Longer polyenyl cations in relation to soliton theory†

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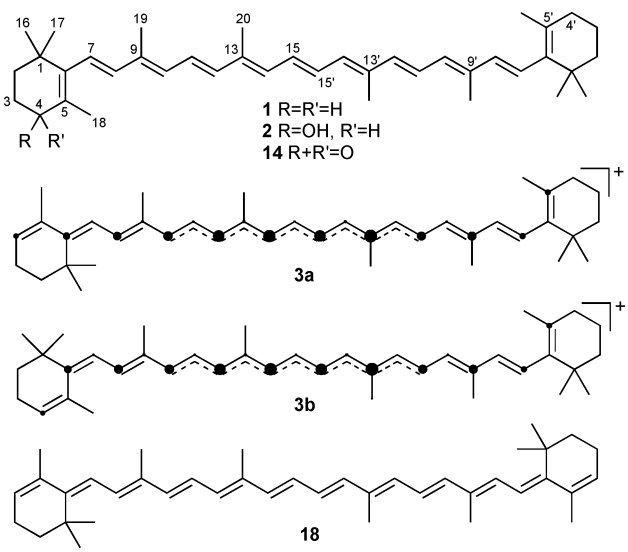
The carotene-like polyenes decapreno-β-carotene (C_{50}), C_{54}-β-carotene (C_{54}, first synthesis) and dodecapreno-β-carotene (C_{60}) with 15, 17 and 19 conjugated double bonds, respectively, were synthesized by double Wittig reactions. Introduction of a leaving group in allylic position failed, and cations were obtained by hydride elimination effected by i) triphenylcarbenium tetrafluoroborate-d_{15}, prepared by a new method, or ii) treatment with trifluoroacetic acid-*d*. Deuterated reagents were employed for product analysis by ^{1}H NMR. Parallel experiments were performed with β,β-carotene (C_{40}). NIR spectra at room temperature and at −15 °C were employed for characterisation and stability studies of the cationic products. In CH_2Cl_2 λ_{max} in the 900–1350 nm region was recorded. NMR data for the cationic product of β,β-carotene obtained by the two new preparation methods were consistent with the two monocations previously characterised. The cationic products of the longer polyenes provided downfield-shifted, broadened signals, compatible with C_{50}-monocation, mixed C_{54}-mono- and dication and C_{60}-dication. Combined NIR and NMR data suggest that the extent of charge delocalisation is limited by the maximum soliton width for cations obtained from linear polyenes with more than *ca.* 20 sp^2-hybridized carbon atoms.

Introduction

The theoretical fundament of charge distribution in very long polyenes, such as doped polyacetylene, was provided by Heeger and co-workers, leading to the Su–Schrieffer–Heeger (SSH) model.[1,2] According to this model, charges are carried in holes or defects in the polyene structure, called solitons. They consist of regions of intermediate bond lengths, in contrast to the strict alternating nature of single and double bonds surrounding them. The charge inside a soliton can mathematically be described as a charge density wave, in the case of a delocalised cation oscillating between finite positive values and zero on alternating carbon atoms, with the highest values in the center of the soliton. In this respect, the model is in agreement with the more familiar concept of resonance structures for smaller delocalised charged species. However, whereas the drawing of resonance structures imposes no limitations as to the extent of delocalisation in the molecule, the SSH-model implies a limiting value for how far a polyenyl cation or anion can delocalise, described by the soliton half-width, *l*. This remains one of the more controversial aspects of the soliton theory.[3] Physically, the parameter *l* describes the width of the region containing half of the charge of the soliton, in terms of the number of bonds.

Experimental studies of soliton properties have been carried out mostly with polyacetylene, both doped and undoped, employing techniques such as resonance Raman spectroscopy, cyclic voltammetry, NIR spectroscopy, EPR and ENDOR.[2,4–7] Using doped polyacetylene, the properties of the bulk of the polyene are superimposed on the characteristics of the solitons contained in the polyacetylene. For accurate description of the physical properties of the soliton itself, its availability in a pure compound is desired. Experimental information about bond lengths and charge distributions is of particular interest.

Carotenoids, such as β,β-carotene (**1**, Scheme 1), are a convenient source of long polyenes. Charged carotenoids, including radical cations, monocations and dications, have been studied experimentally using the techniques mentioned above.[8] Moreover, it is possible through the study of smaller molecules to prepare spinless charge-delocalised polyenes in a controlled manner, and thereby study the charged polyene by ^{1}H and ^{13}C NMR. The ^{13}C chemical shift is of particular importance in this respect, because



Scheme 1

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† Electronic supplementary information (ESI) available: ^{1}H NMR (olefinic region) of cations from β,β-carotene (**1**), decapreno-β-carotene (**4**) and dodecapreno-β-carotene (**6**). See DOI: 10.1039/b706212e

of the empirical correlation of the shift with atomic charge, as first shown by Spiesecke and Schneider for aromatic compounds,[9] and later extended to other systems with sp^2-hybridised carbon atoms.[10] NMR studies of α,ω-diphenylpolyene anions of various length have been reported, employing these empirical correlations to give a description of the charge distribution.[3,11,12]

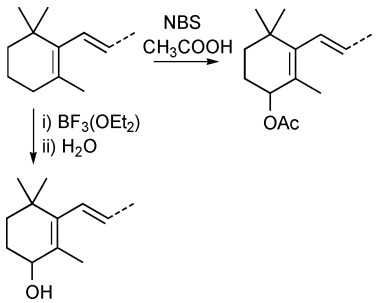
We have previously reported on the formation of delocalised carotenoid monocations formed by acid-induced dehydration of the allylic alcohol β,β-caroten-4-ol (**2**, isocryptoxanthin), creating the longest delocalised carbocation **3a,b** fully characterised by NMR to date (Scheme 1).[13,14] By comparison of the ^{13}C chemical shifts of the resulting monocations **3a,b** with model compounds, we were able to provide an estimate for the charge distribution, and thereby also the extent of delocalisation, as described by the soliton half-width l, yielding $l = 7.8$. In the present work we aimed at the preparation of even longer delocalised polyenyl carbocations, and by NIR and NMR studies to gain insight on the extent of delocalisation in these systems.

Results

Preparation of substrates

The elongated, carotene-like compounds referred to as decapreno-β-carotene (**4**, C_{50}), C_{54}-β-carotene (**5**) and dodecapreno-β-carotene (**6**, C_{60}) were prepared as substrates. Decapreno-β-carotene (**4**) has previously been synthesized *via* a 15,15′-didehydro derivative,[15] and dodecapreno-β-carotene (**6**) by a $C_{15} + C_{30} + C_{15}$ approach.[16] In the present work the C_{50}- (**4**), C_{54}- (**5**) and C_{60}- (**6**) polyenes were prepared by an analogous scheme by Wittig coupling reaction between β-ionylidenethyltriphenylphosphonium bromide (**7**), synthesised from β-ionone (**8**) *via* vinyl-β-ionol (**9**), and the appropriate diapocarotenals **10–12**, using NaH for generation of the ylide[17] (Scheme 2). This approach yielded the desired target molecules in satisfactory quantities.

Various strategies were employed for the introduction of a leaving group in allylic position of the parent polyene (Scheme 3). Addition of NBS in the presence of excess acetic acid to β,β-carotene (**1**) gave the diacetate, as reported by others,[18] whereas attempts to obtain the monoacetate failed. Reaction with BF_3–diethyl etherate, followed by quenching with water,[19,20] gave the desired mono-ol product **2**, albeit in a poor yield in experiments with β,β-carotene (**1**). When applied to the longer C_{54} polyene **5**, it became apparent that the resulting allylic alcohol was rather labile, and another strategy had to be considered.

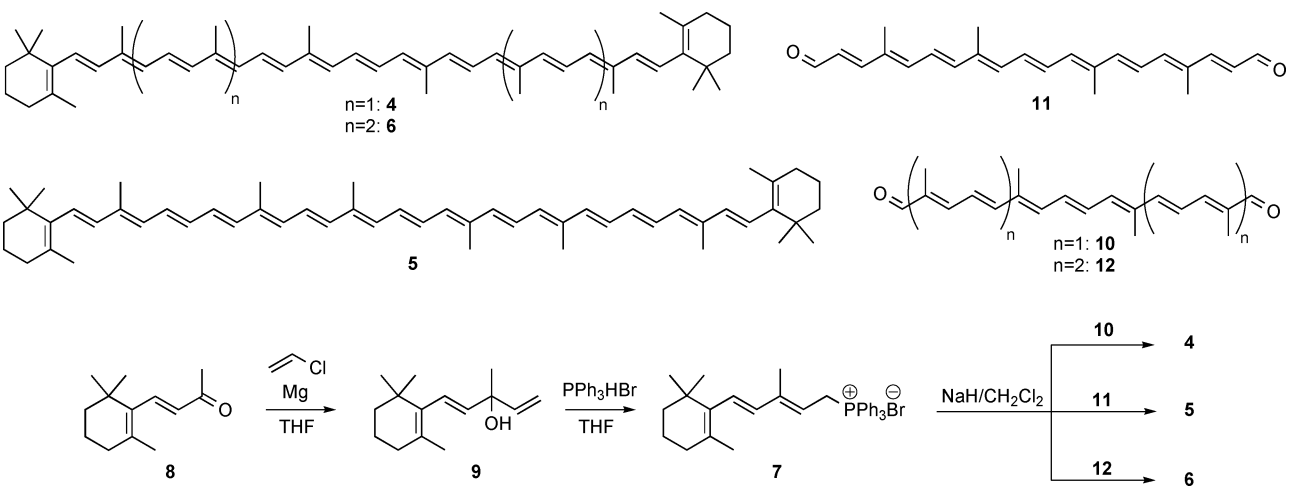


Scheme 3

We have previously noted the ability of carotenoids to eliminate hydride in allylic positions under acidic conditions.[13,21] This was first observed by the formation of blue oxonium ions from a 5,8-furanoid derivative neochrome (**13**) (Scheme 4, i),[21] and later during NMR studies of β,β-caroten-4-one (**14**, echinenone, Scheme 1) treated with dilute trifluoroacetic acid-*d* (Scheme 4, ii).[13] It is known that hydride abstractions can be achieved by treatment with triphenylcarbenium ions.[22] Triphenylcarbenium tetrafluoroborate-d_{15} (**15**) was therefore prepared as an NMR-compatible hydride abstraction reagent. The initial triple Grignard reaction from bromobenzene-d_5 (**16**) and diethyl carbonate offered a convenient pathway to triphenylmethanol-d_{15} (**17**), and represented an alternative to a published method.[23] Treatment of **17** with tetrafluoroboric acid in propionic anhydride provided the carbenium ion **15** (Scheme 5).[22]

Preparation of polyenyl cations

The polyenyl cations were prepared from the parent polyenes **1**, **4**, **5** and **6** using two main strategies, i) either by employing triphenylcarbenium tetrafluoroborate, or ii) by treatment with trifluoroacetic acid. Both reagents were used in dilute solution in



Scheme 2

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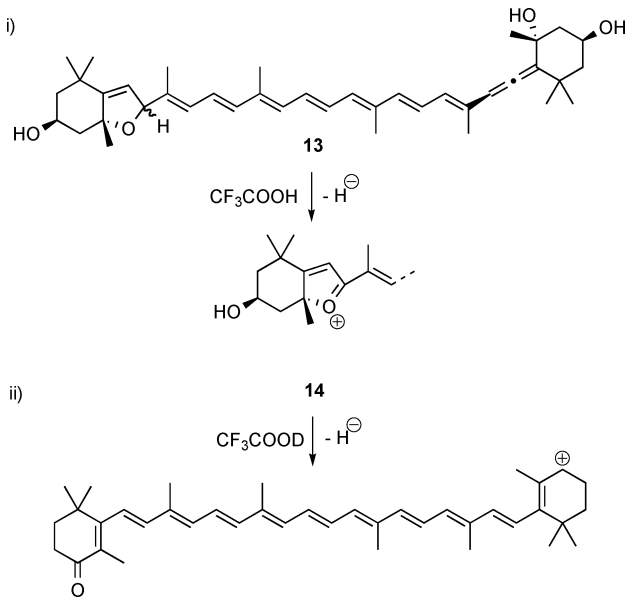
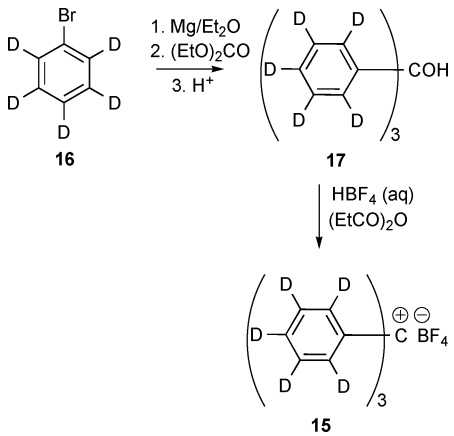


Scheme 4



Scheme 5

chlorinated solvents. For NMR experiments, deuterated analogs were employed.

VIS/NIR spectra

i) With triphenylcarbenium tetrafluoroborate. The VIS/NIR absorption spectra were recorded for β,β-carotene (**1**) and the polyenes **4–6** both at room temperature and at −15 °C in a dichloromethane solution containing triphenylcarbenium tetrafluoroborate. Large bathochromic shifts, characteristic for the formation of positively charged polyenes, were observed at both temperatures, illustrated by the initial room temperature absorptions depicted in Fig. 1.

At room temperature, the stability of the cationic products from the polyenes **4–6** was considerably lower than for the products from β,β-carotene (**1**). The position of the absorption maxima also drifted during the experiments. When the temperature was lowered to −15 °C, constant absorptions were observed. Data for stability and λ_{max} are given in Table 1.

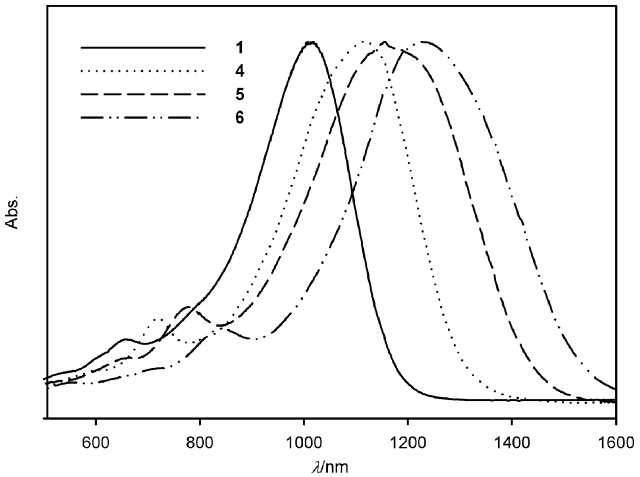


Fig. 1 Initial absorptions at room temperature of cationic products from β,β-carotene (**1**), decapreno-β-carotene (**4**), C_{54}-β-carotene (**5**) and dodecapreno-β-carotene (**6**) in dichloromethane containing 4 mg mL^{-1} Ph_3CBF_4.

Table 1 Absoption maxima and relative stability of cationic products formed in 4–6 mg mL^{-1} solution of triphenylcarbenium tetrafluoroborate in CH_2Cl_2

	Room temperature			−15 °C
Starting polyene	λ_{max}/nm, 0 h	λ_{max}/nm, 1 h	Rel. ε, 1 h	λ_{max}/nm [a]
β,β-Carotene (**1**)	1011	966	0.88	1033
C_{50}-β-Carotene (**4**)	1123	1031	0.40	1130
C_{54}-β-Carotene (**5**)	1180	1140	0.57	1215
C_{60}-β-Carotene (**6**)	1229[b]	1241	0.60	1290

[a] Constant for 1 h. [b] After 5 min λ_{max} 1260 nm was measured.

ii) With trifluoroacetic acid. VIS/NIR measurements of the absorption spectra for the polyenyl cations from the polyenes **1** and **4–6** were performed in an analogous manner to that described above. In addition to varying the temperature from −15 °C to room temperature, two different acid concentrations were used. Data for the lower concentration, 0.013 M, are given in Table 2, and for the higher concentration, 1.3 M, in Table 3.

The influence of the acid concentration is obvious; a higher concentration of acid gives in general a hypsochromic shift of the λ_{max} of the resulting polyenyl cation. Compared to the trityl experiments above, the stability at room temperature is considerably higher when trifluoroacetic acid is used, although higher acid concentrations reduce the stability.

Table 2 Absoption maxima and relative stability of cationic products formed in 0.013 M solution of trifluoroacetic acid in CH_2Cl_2

	Room temperature			−15 °C
Starting polyene	λ_{max}/nm, 0 h	λ_{max}/nm, 1 h	Rel. ε, 1 h	λ_{max}/nm [a]
β,β-Carotene (**1**)	1022	1010	2.00	980
C_{50}-β-Carotene (**4**)	1207	1199	0.99	1153
C_{54}-β-Carotene (**5**)	1277	1263	0.96	1238
C_{60}-β-Carotene (**6**)	1330	1307	0.99	1300

[a] All absorptions unstable, with λ_{max} drifting significantly. Initial values are given.

Table 3 Absoption maxima and relative stability of cationic products formed in 1.3 M solution of trifluoroacetic acid in CH_2Cl_2

	Room temperature			−15 °C
Starting polyene	λ_{max}/nm, 0 h	λ_{max}/nm, 1 h	Rel. ε, 1 h	λ_{max}/nm [a]
β,β-Carotene (**1**)	997	967[b]	0.49	853, 922
C_{50}-β-Carotene (**4**)	1099	1076	0.80	1123
C_{54}-β-Carotene (**5**)	1152	1154	0.88	1216
C_{60}-β-Carotene (**6**)	1236	1222	0.88	1308

[a] Unstable absorptions with significant drift. [b] Another peak at λ_{max} 798 nm apparent after 1 h.

NMR spectra

Several polyenes were treated with the deuterated trityl reagent **15**, namely β,β-carotene (**1**), decapreno-β-carotene (**4**), echinenone (**14**, Scheme 1) and neochrome (**13**, Scheme 4) for NMR characterisation. All polyene/trityl cation mixtures yielded blue or green solutions, compatible with the formation of delocalised cations.[8] However, except for β,β-carotene (**1**), no detailed interpretation of the ^{1}H spectra was possible. For β,β-carotene (**1**), the expected monocationic product **3** was observed, as part of a mixture with other unidentified polyene compounds. The chemical shifts deviated significantly from those earlier reported for **3a,b** (Scheme 1),[14] which may be ascribed to different counterions, *i.e.* tetrafluoroborate *versus* trifluoroacetate.

β,β-Carotene (**1**) treated with trifluoroacetic acid-*d* in $CDCl_3$ at −15 °C also gave the monocation **3**, with only minor differences in ^{1}H and ^{13}C chemical shifts from values reported earlier in CD_2Cl_2.[14] NMR chemical shift data of the main isomer **3a** are given for the two new preparation methods in Table 4, as well as a chemical shift comparison of their respective ^{13}C chemical shifts.

The NMR spectra of C_{50}-β-carotene (**4**), C_{54}-β-carotene (**5**) and C_{60}-β-carotene (**6**) treated with trifluoroacetic acid-*d* yielded downfield-shifted, but severely broadened signals. No accurate assignments of the olefinic parts could be made for either cationic product. However, the mean chemical shifts of olefinic protons were calculated from the broadened signals using Simpson's formula,[24] giving average chemical shifts of 6.88 ppm and 7.11 ppm for the cations formed from **4** and **6**, respectively. For the cations formed from **5**, an initial product with an average chemical shift of 6.80 ppm is formed, which later shifts further downfield to 7.13 ppm. These numerical estimates of the average olefinic chemical shift compared to the average chemical shift of the neutral polyenes gives a total change of chemical shift of 10.0 ppm and 18.5 ppm for cations prepared from **4** and **6**, respectively, and 10.3 ppm and 18.2 ppm for the two different forms from **5**. This was calculated by multiplying the difference in average shift by 20 (for **4**), 24 (for **5**) and 26 (for **6**), which equals the number of sp^2-hybridised protons for the three polyenes.

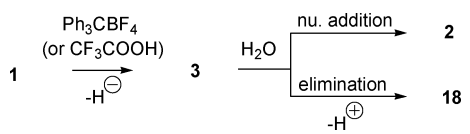
Quenching experiments

Addition of water as a nucleophile to β,β-carotene (**1**) treated with triphenylcarbenium tetrafluoroborate yielded products compatible with formation *via* cation intermediates. Judging by UV/VIS spectra and HPLC-DAD analysis, β,β-caroten-4-ol (**2**) and isocarotene (**18**, Scheme 1) were formed, demonstrating an alternative pathway for the introduction of new functional groups in an allylic postition to the polyene chain (Scheme 6). Both products can mechanistically be explained by initial removal of a hydride by the trityl reagent, and subsequent nucleophilic addition or deprotonation. Exchange of water for aqueous potassium acetate yielded a mixture of the mono-ol **2** and its corresponding acetate, in addition to small amounts of isocarotene (**18**).

Table 4 Chemical shifts of C_{40}-monocations **3a**, prepared from β,β-carotene (**1**) in $CDCl_3$ at −15 °C by treatment with (a) deuterated trityl reagent **15** and (b) CF_3COOD

	δ_H/ppm		δ_C/ppm		$\Delta\delta_C$/ppm
Carotenoid numbering[a]	(a)	(b)	(a)	(b)	(a) − (b)
1			35.9	36.0	−0.1
2	1.58	1.59	39.7	39.7	0
3	2.24	2.25	23.2	23.2	0
4	6.18	6.21	137.3	137.8	−0.5
5			135.5	135.1	0.4
6			159.9	160.1	−0.2
7	6.55	6.58	121.4	121.7	−0.3
8	7.63	7.57	147.5	147.3	0.2
9			138.5	138.7	−0.2
10	7.51	7.29	160.6	158.9	1.7
11	6.92	6.97	126.5	126.6	−0.1
12	7.71	7.29	162.3	159.5	2.8
13			140.5	140.4	0.1
14	7.95	7.41	164.6	161.4	3.2
15	6.98	6.97	132.0	131.8	0.2
16	1.38	1.36	29.1	29.1	0
17	1.38	1.36	29.1	29.1	0
18	1.97	1.97	21.5	21.4	0.1
19	2.06	2.08	11.8	11.8	0
20	2.12	2.14	12.4	12.5	−0.1
1′			34.1	34.1	0
2′	1.48	1.49	39.7	39.5	0.2
3′	1.62	1.62	18.9	18.6	0.3
4′	2.10	2.13	33.6	34.0	−0.4
5′			135.7	138.7	−3.0
6′			137.7	138.0	−0.3
7′	6.71	6.88	135.1	137.4	−2.3
8′	6.38	6.47	136.7	136.6	0.1
9′			150.9	153.5	−2.6
10′	6.45	6.52	132.3	133.1	−0.8
11′	7.55	7.67	140.6	142.6	−2.0
12′	6.67	6.71	137.2	137.3	−0.1
13′			—[b]	163.1	—
14′	6.78	6.79	135.9	136.3	−0.4
15′	8.08	7.76	156.0	153.9	2.1
16′	1.08	1.10	28.8	28.9	−0.1
17′	1.08	1.10	28.8	28.9	−0.1
18′	1.81	1.84	22.1	22.1	0
19′	2.19	2.22	13.5	13.5	0
20′	2.38	2.35	14.4	14.0	0.4

[a] See Scheme 1. [b] Not observed due to missing long-range correlation from 20′-CH_3 caused by broadening in the ^{1}H dimension. A δ_C value of 163.1 ppm was used for 13′-C in subsequent calculations.



Scheme 6

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Discussion

Hydride abstraction

Due to the steric requirements of the triphenylcarbenium ion, the competition between hydride abstraction and addition to the polyene chain should favour the former reaction, which is in agreement with the NMR data and the quenching trials for β,β-carotene (**1**). However, the preference for elimination of hydride over protonation of β,β-carotene (**1**) treated with dilute trifluoroacetic acid (0.01–0.2 M) was surprising. In concentrated trifluoroacetic acid-*d*, only complicated mixtures were previously observed in the NMR spectra.[25] In dilute solutions a mixture of C-7 and C-5 protonated products was expected, as suggested by previous AM1 studies.[26]

NMR data

From earlier experience, we expected the polyenyl cations from the extended polyenes **4–6** to yield readily interpretable NMR spectra, in which downfield shifts could be assigned to specific positions in the chain.[13,20] It turned out that for the longer symmetrical polyenes **4–6**, treatment with trifluoroacetic acid-*d* yielded broad ^{1}H NMR spectra with few distinct spectral features in the olefinic region. The broadening could be caused by various reasons, including aggregation, precipitation, free radicals and dynamic aspects. Care was taken to ensure non-viscous solutions at lowered temperatures, and the samples were visually inspected for precipitates. Although aggregation can not be ruled out, the broadening most likely arises from other phenomena. It has been noted during work with long polyene anions that the longest polyene anions gave broadened spectra, and EPR analysis revealed the formation of radicals, although no radical initiators were present.[11] Radical formation has also been observed by treatment of concentrated carotenoid solutions with trifluoroacetic acid.[26] Radical species cannot be definitely ruled out in our experiments.

If the longer charge-delocalised cations contain free solitons, the charge density wave may travel along the polyene chain with only little cost of energy,[2,6,7] a dynamic process which hypothetically may give rise to signal broadening in the NMR spectra. Consequently, NMR may not be a suitable method for the study of free solitons, as the continuous rapid translational motion of the delocalised charge would yield averaged signals only, and would not provide information about the charge distribution of the soliton itself. This phenomenon seems to have been overlooked in the past, where the preparation of longer, charged polyenes was proposed as a solution to the soliton half-width problem,[27] and followed up here. The broadened appearance of the polyenyl cation from the longer C_{50}-, C_{54}- and C_{60}-polyenes (**4**, **5** and **6**) may suggest signal averaging, whereas the sharper signals of the C_{40} monocation **3** is compatible with restricted movement of the soliton.

Although broadened, the ^{1}H NMR data of the polyenes **4–6** treated with trifluoroacetic acid-*d* in $CDCl_3$ and CD_2Cl_2 show considerable downfield shifts in the olefinic region, compared to the parent polyenes. The calculated values for total downfield shift correspond nicely with values found for other polyenyl cations of carotenoid origin.[13,14] For instance, in the monocation **3** prepared from β,β-caroten-4-ol (**2**), a value of 9.7 ppm per charge is obtained when only the protons originally in the polyene chain are taken in account, whereas the Spiesecke–Schneider relationship for ^{1}H estimates 10.6 ppm per charge.[9] The value of 10.0 ppm for the cationic product of the C_{50}-polyene (**4**) and 10.3 ppm for the initial product of the C_{54}-polyene (**5**) indicates formation of monocations. The higher values found for the second product of **5** and from the C_{60}-polyene (**6**), 18.2 ppm and 18.5 ppm, respectively, point towards dication formation. Additional information on the charge distribution of the longer polyenyl cations is not provided by this crude numerical treatment. However, according to previous experience it would be expected that the charge was located at the centre of the polyene for monocations, whereas electrostatic repulsion would force the two solitons in a dication towards the ends of the polyene chain.[13,14,20]

The data for the monocation **3a** prepared from β,β-carotene (**1**), as given in Table 4, show only small differences from earlier published results.[14] Most notably, by employing the deuterated trityl cation **15**, some characteristics of the soliton shape are altered. The centre has shifted slightly, *cf.* the values of $\Delta\delta_C$ in Table 4 for C-10,12,14,15′ compared to C-5′,7′,9′,11′. The soliton half-width, determined empirically as given previously,[13] is also 10% smaller (calculation not included here). This shows that in addition to the averaging effects discussed above, the picture is further complicated by the influence of different counterions, here CF_3COO^- and BF_4^-.

NIR data

The free-electron model, in which electrons are allowed to move freely along the polyene chain at a constant potential energy, states a linear correlation between absorption maxima and polyene chain length.[28] Work on shorter polyenes revealed a good linear fit to data for polyenyl monocations in the range of 3–13 sp^2-carbons involved in the delocalisation, with the absorption maxima varying from 300 nm to 700 nm (Fig. 2).[29] In the upper end of the spectrum, measurement of the so-called midgap absorption in doped polyacetylenes has been determined to be 0.65–0.75 eV, or 1650–1900 nm when converted to wavelength units.[4,5] The NIR absorption of charged polyenes is therefore expected to converge

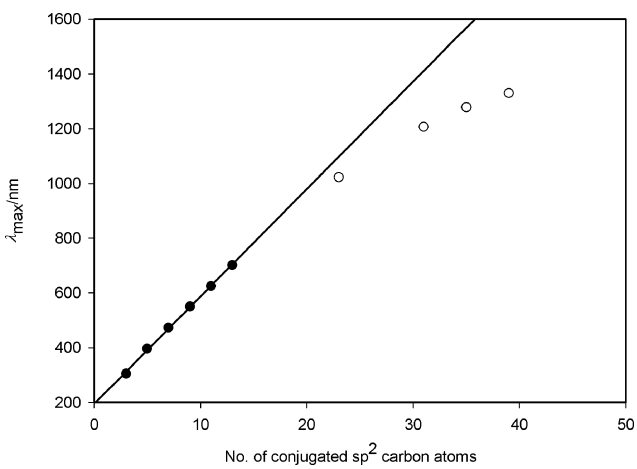

Fig. 2 Absorption maxima λ_{max} at room temperature as function of the number of conjugated sp^2 carbon atoms in polyenyl cations. ●: Data from monocations in ref. 29, measured in 80–96% sulfuric acid. ○: Present data, polyenes **1**, **4–6** dissolved in 0.013 M trifluoroacetic acid in CH_2Cl_2.

in this range. Absorption maxima for radical cations of the C_{50}- and C_{60}-polyenes **4** and **6** are reported at 1250 nm and 1480 nm, respectively.[30] For shorter polyenes, similar values are expected for their spinless counterparts.[26] However, lower values are measured in our experiments.

The ease with which dications are formed, as demonstrated by NMR experiments for **5** (C_{54}) and **6** (C_{60}), add uncertainty to the interpretation of the NIR results. Formation of dications is expected to shift the absorption to lower wavelengths relative to monocations.[31] With the exception of the monocation **3** from β,β-carotene (**1**), the relatively low values in Table 1 point towards dication formation upon treatment with triphenylcarbenium tetrafluoroborate. When trifluoroacetic acid is employed (Tables 2 and 3), the effect of the concentration is compatible with dication formation at the highest acid concentration. Shortening of the polyene chain by in-chain protonations can also be envisaged. However, the values in Tables 1 and 3 are in fair agreement, disfavouring in-chain protonation.

The assumption is made that the absorptions measured in dilute trifluoroacetic acid in Table 2 correspond to monocation formation. Compared to the linear fit for the shorter monocations,[29] all our measured values are markedly lower, as shown in Fig. 2, for the room temperature absorptions. This result indicates deviations from the free-electron model, and may instead be taken as evidence for the emergence of free solitons in these longer polyenes.

Delocalisation limits

The extent of delocalisation can be described through the soliton half-width l, and the physical implications of l on bond lengths and distribution of charge are thoroughly discussed elsewhere.[27] In the absence of bond length and charge distribution data, a more qualitative approach has been employed by several workers,[16,32] using the absolute number of double bonds in which the charge resides. Due to the shape of the charge distribution as a hyperbolical cosine function,[1] these numbers are not easily correlated. The latter approach will now be considered here.

We interpret the deviation of linearity in Fig. 2 as an indication of at which stage the primary assumption of the free-electron model, namely delocalisation over the entire π-electron system, is no longer valid. This occurs at approximately 20 sp^2 carbon atoms, which corresponds to 10 conjugated double bonds. It is interesting to note that the electronic properties of long dicationic polyenes examined by cyclic voltammetry has shown that a limiting oxidation potential is reached for conjugation lengths of 25–30 double bonds,[16] implying that two positively charged solitons in the same polyenyl dication can reach a state of minimal energy with 12.5–15 double bonds per charge. These results are in fair agreement with our findings. For polyenes, a charge carrier length of more than 20 double bonds, which has been suggested,[32] is not supported by our data.

Conclusions

Elimination of hydride ion from β,β-carotene (**1**) was demonstrated upon treatment with both trifluoroacetic acid and triphenylcarbenium tetrafluoroborate. Characterisation of the resulting carotenyl monocation **3** by NMR was supported by product analyses after quenching of the cation with nucleophiles.

For polyenes with longer polyene chains, C_{50}-β-carotene (**4**), C_{54}-β-carotene (**5**) and C_{60}-β-carotene (**6**), NMR spectra after trifluoroacetic acid-*d* treatment revealed broadened peaks. Charge distributions of these longer cations were therefore not determined. The number of delocalised charges in the polyenes could be estimated by numerical methods. The two longest polyenes, **5** (C_{54}) and **6** (C_{60}), were susceptible to dication formation.

NIR data recorded for the cationic products of the longer polyenes showed deviations from the linearity expected from the free-electron model for delocalised elctrons.[28,29] The lower than expected bathochromic shifts for the linear polyenes with 20 or more sp^2-hybridized carbon atoms indicate the transition from charge delocalisation limited by chain length to delocalisation limited by the maximum soliton width.

Experimental

Materials

Synthetic samples of β,β-carotene (**1**), echinenone (**14**), 2,7-dimethyl-2,4,6-octatriene-1,8-dial (**10**), 6,6′-diapo-ψ,ψ-carotenedial (**11**) and 4,4′-diapo-ψ,ψ-carotenedial (**12**) were obtained from Hoffmann–La Roche. Neoxanthin, extracted from *Spinacea oleracea*, was converted to neochrome (**13**) according to literature procedures.[33] β-Ionone (**8**, pract. 90%) was obained from Fluka. Vinyl chloride was supplied by Matheson Gas Products. All other reagents were available in analytical grade from commercial chemical suppliers and used without further purification. Dichloromethane, diethyl ether and tetrahydrofuran were dried and distilled before use. The ethanol stabiliser present in chloroform was removed prior to quenching trials by running the solvent through an alumina column.

Methods

All polyenes were stored in a freezer (−20 °C) under nitrogen atmosphere. Reactions and manipulations were carried out as far as possible in darkness and under nitrogen atmosphere. Ultraviolet (UV) and visible light (VIS) spectra were recorded on a Varian Cary 50 UV-VIS spectrophotometer or a Shimadzu UV160-A spectrophotometer. Visible light (VIS) and near infrared (NIR) spectra of charged compounds, with cooling as described previously for the characterisation of charged species, was performed on a Varian Cary 5 UV–VIS–NIR spectrophotometer.[20] For quantitative estimates, $E_{1\%,1\,cm} = 2500$ at λ_{max} was employed throughout. EI mass spectra were recorded on a Finnigan MAT 95XL ThermoQuest spectrometer. NMR spectra of intermediates were obtained on a Bruker Avance DPX 400 MHz instrument using a 5 mm $^{13}C/^{1}H$ dual probe, whereas data for the polyenes was recorded on a Bruker Avance 600 MHz instrument, using a 5 mm cryoprobe (TCI). Spectra of charged species at temperatures below 0 °C were obtained on a Bruker Avance DRX 500 MHz instrument, using a 5 mm inverse probe (TXI), equipped with a nitrogen dewar for cooling. Multidimensional pulse sequences were used for complete assignment, *i.e.* COSY, ROESY, HMSC,[34] HSQC, HSQC-TOCSY. Chemical shifts are cited relative to TMS with calibration against residual $CHDCl_2$ at 5.32 ppm and 53.8 ppm for ^{1}H and ^{13}C respectively for samples with dichloromethane-d_2, or against residual chloroform at 7.27 ppm for ^{1}H in chloroform-*d*

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and 77.0 ppm for ^{13}C. HPLC was carried out on a Hewlett Packard Series 1050 instrument equipped with a diode array detector (DAD). Detection wavelength was set according to λ_{max} of the crude products recorded by VIS-spectroscopy. For analytical separations, a 250 × 4.6 mm Interchrom Uptisphere 5 ODB column was employed. Mobile phase: 0 min: methanol–acetone (90 : 10 v/v, 1.0 mL min^{-1}), 60 min: methanol–acetone (30 : 70 v/v, 1.0 mL min^{-1}). A similar column with 10 mm inner diameter was used for preparative separations.

Vinyl-β-ionol (9)

Alcohol **9** was prepared in a Grignard reaction,[35] using gaseous vinyl chloride bubbled through a tetrahydrofuran suspension of magnesium (6.5 g, 0.27 mol, activated with iodine and ethyl bromide) for preparation of the Grignard reagent. Addition of β-ionone (**8**, 30.1 g, 0.156 mol) gave after work-up 33.1 g crude product, 96% yield. δ_H(400 MHz, $CDCl_3$) 0.99 (s, 6H), 1.43 (s, 3H), 1.45 (m, 2H), 1.61 (m, 2H), 1.67 (d, 3H, J = 0.9 Hz), 1.98 (m, 2H), 5.09 (dd, 1H, J = 1.2 Hz, J = 10.6 Hz), 5.28 (dd, 1H, J = 1.2 Hz, J = 17.3 Hz), 5.55 (d, 1H, 16.2 Hz), 6.02 (dd, 1H, J = 10.6 Hz, J = 17.3 Hz), 6.09 (m, 1H); m/z (EI) 221 (5.5%, M + 1), 220 (M$^+$, 12.6), 205 (43), 202 (23), 193 (32), 189 (31), 187 (35), 177 (100), 175 (34), 161 (39), 159 (32), 149 (32), 147 (41), 145 (29), 137 (67), 121 (75).

β-Ionylidenethyltriphenylphosphonium bromide (7)

Vinyl-β-ionol (**9**, 10.0 g, 45.5 mmol) and triphenylphosponium hydrobromide (15.5 g, 45.2 mmol) were mixed in tetrahydrofuran solution.[36] The product salt failed to crystallize, and was used as a crude oil in subsequent reactions.

General procedure for preparation of polyenes[17]

β-Ionylidenethyltriphenylphosphonium bromide (**7**, *ca.* 800 mg), sodium hydride (*ca.* 300 mg) and the appropriate diapocarotenedial (**10–12**, 10–20 mg) was stirred in dichloromethane overnight. Excess sodium hydride was decomposed by dropwise addition of acetic acid. The products were extracted with hexane, and washed with water and saturated sodium chloride solution. Initial purification was carried out by column chromatography on a silica column, with 1–2% acetone in hexane as eluent. Final purification was achieved by preparative HPLC (mobile phase: various methanol–acetone gradients, 2.5 mL min^{-1}). Multiple injections of each compounds from dichloromethane solution were required.

3,7,11,16,20,24-Hexamethyl-1,26-bis(2,6,6-trimethylcyclohex-1-enyl)hexacosa-1,3,5,7,9,11,13,15,17,19,21,23,25-tridecaene (decapreno-β-carotene, 4). Yield 77%, spectrophotometrically determined. λ_{max}/nm (acetone) 477sh, 502, 534; %III/II 15; R_T = 45.6 (7%, λ_{max}/nm 473sh, 497, 531), R_T = 46.8 (84%, λ_{max}/nm 477sh, 501, 535), R_T = 48.0 (8%, λ_{max}/nm 479sh, 501, 525); δ_H(600 MHz, $CDCl_3$) 1.04 (6′/6″-CH_3), 1.48 (5′/5″-CH_2), 1.63 (4′/4″-CH_2), 1.73 (2′/2″-CH_3), 1.98 (3/24-CH_3), 1.99 (11/16-CH_3), 2.00 (7/20-CH_3), 2.03 (3′/3″-CH_2), 6.16 (2/4/23/25-CH), 6.18 (1/26-CH), 6.24 (8/19-CH), 6.29 (12/15-CH), 6.38 (6/21-CH), 6.39 (10/17-CH), 6.65 (13/14-CH), 6.66 (5/9/18/22-CH); δ_C(150 MHz, $CDCl_3$) 12.6 (3/7/20/24-CH_3), 12.7 (11/16-CH_3), 19.1 (4′/4″-CH_2), 21.6 (2′/2″-CH_3), 28.8 (6′/6″-CH_3), 32.9 (3′/3″-CH_2), 34.1 (6′/6″-C), 39.4 (5′/5″-CH_2), 124.8 (5/22-CH), 125.0 (9/18-CH), 126.4 (1/26-CH), 129.2 (2′/2″-C), 130.0 (13/14-CH), 130.7 (4/23-CH), 132.3 (8/19-CH), 132.8 (12/15-CH), 135.8 (3/24-C), 136.3 (7/20-C), 136.5 (11/16-C), 137.2 (6/21-CH), 137.6 (2/25-CH), 137.7 (10/17-CH/1′/1″-C); m/z (EI) 670 (21%, M + 2), 669 (24, M + 1), 668 (M$^+$, 46), 666 (11, M − H_2), 563 (10), 562 (22, M − 106), 510 (9), 91 (100); *cf.* properties reported in early work,[15] and compatible with reported VIS, ^{1}H NMR and MS data.[16]

3,9,13,18,22,28-Hexamethyl-1,30-bis(2,6,6-trimethylcyclohex-1-enyl)triaconta-1,3,5,7,9,11,13,15,17,19,21,23,25,27,29-pentadecaene (C_{54}-β-carotene, 5). Yield 66%, spectrophotometrically determined. λ_{max}/nm (hexane) 487, 513, 548; %III/II 29; R_T = 50.6 (99%, λ_{max}/nm 493sh, 521 553); δ_H(600 MHz, $CDCl_3$) 1.04 (6′/6″-CH_3), 1.48 (5′/5″-CH_2), 1.63 (4′/4″-CH_2), 1.73 (2′/2″-CH_3), 1.96 (13/18-CH_3), 1.98 (9/22-CH_3), 1.99 (3/28-CH_3), 2.03 (3′/3″-CH_2), 6.15 (2/29-CH), 6.16 (10/21-CH), 6.18 (1/30-CH), 6.21 (4/27-CH), 6.28 (14/17-CH), 6.36 (8/12/19/23-CH), 6.40 (6/25-CH), 6.47 (7/24-CH), 6.64 (15/16-CH), 6.65 (5/26-CH), 6.66 (11/20-CH); δ_C(150 MHz, $CDCl_3$) 12.5 (13/18-CH_3), 12.6 (3/9/22/28-CH_3), 19.2 (4′/4″-CH_2), 21.7 (2′/2″-CH_3), 28.9 (6′/6″-CH_3), 33.0 (3′/3″-CH_2), 34.1 (6′/6″-C), 39.5 (5′/5″-CH_2), 124.9 (11/20-CH), 126.7 (1/30-CH), 129.2 (7/24-CH/2′/2″-C), 129.7 (15/16-CH), 130.0 (5/26-CH), 130.7 (10/21-CH), 131.9 (4/27-CH), 132.8 (14/17-CH), 133.9 (6/25-CH), 134.5 (9/22-C), 135.9 (3/28-C), 136.3 (13/18-C), 137.2 (8/12/19/23-CH), 137.6 (2/29-CH), 137.7 (1′/1″-C); m/z (EI) 722 (19%, M + 2), 721 (29, M + 1), 720 (M$^+$, 51), 628 (16, M − 92), 91 (100).

3,7,11,15,20,24,28,32-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). Yield 67%, spectrophotometrically determined. λ_{max}/nm (hexane) 503sh, 530, 564; %III/II 14; R_T = 56.9 (42%, λ_{max}/nm 504sh, 529, 561sh), R_T = 57.9 (58%, λ_{max}/nm 509sh, 536, 571); δ_H(600 MHz, $CDCl_3$) 1.04 (6′/6″-CH_3), 1.48 (5′/5″-CH_2), 1.63 (4′/4″-CH_2), 1.73 (2′/2″-CH_3), 1.99 (3/32-CH_3), 2.00 (7/11/24/28-CH_3), 2.01 (15/20-CH_3), 2.03 (3′/3″-CH_2), 6.16 (1/2/33/34-CH), 6.17 (4/31-CH), 6.25 (8/27-CH), 6.27 (12/23-CH), 6.30 (16/19-CH), 6.39 (6/29-CH), 6.41 (10/14/21/25-CH), 6.65 (5/9/26/30-CH), 6.66 (17/18-CH), 6.67 (13/22-CH); δ_C(150 MHz, $CDCl_3$) 12.6 (3/32-CH_3), 12.7 (7/11/15/20/24/28-CH_3), 19.1 (4′/4″-CH_2), 21.7 (2′/2″-CH_3), 28.8 (6′/6″-CH_3), 32.9 (3′/3″-CH_2), 34.1 (6′/6″-C), 39.4 (5′/5″-CH_2), 124.6 (5/30-CH), 124.7 (9/26-CH), 125.0 (13/22-CH), 126.3 (1/34-CH), 129.2 (2′/2″-C), 130.1 (17/18-CH), 130.7 (4/31-CH), 132.4 (8/27-CH), 132.9 (12/23-CH), 133.0 (16/19-CH), 135.8 (3/32-C), 136.5 (7/11/24/28-C), 136.7 (15/20-C), 137.1 (6/29-CH), 137.6 (2/33-CH), 137.7 (1′/1″-C), 137.8 (10/25-CH), 137.9 (14/21-CH); m/z (EI) 802 (10%, M + 2), 801 (22, M + 1), 800 (M$^+$, 35), 695 (12), 694 (21, M-106), 386 (16), 119 (100); compatible with reported VIS, ^{1}H NMR and MS data.[16]

Allylic functionalization of polyenes

a) With NBS. [18] To β,β-carotene (**1**, 5.9 mg, 11 μmol) in 5 mL $CHCl_3$, cooled to −20 °C in a CO_2–ethylene glycol bath, a mixture of *N*-bromosuccinimide (1.8 mg, 10 μmol) and acetic acid (50 μL, 0.87 mmol) in 4 mL $CHCl_3$ was added, giving a brown solution.

After 1 min, methylmorpholine (40 μL, 0.36 mmol) was added, restoring the orange colour. The organic phase was washed with water and saturated NaCl (aq.). After purification on a neutral alumina column, developed with 10% acetone in hexane, HPLC analysis revealed two main peaks: $R_T = 13.4$ (43%, λ_{max}/nm 427sh, 450, 477; %III/II 29), $R_T = 14.7$ (31%, λ_{max}/nm 423sh, 445, 473; %III/II 33). An authentic sample of the monoacetate of β,β-caroten-4-ol gave: $R_T = 22.8$ (λ_{max}/nm 425sh, 451, 481; %III/II 54). Alteration of the β,β-carotene/acetic acid stoichiometry from ~1 : 100 to 1 : 4 gave destruction of the carotenoid, as evidenced by HPLC.

b) With BF_3–diethyl etherate. The β,β-carotene dication, prepared from addition of BF_3–diethyl etherate to β,β-carotene (**1**), was reacted with water in the same manner as reported before,[20] except for modification of the temperature to −20 °C. Pigment recovery was 23%. HPLC analysis showed only one main region containing peaks, and only traces of other compounds: $R_T = 16.4$ (72%, λ_{max}/nm 427sh, 450, 476; %III/II 16), $R_T = 17.0$ (12%, λ_{max}/nm 422sh, 446, 471; %III/II 25), $R_T = 17.6$ (5%, λ_{max}/nm 421sh, 445, 473; %III/II 45). An authentic sample of β,β-caroten-4-ol (**2**) gave: $R_T = 17.0$ (λ_{max}/nm 427sh, 451, 479; %III/II 32).

Employing the same methodology with C_{54}-β-carotene (**5**, 5.7 mg), a pigment recovery of 50% was obtained. The HPLC analysis showed peaks appearing in two main regions, $R_T = 29.0$–35.0 (57%, functionalised polyenes) and $R_T = 47.8$–53.2 (38%, unpolar polyenes). Main peaks: $R_T = 30.1$ (22%, λ_{max}/nm 491, 517, 553; %III/II 30), $R_T = 48.8$ (16%, λ_{max}/nm 493, 518, 554; %III/II 25). The more polar fraction was purified by preparative HPLC and partially characterised by NMR; δ_H(500 MHz, CD_2Cl_2) 1.47 (5″-CH_2), 1.62 (4″-CH_2), 1.66 (4′-$CH_\alpha H_\beta$), 1.71 (2″-CH_3), 1.89 (4′-$CH_\alpha H_\beta$), 2.02 (3″-CH_2), 3.97 (3′-C*H*OH). Decomposition products arising from elimination of the allylic hydroxy group emerged during acquisition in one of two samples.

Triphenylmethanol-d_{15} (17)

Bromobenzene-d_5 (**16**, 5.17 g, 31.9 mmol) was mixed with 10 mL diethyl ether and added dropwise to magnesium (0.78 g, 32.1 mmol) containing a few iodine crystals. The reaction started immediately and the mixture was refluxed for 1 h. Diethyl carbonate (1.22 g, 10.3 mmol) in 5 mL diethyl ether,[37] was added dropwise, and spontaneous boiling started. After addition of the carbonate and reflux for another hour, the mixture was poured over 20 g ice and 25 mL 1 M H_2SO_4. The organic phase was washed with additional 1 M H_2SO_4 and saturated sodium chloride solution and then dried over anhydrous $MgSO_4$. Hexane (20 mL) was added and the ether was boiled off under an aspirator until crystalization was initiated. This afforded 1.48 g white crystals, 52% overall yield; mp 158–161 °C; *m/z* (EI) 276 (4.6%, M + 1), 275 (20, M^+), 194 (16), 193 (100), 192 (22), 174 (16), 165 (21), 164 (19), 110 (82), 82 (39).

Triphenylcarbenium tetrafluoroborate-d_{15} (15)

From 0.78 g triphenylmethanol-d_{15} (**17**), 0.62 g of a red/orange crystalline product was obtained.[22] NMR of the corresponding undeuterated product is given below. Traces of propanoic acid and some unreacted triphenylmethanol were observed. δ_H(600 MHz, $CDCl_3$) 7.71 (d, 2H, *ortho*-CH, $J = 7.4$ Hz), 7.88 (t, 2H, *meta*-CH, $J = 7.6$ Hz), 8.23 (t, 1H, *para*-CH, $J = 7.4$ Hz); δ_C(150 MHz, $CDCl_3$) 130.4 (*meta*-CH), 140.1 (1-CH), 142.8 (*ortho*-CH), 143.2 (*para*-CH), 211.3 (Ph_3C).

VIS/NIR experiments

a) With triphenylcarbenium tetrafluoroborate. To 3 mL of a 4–6 mg mL^{-1} dichloromethane solution of triphenylcarbenium tetrafluoroborate (from a commercial source) in a cuvette, were added polyenes *via* a syringe from dichloromethane stock solutions. The VIS/NIR spectra (500–1600 nm) were recorded repeatedly at maximum 10 min intervals for at least 1 h. Experiments were performed both at room temperature and at −15 °C, although the latter experiments suffered from condensation problems. Polyenes employed: β,β-carotene (**1**), decapreno-β-carotene (**4**), C_{54}-β-carotene (**5**) and dodecapreno-β-carotene (**6**).

b) With trifluoroacetic acid. VIS/NIR spectra were recorded in the same manner as described above for the four polyenes **1**, **4**, **5** and **6** in dichloromethane solutions of trifluoroacetic acid, using concentrations of 0.013 M and 1.3 M. The measurements were performed both at room temperature and at −15 °C.

NMR of polyenes reacted with triphenylcarbenium tetrafluoroborate-d_{15} (16)

a) Low temperature preparation. The polyene (1–2 mg) was dissolved in 0.25 mL $CDCl_3$, and cooled to −78 °C under N_2. Trityl cation **16** (2–4 mg), dissolved in 0.25 $CDCl_3$, was added, and the mixture was allowed to heat slowly. NMR spectra were recorded at 5 °C. Polyenes employed: β,β-carotene (**1**), decapreno-β-carotene (**4**) and neochrome (**13**).

b) Ordinary preparation. To 1 mg trityl cation dissolved in 0.5 mL $CDCl_3$, solid polyene (1–2 mg) was added. NMR spectra of the mixture were recorded at 5 °C. Polyenes employed: β,β-carotene (**1**), echinenone (**14**).

c) Low temperature NMR. The polyene (1–2 mg) was dissolved in 0.4 mL $CDCl_3$, and kept at −15 °C while 2–4 mg of the trityl reagent, dissolved in 0.1 mL $CDCl_3$, was added. NMR spectra were obtained at −15 °C. Polyenes employed: β,β-carotene (**1**), decapreno-β-carotene (**4**) and neochrome (**13**).

All polyene/trityl cation mixtures yielded blue or green solutions. In the case of neochrome (**13**), precipitates were formed upon addition of the trityl reagent **15**. Initially, ^{1}H and ^{1}H,^{1}H COSY were recorded, with additional 2D experiments performed on samples showing promising proton spectra.

NMR of polyenes reacted with trifluoroacetic acid-*d*

To a solution of polyene (1–2 mg) in $CDCl_3$ at −15 °C (for C_{54}-β-carotene (**5**) and dodecapreno-β-carotene (**6**) in CD_2Cl_2), 10 μL of trifluoroacetic acid-*d* was added. NMR spectra were recorded at this temperature or slightly higher, as indicated below. Polyenes employed: β,β-carotene (**1**), decapreno-β-carotene (**4**), C_{54}-β-carotene (**5**, spectra recorded at −10 °C) and dodecapreno-β-carotene (**6**, spectra recorded at −5 °C).

The average olefinic chemical shift for the cations from from **4**, **5** and **6** was estimated using Simpson's formula[24] on 1D ^{1}H spectra

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for evaluation of the integrals in the quotient

$$\frac{\int (\text{intensity} \times \delta_H)\, d\delta_H}{\int (\text{intensity})\, d\delta_H}.$$

Quenching trials with β,β-carotene (1)

To a stirred solution of triphenylcarbenium tetrafluoroborate (72 mg) in 5 mL $CHCl_3$, β,β-carotene (**1**, 5 mg), dissolved in 5 mL $CHCl_3$, was added. The resulting green solution was mixed with water in a separation funnel and washed with 2% aqueous sodium bicarbonate solution until the orange colour was restored. The organic phase was washed with saturated NaCl (aq.), and VIS/NIR analysis showed a pigment recovery of 16%. HPLC analysis revealed three main peaks: $R_T = 16.8$ (55%, λ_{max}/nm 427sh, 450, 477; %III/II 25; **2**), $R_T = 34.4$ (15%, λ_{max}/nm 442, 465, 491; %III/II 29; **18**), $R_T = 35.2$ (17%, λ_{max}/nm 449, 472, 505; %III/II 40; **18**).

When the resulting green solution instead was shaken with 20 mL 5% potassium acetate, the following results were obtained by HPLC analysis: $R_T = 16.7$ (26%, λ_{max}/nm 427sh, 450, 476; %III/II 21; **2**), $R_T = 22.7$ (15%, λ_{max}/nm 427sh, 451, 478; %III/II 21; monoacetate of **2**), $R_T = 25.2$ (3%, λ_{max}/nm 457), $R_T = 34.2$ (5%, λ_{max}/nm 463, 491; **18**), $R_T = 35.0$ (6%, λ_{max}/nm 449, 473, 499; **18**).

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