

Conformation and Circular Dichroism of β,β -Carotene Derivatives with Nitrogen-, Sulfur-, and Selenium-Containing Substituents

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The CD spectra of several 3-substituted azido-, amino-, thio-, phenylseleno- and (phosphonoseleno)- β,β -carotene derivatives with one or two stereogenic centers are discussed with respect to conformational changes of the cyclohexene end group. N- and S-Substituents (N_3 , NH_2 , SH) have no influence on the conformer equilibrium compared to O-substituents, whereas Se-substituents (SePh, $SePO(OC_3H_7)_2$) slightly destabilize the preferred conformer of the β -end group.

1. Introduction. – In β,β -carotenoid derivatives, steric hindrances induced by the close contact of H–C(8) and Me–C(5) forces the ring bond C(5)=C(6) to bend out of the plane of the polyene chain π -electrons by 39° [1–4]. The bond C(5)=C(6) is, therefore, unavailable for π -complex formation and participates only partially in conjugation [5][6]. The out-of-plane deviation of the β -end group C=C bond relative to the chain C=C bonds creates a helical, intrinsically chiral chromophore. In β,β -carotene (**1**; $X^1 = X^2 = H$), each of the half-chair cyclohexene rings occurs in rapidly interconverting conformers with a formal *s-cis* single bond C(6)–C(7) [7][8]. By replacing a Me at C(1) with CD_3 , one of the conformers becomes slightly stabilized [9]. Substituents at the β -end group change the conformational equilibrium even more, and the energetically favored conformer becomes increasingly populated. It has been found that RO substituents at C(3) of the β -end group adopt the equatorial position [10][11]. In (3*R*,3'*R*)-zeaxanthin (**7**), each of the β -end groups occurs in two conformations: B^{up} and B^{down} (Fig. 2). Other theoretically possible conformations (*s-trans*, planar and boat forms, axial OH substituent) can be excluded [7][12–14]. Conformers B^{up} and B^{down} give opposite Cotton effects despite of the same configuration at C(3). No CD spectrum would be recorded if both conformers were present in the same amount. However, X-ray measurements indicate that B^{up} (C(2) and C(8) opposite) is the energetically more stable conformer of **7** and is, therefore, found abundantly in the conformational equilibrium [7][10][15].

So far, data on the conformation and the electronical optical activity (EOA) of ring-substituted β,β -carotene derivatives have been obtained solely for compounds with OH

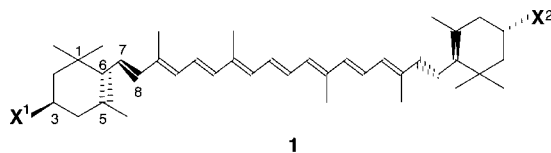


Fig. 1. 3,3'-Disubstituted (3*R*,3'*S*)- β,β -carotene derivatives

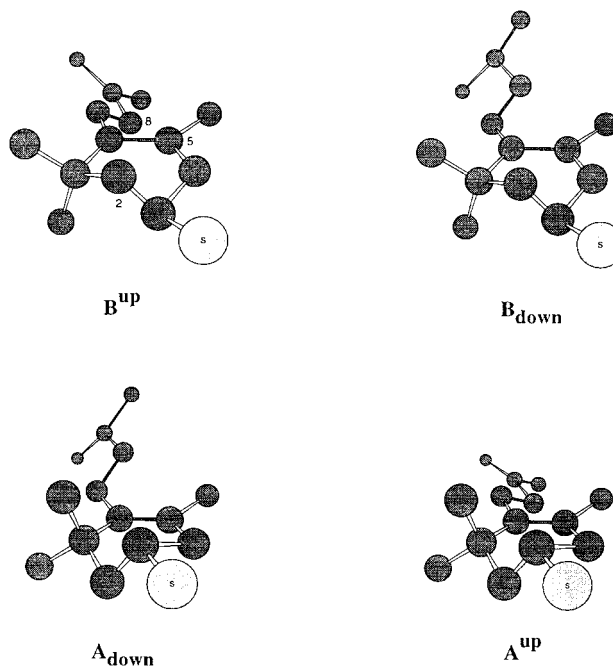


Fig. 2. Conformers **A** with equatorial SH-substituent ((3*S*)- or (3'*S*)-configuration) and conformers **B** with equatorial ((3*R*)- or (3'*R*)-configuration). 'up'/'down' refers to the position of C(5) relative to the plane of the polyene chain [7]. The energetically favored conformers have C(2) and C(8) opposite.

and OR substituents [16–19]. Nevertheless, it was hypothesized that the CD spectra of these carotenoids are independent of the type of substituents and the detailed nature of the cyclic end groups [7][10][20]. This postulate has never been confirmed experimentally. If it would be generally valid, then heteroatom-substituted compounds such as **11**–**14** with two stereogenic centers should all be optically inactive, just as *meso*-(3*R*,3'*S*)-zeaxanthin (**1**; X¹ = X² = OH). Indeed, the carotenoids **11** and **12** with S- and N-substituents were found optically inactive by the dichrograph. However, the Se-compounds **13** and **14** exhibit optical activity.

Conformational changes of β -end groups induced by substituents have not yet been observed. *Cotton* effects of substituents directly bound to the end groups have so far not been assigned because of the inaccessibility of chirally perturbed C–O transitions by usual dichrographs [21][22]. Racemic β,β -carotene derivatives with N-, S-, Br-, and Cl-substituents have been known for a long time [23][24], but it was only recently that optically active heteroatom-substituted β,β -carotene derivatives were synthesized [25–28]. It was, therefore, of interest to study the impact of different substituents on the ring conformation, and to detect possible substituent contributions.

2. Results and Discussion. – 2.1. *Preamble.* By excluding energetically unfavored conformers, it can be calculated from the two minima in the potential energy curve of (3*R*,3'*R*)-zeaxanthin (**7**) [7] that the conformation **B**^{up} occurs to *ca.* 60%, whereas the

less favored conformer \mathbf{B}_{down} amounts to 40%. The 20% excess of \mathbf{B}^{up} in **7** determines the sign and the intensity of $\Delta\epsilon$ in the CD spectra. Similarly, in (3*S*,3'*S*)-zeaxanthin, the cyclohexene rings with the favored equatorial OH substituents adopt the \mathbf{A}_{down} and \mathbf{A}^{up} conformations with \mathbf{A}_{down} (C(2) and C(8) opposite) in 20% excess (Fig. 2). The more the favored conformer of the β -end group is populated, the more this is expressed in the CD intensity. Substituents bound to β -end groups can influence the Cotton effects in four different ways: *a*) By stabilizing one of the two ring conformers: a change in the population of the conformers would result in a variation of the $\Delta\epsilon$ magnitude without substantially changing the CD pattern; *b*) by changing the out-of-plane angle of the bond C(5)=C(6) relative to C(7)=C(8): a deviation in the torsion angle of the ring vs. the chain C=C bond will affect the partial conjugation; a small angle deviation is expected to be detectable by a change in the CD intensity, greater deviations will in addition be seen in shifted positions of the extrema; *c*) by transitions of the substituents X^1 and X^2 (see **1**): substituents could change the shape of the Cotton effects by distinct substituent transitions; *d*) by through-space interaction of the substituents with the polyene chain: coupling of the substituent X^1 and X^2 (see **1**) transitions with those of the polyene chain will change the CD curve, giving rise to bisignate curves [29].

2.2. Change of Conformational Equilibrium. Cyclic end groups in carotenoids contribute independently and additively to the EOA [30]. Accordingly, the chiral β,β -carotene derivatives **2–6** with one stereogenic center (1*C**; see Fig. 3) showed similar, Cotton effects, but of lower intensity, than the compounds **7–10** with two stereogenic centers (2*C**; see Fig. 4), as shown in Figs. 5–8 and 11. The Cotton effects of the (3*S*)-carotenoids **3**, **4**, and **6** (1*C**) and the (3*S*,3'*S*)-derivative **9** (2*C**) appeared as nearly symmetrically reflected bell curves compared to the (*R*)-compounds **2** and **7** (Figs. 5 and 6, and Figs. 1 and 2 in [26]). This was not predictable since it was possible that the heteroatom substituent in the (3*S*)-compounds **3**, **4**, **6**, **8**, and **9** could have stabilized conformer \mathbf{A}^{up} with the same sign as the \mathbf{B}^{up} conformer of a (3*R*)-compound.

Distinct Cotton effects were not measured for the mercapto alcohol **11** and the amino alcohol **12** (Fig. 9). Evidently, the amount of the favored conformers \mathbf{B}^{up} (O-substituted (3*R*)-ring) and \mathbf{A}_{down} (S- and N-substituted (3*S*)-rings) are alike and, therefore, internally compensate each other. Again, this was not possible to prognosticate since the heteroatom substituent could also have stabilized \mathbf{A}^{up} with the same sign as \mathbf{B}^{up} . The low-temperature spectra of **11** and **12** did not exhibit distinct

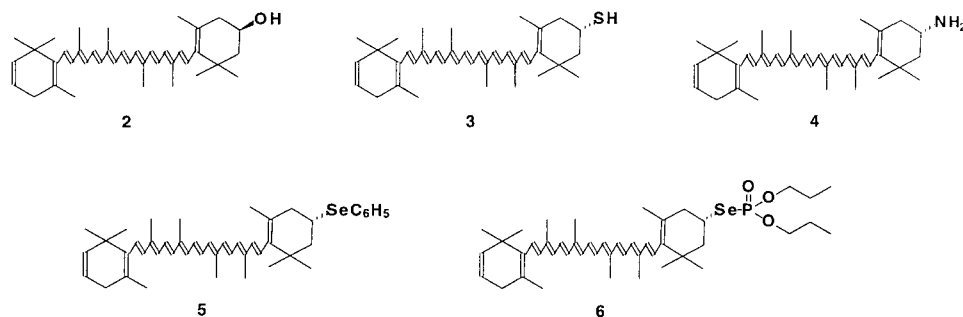
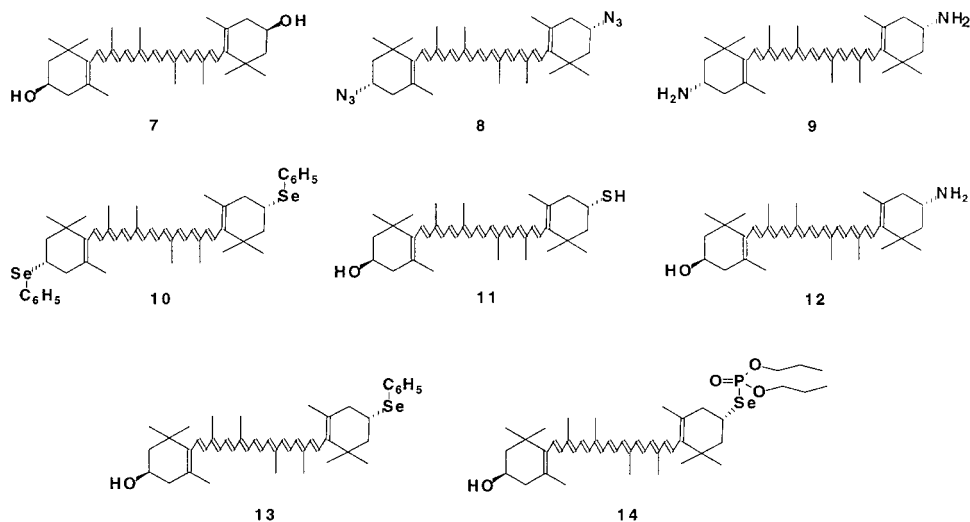


Fig. 3. Chiral β,β -carotene derivatives with one stereogenic center

Fig. 4. β,β -Carotene derivatives with two stereogenic centers

Cotton effects and were similar to the spectra recorded at room temperature (Fig. 9). The pseudo-*meso*-derivatives **11** and **12** may be added to the class of chiral molecules with accidental optical inactivity [31]. This is, of course, only correct when optical activity is used synonymously with EOA. Compounds **11** and **12** could show vibrational or Raman optical activity (VOA and ROA, resp.) [32] [33]. Optically active vibration modes have been detected for secondary $C^*-\text{OH}$, $C^*-\text{NH}_2$, $C^*-\text{SeR}$, and sulfur compounds in VOA and ROA [34–40].

The CD spectrum of selenophosphate **14**, albeit weak, is similar to the spectrum of **2** (Figs. 6 and 10, and Fig. 1 in [28]). Obviously, in **14**, the amount of conformer \mathbf{A}_{down} (Se-substituted ring) does not counterbalance the amount of conformer \mathbf{B}^{up} (O-substituted ring). As stated before, the CD of **2** is generated by a 20% excess of \mathbf{B}^{up} relative to \mathbf{B}_{down} which gives $\Delta\epsilon = -7$ for the most intense extrema at 290 nm (Fig. 5) in accordance with reported values obtained for (3*R*)-cryptoxanthin (**1**, $X^1 = \text{OH}$, $X^2 = \text{H}$; $\Delta\epsilon = -7.7$ [7]); (cf. **7**: $1/2 \Delta\epsilon = -7.3$ [7]; see below). In **14**, at the same wavelength, $\Delta\epsilon = -0.8$ is observed (Fig. 10). If 20% \mathbf{B}^{up} creates $\Delta\epsilon = -7$, then $\Delta\epsilon = -0.8$ corresponds to ca. 2% of \mathbf{B}^{up} . The 20% excess of \mathbf{B}^{up} (O-substituted ring) is opposite to 18% excess of \mathbf{A}_{down} (Se-substituted ring) resulting in a weak spectrum generated by ca. 2% of non-compensated \mathbf{B}^{up} , (see Table). Accordingly, the CD maximum of **6** at 290 nm is expected to be less intense than that of **2**. However, this difference in $\Delta\epsilon$ was not detected (Fig. 6).

$\Delta\epsilon$ Values for zeaxanthin (**7**) vary: -14.6 [7], -16 [20], -18 (taken from Fig. 1 in [10]), and -23 (Fig. 8; see *Exper. Part*). It may, therefore, be dubious to conclude from a single CD spectrum on the exact population of a preferred conformer. However, the concurrent occurrence of two different end groups in **13** and **14** make the measured $\Delta\epsilon$ a credible expression of conformational excess.

It is likely that the conformational part in the CD spectrum of phenyl selenide **13** is comparable in intensity to that of selenophosphate **14**, although **13** has no extrema

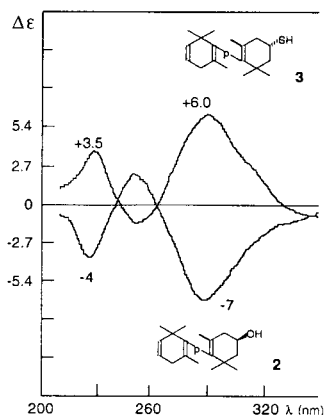


Fig. 5

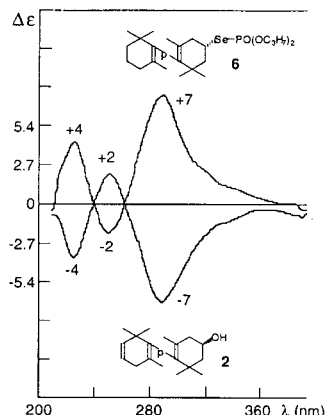


Fig. 6

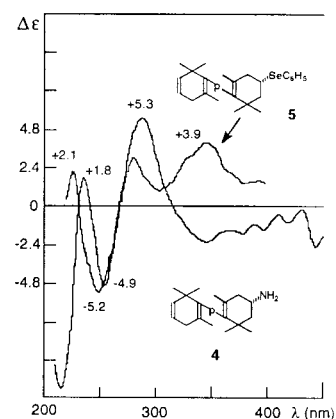


Fig. 7

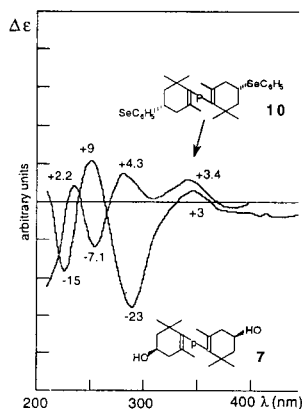


Fig. 8

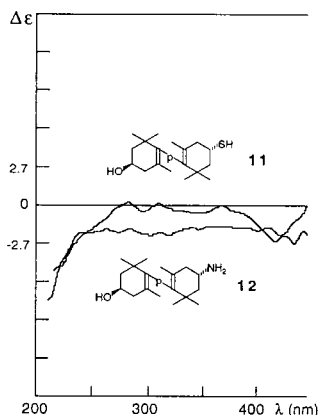


Fig. 9

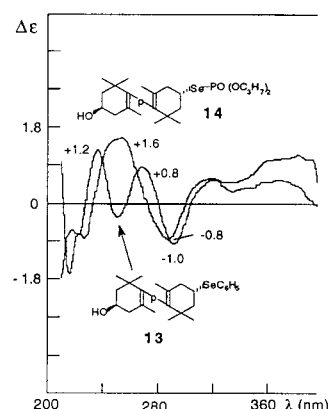


Fig. 10

without substituent contribution (Figs. 10 and 15). It can be assumed that the Se-substituted ring conformers of compounds **5**, **6**, **10**, **13**, and **14** are probably populated to the same extent.

Similarly to the cancelation of *Cotton* effects from the addition of the equally populated opposite ring conformers in **11** and **12** (Fig. 9), the CD spectrum of **13** is the result of non-equal additive contributions (Fig. 10). The intramolecular overlapping effects of the different end groups in **13** could be simulated by the addition of the CD spectra of **2** and **5**, or, analogously, by subtracting those of **3**, **4**, or **6** from that of **5**. The extrema of these generated spectra agreed with the recorded spectrum of **13** (Fig. 14).

2.3. Change of Torsional Angle. Conformational changes resulting in a significant increase or decrease in the conjugation of the β -end group C=C bond with the polyene chain were not detected by CD and VIS spectroscopy for the heteroatom-substituted

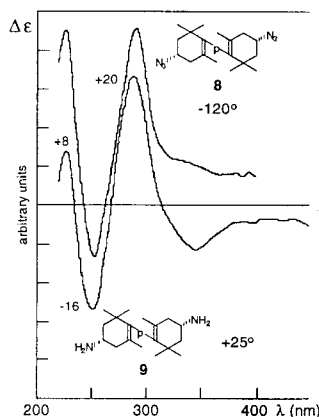


Fig. 11

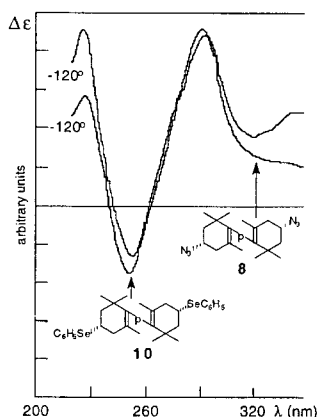


Fig. 12

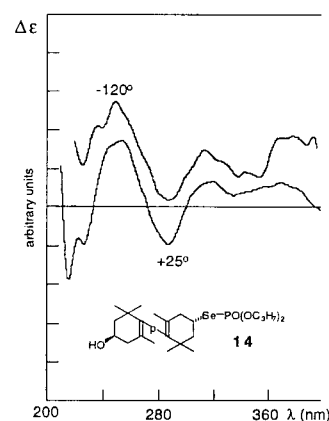


Fig. 13

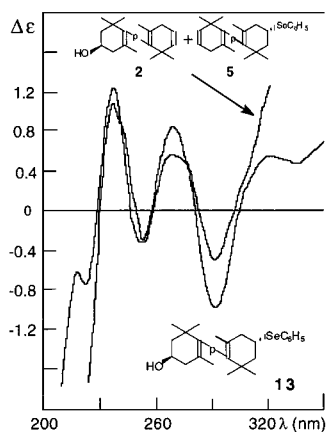


Fig. 14

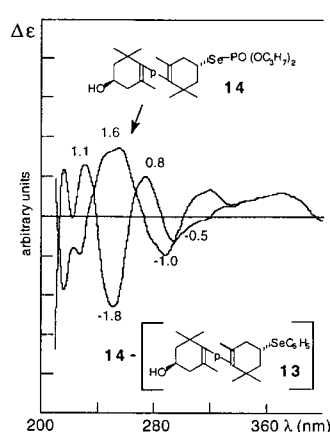


Fig. 15

Fig. 5.–15. CD Spectra (EtOH/isopentane/Et₂O 2:5:5) of **2–14**. p = Polyene chain.

carotenoids **3–6** and **8–14**. Since the VIS spectrum of zeaxanthin (**7**) is identical to that of β,β -carotene (**1**; $X^1 = X^2 = H$) and of compounds **2–6** and **8–14**, and because the electronic spectrum of zeaxanthin (**7**) in the solid state is comparable to that in solution [41], the out-of-plane deviation of bond C(5) = C(6) with respect to bond C(7) = C(8) should have the same magnitude both in the derivatives **2–6** and **8–14** and in **7** and crystalline **1** ($X^1 = X^2 = H$).

2.4. Substituent Transitions. The $n \rightarrow \sigma^*$ transition for the NH_2 substituent in compounds **4** and **9** is out of range (< 200 nm) to be detected [42–45] and the $n \rightarrow \pi^*$ transition for the N_3 substituent (290 nm) in **8** may coincide with the conformational Cotton effect at the same wavelength (Fig. 11) [46] [47]. In chiral sulfides, weak Cotton effects occur between 235 and 255 nm [48–51]. However, in the CD spectra of thiol **3**, these weak S transitions could not be detected (Fig. 5).

Table. Conformer Distribution in 3-Substituted β -End Groups. $\Delta\epsilon$ for maximum/minimum at λ 290 nm.

R = OH, N ₃ , NH ₂ , SH				R = C ₆ H ₅ , PO(OC ₃ H ₇) ₂			
60% ^{a)} B ^{up}	$\Delta\epsilon = -21^b)$	60% ^{a)} A _{down}	$\Delta\epsilon = +21^b)$	60% ^{a)} B ^{up}	$\Delta\epsilon = -21^b)$	59% ^{b)} A _{down}	$\Delta\epsilon = +20.7^b)$
40% ^{a)} B _{down}	$\Delta\epsilon = +14^b)$	40% ^{a)} A ^{up}	$\Delta\epsilon = -14^b)$	40% ^{a)} B _{down}	$\Delta\epsilon = +14^b)$	41% ^{b)} A ^{up}	$\Delta\epsilon = -14.4^b)$
20% ^{a)} B ^{up}	$\Delta\epsilon = -7^c)$	20% ^{a)} A _{down}	$\Delta\epsilon = +7$	20% ^{a)} B ^{up}	$\Delta\epsilon = -7^c)$	18% ^{b)} A _{down}	$\Delta\epsilon = +6.3^b)$
cancellation				2% ^{b)} excess B ^{up}			
$\Sigma \Delta\epsilon = 0$				$\Sigma \Delta\epsilon = -0.7^b)$			
(Fig. 9)				(Fig. 10, $\Delta\epsilon = -0.8$)			

^{a)} Data calculated from the two minima in the potential-energy curve of **7** [7]. ^{b)} Approximative calculated values related to $\Delta\epsilon = -7$ at 290 nm for **2**. ^{c)} See Fig. 5; reported value for (3*R*)-cryptoxanthin (**1**, X¹ = OH, X² = H), $\Delta\epsilon = -7.7$) [7] (cf. **7**: 1/2 $\Delta\epsilon = -7.3$) [7]).

A fine structure was seen in the CD spectra of the hydroxy-selenophosphate **14**, (Fig. 13): the weak band at 226 nm increased at -120° , and a new weak positive maximum appeared at 235 nm. Cotton effects of C–Se $n \rightarrow \sigma^*$ transitions have been recorded at 200, 218, and 273 nm [52]. Weak C–Se as well as Se–P, P=O, and P–O transitions may also contribute to the CD of **14**. In the CD spectra of the (*S*)-selenides **5** and **10**, the band at 350 nm appeared more intense and inverted compared to the (*S*)-amino compound **4** and not inverted compared to the (*R*)-hydroxy compound **7** (Figs. 7 and 8).

In contrast to the predominantly conformational CD spectrum of **14**, the spectrum of **13** shows in addition considerable substituent contributions (Figs. 7, 8, and 10). The subtraction of the CD spectrum of **13** from that of **14** annulled the conformational part of the Cotton effects in **13** so that the transitions of the phenyl-selenide substituent became visible (Fig. 15). The spectra of **5**, **10**, and **13** are, therefore the result of overlapping, cancelation, and coincidence of the substituent's Cotton effects with the Cotton effects of the favored ring conformers (Figs. 7, 8, and 10). The UV spectrum of methyl phenyl selenide shows a band at 270 nm (ϵ 4100) characterized as the π - π^* benzene transition modified by n - π conjugation with the unshared 4p electrons of Se. Another band at 248 nm (ϵ 6600) was attributed to transitions of the unshared electrons of Se [53]. Optically active phenyl selenides have been reported to exhibit weak Cotton effects at 242, 251 (most intense), 278, and 305 nm (n - π^* benzene-Se transitions) and at 284 nm ($\pi \rightarrow \pi^*$ aromatic transition) [52].

The only slightly temperature-dependent effects of the phenylseleno substituent become negligible when compared to the enormous increase of $\Delta\epsilon$ caused by the significant augmentation of the favored ring conformer at low temperature (**7**; $\Delta\epsilon = -80$ at -180° and 290 nm [7]). The CD spectrum of **10** at -120° resembles, therefore, that of **8** and, analogously, those of the carotenoids **2–4** and **6–9** (Figs. 11 and 12).

2.5. Through-Space Interactions. Through-space interactions of 3-RO-substituted β,β -carotene derivatives have not yet been observed [54] and are not expected to occur in **5**, **10**, and **13**. The intensity difference of the chromophores (phenyl selenide: ϵ 6600, 248 nm, EtOH [52][53]; β,β -carotene: ϵ 140400, 450 nm, EtOH [55]), the large projection angle near 180° of the benzene ring relative to the polyene chain and the distance of the chromophores disfavor a chromophoric coupling.

3. Conclusion. – The recorded CD spectra demonstrate that β -end groups of carotenoids substituted at C(3) with a OH, NH_2 , N_3 , and SH group occur in identically populated conformers. Se-Substituents slightly decrease the amount of the preferred conformer in the conformational equilibrium. Thus, the type of substituent and, consequently, the detailed nature of the cyclic end group cannot always be disregarded. It can be assumed that similar conformational effects may arise in not yet resolved or not yet synthesized carotenoids with other substituents from higher-period elements, such as As, Te, Br, and I.

The discussion of the spectra with Prof. *Nina Berova*, Columbia University, New York, and Dr. *Kurt Noack*, *F. Hoffmann-La Roche Ltd.*, Basel, and their decisive comments are highly appreciated.

Experimental Part

General. The synthesis of the compounds is described elsewhere [25–28]. The compounds were purified by prep. TLC and checked by UV/VIS spectroscopy, HPLC, or HPTLC prior to the CD measurements.

CD Spectra. The spectra were recorded in EPA (EtOH/isopentane/ Et_2O 2:5:5) at 25° or -120° on a *Jobin-Yvon-Mark-4* dichrograph (only relevant short-wavelength part shown). The spectra were registered by a data program not allowing the addition of CD spectra. The $\Delta\epsilon$ data of **2**, **5**, and **14** were, therefore, transferred to a computer program, the spectra of **2** and **5** added and compared with that of **14**. The additive spectra of **2** and **5** were in accordance with the spectra obtained by subtracting that of **3**, **4**, or **6** from that of **5**. The $\Delta\epsilon$ data in *Figs. 6* and *8* were taken from single CD spectra of **6**, **7**, and **10**. Too high $\Delta\epsilon$ values for **7** have often been measured on our dichrograph (*Fig. 8*) and were also found for **9** (*Fig. 11*). The large $\Delta\epsilon$ at low temperature were not properly processed by the computer program. The intensity of the spectra at -120° were, therefore, not recorded in relation to the room-temperature spectra (*Figs. 11–13*). The CD program could not plot both spectra in *Figs. 14* and *15*. The addition and the subtraction spectra were, therefore, fitted manually (*Fig. 15*) or with the help of a computer program (*Fig. 14*).

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Received September 16, 1998