

Linear Dichroic Spectra of Cross-Conjugated Carotenals and Configurations of In-Chain Substituted Carotenoids

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Abstract: The polarization angles between the transition moments of the main absorption (${}^1B \leftarrow A$) and "cis" (${}^1C \leftarrow A$) bands are estimated to be in the range of $32\text{--}38^\circ$ for reinerapurpurin-20-al (6), 20-(2,3,4-trimethylbenzal)reinerapurpurin (7), and 8,8'-diapocaratene-8,20,8'-trial (3) from the linear dichroic spectra in stretched polyethylene films. These polarization angles are in good agreement with the theoretically predicted values based on the SCF-MO-CI P-P-P calculations. The most likely configurations of reinerapurpurin-20-al (6) and the triaryl carotenoid (7) are deduced to be 13-cis, while the configuration of the trial 3 cannot be definitively deduced from the present theoretical study. The absorption spectra at 77 K were also recorded in order to enhance the spectral resolution of near-UV and visible bands. Carotenoids containing cross-conjugated aldehyde groups show weak, structured bands at the long wavelength edge of the main absorption band. The assignment of these bands remains unresolved. Additional evidence for the configuration of 18 in-chain substituted carotenoids, 1-18, including 1H NMR data, is discussed. The generality of 13-cis configuration of cross-conjugated caroten-20-als and the relatively high percentage of 13-cis of caroten-20-ols and caroten-20-acetates in solution now seem to be reasonably well established.

In previous work^{2,3} we have analyzed the electronic spectra of β -carotene, rhodopinal (9), and carotenone and carotenal Schiff's bases. Carbonyl containing carotenoids and their Schiff's bases are of special interest as spectroscopically and photochemically useful analogues of the visual pigment chromophores, retinal and retinal Schiff's base. Although photobiological roles of long chain carotenals and their Schiff's bases are yet to be established,⁴ spectroscopic studies of these carotenoids provide useful information in elucidating the electronic structure of carotenoids in general and carbonyl or Schiff's base containing carotenoids in particular. At least in one case the photobiological role of the carbonyl containing carotenoid peridinin has been well established by spectroscopic methods.⁵

In the present paper, we describe the linear dichroic spectra of three cross-conjugated carotenoids, reinerapurpurin-20-al (6), 20-(2,3,4-trimethylbenzal)reinerapurpurin (7), and 8,8'-diapocaratene-8,20,8'-trial (3), with the objectives of (a) establishing the polarization directions of the visible and UV bands, (b) on this basis deducing the spectroscopically consistent configurations of these cross-conjugated polyenes, and (c) comparing these results with 1H NMR evidence, for configurational assignments (i.e., 13-cis) of in-chain substituted carotenoids (Scheme I). The 13-cis carotenoid aldehydes (Scheme II) are of particular interest as a possible photobiological receptor analog.⁴

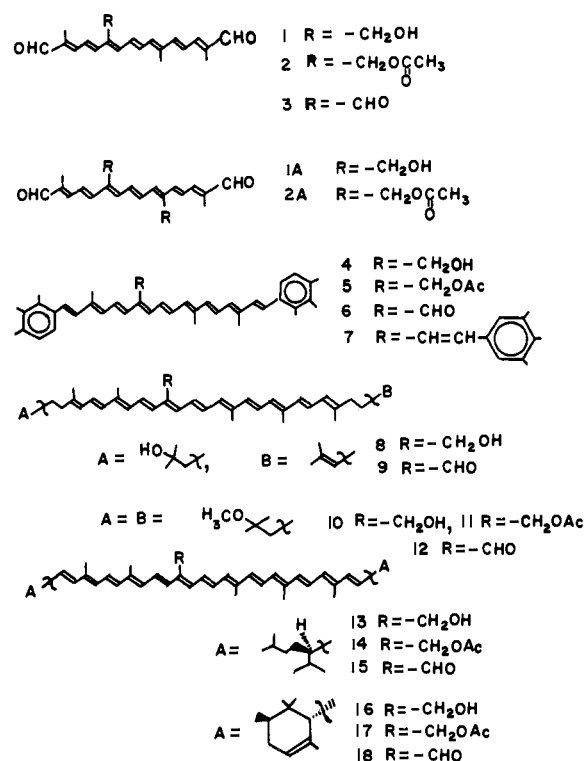
Experimental Section

The cross-conjugated carotenals 3, 6, and 7 were synthesized as described elsewhere.^{6,7}

Crystalline samples were used for spectral measurements. Polyethylene films used for linear dichroic measurements were obtained as described previously.^{2a}

The polyethylene film was swelled in chlorobenzene overnight. The swollen film was immersed in the sample solution (in chlorobenzene) for 1 day in darkness. The dyed film was washed with ethanol and dried in the dark at room temperature under N_2 atmosphere. The dried polyethylene film was stretched 8-9 times from its original length by employing a homemade film stretcher. The best portion of the stretched film was cut and mounted to the cell holder which can be fitted into the cell compartment of a Cary 118C spectrophotometer. The reference was a swollen polyethylene film prepared under exactly the same conditions but without the dyeing samples. In order to record sufficient optical density of the stretched film, three superimposed

Scheme I. Structures of Carotenoids Discussed Including 1H NMR Data



layers of the stretched film were used. Errors due to various optical bias (intrinsic dichroism of the polarizers themselves, reflection, and scattering) have been corrected by the use of carefully prepared reference films. The linear dichroic spectra (parallel and perpendicular components of the absorption with respect to the stretching axis) were recorded on a Cary 118C spectrophotometer at room temperature. The polacoat UV polarizers⁸ were employed for dichroic measurements. The low-temperature (77 K) absorption spectra were measured using optical cells immersed in liquid nitrogen.

Results and Discussion

Linear Dichroic Spectra and Low-Temperature Absorption Spectra. Figure 1 shows the linear dichroic spectra of reinerapurpurin-20-al (6) and 20-(2,3,4-trimethylbenzal)reinerapurpurin (7).

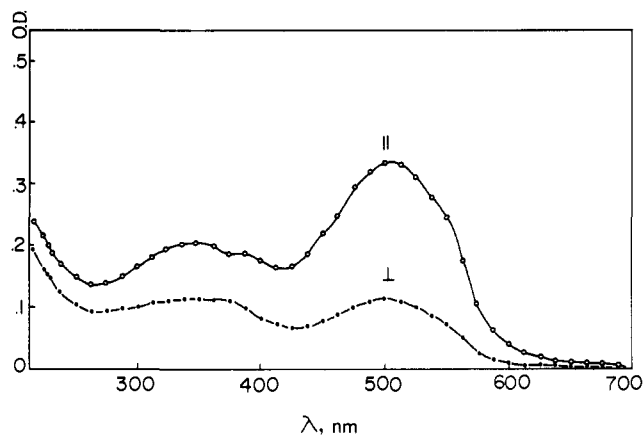


Figure 1. Linear dichroic spectra (\parallel , parallel to the stretching axis; \perp , perpendicular to the stretching axis) of renierapurpurin-20-al (**6**) in polyethylene films (stretched eight times the original length).

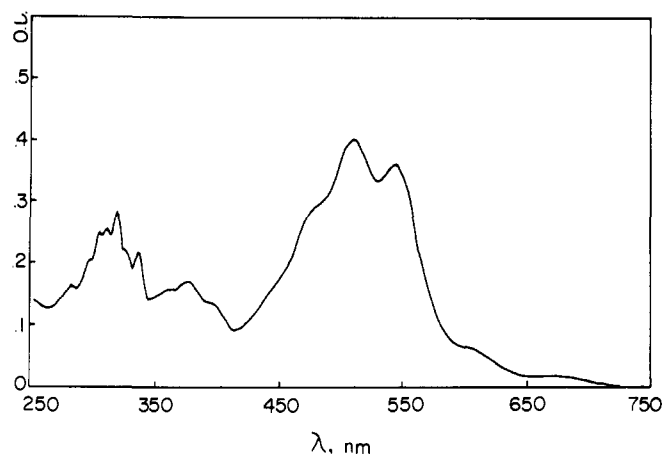
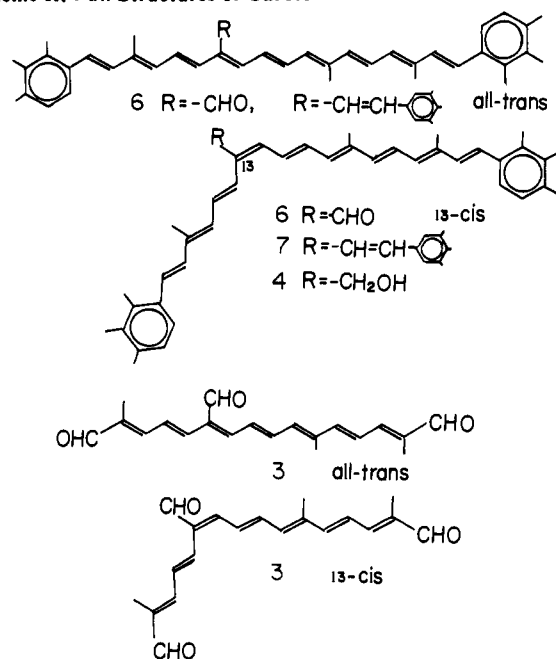


Figure 2. The absorption spectrum of renierapurpurin-20-al (**6**) in ethanol at 77 K.

Scheme II. Full Structures of Carotenoids Studied



erapurpurin-20-al (**6**). The dichroic ratio of the main absorption band (${}^1B \leftarrow A$) is 3.0. Under the assumption that the effective orientation axis and the ${}^1B \leftarrow A$ transition moment are parallel to or very close to the long axis of the molecule, it is possible to calculate the fraction of the aligned molecules in the stretched film. The assumption made is justifiable in view of the linear nature of both the transition moment and the geometry of the molecule, as in the case of β -carotene.^{2a} The fraction of the aligned molecules (f) can be calculated from eq 1,⁹⁻¹¹

$$d_0 = \frac{OD_{\parallel}}{OD_{\perp}} = \frac{f \cos^2 \alpha + \frac{1}{3}(1-f)}{\frac{1}{2}f \sin^2 \alpha + \frac{1}{3}(1-f)} \quad (1)$$

where d_0 is the dichroic ratio, OD_{\parallel} and OD_{\perp} are absorbances of the polarized light parallel and perpendicular to the stretching axis of the film, respectively, and α is the angle between the transition moment direction and that axis of the molecule which is parallel to the stretching axis. The ${}^1B \leftarrow A$ transition in carotenoids is polarized along the long molecular axis.^{2a,12-16} Furthermore, the preferential orientation of *all-trans*- and 15,15'-*cis*- β -carotene is essentially parallel to the stretching axis of the film.^{2a} Thus, it is reasonable to assume that the long molecular axis of carotenoids such as **6** corre-

sponds to the ${}^1B \leftarrow A$ transition moment direction (as also supported by the present theoretical calculations, vide infra) and is essentially parallel to the stretching axis, i.e., $\alpha = 0^\circ$. This justification enables us to calculate f values from eq 1, as mentioned above.

Substituting $d_0 = 3.0$ and $\alpha = 0^\circ$ in the above equation for the first absorption band (${}^1B \leftarrow A$), we obtain $f = 0.398$ for renierapurpurin-20-al (**6**). Values of α for the other transitions, particularly the ${}^1C \leftarrow A$ band (occurring in the so-called "cis" peak region),¹⁷ can be calculated using $f = 0.398$ in eq 1. The angle (θ) between the polarization directions of the two transitions (${}^1B \leftarrow A$ and ${}^1C \leftarrow A$) is then estimated to be 32° . This value agrees well with the theoretically calculated value based on the mono-*cis*, 13-*cis*-12-*s-trans* configurations given in Scheme II and the SCF-MO-CI P-P-P method (Table I).^{18,19} [See ref 20 and 21 regarding the importance of doubly excited configurations in polyenes.] The spectral characteristics (i.e., intensity of the *cis* peak region, polarization directions, and *cis* configurations at the double bond with the formyl substituent) of this carotenoid are, thus, very similar to those of rhodopin (**9**).

It is likely that the *cis* peak region (300–400 nm) in Figure 1 includes the ${}^1D \leftarrow A$ transition, since the calculated energy and polarization direction of the latter are similar to those of the former (Table I). In fact, this is clearly indicated in the low-temperature absorption spectrum shown in Figure 2. The broad band in the 300–400-nm region in the linear dichroic spectrum is now clearly resolved into two bands, each having some vibronic features. The bands at 376 and 320 nm can be assigned to ${}^1C \leftarrow A$ and ${}^1D \leftarrow A$ transitions, respectively, in accordance with the Platt notation.²² Since the dichroic ratios over the 300–400-nm region are essentially identical ($d_0 = 1.72$ at 300 nm, 1.77 at 325 nm, 1.81 at 350 nm, 1.68 at 375 nm, and 2.09 at 400 nm; Figure 1), the polarization direction of the ${}^1D \leftarrow A$ transition is expected to be nearly parallel with that of the ${}^1C \leftarrow A$ transition. This interpretation is supported by the theoretical prediction (Table I).

The spectral resolution is insufficient to make unambiguous assignments in the UV region (<300 nm) of the spectrum at present.

Figure 3 presents the linear dichroic spectra of trial 3. The values of d_0 for this carotenoid are 5 and 2 for the main- and near-UV bands, respectively. In this case, we obtain $f = 0.57$ and $\alpha = 37^\circ$ for the *cis* band. The predicted polarizations and oscillator strengths of trial 3 (Table I) with a fully linear, *all-trans* configuration in polyethylene film are consistent with the dichroic data.

However, the mono-*cis* configuration is not inconsistent with the observed dichroic data, the predicted oscillator strengths,

Table I. The SCF-MO-CI Pariser-Parr-Pople Calculated Spectroscopic Parameters^a

Carotenoid	Transition	Energy, eV	<i>f</i>	θ_i , deg	Geometry	
Renierapurpurin-20-al (6)	$S_1 \leftarrow S_0(B)^b$	3.15	2.27	$\theta_1 = 7.1$	all-trans	
	$S_2 \leftarrow S_0(C)$	3.82	0.13	$\theta_2 = 15$		
	$S_3 \leftarrow S_0(D)$	3.99	0.86			
	$S_4 \leftarrow S_0$	4.29	0.006			
	$S_5 \leftarrow S_0$	4.59	0.04			
	$S_6 \leftarrow S_0$	4.82	0.002			
		$S_1 \leftarrow S_0$	3.22	2.19	$\theta_1 = 51$	13-cis
		$S_2 \leftarrow S_0$	3.85	0.47	$\theta_2 = 45$	
		$S_3 \leftarrow S_0$	4.12	0.68		
		$S_4 \leftarrow S_0$	4.31	0.002		
		$S_5 \leftarrow S_0$	4.63	0.03		
		$S_6 \leftarrow S_0$	4.85	0.03		
8,8'-Diapocarotene-2,20-8'-trial (3)	$S_1 \leftarrow S_0$	3.20	1.95	$\theta_1 = 35$	all-trans	
	$S_2 \leftarrow S_0$	3.84	0.02	$\theta_2 = 18.3$		
	$S_3 \leftarrow S_0$	4.07	0.34			
	$S_4 \leftarrow S_0$	4.45	0.03			
	$S_5 \leftarrow S_0$	4.66	0.06			
	$S_6 \leftarrow S_0$	4.91	0.13			
		$S_1 \leftarrow S_0$	3.30	2.03	$\theta_1 = 60$	13-cis
		$S_2 \leftarrow S_0$	3.95	0.16	$\theta_2 = 35$	
		$S_3 \leftarrow S_0$	4.19	0.30		
		$S_4 \leftarrow S_0$	4.48	0.06		
		$S_5 \leftarrow S_0$	4.77	0.02		
		$S_6 \leftarrow S_0$	4.97	0.22		
20-(3,4,5-Trimethylbenzal)-renierapurpurin (7)	$S_1 \leftarrow S_0$	3.22	2.71	$\theta_1 = 60$	all-trans	
	$S_2 \leftarrow S_0$	3.84	0.003	$\theta_2 = 35$		
	$S_3 \leftarrow S_0$	3.91	0.57			
	$S_4 \leftarrow S_0$	4.32	0.01			
	$S_5 \leftarrow S_0$	4.46	0.12			
	$S_6 \leftarrow S_0$	4.65	0.06			
		$S_1 \leftarrow S_0$	3.24	2.24	$\theta_1 = 40$	13-cis
		$S_2 \leftarrow S_0$	3.87	0.29	$\theta_2 = 62.2$	
		$S_3 \leftarrow S_0$	4.02	0.80		
		$S_4 \leftarrow S_0$	4.43	0.01		
		$S_5 \leftarrow S_0$	4.52	0.09		
		$S_6 \leftarrow S_0$	4.74	0.03		

^a *f*, oscillator strength; θ_1 and θ_2 , angle between $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ and between $S_1 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transition moments, respectively.
^b Platt notation.

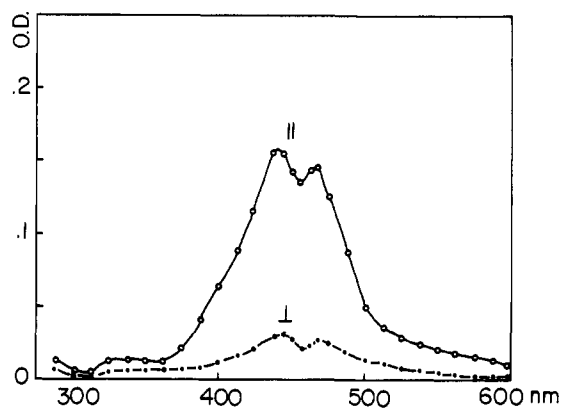


Figure 3. Linear dichroic spectra of 8,8'-diapocarotene-8,20,8'-trial (3) in polyethylene films (stretched nine times). See Figure 1 caption for notations used.

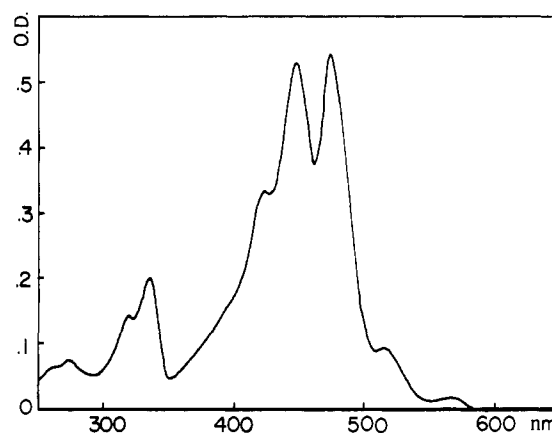


Figure 4. The absorption spectrum of 8,8'-diapocarotene-8,20,8'-trial (3) in ethanol at 77 K.

and polarization directions (Table I), since the large dichroic ratio of the main band can be obtained for the cis configuration (Scheme II) with retention of the parallel orientation of the long molecular axis to the stretching direction. The low-temperature absorption spectrum (Figure 4) seems to reflect the cis configuration of trial 3, as the relatively strong band at 335 nm is assigned as "cis" peak ($S_2 \leftarrow S_0$, Table I). The ${}^1D \leftarrow A$ transition of trial 3 is then assignable to the 275 nm band

(Figure 4), consistent with the linear dichroic deduction (vide supra) and MO data (Table I).

The ambiguity described above arises from the difficulty of dyeing the polyethylene film with trial 3, particularly in the 300–400-nm region where absorbance is low, thus making it difficult to ascertain the accuracy of the dichroic ratio in this region. It is also possible that cis \leftrightarrow trans isomerization occurred during film treatment; such a facile isomerization is

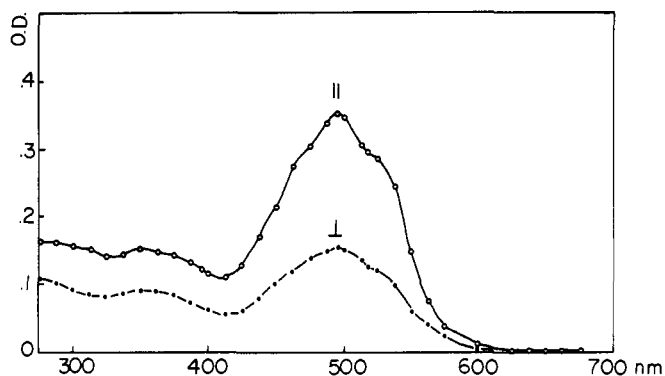


Figure 5. Linear dichroic spectra of 20-(2,3,4-trimethylbenzyl)renierapurpurin (7) in polyethylene films (stretched eight times). See Figure 1 caption for notations used.

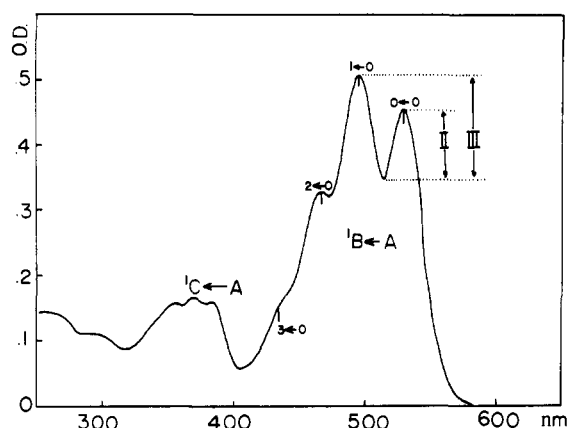


Figure 6. The absorption spectrum of 20-(2,3,4-trimethylbenzyl)renierapurpurin (7) in ethanol at 77 K. Intensity parameters given in Table III are also defined.

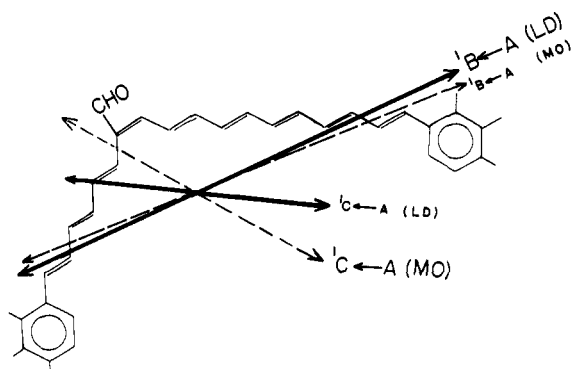


Figure 7. Polarization directions of $S_1(^1B \leftarrow)$ and $S_2(^1C \leftarrow)$ transitions in **6**. LD, deduced from the linear dichroic data in Figure 1; MO, calculated from the SCF-MO-Cl P-P-P method. The polarization direction of the $^1B \leftarrow A$ transition is assumed to be parallel to the effective molecular orientation axis with respect to the film stretching direction. This axis was determined by inspection of the molecular dimension. See text for further discussion.

feasible in view of the NMR data (not shown here), which shows a substantial isomerization of crystalline *cis*-trial **3** in solution.

The location and intensity of $n \rightarrow \pi^*$ transitions for trial **3** and other carotenals studied here are unknown at present, further adding to the complexity to the absorption bands in the near-UV and UV regions. Birge et al.²³ observed vibronic fine structure between the main and “*cis*” bands of retinals at 77 K and this resolved band has been assigned to the $n \rightarrow \pi^*$ transition. Similar fine structure has been observed for peridinin (containing a carbonyl group) at 77 K, superimposed over

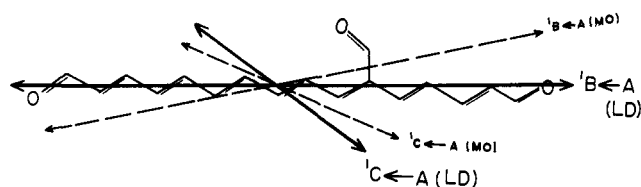


Figure 8. Polarization directions in trial **3**. See Figure 7 caption for notations used (cf. Figure 3).

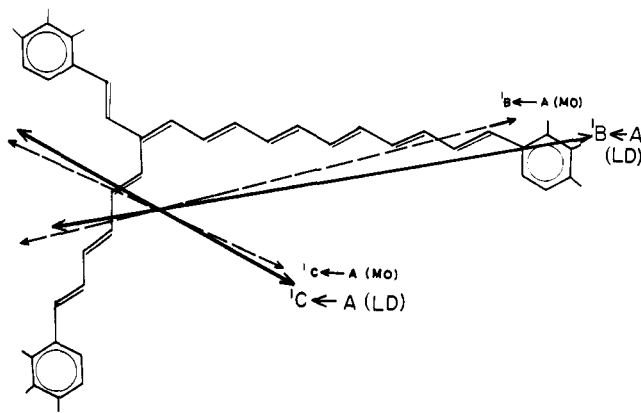


Figure 9. Polarization directions in the triaryl carotenoid **7**. See Figure 7 caption for notations used (cf. Figure 5).

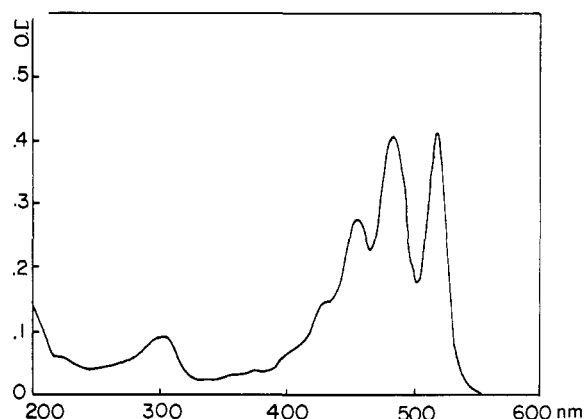


Figure 10. The absorption spectrum of renierapurpurin-20-ol (**4**) in ethanol at 77 K.


the “*cis*” band region.²⁴ Trial **3** does not show such fine structure (Figure 4), while renierapurpurin-20-al (**6**) develops fine structure over the UV (314 nm) band (Figure 2).²⁵ Thus, no definitive assignment of the $n \rightarrow \pi^*$ transitions for these carotenals can be made as an alternative to the $^1D \leftarrow A$ transition.

Figure 5 shows the linear dichroic spectra of the triaryl-carotenoid (**7**) giving $f = 0.31$ and $\alpha = 38^\circ$ for the 350-nm band. The relative polarizations and intensities of the $^1B \leftarrow A$ and $^1C \leftarrow A$ bands of this polyene are consistent with the 13-*cis*-12-*s-trans* configuration (Scheme II, Table I).

The low-temperature absorption spectrum of triaryl carotenoid **7** (Figure 6) shows relative $^1B \leftarrow A$ and $^1C \leftarrow A$ intensities similar to those of renierapurpurin-20-al (**6**) (Figure 2). However, there is no vibrational fine structure in the $^1D \leftarrow A$ band region of the former which has no styryl substituent.

It should be noted that the fraction of the aligned molecules (f) is the highest for trial **3**, as expected from a linear chain (all-*trans* or mono-*cis*) configuration. The f value of the triaryl carotenoid **7** is lower than that of renierapurpurin-20-al (**6**).

Table II. ¹H NMR Signals (δ CDCl₃) of Compounds Studied Relevant for Configuration of the 13 Double Bond^a

Compd ^b	CHO	R = CH ₂ OR'				$\Delta\delta$	
		13-Cis	% ^c	13-Trans	% ^c		
R = CHO	3 c	9.64					
	6 sol	9.58					
		9.58					
	15 sol	9.56					
R = CH ₂ OH	18 sol	9.56					
	1 sol		4.49	65	4.61	35	0.12
		c		4.43	50	4.53	50
	1A sol		4.80 ^d	40	4.86 ^d	60	0.06
		c		4.79 ^d	40	4.86 ^d	60
	4 sol		4.43	60	4.55	40	0.12
		c			4.56	100	
	13 sol		4.43	50	4.54	50	0.11
	16 sol		4.41	70	4.53	30	0.12
	R = CH ₂ OCCH ₃ 	2 c	4.91	100			
2A sol			4.93	30	5.06	70	0.13
		c			5.04	100	
5 sol		i	4.93	30	5.04	70	0.11
			4.85	50	4.98	50	0.13
14 sol			4.87	10	5.02	90	0.15
			4.86	50	4.99	50	0.13
17 sol			4.84	55	4.99	45	0.15

^a For structures compare Scheme I. ^b sol = in solution before crystallization; c = crystallized, i = I₂ isomerized. ^c Estimated from the CH₂OR' signals ($\pm 10\%$). ^d In pyridine-*d*₅.

Table III. UV-Visible Light Absorption of Compounds Studied

Compd isomer			λ_{\max}					Solvent	% ^c 1C/1B ₁₋₀	% ^c III/II	ϵ
1	cis + trans	460	434.5					Acetone		51	92 500
		449.5	423.5	401	324	312	261	Hexane	40	91	
2	13-cis	458	432.5					Acetone		52	102 000
		457	433.5		328		265.6	Methanol	23	0	
1A	cis + trans	454.5	429.8					Acetone		13	79 000
		462	436		325		267	Ether	11	55	
2A	all-trans	452	427	(410)	319	308	260	Acetone		51	
		459	437					Hexane	6	78	
3	13-cis	455.5	431.5	322	311.5	209	260	Acetone		42	115 000
		462	443.5					Hexane	38	35	
4	all-trans	498	470		298.5			Acetone		5	73 500
		501.5	472.5					Hexane	6	3	
5	all-trans ^a	468	(363)	296				Acetone	7	7	140 000
		471.5						Hexane	13		
6	13-cis	490.5	369	314	(232)			Acetone	9	0	130 000
		496.5	365					Hexane	44	0	
7A	13-cis	485	370					Acetone	42	0	79 000
		518	390.5	340				Acetone	37	0	110 000
15	13-cis ^b	529	392					Ether	59	0	
		515	392.5	333				Acetone	63	0	
18	several isomers	518	392					Hexane	46	0	92 000
		520	392	340				Acetone	52	0	
	13-cis ^b	525	392					Hexane	55	0	
								Acetone	61	0	

^a 10% 13-cis. ^b All samples except for **15** and **18** were crystalline. A solid precipitate was used for ϵ measurement of **18**.

The lower f value of the former is consistent with the fact that it possesses a 13-styryl type substituent, thus making it somewhat less vulnerable to the forced alignment in the stretched film than the latter.

Figures 7–9 compare the linear dichroic deductions and predicted polarization directions for the configurations which are assumed to be most likely (vide supra). It can be seen that the agreement between the two sets of data is surprisingly good, although absolute polarization assignments must await polarized single-crystal spectroscopic studies.

Cross-conjugated carotenals such as renierapurpurin-20-al (**6**) (Figure 2), trial **3** (Figure 4), and rhodopinal (**9**)⁸ exhibit unusual ("Franck-Condon forbidden") bands in the long wavelength edge of the main absorption band. Whether this

weak absorption represents the symmetry-forbidden transition of the ¹A_g⁻ ← A_g (or 3 ¹A₁ ← A₁) character²⁰ cannot be determined from the linear dichroic data, since the dichroic ratio of the long wavelength edge remains essentially identical with that of the main band. For example, d_0 values for renierapurpurin-20-al (**6**) (Figure 1) are 3.4 at 550 nm, 4.0 at 575 nm, 4.0 at 600 nm and 3.5 at 625 nm, while d_0 values of the C₂₀-trial **3** (Figure 3) are 5.0 at 475 nm, 4.5 at 550 nm, and 5.0 at 563 nm. The arylcarotenoid, 20-benzal- χ,χ -carotene (**7**) (Figure 6), renierapurpurin-20-ol (**4**) (Figure 10), peridin, ²⁴ *all-trans*- and 15,15'-*cis*- β -carotene¹ show the structured absorption bands without analogous long wavelength edge at 77 K, although the likely configurations (except for *all-trans*- β -carotene) are of the *cis* type which would render some

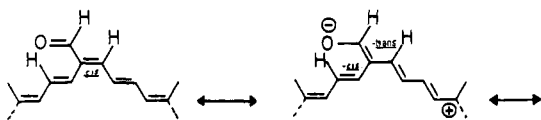
allowedness to the ${}^1A_g^- \leftarrow A_g$ transition. Thus, it is ambiguous to assign the weak band in the long wavelength edge of carbonyl carotenoids to the ${}^1A_g^-$ -like band.²⁶ Alternatively, the long wavelength edge may well be associated with the absorption of a frozen, twisted (about C=C bond) conformer.

Configurational Assignment of In-Chain Substituted Carotenoids. Several 20-substituted carotenoids with known cis/trans isomeric ratios are compiled in Scheme I. In previous work rhodopinal (**9**)^{2b,27,28} and in the present work renierapurpurin-20-al (**6**) are shown to have the 13-cis configuration (Scheme II). This evidence allows a more definite interpretation of previous findings regarding the carotenoids compiled in Scheme I.

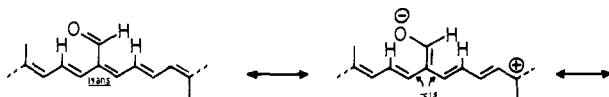
From the following compilation, the preference for the exclusive 13-cis configuration of the polyene chain appears to be dictated by the conjugated 20-aldehyde group for electronic and steric reasons. Thus, the maximum delocalization over the all-trans chain (right-half) is favored in resonance structure A, compared to structure B (Scheme III). Furthermore, the

Scheme III. Resonance Structures

A



B



A >> B

all-trans configuration is sterically hindered due to the two hydrogens as shown in structure B.

In-chain allylic 20-hydroxy and 20-acetoxy functions are also known to be responsible for a remarkable abundance of 13-cis configuration in solution. However, in these cases the all-trans isomer may also be isolated, as is apparently the case in polyethylene film (see the previous section).

Relevant 1H NMR data for the compounds studied before and after crystallization are given in Table II. Approximate ratios for 13-cis and -trans configuration in the 20-substituted alcohols and acetates are estimated from the CH_2OH and CH_2OAc signals. In $CDCl_3$ the CH_2OH singlet for all-trans is observed at δ 4.53–4.61 and for 13-cis isomers at δ 4.41–4.49 ($\Delta\delta$ 0.10–0.12 ppm). Similar shift differences (0.11–0.15 ppm) are observed for the acetates: δ 4.99–5.06 for CH_2OAc in all-trans and δ 4.84–4.93 for 13-cis.

The aldehyde proton signal of δ 9.56–9.64 with cisoid allylic coupling ($J = ca. 1.9 Hz$)²⁹ is characteristic for in-chain carotenoids such as the crystalline trial **3** (13-cis).

Renierapurpurin-20-ol (**4**) in solution is a 3:2 13-cis/13-trans mixture but crystallizes as all-trans. The corresponding acetate **5** again is a 1:1 13-cis/13-trans mixture in solution but crystallizes mainly as all-trans according to the 1H NMR data (Table II).

However, renierapurpurin-20-al (**6**) showed one aldehyde signal only (δ 9.58, d, $J \approx 1.9 Hz$), consistent with the present 13-cis findings. The cross-conjugated triaryl carotenoid **7** in

solution is a 2:1 13-cis/di-cis (?) mixture. In solution 13-cis rhodopinal (**8**) represents ca. 75% and all-trans ca. 25% of the total, whereas rhodopinal (**9**) is 13-cis.²⁷

The 1H NMR data for compounds listed in Table II are supplemented by the UV-visible light absorption data presented in Table III for the 13-cis and all-trans isomers. The ratio percent ${}^1C/{}^1B_{1\leftarrow 0}$ (see notation in Figure 6) gives the relative intensity of the highest cis peak (1C) and the band maximum ($1 \leftarrow 0$) of the ${}^1B \leftarrow A$ absorption, whereas the ratio percent III/II is a measure of spectral fine structure of the main band.²⁸ The 13-cis isomer generally has a high percent ${}^1C/{}^1B_{1\leftarrow 0}$ value and a low percent III/II value.

In conclusion, the generality of 13-cis configurations of cross-conjugated 20-als and the relatively high percentage of 13-cis of caroten-20-ols and caroten-20-acetates in solution seems well established.

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