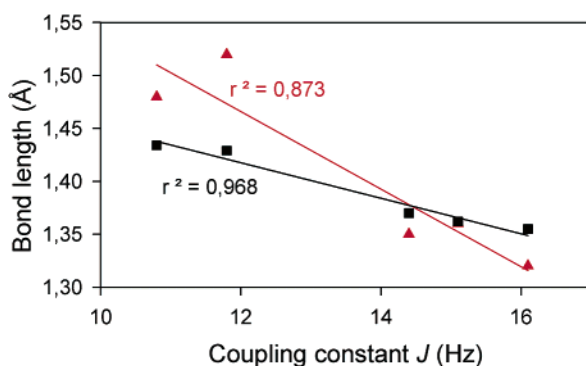
where  $\Delta r_{\infty}$  is the difference between single and double bond lengths in an infinite chain, and  $l$  is the soliton half-width.<sup>33</sup> In principle, the bond lengths of the  $E$  and  $s$ -*trans* bonds in polyenes may be determined from the  $^3J_{\text{H,H}}$  coupling constant.<sup>72</sup> For the carotenoid monocations, the methyl groups on the polyene chain complicate this determination (although simplify-

(72) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Verlagsgesellschaft: Weinheim, 1993.





**Figure 3.** Charge distribution for monocation **23**, calculated from eq 1 (red) and eq 3 (black) (top). Accumulated charge,  $Q_i$ , plotted against carbon atoms along the polyene chain for **23** (black), and curve fitting (red), giving  $Q_i = 0.5 \tanh(i/6.2)$ ,  $R^2 = 0.998$  (bottom).



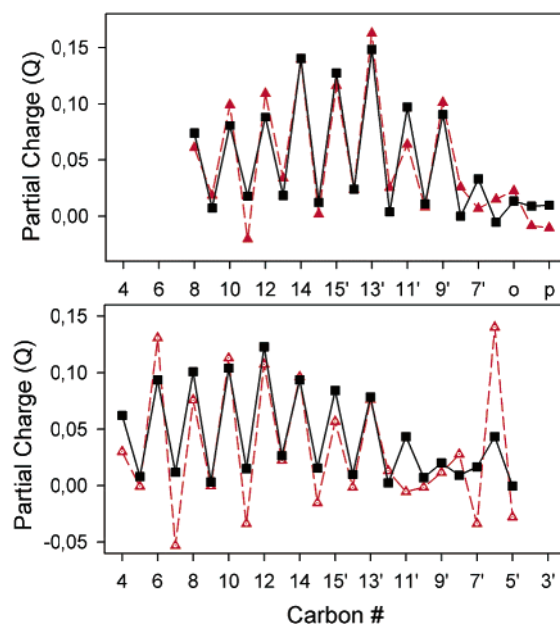
**Figure 4.** Correlation between coupling constants and experimental (red) and calculated (black) bond lengths for  $\beta,\beta$ -carotene (**1**).

ing the determination of the cation structure itself) by affecting the coupling constants through substituent effects, and by reducing the number of  $^3J_{\text{H,H}}$  coupling constants available for bond-length determination. The coupling constants of  $\beta,\beta$ -carotene (**1**) did not give a good correlation with the bond lengths determined by X-ray crystallography;<sup>73</sup> see Figure 4. A better correlation was obtained by correlation to bond lengths determined using AM1 calculations.<sup>65</sup> A reason for this difference may be a difference in structure in the solid state, but a higher resolution X-ray structure might have given better correlation. This approach for determination of the soliton width was abandoned due to the low correlation between the bond length and the determined coupling constants combined with the few coupling constants available for the cations.

#### Charge Distribution of Other Carotenoid Monocations.

The charge distribution for monocations **17** and **21**, prepared from echinenone (**9**) and isorenieratene (**20**), respectively, was determined from the change in chemical shifts according to eq 3. Isocarotene (**10**) was used as model for the left half, while

(73) Sterling, C. *Acta Crystallogr.* **1964**, *17*, 1224.



**Figure 5.** Charge distribution for the 7-hydro- $\phi,\phi$ -carotenyl cation (**21**) (top), and for the 4-dehydro-4'-oxo- $\beta,\beta$ -carotenyl cation (**17**) (bottom), calculated using eq 1 (red) and eq 3 (black). For **21**, the charge in the ortho and meta positions in the aromatic end group has been added (bottom).

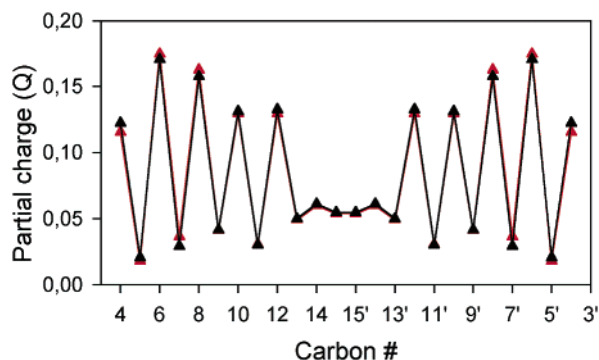
$^{13}\text{C}$  chemical shifts for echinenone (**9**)<sup>67</sup> and  $^1\text{H}$  chemical shifts for canthaxanthin (**3**)<sup>74</sup> were used as a model for the right half in the neutral reference for monocation **17**, the cation formed by elimination of hydride from the 4'-position of echinenone (**9**). For the isorenieratene monocation (**21**), 7,8-dihydro-8,7'-retro- $\beta,\beta$ -carotene-4,4'-dione (**24**)<sup>67</sup> was used as neutral model for C-7 – C-11, C-19, H-7 – H-10 and H-19 and isorenieratene (**20**) for C-12 – C-15, C-20, C-1' – C-20', H-11 – H-15, H-20 and for H-3' – H-20. No suitable model for the nonconjugated aromatic end group of monocation **21** was available, but as this end group is not carrying the charge, these data were not necessary for the determination of the charge distribution. The change in chemical shifts at each position is given in Table B in the Supporting Information, and the charge at each position is shown in Figure 5 and by the diameter of the filled circles on the structures in Chart 2. For comparison, the charge distribution calculated using eq 1 is also shown in Figure 5.

Also, for these carotenoid cations, it may be seen that eq 3 gives a better estimate for the charge distribution than does eq 1. When the charge distribution of monocation **17** is compared to that of monocation **23**, prepared from canthaxanthin (**3**), it is interesting to note the strong charge repulsion from the carbonyl moiety. Some charge is stored in the carbonyl moiety, as evidenced from the downfield shifts of the C-6' carbon in the  $\beta$ -position to the carbonyl. The chemical shift difference of the carbonyl carbon does not provide a good measure for the charge on this carbon, as charge delocalization to the carbonyl will lead to a change in C=O bond hybridization, which will also influence the chemical shift.<sup>55,75,76</sup> However, in comparison with carotenoid cations previously analyzed,<sup>55</sup> it is clear that

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(75) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 2373.

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**Figure 6.** Charge distribution on the polyene chain as determined by eq 3 for the all-*E* (**8c**) (black) and 6,6'-di-*Z* (**8a**) (red) dication of isocarotene (**10**).

the data obtained for monocation **17** are not compatible with a protonation of the carbonyl moiety.

For monocation **21**, prepared from isorenieratene (**20**), the most important feature is the negligible contribution to the charge delocalization of the aromatic end group. There is a strong driving force to avoid a reduction in electron density in the aromatic ring, which would cause a reduction in the Hückel ( $4n + 2$ ) aromaticity.

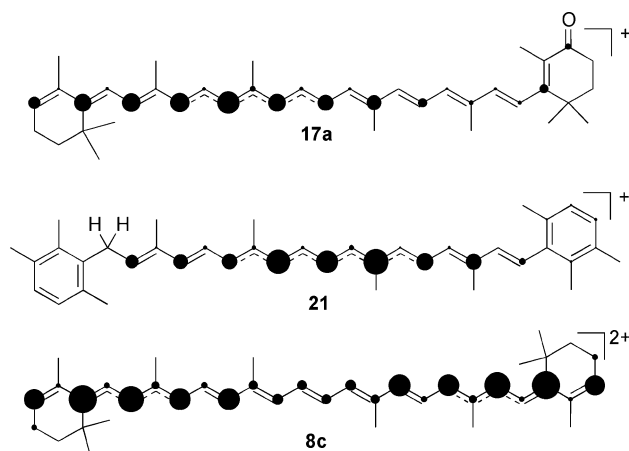
Both the carotenoid monocations **17** and **21** have soliton widths that are smaller than that of monocation **6**, providing no further insight into the width of a free soliton. The total  $^{13}\text{C}$  chemical shift change for **17** and **21**, 253.2 and 240.8 ppm (not including the nonconjugated end group), respectively, is consistent with the carotenoid cations studied previously.<sup>53–55,57</sup>

**Structures of Dications 8 and 13, and the Structural Relationship between Dications 2 ( $20 \pi e^-$ ) and 8 ( $22 \pi e^-$ ).** By the determination of all  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of dication **8** (Scheme 3) and of isocarotene (**10**), it became possible to calculate the chemical shift change of all of the  $\text{sp}^2$ -hybridized carbon atoms for the isocarotene dication (**8**) relative to neutral **10**. The chemical shift differences for all positions in the two *E/Z* isomeric half-molecules of **8** are shown in Table C in the Supporting Information.

The total  $^{13}\text{C}$  downfield shift for dication **8** is 240 ppm per charge, in good agreement with the 252 ppm  $^{13}\text{C}$  downfield shift previously found per charge for the  $\beta,\beta$ -carotene dication (**2**),<sup>53</sup> and the value found for monocation **6** (259.8 ppm). The total downfield chemical shift for  $^1\text{H}$  upon the formation of a carotenoid cation is also surprisingly uniform in the range 12.4–13.8 ppm per charge.<sup>54,55,57</sup>

From the chemical shift change data, the charge distribution for the *E/E* (**8c**) and *Z/Z* (**8a**) isomers was calculated, as shown in Figure 6, where two solitons are apparent. Due to the Coulombic repulsion of the two charges, they are located toward the ends of the polyene chain, as predicted by the SSH theory, rather than being centered in the middle, or being evenly distributed. For the *Z/Z* isomer (**8a**), it may be seen that the charge delocalization to the C-4,5 double bond is smaller than that for the *E/E* isomer (**8c**), as may be expected from the lower overlap of the  $\pi$ -orbitals of the terminal C-4,5 double bonds. The lower charge on the terminal double bond is compensated by a somewhat higher charge on the carbons next to the terminal double bonds in the *Z/Z* isomer (**8a**). The charge density on each carbon for the all-*E* isomer **8c** is illustrated by the diameter of the filled circles on the structure in Chart 2.

**Chart 2**

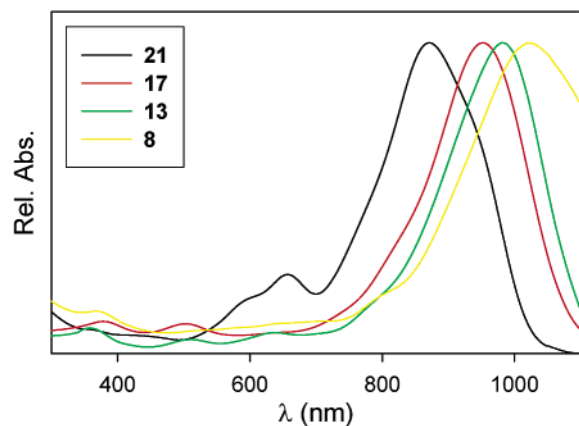


Using eq 5 for the analysis of the solitons in dication **8** is not straightforward. In principle, the dication could be treated as the sum of two solitons. However, the shape of the charge distribution shows large deviations from the shape of a soliton due to the strong Coulombic repulsion between the two charges, and in the center of the polyene chain the contributions from the two solitons are overlapping.

Some information may be gained, however, by comparison of the isocarotene dication (**8**) with the  $\beta,\beta$ -carotene dication (**2**) previously reported,<sup>53,54</sup> which is 2 carbon units shorter, and contains 20, rather than 22  $\pi$ -electrons. The most interesting feature is the decreasing charge on the terminal carbon atoms in **8**. In the  $\beta,\beta$ -carotene dication (**2**), the Coulombic repulsion is high enough to completely erase the wave-shape of the soliton, forcing the highest charge density to the terminal carbons. Opposing the Coulombic repulsion force is the energy gain in storing the charge in a wave-shaped soliton. The longer polyene chain in dication **8** allows one more carbon for delocalization of each charge, and the lower charge on the terminal carbons may be an indication that the Coulombic repulsion is reduced sufficiently to make the wave-shape of the soliton apparent. However, some caution must be exercised not to interpret these data too far. The stabilization of the charge by the tertiary terminal carbons in **2**, as compared to the secondary terminal carbons in **8**, may play a role, and a longer conjugated dication would be needed to confirm this hypothesis.

The charge distribution for dication **13**, containing a protonated hydroxy group, Scheme 3, could not be completely determined from the recorded NMR data. As judged by the available  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift differences, the charge distribution of **13**, with one charge on the polyene chain, is very similar to that of monocation **6**, as expected. However, the center of the soliton is shifted somewhat away from the end of the molecule carrying the protonated hydroxy group. This is interpreted as a result of the Coulombic repulsion from the charge on the protonated hydroxy group and is another piece of indirect evidence for the presence of charge on an oxonium moiety in one end group.

**NIR Absorption and Stability of Carotenoid Cations.** Comparison of the NIR spectra of the carotenoid carbocations studied revealed increasing  $\lambda_{\text{max}}$  for the isorenieratene monocation (**21**, 871 nm, Figure 7) <  $\beta,\beta$ -carotene dication (**2**, 925 nm<sup>54</sup>) < echinenone carbocation (**17**, 953 nm, Figure 7) < dication **13** (982 nm, Figure 7) < isocarotene dication **8** (1022



**Figure 7.** VIS/NIR spectra of isocarotene dicarbocation (**8**), dication **13**, monocation **17**, and the isorenieratene monocation (**21**).

nm, Figure 7) < monocation **6** (1028 nm<sup>57</sup>). A rationalization of these data is not simple because the method of preparation/counterion, size of the charge, length of the polyene chain, solvent, and temperature have to be considered.

In the VIS/NIR spectra of the carotenoid cations, the charged state seems to be more important than the length of the polyene chain. This may explain why the stability measured for the cations is much higher when determined from the NIR spectra as compared to what is found in the NMR experiments. Even though there are reactions going on, which makes the reaction mixture more and more complex, and thereby making it impossible to perform NMR experiments on the sample, there are still cations present that will show an absorption around 900–1000 nm in the VIS/NIR spectrum. This also provides an explanation as to why the color of the cation solution may retain its black color for weeks on the lab bench.

## Conclusion

The stereoisomeric monocations **6a**, **6b**, **6c**, and **6d** with 22 delocalized  $\pi$ -electrons were prepared from  $\beta,\beta$ -caroten-4-ol (**5**) by reaction with CF<sub>3</sub>COOH. Treatment of  $\beta,\beta$ -carotene-4,4'-diol (**7**) with the same acid resulted in a dication (**13**) with the protonated hydroxy group intact.

Three stereoisomeric dicarbocations **8a**, **8b**, and **8c** also with 22 delocalized  $\pi$ -electrons were obtained from  $\beta,\beta$ -carotene-4,4'-diol (**7**) by reaction with the stronger Brønsted acid CF<sub>3</sub>-SO<sub>3</sub>H.

Another four carotenoid cations were prepared and completely characterized by treatment of echinenone (**9**) with CF<sub>3</sub>COOH (**17**, **18**, **19**) and by treatment of isorenieratene (**20**) with BF<sub>3</sub>-THF-*d*<sub>8</sub> etherate (**21**).

Detailed structures of these delocalized cations including the charge distribution, bond types, and regions of bond inversion

were elucidated by NMR spectroscopy in the temperature range from -10 to -20 °C.

The NMR analysis was based on 1D <sup>1</sup>H, and a series of 2D (<sup>1</sup>H-<sup>1</sup>H COSY, 2D ROESY, <sup>1</sup>H-<sup>13</sup>C HSQC, and <sup>1</sup>H-<sup>13</sup>C HMBC) experiments. A general strategy used for the determination of mixtures with up to four stereoisomers is outlined.

For determination of the charge distribution of the carotenoid monocations **6**, **17**, **21**, and **23**, it was found that correlation of the change in <sup>13</sup>C chemical shift of the charged versus the neutral carotenoid model gave a better result than correlation of the charge against <sup>13</sup>C chemical shift, in accordance with the O'Brien implementation<sup>70</sup> of the Spiess-Schneider relationship.<sup>69</sup> It may be inferred that this result is generally valid for sp<sup>2</sup>-hybridized polyene cations, while for a nonsubstituted polyene (or polyacetylene) cation of infinite chain length, the result from using this method and the results from using the O'Brien postulate<sup>70</sup> should be equal, because the chemical shifts of all carbon atoms are equal. The disadvantage of the method employed here is the necessity of knowing the chemical shifts of a relevant neutral model.

The charge distribution determined by the change in <sup>13</sup>C chemical shifts was used to calculate the soliton width. For monocation **6**, with charge delocalized over 23 carbon atoms, the soliton half-width was found to be 7.8 carbons, in good agreement with previous AM1 calculations for a free soliton. For the shorter-chain monocation **23**, with the charge delocalized on 19 sp<sup>2</sup> carbon atoms, the soliton half-width was found to be only 6.2 carbons, indicating that cations with longer delocalization of the charge than over 23 carbon atoms may be necessary for unequivocal determination of the half-width of a free soliton.

The charge distribution of the 22  $\pi$  electron dication **8** showed that upon increasing the number of carbons available for charge delocalization from 22 (20  $\pi$  electron cation **2**) to 24, the Coulombic repulsion is no longer strong enough to force the charge to the far ends of the polyene chain. Thus, the appearance of two solitons can be seen in the isocarotene dication **8**.

Uncritical use of NIR spectra for the identification and determination of the stability of carotenoid cations has been discussed.

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**Supporting Information Available:** Detailed experimental procedures and additional spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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