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Novel diapocarotenoid dications with VIS/NIR absorption

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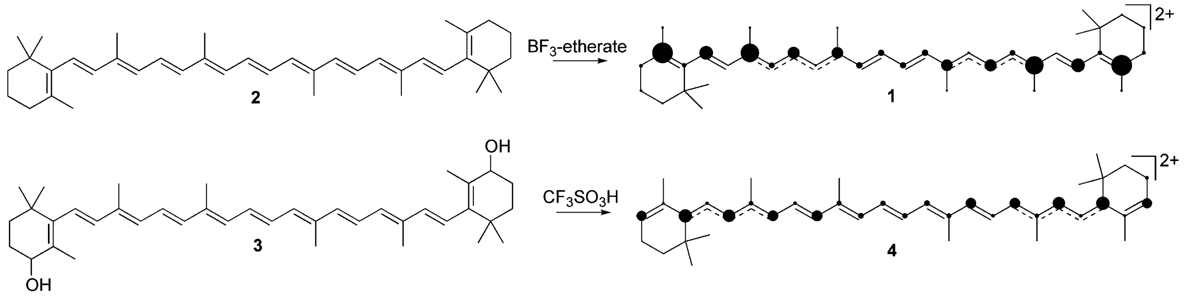
Abstract—Isoprenoid acyclic polyene carbodications with 6, 14 and 18 π electrons have been synthesized and characterized in comparison with previously prepared dicyclic C_{40}-carotenoid dications. An equation correlating λ_{max} (400–1100 nm region) and the number of sp^2 hybridized carbon atoms in the dication is presented.

UV/vis absorption shifts to longer wavelengths is a characteristic feature of aryl and alkenyl cations and of cations with cyclic π-systems.[1,2] Also, in the porphyrin field, there is interest in the preparation of carbocations absorbing in the near infrared (NIR) region.[2] Recently, we have prepared and fully characterized C_{40}-carotenoid dications, including the β,β-carotene dication **1** (λ_{max} 920 nm in $CHCl_3$ at −25 °C) obtained from β,β-carotene **2**,[3,4] and the isocarotene dication (λ_{max} 1022 nm in CH_2Cl_2 at −15 °C) prepared from β,β-carotene-4,4′-diol **3** as three diastereomers, exemplified by the dication **4**,[5] Scheme 1. These long-lived dicyclic dicarbocations with extended π-systems are stable enough to have their NMR spectra recorded. The filled circles demonstrate the distribution of charge as established by NMR methods in comparison with relevant neutral models.[3–5]

Whereas the dication **1** was obtained by reaction of the substrate **2** with a Lewis acid, the dication **4** was prepared by treatment of a bisallylic carotenol **3** with a suitable Brønsted acid.[3–5]

The aim of the present work was to prepare and characterize dications with shorter polyene chains, absorbing in the 600–900 nm region, thus filling the gap in the VIS–NIR spectra of neutral carotenoids with λ_{max} below 550 nm and the C_{40}-carotenoid dications absorbing in the 900 nm range. Relative dication stability was also of interest. The appropriate synthetic diapocarotenedials,



Scheme 1.

Keywords: Acyclic C_{10}, C_{20} and C_{24} diapocarotenoid dications; Preparation; VIS/NIR-correlation.

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C_{10}-dial **5** (2,7-dimethyl-2,4,6-octatriene-1,8-dial),[6] C_{20}-dial **6** (crocetindial)[6,7] and C_{24}-dial **7** (bixindial),[6] were available. These dialdehydes were transformed via the bisallylic carotenediols (**8**, **9** and **10**) and the diacetates (**11**, **12** and **13**) to the corresponding dications (**14**, **15** and **16**), Scheme 2. The diacetates (**11**, **12** and **13**) were preferred rather than the diols due to the presence of better leaving groups.

Fully characterized diacetates (**11**,[†] **12**[‡] and **13**[§]) were treated with trifluoromethanesulfonic acid in CH_2Cl_2 at −15 °C[¶] and VIS/NIR spectra recorded for stability studies. The C_{10}-diacetate **11** provided an initial absorption at λ_{max} 469 nm which progressed partially to a stable absorption at λ_{max} 438 nm (dication **14**). It is likely that the initial absorption arises from formation of the monocation, that is, with single instead of a double elimination of acetate, based on the absorption maxima observed for structurally related polyene monocations.[11] The stability of dication **14** was monitored by NIR spectroscopy at −15 °C. An intensity loss of only 13% was observed during 50 min. Cleaner reactions were obtained from the C_{20}-diacetate **12** to the blue dication **15** with λ_{max} 735 nm (Fig. 1) and $t_{1/2} = 70$ min. A clean reaction was also observed for the C_{24}-diacetate **13** to the blue C_{24}-dication **16** with λ_{max} 850 nm (Fig. 2) and $t_{1/2} = 10$ min. A dramatic change in the VIS/NIR absorption upon dication formation was observed for λ_{max} in the triene ($\Delta = 154$ nm in CH_2Cl_2), heptaene ($\Delta = 336$ nm from peak II and 311 nm from peak III) and nonaene ($\Delta = 419$ nm) series (Figs. 1 and 2).

NMR studies (500 MHz) of the dications **14**, **15** and **16** in dichloromethane-d_2 (0.75 ml), containing trifluoromethanesulfonic acid-d (10 µl), were pursued at various concentrations and temperatures (−15 °C to −20°C).[4,5] For the dication **16** NMR was also attempted in THF-d_8. Downfield shifts of the olefinic protons, characteristic of carotenoid cations,[2–5] were observed. However, NMR spectra of the quality obtained for the C_{40}-dications **1** and **4**,[4,5] could not be obtained due to solubility problems and precipitation.

Due to the shorter π-systems of the diapocarotenoid dications (**14**, **15** and **16**) than for the C_{40}-dications (**1**, **4**), with less delocalization and proximity of the two positive charges, lower stability was anticipated. Stability studies for β,β-carotene dication **1** ($t_{1/2}$ more than several hours)[4] and isocarotene dication **4** (after 21 h no greater intensity loss than 22%)[5] revealed considerably higher stability (NIR) for the dicyclic C_{40}-dications. The recorded stability is in the order **14** > **15** > **16** for the dications and may be ascribed to side reactions of the acyclic dications.

Finally, the prediction of absorption maxima for polyene dications is considered. Sorensen has published a linear equation 1 for calculating λ_{max} of polyene monocations. The number n reflects the number of additional conjugated double bonds to the allylic cation,[11] previously misinterpreted as the total number of effective double bonds.[12,13] This relationship is erroneous judged by the experimental data provided. Eq. 2, subsequently published,[14] gives a much better fit to the data.

Based on Sorensen's approach, we have developed a linear equation for carotenoid dications by correlating our observed λ_{max} with the number m of sp^2 hybridized carbon atoms in the dication, Eq. 4

$$\text{Monocations: } \lambda_{max} = (330.5 + 65.5n)\ \text{nm} \quad (1)$$

$$\lambda_{max} = (319.5 + 76.5n)\ \text{nm} \quad (2)$$

$$\lambda_{max} = (204.8 + 38.3m)\ \text{nm} \quad (3)$$

$$\text{Dications: } \lambda_{max} = (156.0 + 35.4m)\ \text{nm} \quad (4)$$

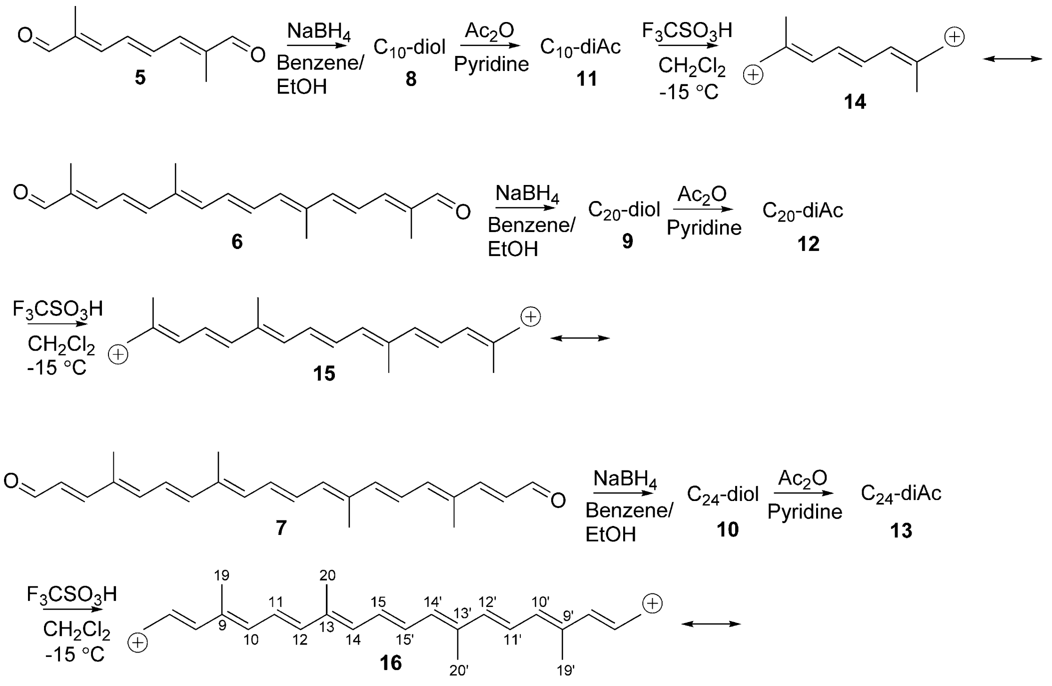
As shown in Table 1, the agreement between the measured λ_{max} and the calculated value for dications according to Eq. 4 is satisfactory. Eq. 3, equal in content to Eq. 2, allows a direct comparison between λ_{max} of dications and monocations with comparable numbers of sp^2 hybridized carbon atoms (m). These correlations demonstrate absorption maxima at shorter wavelengths for carotenoid dications than for polyene monocations, Eqs. 3 and 4. The same observation has also been made previously for dications versus cation radicals.[15] Concentration, solvent, temperature and counterion effects are not accounted for.

[†] 1,8-Diacetoxy-2,7-dimethyl-2,4,6-octatriene (**11**). λ_{max} (CH_2Cl_2)/nm 275 284 297, %III/II[8] 15; δ_H (400 MHz, $CDCl_3$) 1.82 (s, 6H, CH_3), 2.10 (s, 6H, $-OCOCH_3$), 4.55 (s, 4H, CH_2), 6.15 (m, 2H, 3,6-CH), 6.46 (m, 2H, 4,5-CH); m/z (EI) 253 (9.7%, M+1), 252 (M^+, 67), 193 (12), 150 (69), 133 (20), 132 (34), 121 (36), 119 (14), 117 (35), 107 (11), 105 (18).

[‡] 8,8′-Diacetoxy-8,8′-diapo-ψ,ψ-carotene (**12**). λ_{max} (acetone)/nm 378 399 424, %III/II 104; δ_H (400 MHz, $CDCl_3$) 1.85 (s, 6H, 19/19′-H), 1.96 (s, 6H, 20/20′-H), 2.10 (s, 6H, H_3CCO-), 4.56 (s, 4H, 8/8′-H), 6.18 (d, 2H, 10/10′-H, $J_{10,11} = 10.7$ Hz), 6.25 (m, 2H, 14/14′-H), 6.35 (d, 2H, 12/12′-H, $J_{12,11} = 15.1$ Hz), 6.43 (dd, 2H, 11/11′-H, $J_{11,12} = 15.0$ Hz, $J_{11,10} = 10.9$ Hz), 6.63 (m, 2H, 15/15′-H); m/z (EI) 385 (27%, M+1), 384 (M^+, 100), 340 (9, $M-H_3CCOH$), 326 (6), 325 (8), 324 (4, M−AcOH).

[§] 6,6′-Diacetoxy-6,6′- diapo-ψ,ψ-carotene (**13**). λ_{max} (diethyl ether)/nm 408 431 460, %III/II 87; δ_H (400 MHz, $CDCl_3$) 1.83 (s, 6H, 19/19′-H), 1.94 (s,6H, 20/20′-H), 2.10 (s, 6H, H_3CCO-), 4.56 (s, 4H, 6/6′-H), 6.15 (d, 2H, 10/10′-H, $J_{10,11} = 11.0$ Hz), 6.26 (m, 2H, 14/14′-H), 6.35–6.40 (m, 6H, 7/8/12/7′/8′/12′-H), 6.49 (dd, 2H, 11/11′-H, $J_{11,12} = 14.7$ Hz, $J_{11,10} = 11.1$ Hz), 6.63 (m, 2H, 15/15′-H); m/z (EI) 437 (26%, M+1), 436 (M^+, 100), 378 (12), 318 (14).

[¶] General procedure for producing the dications **14** and **16**: Trifluoromethanesulfonic acid solution (3 ml, 1.7 mg/ml in CH_2Cl_2) was cooled in a cuvette to −15 °C prior to addition of a CH_2Cl_2 stock solution of the diacetate **11** (0.25 mg/ml, 250 µl, 0.06 mg) or **13** (0.8 mg/ml, 5 µl, 4 µg). Molar extinction coefficients for phytoene (triene), ζ-carotene (heptaene) and neurosporene (nonaene) were used for the diacetates **11**, **12** and **13**, respectively.[9] Procedure for producing the dication **15**: The diacetate **12** (0.61 mg/ml, 10 µl, 6 µg) from a stock solution was placed in an empty cuvette and blown to dryness with nitrogen. The cuvette was cooled to the desired temperature. Precooled trifluoromethanesulfonic acid solution (3 ml, 1.7 mg/ml in CH_2Cl_2) was added. The formation and stability of the dications **14**, **15** and **16** was monitored by UV/VIS/NIR spectroscopy at −15 °C. General precautions for work with carotenoids were taken. For carotenoid numbering of **12** and **13**, see Scheme 2.[10]



Scheme 2.

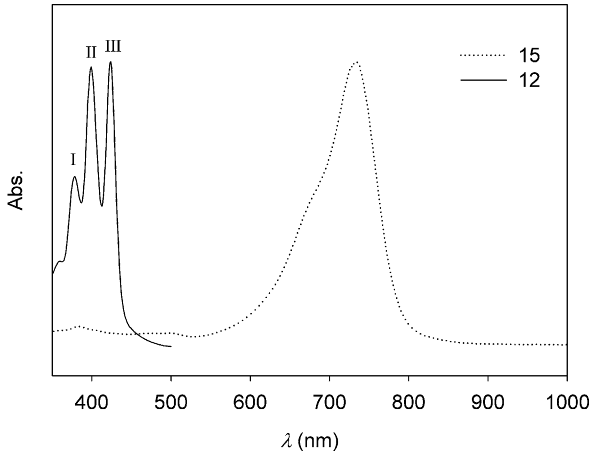


Figure 1. VIS/NIR spectra of C_{20}-diacetate **12** at rt and the C_{20}-dication **15** at −15 °C in CH_2Cl_2.

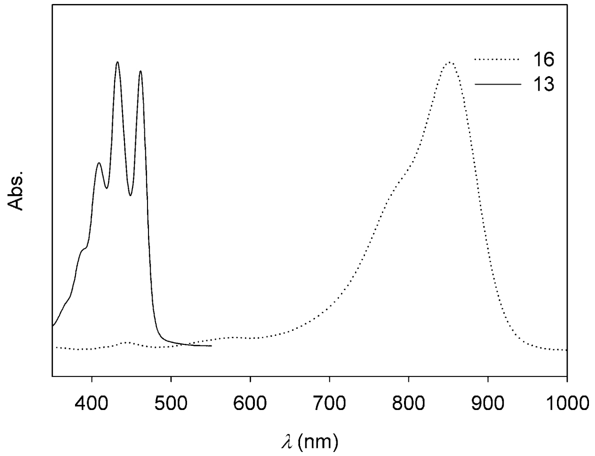


Figure 2. VIS/NIR spectra of C_{24}-diacetate **13** at rt and the C_{24}-dication **16** at −15 °C in CH_2Cl_2.

Table 1. Measured and calculated values for the absorption maximum of dications

Dication	Observed λ_{max} (nm)	Calculated λ_{max} (nm)	m[a]
C_{10}-dication **14**	438	439	8
C_{20}-dication **15**	735	722	16
C_{24}-dication **16**	850	864	20
β,β-Carotene dication **1**	920[3,4]	935	22
Isocarotene dication **4**	1022[5]	1005	24

[a] m: Number of sp^2 carbons.

Acknowledgements

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