The Free-Electron Model, "Overtone" Bands, and Vibrational Structure in Absorption Spectra of Polyenes and Polyenynes

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An analysis of the free-electron model for polyenes has provided theoretical justification for the empirical spectral rule correlating electronic "overtone" bands with the main band of shorter polyenes of lengths equal to integral fractions of the polyene considered. It is further shown how the vibrational structure of the various bands of polyenynes can be predicted by considering the detailed π-electron density displacement pattern along the chain during the transition. The relative intensities of the short wave length bands of polyenynes, in particular of dehydro-carotenoids, indicate that these bands are never due to independent partial chromophores, but must be regarded as overtone transitions. It is also concluded that the most stable configuration around an acetylenic (or odd-cumulenic) link in a polyene chain must be the planar *trans*-configuration.

In an earlier paper [1] it was shown that the minor bands, or "overtone" bands, of polyenes with n conjugated double bonds correspond in wave length location to the main band of polyenes with n/s conjugated bonds, where s is the band order (= 1 for the main band, 2 for the first overtone, and so on). The experimental data available at that time, and, in addition, numerous recently published spectra, fully confirmed the general validity of this rule. However, no theoretical interpretation was attempted.

The success of the free-electron gas model in making spectral predictions for conjugated systems would indicate that it might be of promise when trying to put the rule on a theoretical basis. A comparison of absolute transition energies is of little interest, since Bayliss [2], and Kuhn [3], have shown that simple quantum mechanical calculations based on this crude model, with the assumption of a uniform potential well with infinitely high walls, give fair results only for the main band of short polyenes. For longer chains, and quite generally for overtone bands, the agreement is very poor. However, as Bayliss has emphasized [4], it is the number and position of the orbital nodes of π-electrons confined to a given space, and not the detailed shape of the force field that
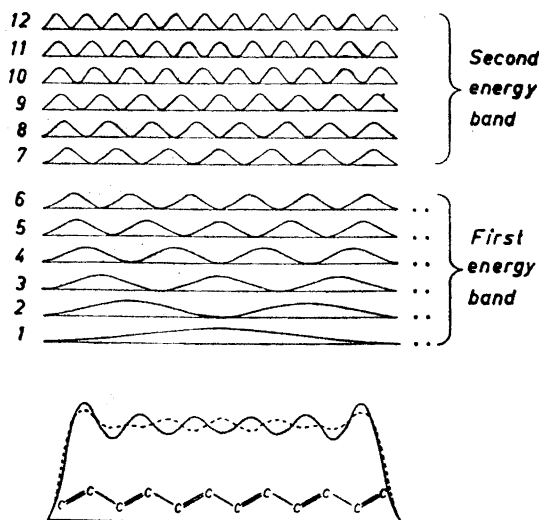
Fig. 1. Top: π-electron density $(\varphi_n{}^2)$ along the chain for free-electron orbitals (φ_n)
of the hexaene chromophore. Energy scale is arbitrary.
Bottom: Total π-electron density for the ground state (full line) and the first excited
state (dashed line). (*Cf.* Bayliss [4].)

keeps the electrons within that space, which are of prime importance in determining the character (polarization, selection rules, intensities, *etc.*) of the electronic transitions as well as the distribution of π-electron charge density, and in this respect the free-electron model, even in its crude shape, is a good approximation.

A qualitative examination of this simple model leads to results in accordance with the observed empirical rule, but it also raises an important question.

As an illustration the hexaene chromophore has been chosen to enable a direct comparison of its first two overtones with the main bands of the triene and diene chromophores. In Fig. 1 the 12 lowest free-electron molecular orbitals (corresponding to all the possible LCAO molecular orbitals) have been represented in their squared form, which is a measure of the π-electron density along the chain. The energy of each orbital is given by $E = \dfrac{h^2 n^2}{8\,m\,L^2} = k\,\dfrac{n^2}{L^2}$

where n is now the quantum number. The length L of the potential well has for simplicity been set equal to 12 times the average C—C distance since there is no more theoretical justification for other choices made by Bayliss and by Kuhn. The orbitals have been split into two groups, or energy bands, corresponding to the introduction of a Kuhn's periodic potential with minima at each formal double bond [3]. In the ground state the lowest energy band is completely filled by the 12 electrons. Summation gives the total electron density distribution given in Fig. 1 (full line) which is seen to correspond roughly
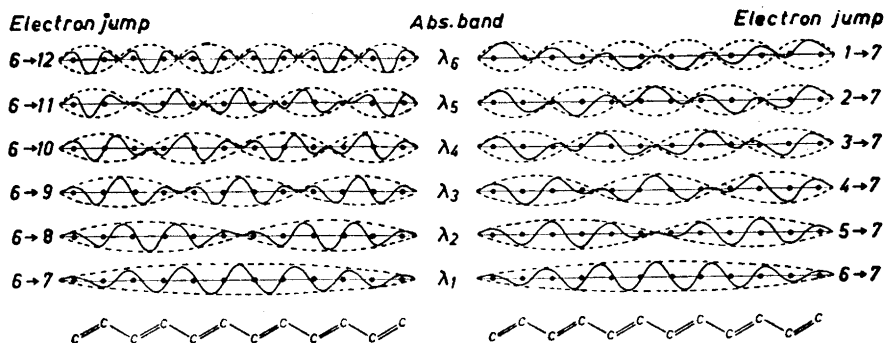
Fig. 2. Differential curves illustrating the displacement of electron density during transitions from the highest filled orbital (left), and similar transitions to the lowest vacant orbital (right). Electronic charge moves from regions where the curve is below the zero line to regions where it is above.

to the classical chemical formula [4,5]. Transfer of one electron from level 6 to level 7 ($\Delta n = s = 1$) gives the first excited state (dashed line) which is seen to correspond to a tendency towards the classical structures

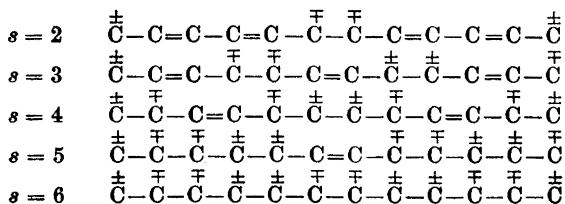$$\overset{\pm}{C}-C=C-C=C-C=C-C=C-C=C-\overset{\mp}{C}.$$
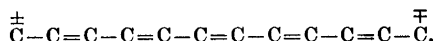
The displacement of electron density that takes place during a transition is more conveniently represented by the differential curves shown in Fig. 2. It is clearly seen that for the 6—7 transition, or in general: f—g transition according to Platt's notation [6], most of the excitation resides in the middle of the chain (*cf.* results from LCAO calculations for stilbene by Coulson and Jacobs [7]), the envelope of the displacement curve ("beat" curve) resembling the fundamental tone of a vibrating string.

OVERTONE BANDS

When the quantum number changes by more than one unit, there will, for a certain change s, be s different transitions; for example, f—h and e—g for $s = 2$; f—i, e—h and d—g for $s = 3$; and so on. Now the experimental data indicate that we have to do in each case with only one electronic transition. Thus, overtone bands show just as distinct vibrational structure as the main band of other polyenes that fall in the same wave length region. That all quasi-degenerate transitions within a group should coincide so perfectly, would only be possible if the energy levels were equidistant (with the exception of the f—g interval), and this possibility can be safely excluded since it conflicts with the convergence of the overtone bands, presumably towards an ionization limit, that is observed in all known spectra. The two remaining possibilities would then be that the transitions are either all from the highest occupied energy level or they are all to the lowest empty level. The pertinent differential curves are given in Fig. 2.

It is at once seen that the envelope of the displacement curves for overtone transitions are identical in both series and resemble the corresponding overtones of a vibrating string. However, the detailed displacement patterns differ more and more with increasing s. For transitions from the highest filled level they are in good accordance with chemical intuition; thus, the structures given below for various values of s are good representations for the corresponding excited states:

$$s = 2 \quad \overset{\pm}{C}-C=C-C=C-\overset{\mp}{C}-\overset{\mp}{C}-C=C-C=C-\overset{\pm}{C}$$

$$s = 3 \quad \overset{\pm}{C}-C=C-\overset{\mp}{C}-\overset{\mp}{C}-C=C-\overset{\pm}{C}-\overset{\pm}{C}-C=C-\overset{\mp}{C}$$

$$s = 4 \quad \overset{\pm}{C}-\overset{\mp}{C}-C=C-\overset{\mp}{C}-\overset{\pm}{C}-\overset{\pm}{C}-\overset{\mp}{C}-C=C-\overset{\mp}{C}-\overset{\pm}{C}$$

$$s = 5 \quad \overset{\pm}{C}-\overset{\mp}{C}-\overset{\mp}{C}-\overset{\pm}{C}-\overset{\pm}{C}-C=C-\overset{\mp}{C}-\overset{\pm}{C}-\overset{\pm}{C}-\overset{\mp}{C}-\overset{\mp}{C}$$

$$s = 6 \quad \overset{\pm}{C}-\overset{\mp}{C}-\overset{\mp}{C}-\overset{\pm}{C}-\overset{\pm}{C}-\overset{\mp}{C}-\overset{\mp}{C}-\overset{\pm}{C}-\overset{\pm}{C}-\overset{\mp}{C}-\overset{\mp}{C}-\overset{\pm}{C}$$

We see from the left side of Fig. 2 that the electrons are mainly displaced from regions with high density ("double bonds") to regions with low density ("single bonds"). In contrast, overtone transitions to the lowest vacant level (right side of Fig. 2) must also involve displacement of electrons from regions with low density to regions with high density.

Furthermore, only transitions from the highest filled level will give the same displacement pattern for each half of the hexaene chromophore when $s = 2$ as for the triene chromophore when $s = 1$, and for each third of the hexaene chromophore when $s = 3$ as for the diene chromophore when $s = 1$, etc., which might be expected from the empirical rule.

It has also been empirically established [1] that steric prevention of coplanarity at certain points, as with *cis*-bonds, both "hindered" and "unhindered", decreases the intensity of bands for which the excitation, as deduced from Fig. 2, is considerable in the part of the molecule where the hindrance is located, but enhances the intensity of bands for which the displacement curve envelope (Fig. 2) is zero at the hindrance. It might therefore be expected that electronic charge transfer is negligible through these zero points, or nodes of the "beat" curve. From Fig. 2 it will be seen that transitions from the highest filled level satisfy this requirement, whereas for overtone transitions to the lowest vacant level electronic charge will have to be transferred through the "nodes". The extreme case is the 1—7 transition where the charge has moved from the double bonds in the middle to the double bonds at both ends.

It is also interesting to observe that if the free-electron expression for the excitation energies [2,3] is developed in a more general form to include also overtones, the following expression is obtained for transitions from the highest filled level:

$$\Delta E_{\frac{N}{2} \to \frac{N}{2}+s} = \frac{h^2}{2\,m\,a_0^2}\left[\frac{s}{N} + \frac{s^2}{N^2}\right]$$

Here N is the number of π-electrons in a polyene with $N/2$ double bonds, and s the change in quantum number (Δn) (which is equal to the band order). The length of the chromophore has been set equal to $\frac{N}{2} \cdot a_0$, where a_0 is the length of one single bond plus one

double bond. The only variables are N and s which occur here as the ratio s/N as would be required in order to satisfy the empirical rule. In contrast, the analogous general expression for transitions to the lowest unfilled orbital

$$\Delta E_{\frac{N}{2}+1-s \to \frac{N}{2}+1} = \frac{h^2}{2\,m\,a_0{}^2}\left[\frac{s}{N} + \frac{s(2-s)}{N^2}\right]$$

also contains the variables in the ratio $(2-s)/N$ in conflict with the requirements.

If Kuhn's sine curve potential [3] is introduced we get in both cases the additional energy term $V_0(1-\frac{s}{N})$, where V_0 is the amplitude of the potential energy variation along the chain (period $= a_0$). This term contains the variables only as the ratio s/N.

It is not easy to explain theoretically why only electrons of the outermost π-electron shell should be excited by light. Neither the LCAO nor the free-electron approximation lead to any such selection rule *.

VIBRATIONAL STRUCTURE IN POLYENE SPECTRA

From Fig. 2 we have seen that the excitation responsible for the main band in polyene spectra is concentrated mainly in the middle of the chain. Now from the Franck-Condon principle one should expect that the stretching frequency of the bonds that receive the greatest change in bond order should be coupled most strongly with the electronic transition and thus contribute most to the vibrational structure of the absorption band. It is therefore not surprising that even in α,ω-diphenylpolyenes [8] it is the polyene frequencies 1 570 cm^{-1} and 1 230 cm^{-1} (in average about 1 400 cm^{-1}) that build up the structure, not only for the long chains, but also in stilbene.

As to the distribution of intensity among the vibrational peaks in the absorption bands of polyenes it is clear that as the number of conjugated double bonds increases, a one-electron jump from a bonding π-orbital to an antibonding π-orbital will have proportionately less and less effect on the binding force, so that the change in bond order decreases and the first peak (vibrationless transition) will have to gain intensity. This is in accord with observations in the unsubstituted polyene series [9] as well as in the diphenyl-polyene series [8]. However, with increasing length *cis*-isomerization will often complicate this behaviour of the main band. It may therefore be more illustrating to compare bands in the same wave length region, that is, overtones of long polyenes with main bands of short polyenes. Numerous examples can be found where the first peak is the strongest in the λ_2-band, although λ_1-bands of comparable chromophores with half the length usually have the second peak the strongest. In the λ_3-band of very long chromophores practically all the intensity may be concentrated in the first peak, as can be seen in the spectrum of lycopene [10]. That the vibrationless transition is by far the strongest in the main band of the spectra of similar ionic compounds, such as the cya-

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* A solution of this problem has been proposed to the writer by Prof. J. R. Platt, who thinks that the observed "selection rule" is only apparent and that the s quasi-degenerate transitions of a group mix to give one with strong transition moment and $s-1$ transitions with zero moment (*cf.* his recent paper on configuration interaction [42]).

nine dyes [11], can also be explained by using the free electron model, from which it is seen that very little change of bond order will occur during excitation, since bonds have now taken the positions occupied by the atoms of polyenes, and *vice versa* [4]. The same deduction has also been made by Platt in his recent paper [42].

VIBRATIONAL STRUCTURE IN POLYENYNE SPECTRA

Since the excitation for the various bands in polyene spectra is located in different parts of the chromophore, it should be possible to predict the vibrational structure of these absorption bands if some of the ethylenic bonds are exchanged with acetylenic bonds. Thus, one acetylenic bond in the middle of a polyene chain should be sufficient to give the λ_1-band acetylenic spacing ($\sim 2\,000$ cm^{-1}) if the chain is very short, as in divinylacetylene [12]. In longer chains both acetylenic and ethylenic spacings should occur and the result may be a smearing out of the structure, especially on the short wave length side of the band, since the number of possible combinations of the vibrational quanta will increase rapidly as more quanta are excited. A greater number of acetylenic bonds are therefore needed to give the band clear acetylenic spacing. However, the λ_2-band should be unaffected and show ethylenic spacing ($\sim 1\,400$ cm^{-1}).

If now the acetylenic bonds are instead at the end, the λ_1-band will remain ethylenic, but it will probably be necessary to have acetylenic bonds located in both halves in order to give clear acetylenic structure to the λ_2-band.
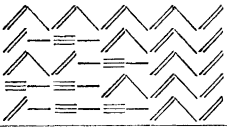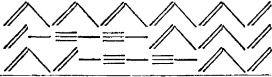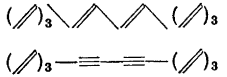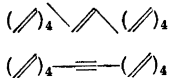
Available experimental data for polyenynes and corresponding polyenes have been compiled in Table 1. It is seen that to the extent that the vibrational structure is resolved, the observed spacings agree well with the spacings that would be expected from the geometry of the chromophores. Compounds in which the acetylenic portion constitutes more than half the chromophore have not been included, since they show the spectral anomalies typical for polyacetylenes. Unfortunately, no examples of chromophores consisting of a polyacetylene chain with a few ethylenic bonds in the middle are known.*

WAVELENGTH SHIFTS AND INTENSITY RELATIONSHIPS IN POLYENYNE SPECTRA

In Table 1 the substitution patterns on the chromophores have not been included. But when substances with equal substitution are compared, it is always found that there is an intensity reduction and a blue-shift of the λ_1-band as compared with polyenes (*cf.* Inhoffen and Bohlmann [13]). This may be connected with the stronger binding of π-electrons to sp-hybridized carbon

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* *Note added in proof:* Very recently Pohlmann and Politt (*Chem. Ber.* **90**(1957)130) have synthesized compounds with the following chromophores: ≡–≡–≡, ≡–≡–, and ≡–≡–≡–≡–≡–≡. The main bands show the vibrational spacings which can be predicted from the arguments given above. As expected, the overtone bands of the second compound have acetylenic structure, but position and intensity are apparently complicated by interaction between the two short π-electron components of the acetylenic portions and the polyene-like "hexaene" component. The overtone bands of the last compound do not show resolved structure.

Table 1. Predicted and observed vibrational structure in spectra of polyenynes (and corresponding polyenes).

Chromophore (substitution not indicated)	λ_1-band			λ_2-band			Ref.
	Wavelength of first peak in mμ	Predicted spacings	Observed spacings in cm⁻¹	Wavelength of first peak in mμ	Predicted spacings	Observed spacings in cm⁻¹	
[polyene/polyenyne chains]	310	eth.	1 500; 1 400	212w	eth.		33
	306	eth.	1 500; 1 200	230w	mixed		34
	308	mixed	1 900; 1 300	224s	mixed		35
	311	acet.	2 000; 2 100	244s	mixed	1 500; 1 000	36
[polyene/polyenyne chains]	341	eth.	1 500; 1 400	236w	eth.		33
	345	eth.	1 500; 1 500	251m	mixed	1 200	26
	341	mixed	1 700; (2 300)	228s	eth.		37
	335	eth.	1 500; (1 600)	253m	mixed	1 600	38
	336	acet.	2 000; 2 100	266s	mixed	2 100; (2 400)	38,39
[polyene/polyenyne chains]	370*	eth.	1 500; 1 400		eth.		33
	354	mixed	2 100; 2 000	277s	mixed	1 700	40
	364	acet.	2 100; 1 800	279m	mixed	2 600; (1 600)	39
$(/)_3 \backslash /\backslash (/)_3$	390	eth.	1 500; 1 400	274w	eth.	1 400; 1 300	9
$(/)_3 — ≡ — (/)_3$	392	mixed	1 900	280m	eth.	1 300	37
$(/)_3 \backslash /\backslash /\backslash (/)_3$	420	eth.	1 500, 1 400, 1 300	296w	eth.	1 200	41
$(/)_3 — ≡ — ≡ — (/)_3$	403	acet.	2 000; 1 500; 600	308m	eth.	1 400; 1 100	34,41
$(/)_4 \backslash /\backslash (/)_4$	441	eth.	1 500; 1 400; 1 300	313w	eth.	1 300	41
$(/)_4 — ≡ — (/)_4$	425	mixed	1 500	314m	eth.	1 300	41
$(/)_4 \backslash /\backslash /\backslash (/)_4$	463*	eth.	1 500; 1 400	331*w	eth.	1 400	41
$(/)_4 — ≡ — ≡ — (/)_4$	435	mixed	2 000; 1 400	342m	eth.	1 500	41

* Data in benzene corrected for solvent shift.
Intensities: w = weak, m = medium, s = strong.

atoms [14]. The effect should be particularly pronounced when the acetylenic bonds are in the middle of the chain where most of the excitation occurs. The λ_2-band may then be wholly unaffected and even undergo a red-shift since the excitation is made easier by the attraction of π-electrons by sp-carbons. Similar observations have been made on replacement of carbon by nitrogen, in a comparison of diphenylpolyenes with diphenylpolyenalazines [1]. Alternatively, these phenomena can be discussed in terms of energy changes of the orbitals

involved as Kuhn has shown for polymethine dyes in which carbon has been replaced by nitrogen [5].

Most of the published spectra of polyenynes show rather weak λ_2-bands except when the acetylenic section is not centrally located. If there were free rotation around the acetylenic bonds one should expect strong λ_2-bands in all cases, so that one is led to conclude that the planar *trans*-configuration, for which λ_2-transitions are forbidden, must be the most stable one. For the very few symmetrical polyenynes which show strong λ_2-bands, the explanation may be that some of the double bonds have a *cis*-configuration or that geometrical isomerism occurs around the acetylene system, so that there can exist also a planar "*cis*-isomer", if both ethylenic π-electron systems remain conjugated with the same component of the acetylenic π-electron system, and a non-planar isomer if they do not conjugate with the same component. According to calculations by Dunitz and Orgel [15] energy differences between such isomers would be small and are further decreased with increasing length of the acetylenic system.

Another effect, which has been observed for *cis*-polyenes, is also encountered in polyenynes. Like *cis*-bonds, acetylenic and cumulenic bonds apparently have a blocking effect for transitions for which there will be excitation in these bonds, but enhance the intensity of transitions for which the bonds are in regions where no excitation occurs ("nodes" of the "beat curve"). Thus, some bisdehydro-lycopenes [16], in which the acetylenic or cumulenic hindrances have divided the chromophore into three roughly equal sections, show degraded λ_1-bands and only weak λ_2-bands, since the chain is essentially straight, but the λ_3-bands at about 300 mμ, the same location as λ_3-bands in the corresponding hindered di-*cis*-lycopenes, have become exceptionally intense, since they have to take over the intensity of the hindered transitions. Even more illustrative material is afforded by the closely related lycopene analogues bis-dehydro-diphenyl-tetramethyl-octadecanonaenes (Fig. 3) synthesized by Karrer and coworkers [17]. It is evident from the spectra that the cumulene system $\diagup$C=C=C=C$\diagdown$ represents a more severe hindrance in a polyene chain than the —C≡C— system. Thus, the dicumulene has a much more degraded λ_1-band and a correspondingly stronger λ_3-band than the diacetylene. The acetylene-cumulene has an intermediate λ_1-band, but the λ_3-band is lower, since because of the unsymmetry (Fig. 3) the λ_2-band (at 360 mμ) and the λ_4-band (at 265 mμ) become allowed and take over much of the intensity. The λ_5-band (at 240 mμ) is also quite distinct in these compounds and its intensity variation can likewise be predicted.

The corresponding unsymmetric monocumulene and monoacetylene have also been obtained [18], and their spectra can be interpreted by similar considerations. The λ_2-bands are here relatively weak since the chains are approximately linear. It is then very interesting to observe that upon *cis*-isomerization of the ethylenic bonds, the λ_2-, λ_4-, and λ_5-bands increase in intensity, while the λ_1- and λ_3-bands decrease correspondingly.

An analogous diacetylenic bisdehydro-methylbixin has been prepared [19]. It shows no λ_2-band but a very strong λ_3-band.
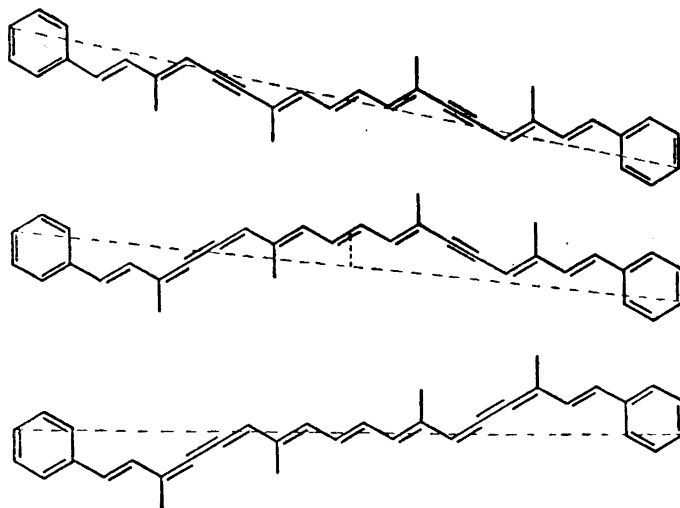
Fig. 3. Skeleton models of bisdehydro-diphenyl-tetramethyl-octadecanonaenes. **Planar** *trans*-configuration around the linear C_4-sections has to be assumed to account for the absorption spectra. Top, diacetylene; middle, acetylene-cumulene; and bottom, dicumulene.

That the spectra of the numerous dehydro-carotenoids with one (or two) centrally located acetylenic bonds prepared by Inhoffen and coworkers [13,20-25] show no corresponding intense band in the λ_2-band region (forbidden by symmetry), and only moderate λ_3-bands, is a very strong support for the idea that in polyenynes, as well as in polyenes, the minor bands are always to be regarded as overtones and never as due to independent partial chromophores as has been suggested by Oroshnik and Mebane [26] for these polyenynes, and earlier by Heilbron *et al.*[27] for polyenynes containing the diacetylene grouping. The present interpretation implies that the planar *trans*-configuration is the most stable one around an acetylenic (or odd-cumulenic) link. The same configuration has been established earlier for a few compounds in the crystalline state by X-ray diffraction [28-32], but these results have not, of course, allowed any conclusion to be drawn as to the configuration of free molecules, since packing effects may come into play in the crystal lattice.

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