113. Classification of the CD. Spectra of Carotenoids

by **Verena Sturzenegger, Richard Buchecker** and **Georges Wagnière**

Institute of Physical Chemistry and Institute of Organic Chemistry, University of Zürich,
Winterthurerstrasse 190, CH-8057 Zürich

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Summary

The CD. spectra of carotenoids in the 220-500 nm region may by inspection be classified as a) essentially *conservative,* b) *intermediate,* or c) essentially *non-conservative.* A conservative spectrum shows in that spectral region a sequence of 5-6 relatively sharp *Cotton* effects of alternating sign, the rotatory strengths of which roughly add to zero. In a non-conservative spectrum $\Delta\varepsilon$ has the same sign over the whole region and its absolute value is in general somewhat smaller. In general, typical conservative spectra invert upon isomerization of the molecule from all-*trans* to mono-*cis*. Non-conservative spectra do not invert. The model of a chiral polyene of the length of the conjugated carotene chromophore reproduces well the main features of the conservative spectra. The theoretical predictions and the experimental data are shown to conform to the C_2-rule [43] [44]. The particular nature of the longest-wavelength transition is interpreted. Based on a summary of the chiroptic data on about 50 naturally occurring compounds, the question is discussed of when conservative spectra arise and when not.

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1. Introduction. - During the last years a wealth of CD. data has accumulated on carotenes, and much attention is being given to establishing correlations with absolute configuration [1-41]. It appears that these CD. spectra may be classified with respect to two extreme types: a) Spectra which are essentially *conservative* in the 220-500 nm region. They consist of 5-6 relatively sharp *Cotton* effects of alternating sign. In an ideal conservative spectrum $\Delta\varepsilon(\lambda)/\lambda$ should integrate to zero over the spectral range here considered. b) *Non-conservative* spectra in which $\Delta\varepsilon$ has the same sign within the 220-500 nm region. The maximum absolute value of $\Delta\varepsilon$ tends to be smaller in non-conservative spectra than in conservative spectra. c) Spectra, which in the spectral region considered have between 1 and 3 changes of sign for $\Delta\varepsilon$, we shall call *intermediate.*

A striking feature of typically conservative spectra is that they invert upon all-*trans* to mono-*cis* isomerization. See [38] [40] and references cited therein. It now seems to be well established that conservative spectra arise when the terminal rings, bearing strongly polarizing substituents at asymmetric centers, have a

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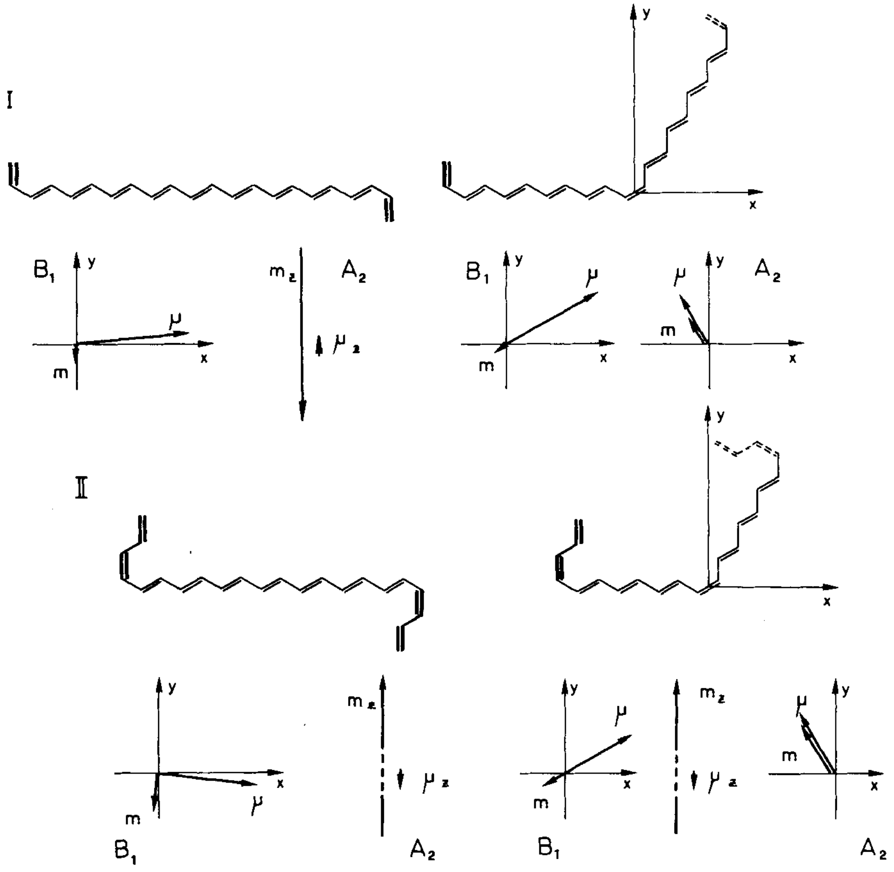
restricted conformational mobility with respect to the polyene chain and impart a well-defined chirality to it. Excellent examples are, for instance, found in the zeaxanthins and astaxanthins where the terminal rings are conjugated to the polyene chain [38] [40]. *Noack & Thomson* [40] discuss the main features of their spectra on the basis of a twisted diene model [42] [43]. In the present investigation we quantitatively investigate the electronic structure of a chiral polyene of the length of the conjugated carotene chromophore. The results are then compared with a variety of measured spectra and interpreted in the light of the C_2-rule [43] [44].



all-*trans* Δ^{11}-*cis*

Fig. 1. *Polyene models considered for the calculations.*

The all-*trans* models (at left) are of righthanded chirality, the Δ^{11}-*cis* models at right of lefthanded chirality. The computed electric $\vec{\mu}$ and magnetic $\vec{m}$ dipole transition moments are shown for the two longest-wavelength transitions B_1 and A_2. Notice in particular: 1) In B_1, $\vec{m}$ is generally small and $\vec{\mu}$ is large. In the all-*trans* cases the two transition moments are almost perpendicular to each other. 2) In A_2 in the all-*trans* models, $\vec{m}$ is large and $\vec{\mu}$ is small, and both are polarized parallel to the twofold symmetry axis in z-direction, thus perpendicular to the plane of the drawing. 3) In A_2 in the Δ^{11}-*cis* models, $\vec{m}$ decreases and $\vec{\mu}$ increases. They are still polarized along the C_2-axis, which now lies in the x,y-plane. 4) In B_1 in II Δ^{11}-*cis*, a strong component m_z appears which is practically absent in model I (see also *Table 1*).

An aspect of central importance is to know when conservative spectra occur and when not. For this reason we present a general overview in *Table 2*. The interpretation of non-conservative spectra is certainly much more difficult than that of conservative spectra. Because of the increased conformational mobility, such an interpretation requires the energy-weighted superposition of a very large number of conformations, presumably of varying chirality. Such an attempt is here not undertaken. With respect to that question, our discussion will remain on a qualitative level.

2. Conservative spectra and the C_2-rule. - We treat the carotene chromophore which gives rise to the transitions in the visible and near-UV. region as a system of

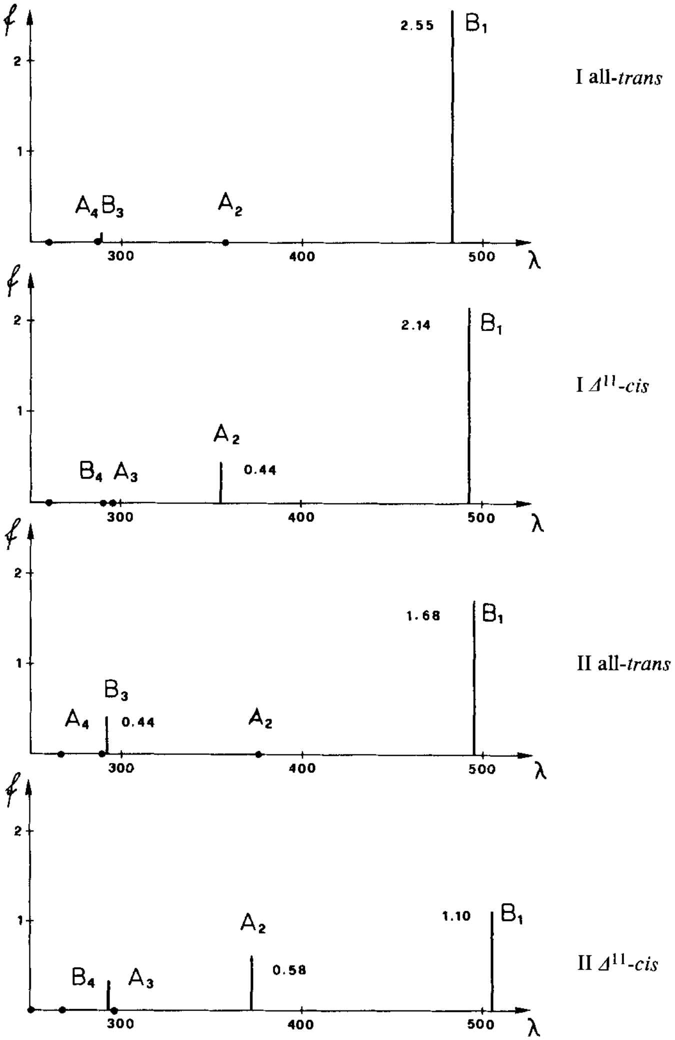


Fig. 2. *Computed oscillator strengths f.* The wavelength-scale is in nm.
Notice the appearance of the '*cis*-peak' A_2 and the concomitant relative decrease of f (B_1).

eleven conjugated double bonds containing 22 (pseudo-)π-electrons. It is assumed that the influence of the asymmetric terminal rings may be simulated by an appropriate twist around a C,C-bond near each end of the conjugated chain. We consider two models (see *Fig. 1*). Model I: The dihedral angles around bonds 2, 3 and 20, 21 are fixed by calibration of the order of magnitude of the rotatory strengths at $-5°$. The formal double bonds 1, 2 and 21, 22 are thereby turned upward. The conjugated system loses its plane of symmetry, adapts the point group C_2 and acquires a righthanded chirality in the case considered. Model II: Here the twist of $-5°$ is around the formal single bonds 4, 5 and 18, 19. Symmetry and chirality are the same as for I. It is immediately apparent that the chirality inverts upon mono-*cis* isomerization.

The computation of the energy levels and wavefunctions of these models were performed by standard SCF-MO-single-CI technique in the frame of the PPP approximation. To take into account the difference in bond length between formal single and double bonds, the adopted resonance integrals β_{CC} were -2.36 and -2.56 eV, respectively. More complete computational details, in particular also concerning the calculation of electric and magnetic transition moments and rotatory strengths, may be found in [45] and [46], and further references cited therein. The computed oscillator strengths f are shown in *Figure 2* and compare satisfactorily with, for instance, the long-wavelength part of the absorption spectrum of β-carotene *(Fig. 3)*. In particular, the appearance of the *cis*-peak (A_2) and concomitant decrease in intensity of the longest-wavelength transition (B_1) upon isomerization from all-*trans* to 15,15'-*cis* is well reproduced. Notice that bond 11 in the model corresponds to bond 15,15' in the actual molecules, in which atoms are conventionally numbered.

We now turn to the CD. spectra and rotatory strengths. The computed rotatory strengths *(Fig. 4* and *5)* are only indicated for transitions above 250 nm. It is very likely that in transitions of higher energy, (pseudo-)π,π^*-electron configurations start mixing with σ,σ^*-electron configurations. This aspect is neglected in our computational model. The predictive value of the model lies in the visible and near

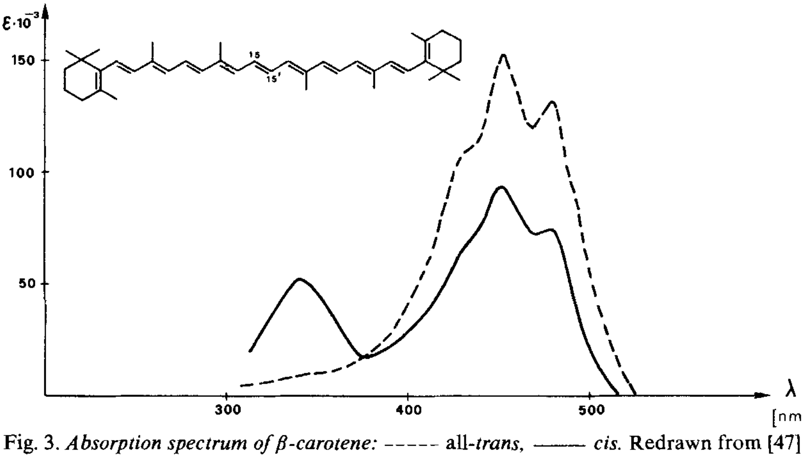


Fig. 3. *Absorption spectrum of β-carotene:* ----- all-*trans*, —— *cis*. Redrawn from [47].

UV. region only. We consider the spectrum of all-*trans* and mono-*cis* astaxanthin *(Fig. 6)*. The chirality of the chromophore is assumed to be determined by the steric position of the two hydroxyl groups. It is apparently *opposite* to the chirality of our models I and II. The sequence of the signs of the three longest-wavelength *Cotton* effects in the computed CD. spectrum of model II *(Fig. 5)* is for all-*trans:* B_1+, A_2-, B_3+, and for Δ^{11}-*cis*: B_1-, A_2+, $(A_3 \approx 0)$, B_4-. In the experimental spectrum of astaxanthin one should encounter the opposite: Coming in from long wavelengths, one should find the sequence of signs for all-*trans*: $-$, $+$, $-$, and for 15,15′-*cis*: $+$, $-$, $+$. This is in agreement with the spectrum actually measured. From this we see that these spectra conform to the C_2-rule. The C_2-rule is applicable to many chromophores of symmetry C_2 and well-defined chirality. In molecules of this point group the transitions (*i.e.* electric dipole and magnetic dipole transition moments) are either of symmetry A: Polarized parallel to the twofold axis, or of symmetry B: Polarized perpendicularly. The rule is here summarized:

Chirality	Transition symmetry	*Cotton* effect
righthanded	A	negative
	B	positive
lefthanded	A	positive
	B	negative

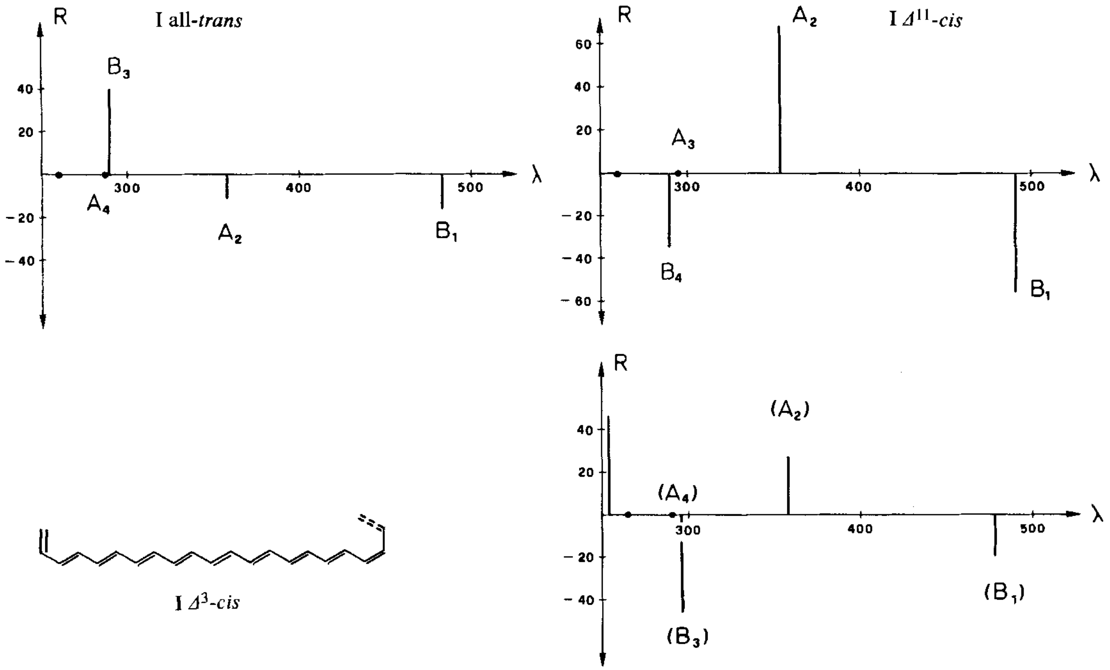
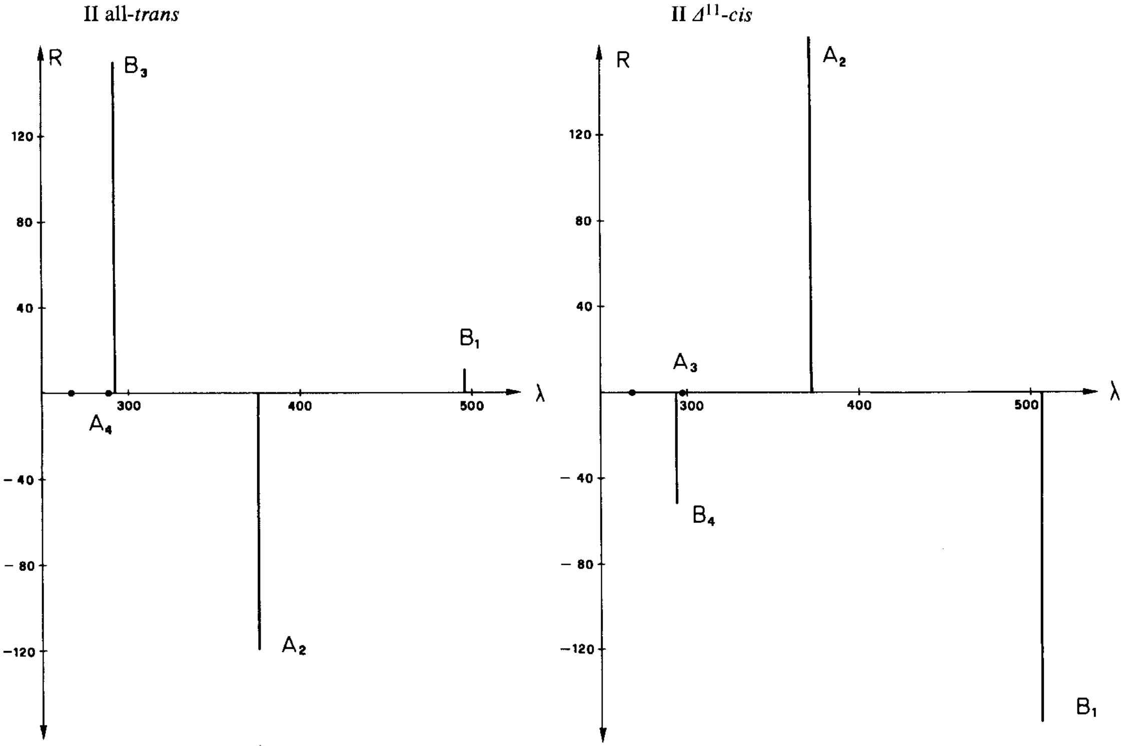


Fig. 4. *Computed rotatory strengths R* (in cgs units × 10^{40}) *of model I.*
Notice that in Δ^3-*cis* one only has pseudo-C_2 symmetry. The values of R nevertheless conform to the C_2-rule. Wavelength-scale λ in nm.


II all-*trans*

II Δ^{11}-*cis*

Fig. 5. *Computed rotatory strengths R of model II* (in cgs units × 10^{40}).
Notice the increase in the absolute value of $R(B_1)$ on going from all-*trans* to Δ^{11}-*cis*. This agrees, with inverted chirality, qualitatively with experiment *(Fig. 6)*.

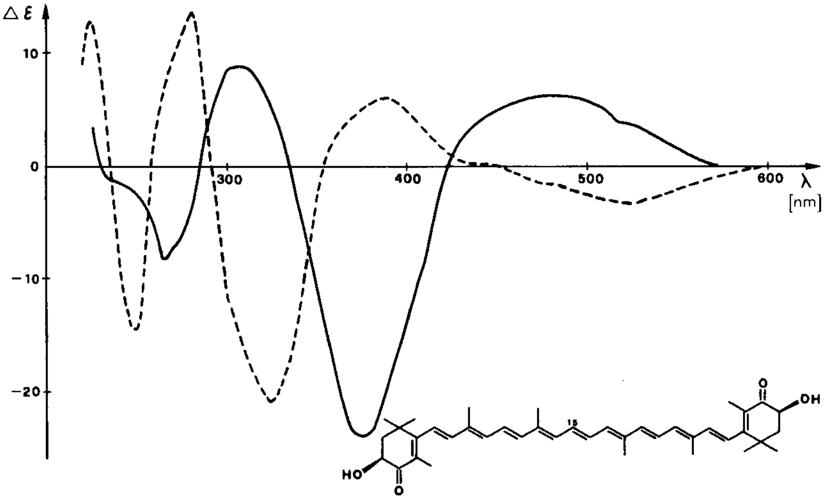


Fig. 6. *CD. spectrum of astaxanthin in* CH_2Cl_2 *at RT.*
- - - - - all-*trans*, ——— Δ^{11}-*cis*. Redrawn from [26].

Table 1. *Components of electric and magnetic transition moments for the four lowest excited states of models I and II.* To identify the frame of reference, see *Figure 1*, the dipole velocity transition moments are in a.u.

		λ (nm)	$\langle\vec{\nabla}\rangle_x$	$\langle\vec{\nabla}\rangle_y$	$\langle\vec{\nabla}\rangle_z$	$\langle\vec{r}\times\vec{\nabla}\rangle_x$	$\langle\vec{r}\times\vec{\nabla}\rangle_y$	$\langle\vec{r}\times\vec{\nabla}\rangle_z$	$R \cdot 10^{40}$ (cgs)	f
I all-*trans*	B_1	483	0.5984	0.0579	0.	−0.0052	−0.0726	0.	−18.3	2.55
	A_2	358	0.	0.	0.0068	0.	0.	−0.8811	−11.6	<0.01
	B_3	289	−0.0830	0.1287	0.	0.0145	0.2116	0.	38.9	0.10
	A_4	288	0.	0.	−0.0002	0.	0.	0.1178	0.	0.
I Δ^{11}-*cis*	B_1	492	0.4719	0.2724	−0.0032	−0.0347	−0.0201	0.0157	−55.7	2.14
	A_2	355	−0.1451	0.2514	0.	−0.0638	0.1105	0.	67.9	0.44
	A_3	295	−0.0021	0.0037	0.	−0.0011	0.0019	0.	0.	0.
	B_4	290	−0.0159	−0.0092	0.0094	0.1011	0.0583	−2.2392	−35.0	<0.01
II all-*trans*	B_1	495	0.4788	−0.0526	0.	−0.0120	−0.1860	0.	10.3	1.68
	A_2	376	0.	0.	−0.0184	0.	0.	3.3526	−120.1	<0.01
	B_3	292	0.1644	0.2768	0.	0.0246	0.3541	0.	154.0	0.44
	A_4	291	0.	0.	−0.0017	0.	0.	0.2687	−0.7	<0.01
II Δ^{11}-*cis*	B_1	506	0.3340	0.1928	−0.0109	−0.0895	−0.0517	1.7427	−154.3	1.10
	A_2	372	−0.1629	0.2821	0.	−0.1320	0.2287	0.	165.5	0.58
	A_3	298	0.0052	−0.0090	0.	0.0080	−0.0138	0.	0.3	<0.01
	B_4	293	−0.2362	−0.1363	−0.0205	−0.1717	−0.0991	4.3082	−52.0	0.32

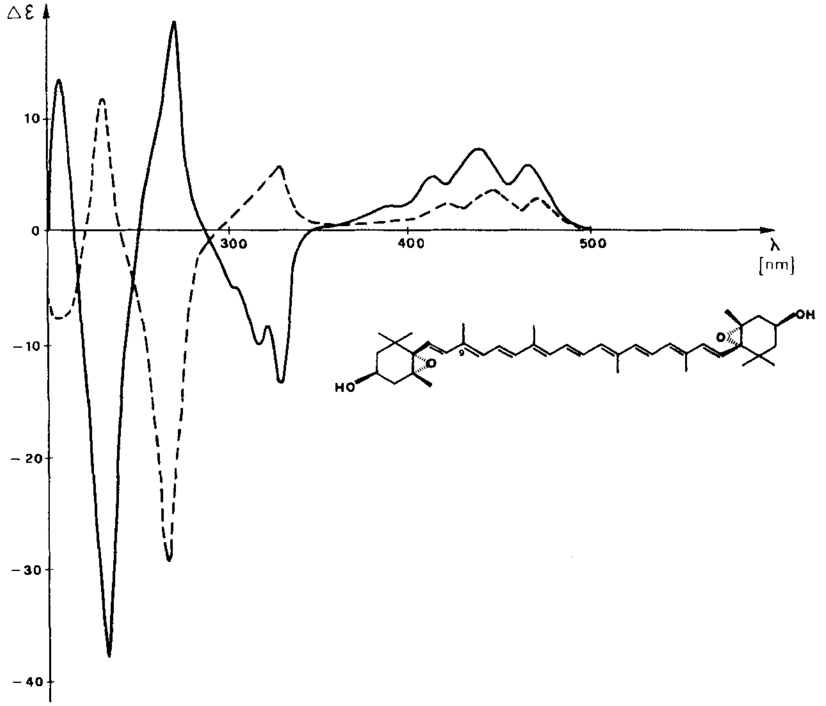


Fig. 7. *CD. spectrum of violaxanthin in ethanol at RT.* ----- all-*trans*, ——— Δ^{11}-*cis*. Redrawn from [18].

Hereby an analogy is established to the CD. spectra of otherwise rather unrelated systems of actual or formal symmetry C_2, such as helicenes [44], the corrin chromophore in vitamin B_{12} [48], bile pigments attached to proteins [45] [46], optically active biphenyls, or even the disulfide chromophore [44].

Whereas in astaxanthin *(Fig. 6)* 15,15′ mono-*cis* isomerization changes the sign in the whole spectrum, in violaxanthin *(Fig. 7)* the spectrum inverts with exception of the longest-wavelength transition. Qualitatively, the spectrum of Model II (with inverted chirality; *Fig. 5*) reproduces better the spectrum of astaxanthin, whereas that of Model I (also with inverted chirality; *Fig. 4*) shows the unexpected behavior of the longest-wavelength transition B_1 of violaxanthin. This situation may be interpreted by looking at the computed electric and magnetic transition moments *(Fig. 1, Table 1).* It is seen that in the all-*trans* models I and II for the transition B_1 the magnetic transition moment $\vec{m}$ is small and almost perpendicular to the large electric transition moment $\vec{\mu}$. Only very small changes in the respective orientations of $\vec{m}$ and $\vec{\mu}$ may lead to a change of sign. In the all-*trans* model of II, where the chirality is more pronounced than in the all-*trans* model of I, the sign of the predicted *Cotton* effect of B_1 actually does conform to the C_2-rule.

To verify if our models predict correct orders of magnitude, we make use of the approximate formula relating the rotatory strength R with the bandwidth Δ, the wavelength of the band maximum λ_0, and $\Delta\varepsilon_{\max}$ for a given CD. band [49]:

$$R \gtrsim 23 \cdot 10^{-40} \sqrt{\pi}\, \frac{\Delta}{\lambda_0} \Delta\varepsilon_{\max}.$$

Although this formula is strictly only applicable to *Gaussian* bands, we make a more general use of it, adopting an estimated average value of Δ/λ_0 of 0.09. From this and the computed rotatory strengths, $\Delta\varepsilon_{\max}$ becomes,

for model I all-*trans*:	B_1: −5.0	A_2: −3.2	B_3: 10.6
for model II all-*trans*:	B_1: 2.8	A_2: −32.7	B_3: 42.0

From *Figures 6* and *7* we notice that measured values tend to lie inbetween the predictions of the two models.

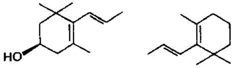
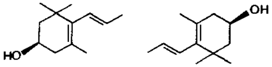
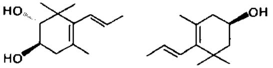
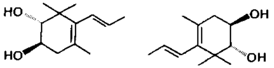
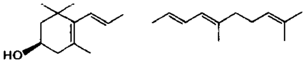
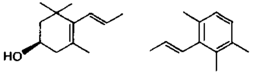
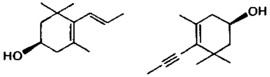
3. Non-conservative spectra. - Over the whole wavelength range ($\lambda = 0$ to $\lambda = \infty$) the CD. spectrum of every molecule is conservative. This is a consequence of the sum rule:

$$\sum_{b \neq a} \operatorname{Im}\{\langle a|\vec{\mu}|b\rangle \cdot \langle b|\vec{m}|a\rangle\} = 0$$

If in a given molecule the spectrum is conservative within a *finite* and *limited* wavelength range, the molecular electrons giving rise to the transitions in that range act as a quasi-independent chiral chromophore. Such are, as we have seen in Section 2, the (pseudo-)π-electrons in a carotene of fixed chirality. We then have a partial sum rule for the (pseudo-)π,π^*-transitions. On this question see [50], in particular *Table 5* and the Appendix.

Table 2. *CD. data on some naturally occurring carotenoids or closely related derivatives thereof.* The wavelength λ is in nm. $\Delta\varepsilon$ designates $\Delta\varepsilon_{\max}$-values in $1\,mol^{-1}\,cm^{-1}$. In all formulae seven conjugated double bonds of the polyene chain are omitted

Table 2a. *Predominantly conservative spectra.* One notices that the $\Delta\varepsilon$-values often do not add to zero. In many cases the sum rule is only very approximately fulfilled, and to verify it, the bandwidth must also be taken into account.

	210-230		230-270		270-300		320-380		>380		Solvent[a])	Ref.
	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$		
β-Kryptoxanthin 	<220	-	*ca.* 248	*ca* + 5,2	*ca.* 288	*ca.* − 7,7	*ca.* 345	*ca.* + 1,9			Dioxane	[40] [2][b])
Zeaxanthin 	225	− 7,7	251	+ 8,1	290	− 14,6	348	+ 3,7	490	− 2,5	CH_2Cl_2	[26] [2][b])
Caloxanthin 	222	− 10,4	244	+ 8,8	283	− 16	337	+ 4,6			EPA	[20]
Nostoxanthin 	220	− 11,9	245	+ 8,8	282	− 16,7	340	+ 3,5			EPA	[20]
Rubixanthin 	<220	-	*ca.* 257	*ca.* + 2,5	*ca.* 296	*ca.* − 7,5	*ca.* 355	*ca.* + 2,0			EPA	[40] [2][b])
Agelaxanthin A 	217	− 6,9	248	+ 4,5	284	− 8,9	338,5	+ 2,3			Ether/Hexane 1:2	[24]
Diatoxanthin 	227	− 5,1	250	+ 4,8	286	− 9,2	343	+ 3,0			EPA	[25] [2][b])

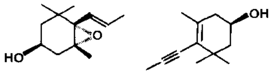
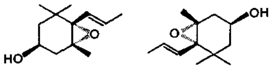
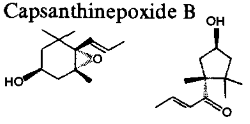
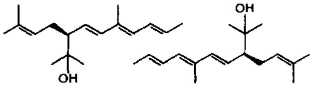
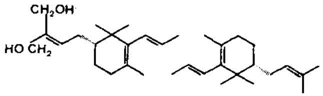
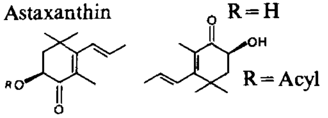
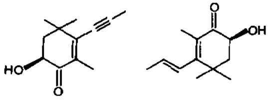
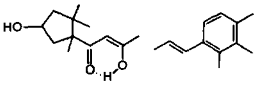
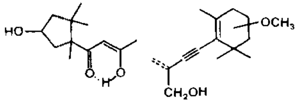
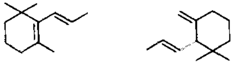
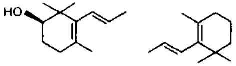
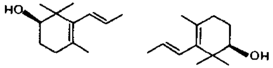
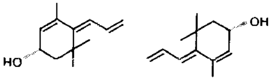
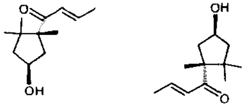
Diadinoxanthin 	<205	-	ca. 235	ca. + 2	ca. 280	ca. − 9	ca. 365	ca. + 2,5			EPA	[25]
Violaxanthin 	205	− 8,0	230	+ 11,6	266	− 29,4	316 328	+ 3,6 + 5,8	395 420 444 471	+ 0,9 + 2,1 + 3,4 + 2,7	Ethanol	[18] [1][b]) [2][b])
Capsanthinepoxide B 	ca. 215	ca. − 4	ca. 245	ca. + 6	ca. 285	ca. − 8,5	ca. 340 ca. 355	ca. + 2,5 ca. + 4			Dioxane	[22]
Bisanhydrobacterioruberin 	ca. 225	ca. − 3	ca. 245	ca. + 2,5	ca. 270	ca. − 8	ca. 320	ca. + 8	ca. 390 ca. 430	ca. − 3 ca. − 1	EPA	[16] [21][b])
C.p. 450 	<220	-	ca. 250	ca. + 3	ca. 280	ca. − 7	ca. 320	ca. + 0,7			EPA	[11]
Astaxanthin  R = H	224	+ 12,8	249	− 14,4	280	+ 12,5	323	− 23,1	384 521	+ 6,7 − 3,2	CH_2Cl_2	[26] [10][b])
R = Acyl	ca. 220	+	ca. 240	-	ca. 270	+	ca. 305	-	ca. 375	+	EPA	[10]
Monoacetylenic Asterinic Acid 	ca. 220	ca. + 5	ca. 247	ca. − 3	ca. 276	ca. + 4	ca. 320	ca. − 13	370–380	ca. + 4	EPA (20°)	[40] [23][b])
Trikentriorhodin 	<215	+	264	− 1,1	301	+ 1,3	ca. 360	− 0,7			Ether/Hexane 1:2	[24]

Table 2a (continued)

	210-230		230-270		270-300		320-380		>380		Solvent[a])	Ref.
	λ	Δε	λ	Δε	λ	Δε	λ	Δε	λ	Δε		
Agelaxanthin C 	<230	+	257	− 0,6	296	+ 0,5	ca. 360	− 0,4			Hexane	[24]
β,γ-Carotene 	ca. 220	ca. + 5	ca. 245	ca. − 5	ca. 275	ca. + 7,5	ca. 325	ca. − 3	>380	-	EPA	[27]
β,β-Carotene-2-ol 	225	+ 2,65	251	− 1,6	281	+ 3,05	334	− 0,80	>380	+	EPA	[6] [12][b])
β,β-Carotene-2,2′-diol 	223	+ 3,95	250	− 2,95	281	+ 4,93	345	− 0,80			EPA	[6] [12][b])
Eschscholtzxanthin 	ca. 215	ca. + 8	ca. 240	ca. − 4,5	ca. 265	ca. +26	ca. 310	ca. −24,5	ca. 360 ca. 380	ca. +11,5 ca. +19,5	EPA	[36]
Capsorubin 	ca. 210	ca. + 2,5	ca. 250	ca. − 1	ca. 300	ca. + 7	ca. 370	ca. − 2				[9] [1][b])

Concerning eschscholtzxanthin, it occurs predominantly in the Δ^6-*trans*-configuration

Table 2b. *Intermediate spectra, close to conservative.*

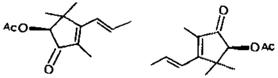
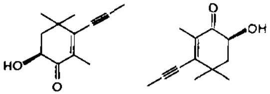
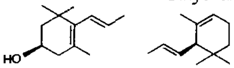
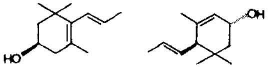
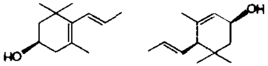
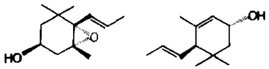
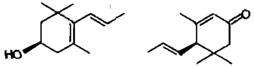
	210–230		230–270		270–300		320–380		> 380		Solvent[a])	Ref.
	λ	Δε	λ	Δε	λ	Δε	λ	Δε	λ	Δε		
Actinioerythrin 	< 230	-	*ca.* 250 *ca.* 260	*ca.* + 0,8 *ca.* + 0,7	*ca.* 280	*ca.* – 0,3	*ca.* 315 *ca.* 345	*ca.* + 1,5 *ca.* – 1,6	*ca.* 415	*ca.* – 1,4	CH_2Cl_2	[34]
Diacetylenic Asterinic Acid 	*ca.* 225	*ca.* + 4,2	*ca.* 260 Sh	*ca.* –2,7	*ca.* 315	*ca.* – 4,2	*ca.* 360	*ca.* + 1,3	> 450	-	EPA (20°)	[40] [23][b])
α-Kryptoxanthin, Zeinoxanthin, Physoxanthin 			241	+ 9,0	280	– 5,0	333	+ 3,8	> 400	+	Hexane/Ether/ Methanol 10:3:1	[30] [1][b])
Lutein 	212	+ 4,2	242	+ 6,8	280	– 2,8	327	+ 1,1	392 447 468	+ 1,0 + 0,8 + 0,5	Hexane	[39] [13][b])
3′-Epilutein 			241	+ 10,6	280	– 6,1	331	+ 4,1			Hexane/Ether/ Methanol 10:3:1	[37] [31][b])
Luteinepoxide 	< 220	+	234	+ 4,1	275	– 0,2	330 352	+ 1,35 + 0,45	*ca.* 417 *ca.* 470	+ 1,35 + 1,5	Dioxane	[14]
3′, O-Didehydrolutein 	215	– 15,4	236 261	+ 3,2 + 8,4	299	– 1,9	332	+ 3,4	389	+ 1,3	Hexane	[31]

Table 2c. *Non-conservative spectra.*

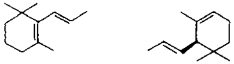
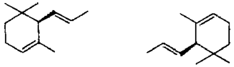
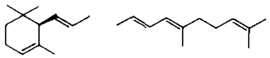
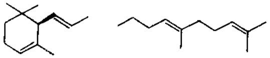
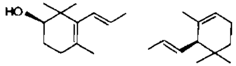
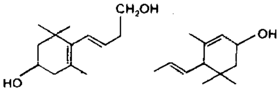
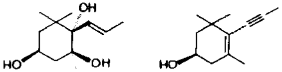
	220–250		250–270		320–340		370–400		>400		Solvent[a])	Ref.
	λ	Δε	λ	Δε	λ	Δε	λ	Δε	λ	Δε		
β,ε-Carotene (α-Carotene) 	243	+ 5,3	254	+ 4,25	334	+ 2,4	394	+ 1,3	410– 490	+ 0,9	Dioxane	[8] [3]b)
ε,ε-Carotene 	*ca.* 220	+	264	+ 19,5	*ca.* 312 325	+ 2,5 + 3,2	*ca.* 392	+ 4,5	411 436 465	+ 7,5 + 10,5 + 9,6	Hexane	[41] [3]b) [4]b)
ε,ψ-Carotene (δ-Carotene) 	<215 242	+ + 6,1	269 285	+ 4,6 + 3,6	347	+ 3,3	400	+ 1,5	415– 480 480– 500	+ 0,8 + 0,5	Dioxane	[8] [4]b)
α-Zeacarotene 			253	*ca.* + 4,5			373	*ca.* + 1,2	457	*ca.* + 0,8	Dioxane	[8]
β,ε-Carotene-2-ol 	<210 240	+ + 4,95	262	+ 6,0	331	+ 2,9	391	+ 1,45			EPA	[6] [12]b)
Loroxanthin 	220	+	265	+	315	+	395	+			EPA	[38]
Alloxanthin  *(ex Microciona prolifera)*	<230	-	*ca.* 270	*ca.* – 6	*ca.* 325	*ca.* – 4					EPA	[23] [2]b)
Heteroxanthin 	*ca.* 230	*ca.* – 3,5	*ca.* 275	*ca.* – 1,5	*ca.* 340	*ca.* – 1	>370	-			EPA	[25]

Table 2d. *Intermediate spectra* (Difficult to classify)

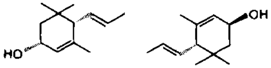
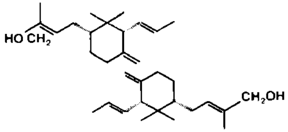
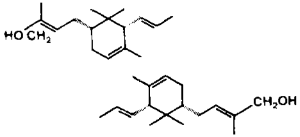
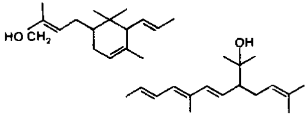
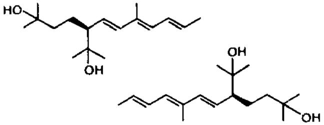
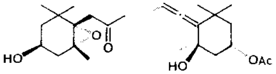
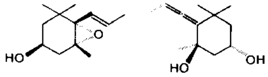
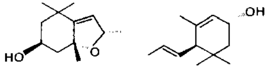
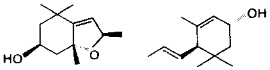
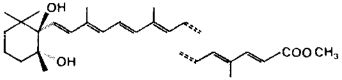
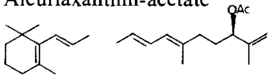
	220-250		265-290		310-360		380-400		>400		Solvent[a])	Ref.
	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$	λ	$\Delta\varepsilon$		
Tunaxanthin 	<210 *ca.* 230	- *ca.* – 5,5	*ca.* 265	*ca.* – 7	*ca.* 335	*ca.* + 0,5					EPA	[35]
Sarcinaxanthin 			*ca.* 270	*ca.* –16	*ca.* 350	*ca.* + 1			>400	-	EPA	[29]
Decaprenoxanthin 	*ca.* 230 Sh	*ca.* – 1	*ca.* 270	*ca.* – 5	*ca.* 310 *ca.* 330	*ca.* – 0,5 *ca.* – 0,5	*ca.* 380	+			EPA	[15]
A.g. 470 	*ca.* 225 *ca.* 245	*ca.* – 5 *ca.* – 4	*ca.* 275 *ca.* 290	*ca.* – 5 *ca.* – 5,5	*ca.* 340 *ca.* 360	*ca.* + 4,5 *ca.* + 5,5			*ca.* 410	*ca.* – 0,5	EPA	[16]
Bacterioruberin 	*ca.* 220 250 Sh	*ca.* – 3 –3	*ca.* 275	*ca.* – 6	*ca.* 315	*ca.* + 8	*ca.* 385	*ca.* – 3	*ca.* 440	*ca.* – 0,5	EPA	[5] [21][b])

Table 2d (continued)

	220-250		250-270		290-330		380-400		>400		Solvent[a])	Ref.
	λ	Δε	λ	Δε	λ	Δε	λ	Δε	λ	Δε		
Fucoxanthin 	*ca.* 225	*ca.* + 0,4	*ca.* 265	*ca.* − 0,6	*ca.* 295	*ca.* + 0,1	>350	+			EPA	[28] [2[b])]
Neoxanthin (Trollixanthin, Trolliflor) 	222	− 2,0	267,5	− 5,9	299 311 328	− 0,5 − 0,5 − 0,1	393	+ 0,6	420 444 475	+ 1,3 + 1,8 + 2,0	Ethanol	[18] [2[b])]
Flavoxanthin 	225	+ 5,0	252	+17,3	303 314	− 1,3 − 1,7	*ca.* 382	+ 1,4			Dioxane	[32]
Chrysanthemaxanthin 	223	− 0,9	256	+ 5,0	291 303 314	+ 1,9 + 3,0 + 3,6			*ca.* 415	+ 0,9	Dioxane	[32]
Azafrinmethylester 	243	− 2,56	270	+ 0,42			380	+ 0,62	450 520	+ 0,78 + 0,23	Dioxane	[33] [17[b])]
Aleuriaxanthin-acetate 	<230	-	*ca.* 250	*ca.* + 0,1	*ca.* 300	*ca.* − 1	*ca.* 350	*ca.* + 0,3	*ca.* 460	*ca.* + 0,3	EPA	[7] [19[b])]

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[a]) EPA = ether/isopentane/ethanol 5:5:2 (*v/v*).

[b]) Contain only the determination of absolute configuration, no CD. data.

Spectra of carotenes which are non-conservative in the region of the (pseudo-)π,π^*-transitions will, however, become conservative if we extend our range of observation far into the vacuum UV. This then means that the (pseudo-)π,π^*-transitions and the energetically higher-lying σ,σ^*-transitions are not independent of each other. This situation is an indication of increased π,σ-interaction. As we shall see in more detail in the next section, such spectra which are non-conservative in the long-wavelength range reflect increased conformational mobility and a decrease of well-definable chirality. Consequently, these spectra become insensitive to *trans, cis*-isomerization: Non-conservative spectra tend not to invert upon *trans, cis*-isomerization. The spectrum of α-carotene [51] gives a striking example *(Fig. 8)* thereof.

4. General discussion. - *Tables 2a–d* summarize the accessible CD. data of about fifty naturally occurring carotenes, or closely related derivatives thereof. It is immediately apparent that a clearcut classification is difficult, but that a general ordering of the spectra with respect to two extremes, conservative and non-conservative, is meaningful.

4.1. *Predominantly* conservative *spectra (Table 2a)* are obtained in the following typical cases: The molecule has two terminal rings, each of which contains a double bond formally conjugated with the polyene chain and one or more asymmetric C-atoms.

The molecule is homodichiral [1], or close to homodichiral. As discussed in detail by *Noack & Thomson* [40], if the double bond is in position 5, 6, different conformations are energetically possible in which the formal single bond 6, 7 is twisted. By the presence of an asymmetric center in position 3 and (or) 2, one of these conformations outweighs, thereby imparting a resulting chirality to the overall system of conjugated double bonds. A similar situation is encountered if the double bond in position 5, 6 is transformed into an epoxy ring at the same position. In particular, we find as typical cases:

4.1.1. *(3*R*,3'*R*)-Zeaxanthin.* The rings are β, the asymmetric carbon center with hydroxy substituent is in position 3.

4.1.2. *β,β'-Carotene-(2*R*,2'*R*)-diol.* The rings are β, the asymmetric carbon center with hydroxy substituent is in position 2. The CD. spectrum is somewhat weaker than in 4.1.1 and of *opposite* chirality.

4.1.3. *(2*R*,3*R*,2'*R*,3'*R*)-Nostoxanthin.* The rings are β; there are two asymmetric carbon centers adjacent to each other at positions 2 and 3 of such absolute

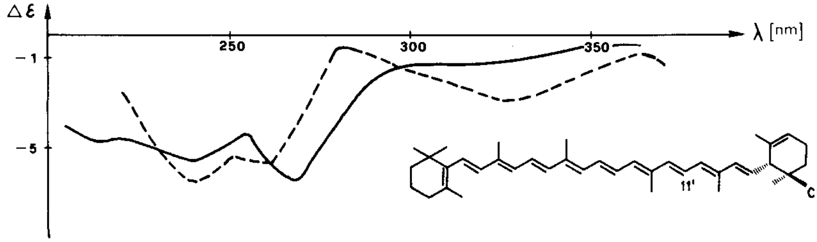

Fig. 8. *CD. spectrum of α-carotene in ethanol at RT.* ----- all-*trans*, ——— Δ^{11}-*cis*. Redrawn from [51]. Notice that the spectrum is non-conservative and that it does not invert upon *trans, cis* isomerization.

configuration as to reinforce one another in leading to the same chirality as in 4.1 and with noticeably larger $\Delta\varepsilon_{max}$-values in the spectrum.

4.1.4. *(3S,3'S)-Astaxanthin.* The rings are *β*, containing a 3-hydroxy-4-oxo-ionone moiety. Conservative spectra tend to show strong temperature dependence. Astaxanthin reveals the particularity that its spectrum inverts upon cooling from room temperature to – 180° [40]. The chirality of the high-temperature form is the same as in 4.1.1.

4.1.5. *The so-called* retro *structure of Eschscholtzxanthin.* It has the intra-annular double bond in position 4, 5 instead of 5, 6 for the cases 4.1.1–4.1.4. The asymmetric carbon center is in position 3 and, theoretically, lies in the plane of conjugation of the polyene chain. Viewing the hydroxy-substituent as part of the chromophore, one may assign to it a well defined chirality. For the absolute configuration *3S,3'S* this chirality is righthanded. The measured spectrum is in accordance with this conclusion.

4.1.6. *(3R,3'R)-Violaxanthin.* The double bond in position 5, 6 encountered in 4.1.1–4.1.4 is here replaced by an epoxy-ring. It appears, upon comparison with 4.1.1, that the epoxy-ring must lead to comparable steric hindrance as the double bond. If the absolute configuration at position 3 is the same, the resulting chirality is the same for 4.1.1 and 4.1.6.

Typical conservative spectra, such as those described under 4.1.1–4.1.6, should invert upon all-*trans* to mono-*cis* isomerization.

4.1.7. Molecules having on one side a *β*-ring with an asymmetric C-atom in position 3 or 2, on the other side an optically inactive ring or substituent, tend to be still predominantly conservative. Examples are: *β*-kryptoxanthin, rubixanthin, agelaxanthin A, *β,β'*-carotene-2-ol. The CD. spectra tend to be weaker than in cases 4.1.1–4.1.6. It is unlikely – but not in all cases excluded –, that they invert on all-*trans* to mono-*cis* isomerization because of the lack of homo-dichirality.

4.2. Intermediate *spectra (Table 2 b)* occur in very many cases, and our discussion of them is by necessity incomplete.

4.2.1. Molecules having on one side an optically active *β*-ring, on the other side an optically active *ε*-ring tend to show such intermediate spectra, some being closer to conservative: *α*-kryptoxanthin, lutein, 3'-epilutein, luteinepoxide, 3',*O*-didehydrolutein.

β,ε-Carotene-2-ol, with the asymmetric substituent of the *β*-ring in position 2, is non-conservative *(Table 2 c)*.

4.2.2. Molecules having on one side an optically active *β*-ring, on the other side an optically active ring connected to a triple bond in position 7, 8 may still be conservative: Diatoxanthin, Monoacetylenic asterinic acid *(Table 2a)*. If there are optically active rings connected to triple bonds on both sides, the spectrum may be intermediate: Diacetylenic asterinic acid *(Table 2b)*, or non-conservative: Alloxanthin *(Table 2c)*.

4.2.3. There are further conformationally mobile homodichiral molecules which, though related to each other, show different types of spectra: Bisanhydrobacterioruberin, conservative; bacterioruberin, intermediate; C.p. 450, conservative; decaprenoxanthin and sarcinaxanthin, intermediate.

4.3. *Typically* non-conservative *spectra (Table 2c)* occur when terminal groups (rings) are conformationally mobile with respect to the polyene chain. Such examples are: α-carotene, ε,ε'-carotene, δ-carotene, α-zeacarotene.

In summary, homodichiral molecules with strongly optically active end groups which are relatively rigidly connected to the polyene chain tend to give conservative spectra. Increased conformational mobility and lack of homodichirality will contribute to making the spectrum non-conservative. With respect to the influence of conformational mobility, it may be interesting to investigate if carotenoids may be found for which the CD. spectrum is conservative at low temperature and becomes non-conservative as the temperature is raised.

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