

Empirical Relationships of the Minor Bands in the Absorption Spectra of Polyenes

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A study of published electronic absorption spectra of polyenes has led to the simple rule that all minor bands at short wave lengths correspond in location with the main band of shorter chromophores of lengths equal to integral fractions of the chromophore considered. The relative intensities of these "overtone" bands are shown to be influenced by stereochemical factors (compare Zechmeister's *cis*-peak). Some new ideas, pertaining to the distribution of extinction value on the various bands, are developed and applied in a discussion of poly-*cis* carotenoids and Karrer's sterically hindered *cis*-compounds. The spectra of retro-polyenes and vitamins A₁ and A₂ are also discussed, and an explanation of the difference between "retro" and "normal" spectra is proposed. The more general validity of the principles established is demonstrated by the spectra of diphenylpolyenes, symmetrical azines, polyazobenzenes, and polyphenyls.

It is well known that the absorption spectra of polyenes in addition to the main band (with its vibrational fine structure) show minor bands (with or without fine structure) at shorter wave lengths. The main band is explained in terms of classical theory as being due to oscillations of the π -electrons from one end of the chromophore to the other, resulting from a transition from the stable ground state to the first excited state of the total conjugated chromophore. (From a quantum mechanical viewpoint the same electronic transition is described as an electron jump from the highest occupied π -orbital, or energy level, to the lowest vacant π -orbital.) The minor bands, however, can be explained as being due either to transitions to higher excited states of the total chromophore, or to electronic transitions of independent partial or localized chromophores. Evidence is put forward here to show that bands of partial or localized oscillation are of importance only in rare cases when special structural features are present, and possibly also in the case of very short systems where the resonance is not very pronounced. The general indications are that the minor bands are to be attributed to higher order transitions of the total chromophore, and that this is always the case with aliphatic polyenes. Such bands have been called overtones^{1,2}, or fundamental

bands of higher order ³, but will here mostly be referred to specifically as the λ_2 -band, the λ_3 -band, and so on, the main band being then the λ_1 -band.

Only two of these overtones have so far been recognized as such: the λ_2 -band, (fundamental band of second order, or first overtone, which represents an electronic transition that is forbidden in the linear all-*trans* compound, but can take place in *cis*-isomers with an angular shape, and hence has been termed "*cis*-peak" by Zechmeister and Polgár ^{4,15}), and the λ_3 -band (second overtone, which is observable in the all-*trans* compound and most *cis*-isomers ^{1,6}). However, many authors have, from theoretical considerations, predicted the existence of further overtones ⁷⁻⁹. Among these only bands of odd order (λ_5 , λ_7 , etc.) represent transitions that are allowed in the essentially one-dimensional all-*trans* molecule, while bands of both odd and even order are to be expected in the spectra of two-dimensional *cis*-isomers ⁸⁻⁹.

A survey of published absorption spectra of polyenes reveals that until recently further bands which may be interpreted as higher overtones (λ_4 - and occasionally λ_5 -bands) have only been observed in the region accessible for solution spectroscopy in the spectra of a few carotenoids ^{10,11,1,6}. It is clear that by extending the length of the conjugated system, whereby the absorption bands are displaced towards longer wave lengths, more overtones should become observable. In fact the spectra of the higher homologues of carotenoids synthesized recently by Karrer and co-workers ¹²⁻¹⁴, show several short

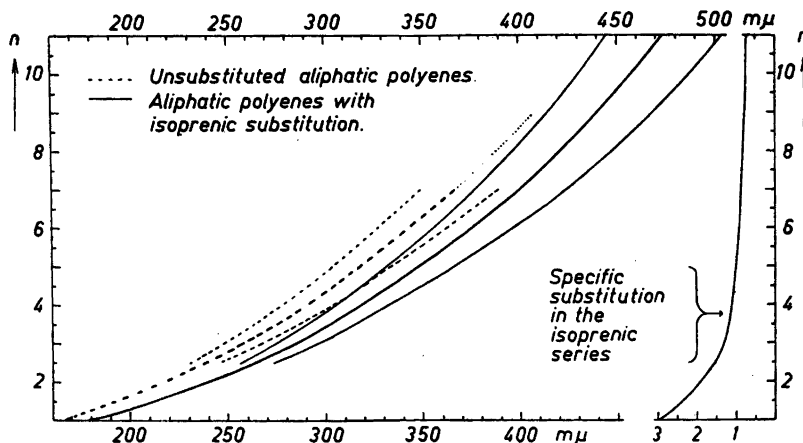


Fig. 1. Wave length positions of the three first peaks in the main absorption band of aliphatic polyenes plotted against number of conjugated double bonds.

The following data were used in plotting the curves: Unsubstituted series: Ethylene, 163, vapor ⁵⁸, butadiene, 217 in hexane ¹⁰, hexatriene 247, 256, 266 in hexane ⁵⁹, octatetraene, 278, 291, 304 in cyclohexane ⁶⁰, decapentaene, 304, 318, 334, in isooctane ⁶¹, tetradecaheptaene, 350, 368, 390 in isooctane ⁶¹.

Isoprenic series: Trimethyl-ethylene, 178, vapor ⁶², phytoene, 275, 285, 297 ⁶³, phytofluene, 331, 348, 367 ⁶⁴, ξ -carotene, 378, 400, 425 ⁶⁵, 5,6-dihydro- α -carotene, 415, 438, 469 ⁴, lycopene, 445, 473, 504 ¹, all in hexane.

The single curve to the right represents number of substituents per double bond as a function of n in the isoprenic series for use when interpolating between the two curves.

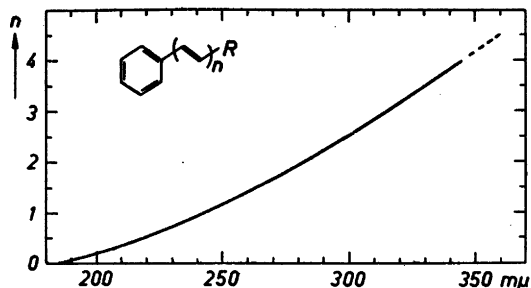


Fig. 2. Wave length position of the main absorption band of α -phenylpolyenes plotted against number of conjugated double bonds in the chain.

The following data were used in plotting the curve: Benzene, 183 in heptane³⁰, styrene, 244 in ethanol⁶⁸, 1-phenylbutadiene, 280⁶⁷, 1-phenyl-3-methyl-octatriene-7-ol, 319 in ethanol⁶⁸, 1-phenyl-3,7-dimethyl-nonatetraene-9-ol, 343 in ethanol⁶⁸.

wave length bands. In the case of dodecapreno- β -carotene with 19 conjugated double bonds, as many as seven bands can be recognized¹⁴.

With regard to the wave length position of the overtones it was observed by Zechmeister and Polgár⁴ that the difference in wave length between the first peak (o-o vibrational transition) in the main band and the *cis*-peak amounted to about 140 $m\mu$ for all carotenoids. In shorter conjugated systems this difference was much smaller.

A simple and exact relationship between the positions of the various absorption bands does not seem to have been demonstrated, although a theoretically

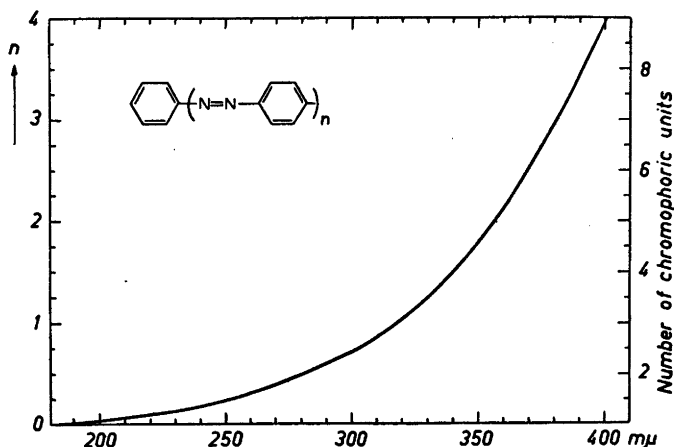


Fig. 3. Wave length position of the main absorption band of "polyazobenzenes" plotted against total number of benzene nuclei and azo groups.

The following data were used in plotting the curve: Benzene, 183 in heptane³⁰, azobenzene, 318⁶³, disazobenzene, 352-359^{65,68}, trisazobenzene, 380⁶³, tetrakisazobenzene, 400⁶³, all in ethanol.

derived formula involving two empirical parameters has been proposed by W. Kuhn⁹. However, this formula fails badly for the higher overtones (see footnotes to Table 1), and thus cannot be used to distinguish reliably between bands belonging to a given all-*trans* polyene and bands due to the presence of *cis*-isomers or to foreign impurities; neither can it be used to determine whether true partial chromophores are active in addition to the main chromophore.

It will be shown here that *if an aliphatic polyene contains n conjugated double bonds, the wave length maximum of the λ_s -band will lie very close to the wave length maximum of the main band of a corresponding polyene with n/s conjugated double bonds* (where n/s need not be an integer). Since alkyl substituents shift the absorption maximum to longer wave lengths compared with the unsubstituted chromophore, due consideration must be given to the degree of substitution. The calculation of the wave lengths (λ_s) is most easily carried out graphically (Fig. 1) by plotting λ_1 against n for two polyene series with different degree of substitution and evaluating λ_s by proper interpolation between the values found for n/s on the two curves.

A similar procedure can be adapted for α,ω -diphenyl-polyenes and symmetrical azines to estimate the position of the λ_2 -band (Fig. 2), for "polyazobenzenes" (Fig. 3), and for "polyphenyls".

The results are compared with observed bands in Tables 1, 2, 3, 4, and 5.

DETAILS OF CALCULATING PROCEDURE

In Fig. 1 the wave length maxima of the first three peaks in the main absorption band are plotted against the number of conjugated double bonds for aliphatic polyenes. Reliable data for a sufficient number of compounds was found in the literature for two series only; unsubstituted polyenes, and polyenes with isoprenic substitution (carotenoids *etc.*). In this last series only the points for polyenes with an odd number of double bonds were used in drawing the curve in order to obtain a continuous curve with a continuous variation in substitution per double bond. This specific substitution is comparatively lower in the even members, and they consequently absorb at slightly shorter wave lengths than evaluated from the curve.

As far as possible only spectra taken in petrol ether, hexane or similar solvents were included. This becomes especially important at longer wave lengths, since the shift of λ_{\max} due to change of solvent has been found to be proportional to the number of double bonds n in the conjugated chain¹⁸.

The curve representing the isoprenic series might have been extended¹⁴ to $n = 19$, but this has not been done here for several reasons. Firstly, most of the compounds reported in this region contain β -ionone rings and because of steric hindrance to coplanarity with resulting decreased resonance in the excited state would be expected to absorb at considerably lower wave lengths than a corresponding true aliphatic polyene, (the shift in λ_{\max} due to one ring closure being known to correspond to a reduction of around 2/3 of a double bond at $n = 11$). Secondly, published spectrophotometric curves are not taken up in hexane or petrol ether. Thirdly, there is much evidence to show that the curves given represent mixtures of *cis-trans*-isomers rather than the true all-*trans*-form (see below), and the shift to shorter wave lengths resulting from isomerization is also known to increase with n .

The curves obtained have been used for a graphical calculation of the data given in Table 1. In the present work only the second peak (heavy line) has been used, since in most cases this represents the peak of highest extinction and, accordingly, would be expected to represent λ_{\max} in cases where the vibrational fine structure is not discernible. A curve representing the degree of substitution per double bond on each point of the

"isoprenic" curve has been introduced into Fig. 1 to allow easy interpolation for obtaining a correction for differences in substitution.

The same procedure can be applied with satisfactory results to carotenoids containing β -ionone rings when a correction in n is made for the effect of ring closure.

Table 1 also contains in the footnotes λ_{\max} values for the same bands for lycopene* and dodecapreno- β -carotene as calculated from Kuhn's formula*

$$\lambda_s = \frac{157 \text{ m } \mu}{\sqrt{1 - 0.922 \cos \frac{\pi \cdot s}{n+1}}}$$

where n is the number of conjugated double bonds and s the band order. A comparison will show the large deviations from observed values at short wave lengths.

Only hydrocarbons with aliphatic or β -ionone-ring chromophores have been included in Table 1. When separated from the chromophore the presence of functional groups containing oxygen *etc.* in the molecule has no influence on the spectra. Examples can be found in a paper by Karrer and Würgler¹¹, but these have not been included in Table 1.

When carboxyl and carbonyl groups are in conjugation it would appear that such groups can be counted as equivalent to slightly less and slightly more than a conjugated C=C double bond, respectively. From Table 2 it can be seen that the agreement between calculated and observed values is not perfect, but fairly good when the heterogeneity of the systems and the sensitivity of λ_{\max} to change of solvents is considered.

A further discussion is given below, where the effect of more unsaturated ring structures conjugated with the chain is also discussed.

GENERAL DISCUSSION

How is it possible then to be sure that the bands observed actually represent overtones of the calculated order? No direct proof is given here**, but to date no feature has been found that does not fit in with the postulate. In the following some indications of the correctness of the correlations made will be mentioned.

Following Pauling's semi-classical treatment of the *cis*-peak phenomenon^{1,88}, in which it is assumed that the λ_1 -band represents electronic oscillations throughout the whole length of the chromophore; the λ_2 -band coupled oscillations in the two halves; the λ_3 -band oscillations in the three thirds, *etc.*; it does not seem unreasonable to expect these overtone oscillations to correspond in wave length to similar λ_1 -band oscillations in shorter chromophores of comparable length and specific substitution.

Furthermore, in all spectra of carefully purified all-*trans* isomers only bands of odd order have been observed, while spectra of established *cis*-isomers also show bands of even order⁵. Whenever bands have been observed other than those predicted from the calculations, it can be shown that an exceptional structural feature has caused a displacement of, what it seems, regular overtone bands, or more rarely has given rise to independent partial chromophores. (See below.)

In cases where it is more or less tacitly assumed that an all-*trans* form has been isolated but no proof of stereochemical homogeneity has been presented,

* In the original paper n for lycopene is set equal to $11 + 2 \cdot 1/2 = 12$. It is not clear why isolated double bonds should be considered as adding to the effective length of the chromophore. Rather, cyclization would reduce the effective length because of steric hindrance to coplanarity^{16,17}.

** Further studies, based on the quantum mechanical picture of polyenes, have led to some interesting results, the discussion of which will be postponed to a later date.

Table 1. Calculated and observed wave length maxima for overtone bands in the absorption spectra of hydrocarbon carotenoids and aliphatic polyenes.

Compound	<i>n</i>	Eff. <i>n</i>	Spec. ^a subst.	Solvent	λ_2^b (n/2) calc. obs.	λ_3 (n/3) calc. obs.	λ_4 (n/4) calc. obs.	λ_5 (n/5) calc. obs.	Ref.
Dodecapreno- β -carotene ^c	19	18d	0.63	cyclo-hexane	437 444 ^e	366 372	323 328	292 288 ^f	14
Decapreno- β -carotene	15	14d	0.67	» »	394 405 ^e	329 328	290~290	253 245	12
Decapreno- ε_1 -carotene	13	13	0.61	» »	378 (392) ^{e,g} 374	318 321	280 280	252 246	13
C ₄₃ -Homo- β -carotene	12	11d	0.67	ether	354 355	296 296			25
Lycopene ^h	11	11	0.73	hexane	355 (362) ^g 348	297 296	260 255	235 234	1,6
γ -Carotene	11	10.3	0.73	» »	345 349	288 282	253 245		1
β -Carotene	11	9.3	0.73	» »	337 339	280 272			4
7,7'-Bis-desmethyl- β -Carotene	11	9.7	0.55	—	330 330	276 270			22
δ -Carotene	10?	10	0.70	iso-octane	340 ~ 345	285 280	249~245		69
α -Carotene	10	9.3	0.70	hexane	330 331	275 267			4
5,6-Dihydro- β -carotene	10	9.3	0.70	» »	330 331	275 268			4
5,6-Dihydro- α -carotene	9	9	0.67	» »	324 (329) ^g 316	270 266			4
ε_1 -Carotene	9	9	0.67	cyclo-hexane	324 332 ^e	270 267			18
1,1'-Dihydro- β -carotene	8	8	0.75	ether	309 (312) ^g 302	258 254			70
"Dehydro-phytofluene"	7?	7	0.86	hexane	294 (297) ^g 287				71
Phytofluene	5	5	1.00	» »	256 (259) ^g 252				72
Tetradecaheptaene	7	7	0	iso-octane	275 265				61
1,12-Dimethyl-dodecahexaene	6	6	0.33	chloroform	264 ~ 265				73
Decapentaene	5	5	0	iso-octane	238 235				61
Hexatriene	3	3	0	vapor		163 175			74
Butadiene	2	2	0	» »	163 170 ⁱ				75
Cyclohexadiene ^j	2	2.5	1.00	» »	185 199 ⁱ				75

^a Because of the minor contribution from ring double bonds, cyclization is not counted as extra substitution.

^b All wave lengths given in μ .

the bands of odd order are always the major ones, while bands of even order are usually less developed. Particularly interesting examples are offered by Karrer's higher homologues of carotenoids. Probably, in most cases isomerization has taken place after dissolution of the substance. Thus the absorption curves of ϵ_1 -carotene¹⁸ in ethanol and in cyclohexane show very nearly the same extinction values in the λ_1 - and in the λ_3 -bands, but widely different values in the λ_2 -band. Dodecapreno- β -carotene¹⁴ affords an even better example. Here all bands from λ_1 to λ_7 are present, and it is evident even in the main band that the solution must have contained *cis*-isomers. The first "vibrational" peak (0—0 transition) is lower than the third peak (0—3 transition), while it is an experimental fact that in the all-*trans* form the first peak is always the higher one and decreases more rapidly upon isomerization to become sometimes even lower than the third peak. Also the degree of fine structure is diminished and would likewise be explained as a consequence of isomerization*. The relatively low melting point** and good solubility might indicate that the crystallized compound is a *cis*-isomer, but this need not be the case. According to calculations by Coulson^{19,20} the double bond character of especially the central bonds becomes very much reduced in such long systems, and consequently the ease of isomerization should increase with chain length^{1,21}. The all-*trans* crystal might well isomerize spontaneously and rapidly upon dissolution, and also during melting point determination.

In a discussion of the relative intensities of the various bands of a polyene one is limited to systems where the steric configuration of isomers has been established beyond doubt by the synthesis, *e. g.*, the synthetic carotenoids prepared by Inhoffen and co-workers²²⁻²⁶. For the all-*trans* isomer the intensity of bands of odd order has been predicted by W. Kuhn⁹ to be inversely proportional to the square of the band order; thus the λ_3 -band = $1/3^2 \times \lambda_1$,

* There is no apparent reason to believe as do Karrer and Eugster¹⁴ that the fine structure should be less pronounced for this all-*trans* form than for all-*trans*- β -carotene. All added double bonds belong to types already present in β -carotene and should not introduce new stretching frequencies or vibrational levels to effect a smearing out of the fine structure²⁸.

** 190—91° as against 192° for decapreno- β -carotene and 180° for β -carotene.

c Calculated from Kuhn's formula: $\lambda_2 = 445$, $\lambda_3 = 371$, $\lambda_4 = 311$, $\lambda_5 = 266$, $\lambda_6 = 232$, $\lambda_7 = 206$.

d In lack of comparative data ring double bonds are here tentatively assumed equivalent to 0.5 of a chain double bond.

e Because of solvent shift and proximity to the main band, the real $\lambda_{2\max}$ is expected to be at shorter wave lengths.

f Two additional bands are observed, one at 265 (calc. 267 for λ_6), and one at 240 (calc. 252, 237, and 225 for λ_7 , λ_8 , and λ_9). (See discussion in text.)

g The first vibrational peak (0—0 transition) is here higher than the second one on which the calculation is based.

h Calculated from Kuhn's formula: $\lambda_2 = 349$, $\lambda_3 = 266$, $\lambda_4 = 214$, $\lambda_5 = 180$.

i The assignment of this band as a λ_2 -band is supported by the fact that in butadiene (straight) it is very weak compared with the λ_1 -band, whereas in cyclohexadiene (bent) the λ_2 -band is strong and the λ_1 -band is rather weak.

j Included for comparison.

or 11 % of the λ_1 -band. This is equivalent to Pauling's statement^{1,27} that since the light absorption is proportional to the square of the regularly reversing electric dipole moment, the intensity of the λ_1 -band is proportional to the square of the distance between the ends of the conjugated system, hence will be lower for a bent *cis*-isomer. Similarly, the extinction of the λ_2 -band in *cis*-isomers should be proportional to the square of the distance between the middle of the conjugated system and the middle of the line connecting the ends of the conjugated system, while λ_3 is supposed by Pauling to vary roughly proportionally to λ_1 . This is demonstrated clearly in the spectra of 7,7'-bis-desmethyl- β -carotene²² and β -carotene²⁴ synthesized by Inhoffen *et al.* where the central double bond assumes a *cis*-configuration resulting from partial hydrogenation of an acetylenic bond. It is especially noteworthy that this mono-*cis*- β -carotene, as would be expected, has a higher *cis*-peak than the mono-*cis*-isomer (*neo* U) isolated by Zechmeister and Polgár and assigned *cis*-configuration around a more peripheral double bond²⁹, and is in fact higher than any other *cis*-isomer of this set. Inhoffen's C₄₂-homo- β -carotene synthesis²⁵ provides both a central di-*cis* and a mono-*cis* isomer. The mono-*cis* behaves as expected, but the di-*cis* does not. It is true that it shows no λ_2 -band or *cis*-peak which, being essentially linear, it should not, but the λ_1 -band has fallen to about 75 % instead of 93 % as calculated from a model, and the λ_3 -band has increased with about 50 % instead of decreasing slightly.

Obviously there must also be other factors than the possibility and estimated magnitude of a reversing dipole moment, connected with electronic oscillations, which determine the probability of light absorption taking place. One might imagine that the two central *cis*-bonds, because they are twisted slightly out of the plane (*cf.* Pauling²⁷), constitute a partially insulating group having a certain blocking effect for oscillations through the whole length of the chromophore, thereby causing an additional decrease in the λ_1 -band. On the other hand the λ_3 -band may increase, since in two of the three thirds of the chromophore there are still no blocking groups, and the overtone oscillation may gain in importance in conformity with the theoretically derived requirement that the total extinction, or oscillator strength (*f*-value), summed over all electronic absorption bands shall be constant and determined only by the number of double bonds or π -electrons^{9,30}.

Ferguson³¹ has depicted the *cis*-peak as due to partial oscillations on each side of a blocking *cis*-bond out to the ends of the system. This cannot be true since in a non-central mono-*cis* compound one would then expect two *cis*-peaks at different wave lengths. There is ample material⁵ to show that the *cis*-peak has very closely the same location in all types of *cis*-isomers of the same compound and hence must be regarded as an overtone band (λ_2 -band). The wave length location of all overtones seems to be determined purely as a function of the total conjugated system in the manner shown above, and in no way by the individual positions of any *cis*-bonds. However, as already pointed out, *cis*-bonds may constitute a hindrance for some of the oscillations even when they represent allowed transitions, thus making other (allowed) transitions more probable. This would especially be the case with oscillations of lowest possible order for which the positions of the *cis*-bonds coincide with the borders between any of the imagined "overtone chromophore-

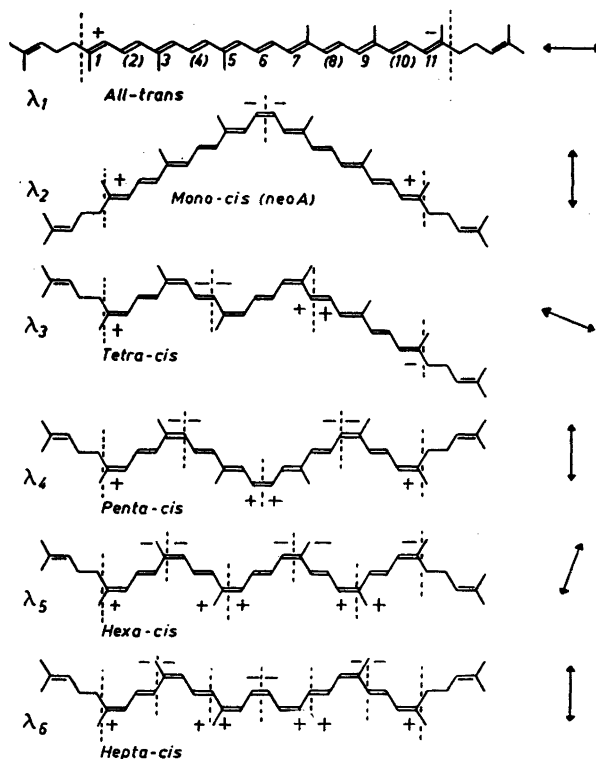


Fig. 4. Polarization diagrams for the electronic transitions responsible for the main absorption band and overtone bands of polyenes, exemplified by some possible "unhindered" isomers of the lycopene set^{1,88}.

res", thereby providing an optimal possibility for transitions without the need for the oscillating electrons to "pass through" blocking *cis*-bonds.*

It might be speculated as to how much the angle of twist at the *cis*-bonds has to be increased before such "overtone chromophores" change to become true partial chromophores taking over the total extinction of longer wave length bands. Even the quite considerable angle of twist at a sterically hindered carotenoid double bond in *cis*-configuration (cf. Pauling²⁷) does not seem to be sufficiently large to prevent π -electron interaction and to cause a splitting up of the main chromophore into partial chromophores³²⁻³⁶.

POLY-CIS CAROTENOIDS AND STERICALLY HINDERED DOUBLE BONDS

The ideas just outlined find an excellent illustration in the spectra of several poly-*cis* lycopenes isolated from plant material by Zechmeister and

* This principle can be more clearly visualized by likening the chromophore to a vibrating string fastened at both ends. Then the preferred overtone vibrations will be those for which the nodes of the associated standing wave coincide with any loosely clamped position (or *cis*-bond).

co-workers^{1,6}. If the double bonds are enumerated as in Fig. 4, then according to Pauling^{27,1,31} only 1, 3, 5, 6, 7, 9 and 11 will be reasonably free of steric hindrance in a *cis*-configuration and would be expected in a poly-*cis* compound. Fig. 4 shows that the four poly-*cis* isomers depicted are essentially linear, and according to Pauling¹ should show an intensity in the λ_1 -band around 80 % of that of the all-*trans*. The measured intensities, however, are considerably lower, in some cases even below 60 %. The geometry of the tetra-*cis* and the penta-*cis* models in Fig. 4 should allow λ_2 -bands of low intensity as seen from the polarization diagrams. None of the isolated poly-*cis* lycopenes has any distinct λ_2 -band, and the reason would be that the *cis*-bonds decrease an already low probability of transition.

Likewise, the λ_3 -band is mostly absent except in a few poly-*cis* isomers with fewer *cis* double bonds, where the intensity is still rather weak. These isomers might be of the type illustrated by the tetra-*cis* in Fig. 4, where one of the three thirds of the conjugated chain is free of blocking *cis*-bonds. The λ_4 - and λ_5 -bands, however, are mostly very well developed, and this is more pronounced the more *cis*-bonds the chain contains. It might be imagined that an isomer of the penta-*cis* type shown in Fig. 4 would give a very intense λ_4 -band and a somewhat lower λ_5 -band, while in the hexa-*cis* model shown the λ_5 -band would be more intense than the λ_4 -band. (Similarly it might be inferred from Fig. 4 that a λ_6 -band, calculated at 217 μ , would be absent or weak in poly-*cis* isomers.) It remains to be emphasized that in the all-*trans* λ_5 is weak and λ_4 absent, while in 6-mono-*cis* lycopene (*neo* A) both λ_4 and λ_5 can be observed as weak bands.

The good agreement found between the models and the spectra of these remarkable poly-*cis* lycopenes would not have been possible if both types of double bonds were able to assume a *cis*-configuration, thus providing a confirmation of the validity of the concept of steric restrictions proposed by Pauling. Certainly, from this it does not follow that isomers with *cis*-configuration at "hindered" double bonds cannot exist, even if Pauling has shown that they are very unlikely to arise in an isomerization mixture²¹. It is, for example, possible to prepare such isomers by making use of the fact that acetylenic bonds can be partially hydrogenated to yield *cis*-ethylenic bonds.

Very recently Garbers and Karrer³⁵ have in this way succeeded in preparing isomers of lycopene in which bond 4, or 4 and 8, are believed to be in *cis*-configuration (possibly also one or more "unhindered" bonds). From a similarity between the degraded main bands in the spectra of these isomers and in the spectra of the poly-*cis* lycopenes the authors find support for the suggestion previously put forward by them³³ that the natural poly-*cis* lycopenes might have *cis*-configuration at one or two "hindered" double bonds rather than at several unhindered bonds. However, they completely disregard the conspicuous fact that their "hindered" isomers show a considerable extinction in the λ_2 -band region as compared with a very low extinction in poly-*cis* lycopenes (see above). Unfortunately, their published spectra do not extend far enough into the ultraviolet to make possible a comparison of higher overtones, but by using arguments similar to those applied in the case of the poly-*cis* lycopenes, one would expect a strong λ_3 -band (*cf.* Fig. 4), while the λ_4 - and λ_5 -bands, although of no special preference, might have to take over some of the extinc-

tion of the degraded longer wave length bands. The presence of strong λ_3 -bands is actually shown in corresponding hindered *cis*-isomers of the β -carotene set³⁶. In fact these λ_3 -bands are much stronger than those of any other known *cis*-isomers of β -carotene⁴.

A further confirmation of the correctness of these assumptions is provided by the spectra of hindered and unhindered *cis*-isomers of 1,18-diphenyl-3, 7, 12, 16-tetramethyl-octadeca-nonaene prepared by Eugster, Garbers and Karrer^{37,33,34}. If the phenyl groups of this compound are assigned the chromophoric value of one double bond, the total chromophore is nearly equivalent to that of lycopene. Furthermore, the aliphatic chain carries exactly the carotenoid pattern of methyl substituents, and the spectrum of the all-*trans* form* is very similar to that of all-*trans* lycopene (see wave length locations in Table 1). Some unhindered *cis*-isomers which have been isolated³⁷ show the normal spectral changes when compared with the all-*trans* form. Among the hindered isomers prepared discussion will be confined to the two isomers with established configuration, the 5,6-mono-*cis* and the 5, 6, 13, 14-di-*cis*. The 5,6-mono-*cis*³⁴ has the chromophore "divided" into two parts approximately 1/3 and 2/3 in length, respectively. As might be predicted, the λ_1 -band (with the third and second vibrational peaks the highest) is here lower than in any unhindered isomer, the λ_2 -band is higher, the λ_3 -band is even higher than that of the all-*trans*, and both λ_4 and λ_5 are moderately developed. In the 5,6,13,14-di-*cis*³³ the chromophore is "divided" into three approximately equal parts, and the spectrum is accordingly further degraded. The λ_1 -band has decreased relative to the 5,6-mono-*cis*, the fine structure is practically absent, and it seems that the third and fourth vibrational peaks are now the highest. A λ_2 -band should not be allowed (no dipole moment) and appears only as a low bump squeezed in between the displaced λ_1 -band and the λ_3 -band, which latter, as expected, has increased relative to the 5,6-mono-*cis*. The λ_4 -band is absent (not allowed), but λ_5 has gained in importance.

Thus it seems that the spectra of these "hindered" *cis*-isomers also conform to the principles now developed, and it will be realized that it is hard to reconcile the overtone part of their spectra with the typical overtone spectra of the natural poly-*cis* lycopenes.

Unfortunately, the published spectrum of the natural poly-*cis* compound pro- γ -carotene¹ does not extend far enough into the ultraviolet to reveal more than the λ_4 -band, but approximately the same relations as found in the lycopene set should be valid also in this stereoisomeric set. However, in possible poly-*cis* isomers of higher or lower homologous carotenoids it is easily seen that if the correlations proposed above are correct, then other bands would have a favoured absorption probability similar to that of the λ_5 -band in the lycopene set, e.g., the λ_7 -band in dehydrolycopene ($n = 15$), the λ_9 -band in dodecapreno- β -carotene ($n = 19$), etc. Since the length of the corresponding "overtone chromophore" is practically identical in all these cases, i.e., the distance between successive tertiary carbon atoms, the wave length position of this "poly-*cis* peak" should be approximately constant, at about 230 μ . Simi-

* A strong λ_3 -band in cyclohexane solution indicates that isomerization has taken place upon dissolution, inasmuch as the band is rather weak in benzene solution³⁷.

larly, when the central double bond is also in *cis*-configuration, the favoured absorption of the λ_4 -band in poly-*cis* lycopenes might be taken over by λ_6 - and λ_8 -bands respectively.

This corollary may give a clue to the problem of the remarkable height of the assumed λ_7 -band in the isomer mixture of dodecapreno- β -carotene¹⁴, and also explain the discrepancy between its calculated and observed position at 252 and 240 $m\mu$ (see Table 1). It is very probable that the observed band is actually a fusion of the λ_7 -, λ_8 - and λ_9 -bands, calculated at 252, 237 and 225 $m\mu$, respectively, the λ_9 -band and possibly the λ_8 -band contributing relatively strongly to the observed extinction, since the corresponding transitions for reasons suggested above should become somewhat more probable in *cis*-isomers, although not of the intensity expected for poly-*cis* compounds. Bands beyond λ_9 should be of no special preference, either in *cis*-isomers or in the all-*trans* isomer, and accordingly the extinction drops very sharply beyond this "fused" band.

NON-ALIPHATIC AND OXYGENATED POLYENES. VITAMINS A₁ AND A₂

It has already been mentioned that although the construction of the curve in Fig. 1 is based on data for aliphatic polyenes, overtone bands can also be estimated from it with reasonable accuracy for carotenoids containing β -ionone rings and for systems with a carboxyl or carbonyl group in conjugation. However, there are types of compounds where the quantitative agreement is not quite as satisfactory, although the qualitative picture is the same.

A complication arises, for instance, with the polyene-dicarboxylic acids. It was observed early by Hausser *et al.*³⁸ that a second carboxyl group in the opposite end can be neglected when estimating the wave length positions of λ_1 -bands for polyene-carboxylic acids. This rule incidentally seems to apply to polyene carbonyl — polyene dicarbonyl pairs as well³⁹. However, when calculating overtone bands it seems that in some cases both C=O bonds have to be taken into account in order to reach good agreement with observed values (see Table 2). This peculiarity can be compared with the abnormal location of the λ_1 -band in azines as against the normal position of the λ_2 -band (see below).

A similar abnormality can be observed in polyenes with "retro"- β -ionylidene ring structures, *i.e.*, where the conjugated system has moved one step into the ring relative to the β -ionylidene compounds. Oroshnik, Karmas and Mebane³² have prepared two members of this series with the vitamin A skeleton but containing four and five conjugated double bonds ending in a "retro" structure (probably similar to anhydrovitamin A). These compounds oddly enough do not seem to be sterically hindered at the ring, and both λ_1 - and λ_2 -bands correspond completely with aliphatic polyenes (see Table 3). However, in longer systems with "retro" structures in both ends the position is more complicated. Thus in dehydro- β -carotene^{40,46} and eschscholtzanthin⁴² with 12 conjugated double bonds the λ_1 -band corresponds in location to 11 only, whereas the overtone bands must be calculated on the basis of $n = 12$ (Table 3). In bisdehydro- β -carotene⁴³ with 13 conjugated double bonds where the unsaturation most probably extends further into one of the rings,

Table 2. Calculated and observed overtone bands of polyenes conjugated with carbonyl and carboxyl groups.

Compound	n	Eff. n	Spec. subst.	Solvent	λ_2		λ_3		λ_4		Ref.
					calc.	obs.	calc.	obs.	calc.	obs.	
Capsanthin	10 + C=O	11	0.54	hexane	350	355	294	284			76
α -Apo-2-carotenal	8 + C=O	9.5	0.56	» »	327	(330) 314	274	265			11
α -Citaurin	8 + C=O	9.5	0.56	» »	327	(330) 315	274	265			11
Hexadecaheptaenal	7 + C=O	8.5	0.13	dioxane	302	305	255~260				51
Tetradecahexaenal	6 + C=O	7.5	0.14	» »	286	285					51
Dodecapentaenal	5 + C=O	6.5	0.17	» »	270	264					51
C ₂₃ -Ketone (vitamin A homologue)	6 + C=O	7	0.71	cyclo-hexane	290	269	240	237			14
Astaxanthin	11 + 2C=O	11	0.61	hexane	351	353	295	289	259	249	11
Bixindialdehyde	9 + 2C=O	12	0.36	ethanol	356	372	300	294			11
β -Carotenone	9 + 2C=O	11	0.55	hexane	350	(367) 352	295	295			11
Methylbixin	9 + 2C=O	10.5	0.36	» »	336	340	282	277	249~245		10cf.77
Bixin	9 + 2C=O	10	0.36	ethanol	330~360		277	286	244	244	11
Apo-3-norbixinal-methyl-ester	7 + 2C=O	8.5	0.33	» »	307	310					11
Crocetin-dimethyl-ester	7 + 2C=O	8.5	0.44	petrol ether	310	314	257	255			26
Corticrocin	6 + 2C=O	8	0	chloroform	291	(295) 287	245~235				78
2,7-Dimethyl-octatriene-dial	3 + 2C=O	4.5	0.40	petrol ether	233	234					79

the λ_1 -band corresponds to $n = 12$ and overtone bands to $n = 14$. In the case of anhydro-eschscholtzanthin^{42,43} with 14 conjugated double bonds (both rings dehydrogenated) the λ_1 -band corresponds to $n = 13$ and overtone bands to $n = 15-17$. Rhodoxanthin¹¹ also has a "retro" structure, but the unsaturated system is terminated by a keto-group in both rings. A similar spectral irregularity is evident here as well.

The most surprising feature is that the λ_2 -band, although present in sterically hindered *cis*-isomers of the retro-vitamin A type compounds, is of very low intensity in the dehydro- β -carotene type polyenes even in cases where all other polyene spectra simultaneously published, and obviously representing isomer mixtures (see above), exhibit very distinct λ_2 -bands. According to Zechmeister and Wallcave^{41,43} isolated *cis*-isomers have λ_2 -bands (or rather

Table 3. Calculated and observed overtone bands of polyenes with "retro-ionylidene" structure.

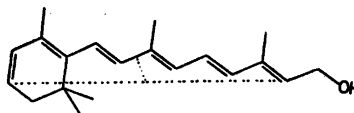
Compound	n	Spec. subst.	λ_2		λ_3		λ_4		λ_5		Ref.
			calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	
1 ring: "Tetra-retro" vitamin A methyl ether	4	1.00	230	232							32
"Penta-retro" vitamin A methyl ether	5	1.00	256	255							32
2 rings: Dehydro- β -carotene	12	0.67	367	(382) 366	308	309	271	269		225 (218)	40, 41
Eschscholtzanthin	12	0.67			308	310	271	272	244	240	42
Bisdehydro- β - carotene	13	0.62	378	(404) 386	316	333					43
Anhydro-esch- scholtzanthin	14	0.57	389	(425) 405	326	353	288	310	261	272	240 245 42, 43

bumps) as low as the all-*trans* form. It is not easy to understand why λ_2 -transitions should be forbidden in such compounds. It might be connected with the fact that the λ_1 -band for some reason (see below) retains its extinction value almost completely in *cis*-isomers of these compounds, thus leaving little over for overtone bands.

The spectrum of vitamin A₁ has been the subject of much speculation because of the abnormally short wave length position and lack of fine structure. Oroshnik *et al.*⁴⁴ have been able to show that this is not due to the allylic hydroxyl group, but rather to the β -ionylidene structure. The explanation put forward is that because of steric conflict between the *gem*-dimethyl group and a hydrogen atom of the chain, a partial chromophore is set up involving only the four double bonds of the chain³², and the resulting observed band is thought to be a fusion of this band and a band due to the complete chromophore.

Farrar *et al.*⁴⁵ similarly resort to the postulation of partial chromophores to explain the confusing (*cf.* Cama *et al.*⁴⁶) subsidiary absorption band in vitamin A₂ and analogous compounds. They suggest that this band represents the combined absorption of two partial chromophores, one consisting of the two double bonds in the ring, and the other of the side chain double bonds only. An estimation of the mean λ -value for the subsidiary band has been made for vitamin A₂ and for several homologues with the same ring systems, assuming the ring chromophore band to absorb at 270 m μ and the chain chromophore band at appropriately varying wave lengths. The justification of such a calculation is very doubtful when it is considered that to explain the band at 315 m μ in retinene₂ it has to be regarded as a combination of one band at 270 m μ and another at 360 m μ ! No evidence of band splitting can be found in any case. Furthermore, the main band of vitamin A₂ (and homologues) shows the same lack of fine structure and is located at abnormally short wave lengths, in the same way as vitamin A₁ (and corresponding homolo-

Fig. 5. Model of vitamin A_2 showing how the subsidiary band can be explained as a λ_2 -band.



gues). The explanation given by Oroshnik *et al.*³² concerning the spectrum of vitamin A_1 is accordingly also made unacceptable, as it is very difficult to understand how the chain partial chromophore band in vitamin A_2 can at the same time combine with both the main band and the subsidiary band, still leaving a minimum between them, and furthermore, why a difference of two double bonds between the partial chain chromophore and the complete chromophore in vitamin A_2 , compared with a difference of one in vitamin A_1 , should not become manifest in the shape of the main band when compared with the main band of vitamin A_1 .

It seems that a more plausible interpretation can be arrived at by simply regarding the subsidiary band in the vitamin A_2 series as a λ_2 -band (forbidden in the vitamin A_1 series). Even without assuming *cis*-configuration at any chain double bond it is easily seen from Fig. 5 that the added double bond in the ring will create a twodimensional chromophore (*cis* single bond) which would make a λ_2 -transition allowed. From Fig. 5 it will also be realized that the λ_2 -band will become relatively less important as the length of the unsaturated chain increases, in accordance with the observed fact that it appears more like an inflection in retinene₂ and similar compounds⁴⁵. It can also be inferred that in mono-*cis* isomers this band should have increased intensity. That the main band is relatively weaker in the A_2 series than in the A_1 series would be a consequence of the distribution of extinction value on two bands instead of one. Also, one half of the system is free of steric hindrance, thus increasing the relative probability of the λ_2 -transition.

A calculation of wave lengths of λ_2 -bands in the A_2 series based on the curve in Fig. 1 gives as a result values which on the average are 20 $m\mu$ too short, even when the true unreduced *n*-values are used. This can be compared with the results for bis-dehydro- β -carotene and anhydro-eschscholtzanthin, which likewise contain two double bonds in the ring, and for which calculated overtone bands are at shorter wave lengths (see Table 3).

In Table 4 the results from overtone calculations are presented for compounds both in the A_2 and A_1 series. The A_1 compounds can of course show λ_2 -bands only as a consequence of isomerization.

To sum up, it seems safe to state that the spectra of all polyenes that contain the β -ionylidene structure (vitamin A_1 , β -carotene, *etc.*) or the dehydro- β -ionylidene structure (vitamin A_2) indicate a spatial conflict between the *gem*-dimethyl group of the ring and the opposing hydrogen of the chain, resulting in a non-coplanar conjugated system. The marked features of the main band in such spectra, compared with the spectra of corresponding aliphatic systems, are: low extinction value, less or complete lack of fine structure,

Table 4. Calculated and observed overtone bands of vitamins A_1 and A_2 and related compounds (in ethanol).

Compound	n	Spec. subst.	λ_1		λ_2		Ref.
			calc.	obs.	calc.	obs.	
<i>A₁ series:</i>							
C_{20} Alcohol	5	1.00	254 ~ 250		210 ~ 208		80
C_{20} Aldehyde	6	0.67			225 ~ 245		81
C_{20} Acid	6	0.67	271 ~ 260		225	233	82
C_{23} Ketone	7	0.71	290	272	240	238	14
<i>A₂ series:</i>							
C_{17} Alcohol	5	0.80	251	269			45
C_{17} Acid	6	0.50	268	287			45
C_{18} Ketone	6	0.67	271	304			45
C_{20} Alcohol	6	0.83	275	288			45
C_{20} Aldehyde	7	0.57	289	315	240	260	45, 83
C_{20} Acid	7	0.57	289	305			45

and displacement to shorter wave lengths. In contrast, all polyenes that contain the "retro"- β -ionylidene structure (anhydrovitamin A_1 , Oroshnik's retro compounds, dehydro- β -carotene, *etc.*) or the dehydro-"retro"- β -ionylidene structure (anhydro-eschscholtzanthin, *etc.*) retain a high extinction value, sharp fine structure, normal location of the main band and a surprisingly low extinction of overtone bands (in particular the λ_2 -band). Evidently, "retro"-polyenes manage in some way to keep the whole conjugated system coplanar.

Oroshnik *et al.*³² have examined molecular models and state that these cannot show that "retro" compounds are less sterically hindered than "normal" compounds. However, the assumption that the *gem*-dimethyl group behaves as a single grouping (*cf.* Farrar *et al.*⁴⁵) is hardly valid. In fact, inspection of such models actually shows that if the ring is planar, one of the methyl groups will lie above and the other below the plane, thus leaving room between them just sufficient to accommodate the opposing hydrogen atom on carbon 8 in the chain (see Fig. 6, c and d), whereby the hydrogens of the methyl groups might have to assume fixed positions. The resistance of the methyl groups against giving up their free rotation is, of course, more than outweighed by the gain in stability upon the attainment of coplanarity of the unsaturated system. On the other hand, if the ring is not planar, one of the methyl groups will collide with the chain hydrogen (Fig. 6, a and b), making it impossible for the

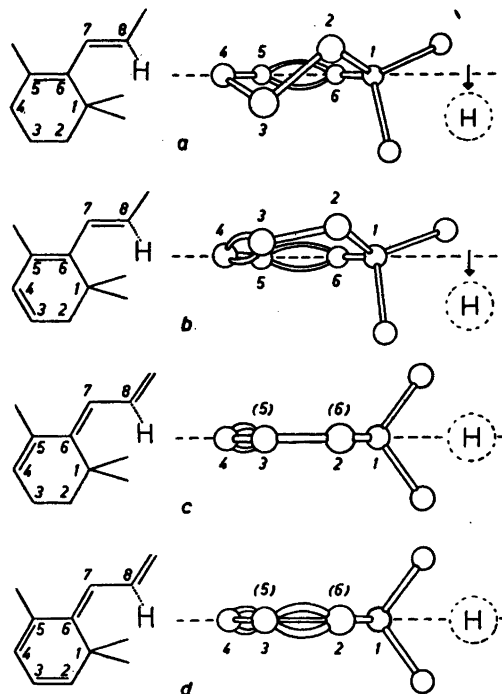


Fig. 6. Sketches of ring systems occurring in vitamins A and in carotenoids showing that "normal" rings (a and b) are skew or puckered, so that one of the 1-methyl groups will repel the opposing chain hydrogen, whereas "retro" rings (c and d) can become planar and accommodate the chain hydrogen between the two methyl groups (see text). The drawings to the right are as viewed in front of the 2—3 bond and parallel to the plane of the paper.

ring double bond (or bonds) to lie in the same plane as the double bonds of the chain.

The models also show just what should then be expected, *viz.*, that "retro" rings can easily become planar, whereas "normal" rings tend to be puckered. The drawings in Fig. 6 will demonstrate this more clearly. In the *cyclohexenyl* ring (Fig. 6a) the carbon atoms 1, 6, 5 and 4 necessarily lie in one plane, while carbons 3 and 2 will lie below and above this plane, respectively, in order to satisfy the four tetrahedral angles^{47,89}. One might at first expect the *cyclohexadienyl* ring (Fig. 6b) to be planar because of the double bond character of bond 4—5. However, such a ring would involve considerable strain, which can easily be relieved by a slight rotation about bond 4—5 in order to lift carbon 2 sufficiently relative to carbon 1 to establish both required tetrahedral angles⁴⁸. That the two double bonds are thus not wholly conjugated is also indicated by the abnormally small resonance energy found for 1,3-*cyclohexadiene*⁴⁹. In the *cyclohexenylidene* ring (Fig. 6c) nothing can be gained by a similar rotation about bond 5—6, and not much by lifting carbon 2 out of the plane; hence this ring can more easily become planar. For the *cyclohexadienylidene*

ylidene ring (Fig. 6d) no other configuration than a planar one can be envisaged*. Also, it should not be overlooked that a "retro" system would have to rotate a greater amount about the single bond 7—8 to move the hydrogen at carbon 8 away from the dimethyl group, than is required when rotation occurs about the single bond 6—7 in a "normal" system, thus making the planar structure still more favourable.

The great decrease in energy connected with the attainment of coplanarity in a conjugated system should lead one to expect "retro" compounds to be more stable than the "normal" ones. It is therefore interesting to note that Oroshnik *et al.*⁵⁰ have pointed out the great ease with which the "retro" system is formed and the fact that "the only really successful synthesis of vitamin A started with a carbinol in which "retro"-ionylidene formation was structurally impossible". Similarly, the various dehydrogenation processes of β -carotene evidently lead exclusively to "retro" configurations⁴³.

One would also expect that since the chain hydrogen atom, as proposed here, is thought to be squeezed in between the two 1-methyl groups of the ring, the coplanar system should be quite fixed in these compounds and more rigid than an aliphatic coplanar system. One consequence would then be that the "loose bolt effect" of Lewis and Calvin³ would be reduced; hence the spectra of "retro" compounds show sharper fine structure than might be expected in such heterogeneous double bond systems. The suggestion is also made that the low extinction of overtone bands even in *cis*-isomers of the "retro" carotenoids can be ascribed to this stiffening effect, since the reverse effect, *viz.*, the loosening up of the rigid molecule by introduction of steric hindrance (at *cis*-bonds, *etc.*) is known to favour a high extinction of overtone bands.

DIPHENYLPOLYENES AND SYMMETRICAL AZINES

The curve in Fig. 1 can be used to estimate overtone bands for diphenylpolyenes if each phenyl group is assigned some arbitrary chromophoric value. However, satisfactory agreement for all overtones is achieved only when the aliphatic chain is predominant, since the phenyl groups become more significant in short systems.

A more direct estimation, involving no choice of chromophoric value, of only the λ_2 -bands in the spectra of α,ω -diphenylpolyenes is possible using the same principle, *i.e.*, a comparison is made with the λ_1 -bands of compounds with chromophores corresponding to half the molecule. Thus in Fig. 2 the wave length maxima of the main band for α -phenylpolyenes have been plotted against number of conjugated double bonds in the chain. The resulting curve can then be used to estimate the wave length positions of λ_2 -bands in diphenylpolyenes. Because of limited selection of data substitutional effects have had to be neglected. Nevertheless, the values calculated from Fig. 2 and given in Table 5 show a good coincidence with observed values. Data for some isomorphous symmetrical azines have also been included assuming a C=N-bond equivalent to a C=C-bond. Although the λ_1 -band of the azines lies at abnormally short wave lengths⁵¹, the λ_2 -band is in perfect agreement.

* Both these planar rings have to be somewhat strained. A practically strainless planar structure, related to 1,4-cyclo-hexadiene⁵⁰, is obtained when one double bond is moved out of conjugation, and is possibly present in anhydrovitamin A₂ and isoanhydrovitamin A₁⁵¹:

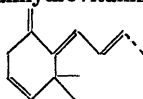


Table 5. Calculated and observed λ_2 -bands of α,ω -diphenylpolyenes and symmetrical azines.

Compound	Aliphatic double bonds (n)	$\lambda_2(n/2)$		Ref.
		calc.	obs.	
Stilbene	1	220	222 ^a	84
Diphenylbutadiene	2	244	240 ^b	85, 86
Diphenyloctatetraene	4	282	283	4
Diphenyldodecahexaene	6	315	315	28
Diphenyl-tetramethyl-octa-decanonaene	9	~360 ^c	365	37
Cinnamalazine	4	280	277	52
Phenylpentadienalazine	6	315	311	52

^a This band is also present in the *trans* form, and is possibly combined with a partial ⁵⁴.

^b Possibly a fused λ_2 and λ_3 -band.

^c By extrapolation.

Another interesting relationship, which has already been noted by Dale and Zechmeister ⁵³, is brought out by the data given in Table 6 for the aldehydes from which the azines are made. Their λ_1 -bands lie very close to the λ_2 -bands or *cis*-peaks of the corresponding azines.

POLYAZOBENZENES AND POLYPHENYLS

To test the more general validity of the ideas put forward it was of considerable interest to examine the spectra of mixed aromatic-aliphatic polyenes, where *para*-disubstituted aromatic links might be expected to maintain a linear chain, whereas *ortho*-disub-

 Table 6. Comparison of λ_2 -bands of polyenal-azines with λ_1 -bands of the parent aldehydes.

Compound	Azine		Parent aldehyde		Ref.
	Aliphatic double bonds	λ_2 obs.	Aliphatic double bonds	λ_1 obs.	
Cinnamalazine	4	277	2	279	52
Phenylpentadienalazine	6	311	3	308	52
Hexadienalazine *	6	~260	3	270	51
Octatrienalazine	8	304	4	312	51
β -C ₁₅ -Aldazine	8	310	4	311	87

* A series of α -furyl-polyenal azines all show inflections at approximately the same wave lengths as the main band of the corresponding α -furyl-polyenals.

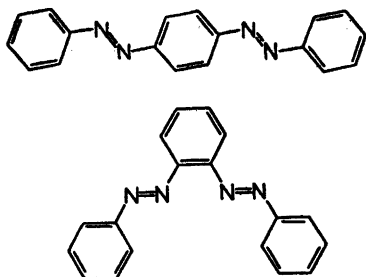


Fig. 7. Models demonstrating the linear, trans-like shape of *p*-disazobenzene and the angular, *cis*-like shape of *o*-disazobenzene.

stituted aromatic links should cause a bend of the chain similar to the bend at *cis*-bonds in aliphatic polyenes (see Fig. 7). As is well known, *meta*-disubstituted links break up the conjugation and are of no interest here.

Unfortunately, the only series for which comparable spectral data have been given for *para*- and *ortho*-compounds are the so-called "polyazobenzenes" described by Ueno⁵² and by Dahn and Castelmur⁵³. Their spectra are not too easy to analyze because the bands are compressed in a narrow region, causing much overlap. In addition to the regular bands that shift position with chain length, there are also two interfering bands with about constant location for all members. It is generally agreed^{53,54} that the weak long wave length band at around 440 $m\mu$ is due to the azo group, and the constant band at 228 $m\mu$ to some transition in the benzene ring, since the extinction of these partial bands is fairly proportional to the number of the respective groups in the molecule.

The migrating band of highest extinction is supposed to involve the total chromophore. In order to estimate wave length positions of overtone bands, one has to choose arbitrary relative chromophoric values of the azo group and the benzene ring, and to plot the wave length maxima against number of chromophoric units. The plot in Fig. 3 has been made by simply assuming them equivalent.

Considering the *para*-series first, λ_2 -bands should of course be forbidden, and no evidence of such bands can be found. λ_3 -bands are estimated at around 265 $m\mu$ for disazobenzene against 275 $m\mu$ observed for a "band shoulder"⁵⁵; at 295 $m\mu$ for trisazobenzene, which may explain the broadening of the λ_1 -band into this region⁵³; and at 318 $m\mu$ for tetrakisazobenzene against a distinct inflection observed at 308 $m\mu$ ⁵³.

In the *ortho*-series only disazobenzene has been prepared by the same authors^{52,53}, who feel very confused by the peculiar shape of the main band with a peak at 305 $m\mu$ and inflection at around 350 $m\mu$. Now the λ_1 -band of *para*-disazobenzene lies at 359 $m\mu$ (or 352 $m\mu$), and if the inflection at 350 $m\mu$ is regarded as a λ_1 -band of decreased intensity, the band at 305 $m\mu$ must be a λ_2 -band or *cis*-peak (estimated from the curve at 303 $m\mu$)^{*}.

Another series for which a more limited number of spectra are available are the "polyphenyls". The benzene nuclei are here directly attached to each other, so that *ortho*-linked chains cannot become coplanar because of steric hindrance. The main bands should therefore become very much degraded in the *ortho*-series.

Published spectra of *para*-polyphenyls include only the very near overtone region⁵⁶ where λ_2 -bands should not and do not occur. The only member of the *ortho*-series, *o*-diphenylbenzene⁵⁷, shows a rudimentary band in the region where *p*-diphenylbenzene has its intense λ_1 -band (λ_{max} at 276 $m\mu$), thus indicating severe inhibition of resonance. However, a new and strong band has grown up at 232 $m\mu$ where the *para*-compound does not absorb. The location is in the region anticipated for $n/2 = 1.5$ (between benzene, 183 $m\mu$, and diphenyl, 246 $m\mu$). It might be argued that this band is a partial band and no overtone. It would then seem natural to expect partial oscillations to involve two benzene rings as evidenced in *m*-diphenylbenzene⁵⁷, where conjugation through all three rings is not possible and the main band has exactly the same

* Recent unpublished investigations by the author on the spectra of *o*- and *p*-distyrylbenzene support these assignments.

location as in diphenyl (246 $m\mu$). That the strong band in *o*-diphenylbenzene corresponds in location neither to one nor two benzene nuclei, lends support to the belief that a true overtone is involved.

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