Vinylogous β -Carotenes: Generation, Storage, and Delocalization of Charge in Carotenoids

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In this paper, we report on the synthesis of β -carotenes of variable chain length with between 5 and 23 double bonds (1-7). These oligoenes were prepared by McMurry and Wittig reactions. The tetradecapreno- β -carotene 7 would seem to be the longest β -carotene yet reported. Furthermore, we investigated the electronic properties using cyclic voltammetry and photoelectron spectroscopy (UPS) to generate openshell and closed-shell ions of carotenoids in solution and in the solid state, respectively. With increasing chain length (\geq 11 double bonds), even the generation of tetracations and tetraanions could be observed by cyclic voltammetry. Extending the number of conjugated bonds causes the potentials to converge to limiting values. All electron-transfer processes occur in one-electron steps, which are close to each other in pairs. The potential difference between the first oxidation

Introduction

Carotenoid radical and closed-shell ions play remarkable roles in several processes: 1. Carotenoids can quench chlorophyll fluorescence by electron transfer from the carotenoid to the singlet excited porphyrin, thereby controlling photosynthetic energy flow^[1], 2. carotenoid radical cation formation may inhibit cyclic electron flow around the photosystem-II reaction center^[2], 3. carotenoid cations or anions are formed by reactions with other radicals, e.g. with superoxide $O_2^{-[3]}$, $CCl_3O_2^{\bullet[4]}$, or with $NO_2^{[5]}$. The structures and the electronic properties of these ions have been investigated using absorption, resonance Raman, IR and ESR spectroscopy and cyclic voltammetry^{[6][7]}, as well as by restricted and unrestricted Hartree-Fock calculations^{[8][9]}.

Similar open-shell and closed-shell ions have been studied in linear polyenes^[10], oligo(phenylenevinylene) chains^{[11][12]}, oligo(perinaphthylenes)^[13], oligo(*para*-phenylenes)^[14], and other conjugated oligomers of defined structure and chain length ("oligomeric approach")^{[11][15][16]}. Variations of chain lengths lead to changes in chemical and potential and the first reduction potential is a linear function of the reciprocal chain length. Despite the different techniques used (CV and UPS) and the different condensed phases, there is an excellent correspondence between the energies of the radical cation states generated by the two methods. This shows that the radical cation formation is principally determined by the chain length. The structures of the ion states were investigated using semiempirical methods at the NDDO level. Charge delocalization and bond relaxation are not identical and do not utilize the same number or the same kind of atoms. It can be shown that from the length of 20 double bonds onwards, the effective conjugation length for doubly-charged cations converges slowly to a limiting value.

physical properties, which allow extrapolation to higher oligomers and even polymers. This approach has also been applied to oligomeric thiophenes, pyrroles, anilines and acetylenes. The band gap for polyacetylene^{[17][18][19][20]}, $\Delta E = 1.7$ eV, was determined from cyclic voltammetrical measurements on α, ω -*tert*-butylpolyenes (by plotting ΔE against the reciprocal number 1/*n* of double bonds)^[10]. Because of the low solubility of these compounds, only small chain lengths up to 8 double bonds could be investigated.

The introduction of several methyl groups should, on the other hand, considerably increase solubility and at the same time improve chemical stability and handling. Therefore, we synthesized carotenoids 1-7 with extended conjugated π sytems of between 5 and 23 π bonds and investigated their redox properties by cyclic voltammetry, ultraviolet photoelectron spectroscopy and semiempirical calculations. Special emphasis was placed on the question as to the localization and delocalization of reactive centers and charges, and whether or not the domains of bond equalization corresponded more or less to the charged areas.

Scheme 1



Scheme 2



Syntheses

Minicarotenoids 1 and 2 were prepared using the McMurry reaction (Zn, TiCl₄, THF/CH₂Cl₂)^[21]. However, we utilized the Wittig reaction in the synthesis of the chain-elongated carotenoids 5–7. To this end, the phosphonium salt $12^{[22a]}$ was treated with dialdehydes 8-10. The C₅-phosphonium salt 11 was used to extend the chain length to C_{30} and C_{40} , as in dialdehydes 9 and 10, respectively^[23]. In this way, decapreno- β -carotene 5 (C₅₀) and dodecapreno- β -carotene 6 (C₆₀) are more conveniently available than by following published procedures^[24-26]. Tetradecapreno- β -carotene 7 was previously unknown. It was isolated by chromatography as a black solid, and was found to be soluble in nhexane and chlorinated hydrocarbons forming violet-colored solutions. Even at low temperatures under argon, slow decomposition was observed. α -Carotene (β , ϵ -carotene) 3 was prepared from the C₂₅-aldehyde, 12'-apo-β,β-caroten-12'-al, and [5-(2,6,6-trimethylcyclohex-2-enyl)-3-methylpenta-2,4-dienyl]triphenylphosphonium bromide^[22b]. β-Carotene (β , β -carotene, BASF AG) was purified by CC prior to use.

Results and Discussion

Cyclic Voltammetry

The experimental conditions are described in the Experimental Section. The results (Table 1, Figures 1 and 2) can be summarized as follows:

a) The number of possible redox states increases with increasing chain length: From β -carotene 4 (11 double bonds) onwards, tetracations and tetraanions are observed.

b) On proceeding in the same direction, all potentials shift to lower values and converge to limiting potentials.

c) The electron-transfer processes occur in one-electron steps, which are close to each other in pairs.

d) With increasing conjugation length, the potential difference between these pairs as well as within these pairs decreases due to the diminishing Coulombic repulsion. The difference between the first oxidation potential $E^{l}_{al/2}$ and the first reduction potential $E^{l}_{cl/2}$ gives an electrochemical indication of the HOMO-LUMO gap:

$$\Delta E(\text{gap}) = E^{1}_{a1/2} - E^{1}_{c1/2}$$

The correlation between this energy difference ΔE and the reciprocal chain length 1/n is linear (at least over this 1/n range, Figure 3). Extrapolation to $n = \infty$ yields a potential difference of $\Delta E = 1.25$ V for polyacetylene void of defects. The band gap between the valence and conduction bands in polyacetylene can therefore be approximated as $E_{\rm g}$ (band gap) = 1.25 eV, which is in good agreement with other experimental and theoretical results (1.2 eV $\leq E_{\rm g} \leq 1.8$ eV^{[10][15][27-30]}). It is not surprising that experimentally determined band gaps tend to be larger than those obtained by extrapolation, since the actual conjugation length in polyacetylene will not be $n = \infty$. The linear correlation of Figure 3 predicts that a "real" conjugation length of $n \approx 33$ double bonds will have a band gap $E_{\rm g} = 1.5$ eV^[28]. This length agrees well with estimates from Raman spectroscopic investigations^[29].

It is remarkable that from a chain length of $n \ge 11$ double bonds onwards, the second anodic (oxidation) electron-transfer step becomes energetically more favorable than the first one. This behavior in the dication formation is also of interest with regard to theoretical aspects^[31], e.g. in describing the charge storage mechanism of conducting polymers. Simple models such as HMO predict the formation of closed-shell ions without a potential separation between the two electron-transfer steps. The experimental data indicate that the redox potential of the first electrontransfer step is influenced by geometrical distortion and interactions with both the solvent and counterions during the monocation formation. These changes require additional

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Comp.	п	Oxidation in SO_2			Reduction in DMA			
1		$E^{1}_{1/2}/E^{2}_{1/2}$	$E^{3}_{1/2}$ -	$E^{4}_{1/2}$	$E^{1}_{1/2}$	$E^{2}_{1/2}$	$E^{3}_{1/2}$	$E^{4}_{1/2}$
1	5	0.82 ^[b]	_	_	-2.36	-2.76	_	-
2	7	0.67 ^[b]	2.04	_	-1.96	-2.27	—	_
3	10	0.56 ^[b]	1.53	-	-1.67	-1.81	-3.11	—
4	11	0.51 ^[b]	1.35	1.54	-1.60	-1.69	-2.89	-3.08
5	15	0.43 ^[b]	0.97	1.11	-1.	47 ^[b]	-2.42	-2.59
6	19	0.33 ^[b]	-	_	-1.	39[b]	-1.99	-2.12
7	23	0.33 ^[b]	_	-	-1.	39[ь]	-2.01	-2.11

Table 1. Cyclic voltammetrical data of 1-7

^[a] $E_{1/2}$ in volts; reference electrodes: Ag/AgCl electrode (SO₂), Ag wire (DMA), T = -60 °C, supporting electrolyte: TBAPF₆, electrode: platinum. - ^[b] Two single-electron-transfer steps at the same potential.

Figure 1. Cyclic voltammograms of 1-7 in DMA/TBABr (reduction) and SO₂/TBAPF₆ (oxidation) at T = 213 K, v = 0.1 V/s. Voltammograms of **6** and **7** in SO₂ are solid-state voltammograms



Figure 2. Redox potentials (see Table 1) of 1-7 versus 1/n (n = number of π bonds). DMA/TBABr (reduction) and SO₂/TBAPF₆ (oxidation) at T = 213 K, v = 0.1 V/s



energy. In this case, the potential of the second electron transfer is not changed and the experimental data give no evidence for an extra stabilization as suggested by the bipolaron model. On the other hand, the limiting oxidation

Figure 3. Electrochemical "HOMO-LUMO gap", $\Delta E(\text{gap}) = E_{a 1/2}^1 - E_{c 1/2}^1$, as a function of 1/n (n = number of π bonds)



potential is seen to be approached for finite conjugation lengths of about 25-30 double bonds. A further extension of the chain length does not seem to result in greater stability of these dications. It is therefore concluded that doubly-charged positive defects in large polyenes and carotenoids can attain a state of minimal energy when allowed to extend over these finite conjugation lengths.

Semiempirical Calculations

The structures of the singly-charged and doubly-charged ion states were investigated using the semiempirical Austin Model 1 (AM1) method^[32]. The complete geometry optimization was carried out for 1, 2 and 4–7 as ground state molecules M, as ground state radical cations M^{•+} [using both the half-electron method and the unrestricted Hartree-Fock (UHF) formalism], and as ground state dications M²⁺. The calculations give information on bond lengths, charge distributions and orbital energies^[33]. Singly-charged ions (spin 1/2) M^{•+} exhibit bond relaxations over the whole π chain between the terminal rings (Table 2, Figures 4 and 6). Areas with considerable changes in charge density ($\Delta q \ge +0.03$) differ somewhat from these relaxation domains within the selected limits of changes (Table 2, Figures 5 and 7).

Doubly-charged cations M^{2+} , on the other hand, possess two spinless charged symmetry-equivalent (c_i) areas, which develop more or less ideal bond equalization (Table 2, Fig-

Table 2. Bond relaxation and charge delocalization as defined in Figures 6 and 7. Calculations: $AM1^{[32]}$, monocations: UHF. In dications, the total domain is composed of two symmetry-equivalent (c_i) subdomains

number of π bonds	number of C a	atoms within	number of C atoms		
	the domain	a of bond	within the domain of		
	relaxa	tion	charge density changes		
	Monocation	Dication	Monocation	Dication	
5	6	4	$\begin{array}{r} 6\\10\\14\\10\end{array}$	6	
7	10	8		10	
11	18	8		18	
15	26	10		22	
19 23		10 12		22 30	

Figure 4. Changes in C–C bond length [pm] upon one-electron and two-electron oxidation of C_{40} and C_{50} β -carotenes (AM1 calculations^[32], monocations: UHF)



ures 4 and 6). In the central part of the molecule, however, there is strong bond alternation and, in comparison with the neutral parent polyene M, a reversal of double and single bonds is seen. The two symmetry-equivalent halves (c_i) of charge density changes ($\Delta q > +0.1$, see Figure 7) in dications turn out to be larger than the bond relaxation domains ($\Delta l = \pm 3-7$ pm, see Figure 6) within these selected limits of changes. This can be interpreted in terms of the

Figure 5. Changes in total electron density at carbon centers upon one-electron and two-electron oxidation of C_{40} and C_{50} β -carotenes (AM1 calculations^[32], monocations: UHF)



concept of the "vertical stabilization" of cations^[34] (vide infra). If theoretical bond relaxation domains and areas of charge density changes in dications are compared with experimental data on the dependence on chain lengths, an interesting result emerges (Figure 8).

Both experimental and theoretical data approach limiting values at 25-30 double bonds. The aforementioned finite domains for states of minimal energy are self-sufficient and clearly do not seek further extension. An approximate "mirror image behavior" of the oxidation curve on the one hand and the theoretical dependencies on the other, is observed. Charge delocalization areas and $\pi(CC)$ and $\sigma(CC)$ bond relaxation domains do not necessarily coincide, at least within the selected limits of changes. Non-relaxed areas with no or little bond equalization can also be used for charge delocalization and, therefore, for stabilization. This is consistent with the aforementioned concept of the "vertical stabilization" of cations^[34]. Vertical stabilization has been defined as that stabilization in $M^{\bullet+}$ which is obtained with the internal geometry of M^{•+} remaining essentially as it was in the reactant M.

The orbital diagrams also reflect the changes during oxidation. Singly-charged radical cations show two orbitals within the "band gap", the lower one being singly occupied. Doubly-charged species exhibit two vacant midgap orbitals



Figure 6. Domains of C-C bond length relaxation upon oxidation (monocations: UHF) where changes Δl amount to $\pm 3-7$ pm for C₄₀ and C₅₀ β -carotenes

Figure 7. Domains of charge delocalization upon oxidation where changes in total electron density Δq amount to more than +0.03 (in monocations, UHF) and +0.1 (in dications) for C₄₀ and C₅₀ β -carotenes



("midgap states"). Because of a more or less efficient overlap of the corresponding wavefunctions, the energy difference between these two unoccupied midgap orbitals is strongly dependent on chain length: 0.87 eV for **1** and 0.01 eV for **6**.

Solid-State Photoelectron Spectra

Solid-state photoelectron spectroscopy is an appropriate method for obtaining threshold energies $e\phi^{th}$ (i.e. the lowest

ionization energies) for carotenoids in the solid state. These values are even more useful than the ionization energies of single carotenoid molecules in the gas phase (sufficient volatility taken for granted!), as in the amorphous or crystalline solid state the carotenoid molecules are surrounded by species of the same kind, a situation which approximates to that in many important natural systems where carotenoids are in close proximity to other carotenoids or different chromophores such as porphyrins (aggregates, light harvesting complexes, eye spots, photosynthetic reaction cen-

Figure 8. Graphical dependence of experimental oxidation potentials (____), domains of calculated charge density changes (- -), and calculated bond relaxation domains (.....) on the number of π bonds for dications of 1, 2 and 4-7



Figure 9. Relationship between ionization threshold energies $e \phi^{th}_{SA}$ and widths ΔE_{SA} of solid-state photoelectron spectra^[a]



^[a] $E_{\rm F}$: Fermi energy, $E_{\rm SA}^{\rm V}$: vacuum level of sample, $E_{\rm SU}^{\rm V}$: vacuum level of substrate, $e\phi_{\rm SU}$: work function of substrate, $e\phi_{\rm SA}$: work function of sample, hv: energy of photons, $E_{\rm kin}$: kinetic energy of photoelectrons in sample and analyser, $E_{\rm g}$: band gap, $e\phi^{\rm th}_{\rm SA}$: ionization threshold energy of sample, $\Delta E_{\rm SA}$: width of spectrum, $E_{\rm VB}$: edge of valence band, $E_{\rm CB}$: edge of conduction band, $e\phi_{\rm A}$: work function of analyser, $e\Delta\phi_{\rm bias}$: negative bias voltage applied to the specimen, $E_{\rm A}^{\rm V}$: vacuum level of analyser, $E_{\rm A}^{\rm F}$: Fermi energy of analyser

ters). These ionization threshold energies will therefore satisfactorily reflect the one-electron donating abilities of carotenoids in solid or semi-solid matrices. Furthermore, it is of interest to ascertain whether or not such solid-state properties show any meaningful correlation with the redox potentials recorded by cyclic voltammetry.

Photoemission, i.e. photoionization, from solids is more complicated than corresponding processes in the gas phase^[35]. In Figure 9, the relationship between the work functions $e\phi$ of sample and analyzer, the negative bias $e\Delta\phi$ bias applied to the specimen, the ionization threshold energy $e\phi^{\text{th}}$, and the final spectrum width ΔE_{SA} are depicted.

This relationship allows the relatively straightforward evaluation of the ionization threshold energy $e\phi^{\text{th}}$ of the sample using the width of the spectrum ΔE_{SA} :

The determination of threshold energies in solid-state spectra may pose some difficulties. Whereas calibration is easily performed using metals such as Au, Ag, or Cu, as well as reference compounds such as polystyrene or anthracene, the edges of the spectrum can sometimes only be deciphered with difficulty. There are several procedures that can ultimately be successful:

1. Inflection points of both the S-shape cut-off edges and the Fermi edges are taken and the intersection of the inflection point tangent with the energy axis is sought^{[36][37]}.

2. Inflection points can be used to directly project the perpendicular onto the abscissa. This method turned out to give precise and reproducible data.

3. In cases where the determination of inflection points is rather uncertain, the following remedial measures can be taken:

a) In most cases, the first derivative allows inflection points to be discerned with sufficient accuracy (β -carotene is successfully reproduced in this way: 5.5±0.1 eV^[38]).

b) The secondary emission of electrons causes an increase in emitted intensity in the lower energy region. A compensation for this increase is possible using the Shirley algorithm^{[39][40]}, which calculates the background secondary emission in an iterative manner. This is subsequently subtracted from the original spectrum. The inflection points are then determined according to method a (β -carotene is satisfactorily reproduced in this way: 5.4±0.1 eV).

c) Multiple smoothing^{[41][42]} (five to ten times) of the spectra reduces the intensity of low-intensity ionization events. The resulting background spectrum is again sub-tracted from the original. The Fermi edge is well resolved using this procedure (β -carotene is satisfactorily reproduced in this way: 5.4 ± 0.1 eV). In Figure 10, the results obtained for carotenoids 1, 2, 4, and 5 are presented.

Figure 10. Correlation between experimental ionization threshold energies $e \phi^{\text{th}}_{\text{SA}}$ [eV] and experimental oxidation potentials for 1, 2, 4, and 5^[a]



 $^{[a]}r$: correlation coefficient. Error limits: threshold energies ± 0.1 eV, oxidation potentials ± 50 mV

It is most remarkable to see that there is a more than satisfactory correlation between the oxidation potentials measured by CV and the ionization threshold energies obtained by UPS. We therefore conclude that these values are true indicators of the one-electron-donating ability of β carotenes either in the highly solvating environment of liquid SO₂ or in the polarizable environment of the solid amorphous or crystalline state.

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Experimental Section

Cyclic Voltammetry: The experiments were performed using a three electrode apparatus equipped with a platinum disc working electrode (d = 1 mm), a platinum counterelectrode, and either an Ag/AgCl reference electrode (SO₂) or an Ag pseudo reference electrode (dimethylamine). Dimethylamine/tetrabutylammonium bromide (reduction) and sulfur dioxide/ tetrabutylammonium hexa-fluorophosphate (oxidation) were used as solvent/electrolyte systems. The purification of the solvents has been described elsewhere^{[43][44]}. All voltammograms were recorded at 213 K and the potentials were calibrated with the redox couples ferrocene/ferrocenium (SO₂) and cobaltocene/cobaltocenium (dimethylamine).

General: All operations were carried out under nitrogen. – IR: Perkin-Elmer 710 B. – UV/Vis: Zeiss DMS 21 114 Q III. – NMR: Varian VXR 300 (300 MHz and 75 MHz, for ¹H and ¹³C, respectively). With CDCl₃ as solvent TMS was used as internal standard. – MS: MAT 311 A (70 eV). – CC: Merck silica gel 60, 0.063-0.040 mm.

UV Photoelectron Spectroscopy: The measurements were made using an ESCA spectrometer (Fisons, VG Instruments, 200X) equipped with a UV source (Leybold UVS 10/35) and a Mark II 127° spherical analyser with an array of 5 channeltrons as detector. The spectra were recorded with a constant pass energy of 5-10 eVand with a negative bias of 10 V to the specimen so as to record an unchanged cut-off edge of the secondary electrons. The energy scale of the spectrometer was routinely calibrated for XPS conditions with pure Au, Ag, and Cu metal standards. In addition, the work function of Au was determined by UPS for calibration: 5.3 eV. This is close to the published value of 5.13 eV^[36]. The work function of polycrystalline Cu was determined in acceptable agreement with the reference value (4.6 eV, as compared with 4.65 eV^[36]). Carotenoids were dissolved in organic solvents such as methanol or CH₂Cl₂ (ca. 10 mg in 100 ml). A small drop of the solution was applied to the gold-plated surface of the specimen holder. The solvent was then evaporated in vacuo and samples were introduced into the analyser chamber via the fast entry lock and the preparation chamber within a period of 5 min. The residual pressure within the analyser chamber was typically 10^{-9} mbar. The concentration of the solution permitted calculation of the thickness of the dye layer assuming a density of about 1.0 g/cm³. Three thicknesses in the range 10-30 nm were prepared by variation of the amount of solution applied. No influence of the thickness on surface charging of the specimen during UPS measurements was observed. On the other hand, the carotenoid layer was sufficiently thick and homogeneous to avoid any distortion of the UP spectrum by contributions from the photoelectrons of the gold substrate. The mean free path of the low energy photoelectrons within the organic layer amounted to about 1.25 nm according to the empirical relation of Seah^[45], thus leading to their complete absorption within a range of about 4 nm.

Dialdehydes **9**/**10**: To a solution of dialdehyde **8** (2.0 g, 6.7 mmol, BASF AG) in dry CH₂Cl₂ (50 ml), a solution of phosphonium salt

11 (17.1 g, 33.5 mmol) in dry CH_2Cl_2 (80 ml) and a solution of sodium methoxide (1.81 g, 33.5 mmol) in dry methanol (50 ml) were added. The mixture was stirred at room temp. for 24 h, dropped into water, extracted with CH_2Cl_2 , and the combined extracts were dried over MgSO₄. The solvent was evaporated and the residue was dissolved in acetone. *p*-Toluenesulfonic acid (0.1 g) was added. After 2 h, the solvent was evaporated. CC (*n*-hexane/ethyl acetate, 3:1) of the residue yielded dialdehyde **9** (1.6 g, 57%)^[23].

Dialdehyde **9** (1.0 g, 1.8 mmol) in dry CH_2Cl_2 (50 ml) was similarly treated with a solution of phosphonium salt **11** (5.9 g, 12 mmol) in dry CH_2Cl_2 (40 ml) and a solution of sodium methoxide (0.62 g, 11.5 mmol) in dry methanol (15 ml), leading after workup to dialdehyde **10** (0.4 g, 31%).

3,4-Dimethyl-1,6-bis-(2,6,6-trimethylcyclohex-1-enyl)-1,3,5-hexatriene (1): At -78°C, 27 ml of a 1 M solution (27 mmol) of titanium(IV) chloride in dry CH₂Cl₂ was added dropwise to 3.3 g (50 mmol) of zinc powder in 20 ml of dry THF. The mixture was stirred for 0.5 h at room temp. and then cooled to -78 °C once more. B-Ionone (1.6 g, 8.0 mmol) in 20 ml of dry THF was added and the resulting mixture was stirred until the β -ionone was no longer detectable by TLC. After addition of 50 ml of a 15% aqueous ammonia solution, the reaction mixture was filtered and the filtrate was extracted with CH2Cl2. Washing with saturated NaCl solution, drying over MgSO₄, and CC (n-hexane/ethyl acetate, 4:1, $R_{\rm f} = 0.7$) yielded 1.9 g of 1 (67%) as an (*E*/*Z*) mixture. - ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 1.02, 1.03$ (s, 12 H, 6'-, 6''-CH₃), 1.48 (m, 4 H, 5'-, 5''-CH₂), 1.62 (m, 4 H, 4'-, 4''-CH₂), 1.71 (d, ${}^{4}J = 0.8$ Hz, 6 H, 2'-, 2''-CH₃ of the 3-Z-isomer), 1.74 (d, ${}^{4}J = 0.8$ Hz, 6 H, 2'-, 2''-CH₃ of the 3-E-isomer), 1.97 (s, 6 H, 3-, 4-CH₃), 2.02 (br. t, ${}^{4}J = 6$ Hz, 4 H, 3'-, 3''-CH₂), 6.15, 6.71 (AB system, ${}^{3}J =$ 16 Hz, 2 H, 1-, 2-CH of the 3-Z-isomer), 6.18, 6.65 (AB system, ${}^{3}J = 16$ Hz, 2 H, 1-, 2-CH of the 3-*E*-isomer). – IR (KBr): $\tilde{v} =$ 3020 cm⁻¹ (=C-H), 2980-2800 (C-H), 1610 (C=C), 1595 (C= C), 940 (=C-H). – UV/Vis (CHCl₃): λ_{max} (lg ϵ) = 323 nm (4.898). - MS (70 eV); m/z (%): 354 (28) [M⁺ + 1], 353 (100) [M⁺], 105 (15), 95 (14), 69 (23), 55 (18), 41 (14). $- C_{26}H_{40}$ (352.6): calcd. C 88.56, H 11.44; found C 88.29, H 11.60.

3,8-Dimethyl-1,10-bis-(2,6,6-trimethylcyclohex-1-enyl)-1,3,5,7,9decapentaene (2): The preparation was carried out in analogy to the procedure described above for 1 using 0.8 g (3.8 mmol) of 3methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,5-dienal in 10 ml of dry CH₂Cl₂, 1.65 g (25.0 mmol) of zinc powder in 10 ml of dry CH₂Cl₂, and 13.7 ml (13.7 mmol) of a 1 M solution of titanium(IV) chloride in dry CH₂Cl₂. Yield: 0.50 g of **2** (33%) ($R_f = 0.9$, *n*-hexane/ethyl acetate, 4:1). - ¹H NMR (300 MHz, CDCl₃): $\delta = 1.03$ (s, 12 H, 6'-, 6''-CH₃), 1.46 (m, 4 H, 5'-, 5''-CH₂), 1.62 (m, 4 H, 4'-, 4''-CH₂), 1.71 (d, ${}^{4}J = 0.8$ Hz, 6 H, 2'-, 2''-CH₃), 1.94 (s, 6 H, 3-, 8-CH₃), 2.02 (br. t, ${}^{4}J = 6$ Hz, 4 H, 3'-, 3''-CH₂), 6.14-6.60 (m, 8 H, 1-, 2-, 4-, 5-, 6-, 7-, 9-, 10-CH). – IR (KBr): $\tilde{v} = 3000$ cm⁻¹ (=C-H), 2960-2800 (C-H), 1700 (C=C), 1360-1340 (C–H), 950 (=C–H). – UV/Vis (CHCl₃): λ_{max} (lg ϵ) = 381 nm (4.913). - MS (70 eV); m/z (%): 406 (31) [M⁺ + 1], 405 (100) [M⁺], 404 (89), 69 (41), 55 (30), 43 (44), 41 (26).

 β .e-Carotene (α -Carotene) (3)^[22b]: A solution of 0.3 g (5.7 mmol) of sodium methoxide in 10 ml of dry methanol was added to a solution of 1.0 g (2.9 mmol) of the C₂₅-aldehyde 12'-apo- β , β -caroten-12'-al and 3.2 g (5.8 mmol) of [5-(2,6,6-trimethylcyclohex-2-enyl)-3-methylpenta-2,4-dienyl]triphenylphosphonium bromide in 30 ml of dry methanol at room temp. over a period of 20 min. After 6 h, 40 ml of methanol was added and the solution was heated under reflux for 1 h. It was then allowed to cool and stored overnight at 0°C. The precipitated product thus obtained was fil-

tered off and washed with methanol. CC (n-hexane) yielded 1.1 g of 3 (72%). - ¹H NMR (300 MHz, CDCl₃): $\delta = 0.92$ (s, 12 H, 16-, 16'-, 17-, 17'-CH₃), 1.01 (s, 12 H, 19-, 19'-, 20-, 20'-CH₃), 1.76 (s, 6 H, 18-, 18'-CH₃), 2.45 (m, 4 H, 2-, 3-CH₂), 2.53 (m, 4 H, 2'-, 3'-CH₂), 6.2–7.5 (m, 14 H, 7- to 15-CH, 7'- to 15'-CH). – ¹³C NMR (75 MHz, CDCl₃): $\delta = 12.0$ (s, 20-C), 12.8 (s, 20'-C), 13.2 (s, 19-C), 13.9 (s, 19'-C), 18.9 (s, 18-C), 19.8 (3-C), 22.5 (s, 3'-C), 23.5 (3'-C), 27.1 (17'-C), 28.7 (17-C), 28.2 (16'-C), 29.0 (16-C), 31.7 (2'-C), 32.4 (1'-C), 33.8 (4-C), 35.0 (1-C), 39.8 (2-C), 54.0 (6'-C), 120.4 (4'-C), 126.8 (7-C), 129.4 (5-C), 130.8 (7'-C), 131.0-137.3 (8- to 15-C, 8'- to 15'-C). – IR (KBr): $\tilde{v} = 3030 \text{ cm}^{-1}$ (=C–H), 2830 (C-H), 1680 (C=C), 1480 (C-H), 960 (=C-H).

Vinylogous β -Carotenes 5–7: Dialdehydes 8, 9, or 10 were dissolved in CH₂Cl₂/methanol (1:1) along with a 10-fold excess of phosphonium salt 12. A solution of sodium methoxide in methanol was then added at room temp. (5-fold excess with respect to the dialdehyde). After 6 h, the solution was dropped into H₂O, and extracted with CH₂Cl₂. The combined extracts were dried over MgSO₄ and the solvent was evaporated. CC (n-hexane/ethyl acetate, 1:1) yielded the respective carotenoids.

3,7,11,16,20,24-Hexamethyl-1,26-bis(2,6,6-trimethylcyclohex-1enyl)hexacosa-1,3,5,7,9,11,13,15,17,19,21, 23,25-tridecaene (Decapreno- β -carotene) (5): 2.0 g (6.7 mmol) of crocetindialdehyde 8, 26.5 g (67.0 mmol) of phosphonium salt 12, and 1.5 g (27 mmol) of sodium methoxide in 25 ml of dry methanol were reacted as described above. Yield: 1.0 g of 5 (42%). - ¹H NMR (300 MHz, CDCl₃): $\delta = 1.03$ (s, 12 H, 6'-, 6''-CH₃), 1.46 (m, 4 H, 5'-, 5''-CH₂), 1.62 (m, 4 H, 4'-, 4''-CH₂), 1.72 (d, ${}^{4}J = 0.8$ Hz, 6 H, 2'-, 2"-CH₃), 1.98 (m, 22 H, 3'-, 3"-CH₂, 3-, 7-, 11-, 16-, 20-, 24-CH₃), 6.13-6.69 (m, 20 H, 1-, 2-, 4-, 5-, 6-, 8-, 9-, 10-, 12-, 13-, 14-, 15-, 17-, 18-, 20-, 21-, 22-, 23-, 25-, 26-CH). – IR (KBr): $\tilde{\nu} = 3000$ cm⁻¹ (=C-H), 2960-2850 (C-H), 1700, 1670 (C=C), 1260, 1195, 1020, 950 (=C-H), 800. – UV/Vis (CHCl₃): λ_{max} (lg ϵ) = 517 nm (5.328), 488 (5.227), 552 (5.235). – MS (70 eV); m/z (%): 670 (3) $[M^+ + 1]$, 669 (6) $[M^+]$, 159 (22), 95 (30), 69 (34), 43 (100).

3,7,11,15,20,24,29,32-Octamethyl-1,34-bis(2,6,6-trimethylcyclohex-1-enyl) tetratriaconta-1,3,5,7,9,11,13,15, 17,19,21,23,25,27,29,31,33-heptadecaene (Dodecapreno- β -carotene) (6): 0.1 g (0.20 mmol) of dialdehyde 9, 1.26 g (2.30 mmol) of phosphonium salt 12, and 0.12 g (2.30 mmol) of sodium methoxide in 2 ml of dry methanol were reacted as described above. Yield: 60 mg of **6** (31%). - ¹H NMR (300 MHz, CDCl₃): $\delta = 1.03$ (s, 12 H, 6'-, 6''-CH₃), 1.46 (m, 4 H, 5'-, 5''-CH₂), 1.62 (m, 4 H, 4'-, 4''-CH₂), 1.72 (d, ${}^{4}J = 0.8$ Hz, 6 H, 2'-, 2''-CH₃), 1.98 (m, 28 H, 3'-, 3''-CH₂, 3-, 7-, 11-, 16-, 20-, 24-, 28-, 32-CH₃), 6.13-6.69 (m, 26 H, 1-, 2-, 4-, 5-, 6-, 8-, 9-, 10-, 12-, 13-, 14-, 16-, 17-, 18-, 19-, 21-, 22-, 23-, 25-, 26-, 27-, 29-, 30-, 31-, 33-, 34-CH). – IR (KBr): $\tilde{v} =$ 3000 cm⁻¹ (=C-H), 2960-2850 (C-H), 1700, 1670 (C=C), 1260, 1095, 1020, 960 (=C-H), 800. – UV/Vis (CHCl₃): λ_{max} (lg ε) = 547 nm (4.969), 519 (4.923), 580 (4.827). - MS (70 eV); m/z (%): 799 (<1) [M⁺], 159 (26), 119 (28), 109 (25), 105 (29), 95 (30), 91 (33), 69 (35), 55 (33), 44 (38), 43 (100), 41 (36).

3.7.11.15,19,24,28,32,36,40-Decamethyl-1,42-bis(2,6,6-trimethylcyclohex-1-enyl)dotetraconta-1,3,5,7,9,11,13,15,17, 19,21,23,25,27,29,31,33,35,37,39,41-henicosaene (Tetradecapreno- β -carotene) (7): 0.20 g (0.40 mmol) of dialdehyde 10, 2.52 g (4.6 mmol) of phosphonium salt 12, and 0.24 g (4.60 mmol) of sodium methoxide in 2 ml of dry methanol were reacted as described above. Yield: 80 mg of 7 (24%). $- {}^{1}$ H NMR (300 MHz, CDCl₃): $\delta = 1.03$ (s, 12 H, 6'-, 6''-CH₃), 1.46 (m, 4 H, 5'-, 5''-CH₂), 1.62 (m, 4 H, 4'-, 4''-CH₂), 1.72 (d, ${}^{4}J = 0.8$ Hz, 6 H, 2'-, 2''-CH₃), 1.98 (m, 34 H, 3'-, 3''-CH₂, 3-, 7-, 11-, 15-, 20-, 24-, 28-, 32-, 36-, 40-CH₃),

6.13-6.69 (m, 32 H, 1-, 2-, 4-, 5-, 6-, 8-, 9-, 10-, 12-, 13-, 14-, 16-, 17-, 18-, 20-, 21-, 22-, 23-, 25-, 26-, 27-, 29-, 30-, 31-, 33-, 34-, 35-, 37-, 38-, 39-, 41-, 42-CH). – IR (KBr): $\tilde{\nu}$ = 3020 cm $^{-1}$ (= С-Н), 2950-2850 (С-Н), 1690 (С=С), 1260, 1090, 1060, 1020, 960 (=C-H), 800. – UV/Vis (CHCl₃): λ_{max} (lg ϵ) = 550 nm (4.956), 485 (4.832), 603 (sh, 4.734). - MS (70 eV); m/z (%): 933 (36) (M⁺). - C₇₀H₉₂ (933.50) high res. MS: calcd. 932.7199; found 932.7190.

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