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THE DISPERSIVE INTERACTION OF NON-POLAR SOLUTES WITH NON-POLAR SOLVENTS: SOLVENT EFFECTS ON ELECTRONIC SPECTRA OF CAROTENOIDS

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Abstract—From the known model for the dispersive interaction of a non-polar solute with a non-polar solvent the following predictions can be derived for the behaviour of the electronic spectrum of a polyene dissolved in binary mixed solvents: (a) With increasing concentration of the more strongly interacting solvent component the $^1A \rightarrow {}^1B^0$ transition is shifted toward longer wavelengths. (b) This bathochromic shift is accompanied by a *decrease* of the oscillator strength f_M of the $^1A \rightarrow {}^1B^0$ transition. (c) Both $\Delta\tilde{\nu}$ and the relative oscillator strength f'_M/f_M are linear functions of the concentration of the more strongly interacting solvent component expressed in volume per cent. (d) Both $\Delta\tilde{\nu}$ and f'_M/f_M are in a first approximation independent of the number of conjugated double bonds of the polyene. The same predictions can be derived from a theoretical model due to *Liptay* which includes second order effects. These predictions have been verified using as model systems solutions of carotenoids (with 5 to 15 conjugated double bonds) in mixtures of hexane/carbon disulfide or cyclohexane/carbon disulfide.

THE subject of solvent effects on molecular electronic spectra is one of central importance in electronic spectroscopy, from both a theoretical and a practical point of view. The underlying theory has been repeatedly reviewed[1] and a critical discussion of its present state has been given by Liptay.[2, 3] Almost all experimental observations available to date refer to polar solutes (e.g. molecules substituted with electron acceptor and/or electron donator groups) dissolved in polar solvents, as it is only under these conditions that large and readily observable effects (e.g. solvatochromic effects) occur.[4] From a theoretical point of view, such effects are essentially the result of first order perturbations and can be linked to the charge distribution of the solute molecule in its electronic ground and excited states (i.e. Ψ_G and Ψ_I).

The uneven charge distribution $|\Psi_G|^2$ of the solute molecule creates a reaction field by orienting the polar solvent molecules surrounding it. This field, which is frozen in the solvent during the Franck-Condon transition $\Psi_G \rightarrow \Psi_I$ will then interfere with the new charge distribution $|\Psi_I|^2$.[5]

The effect of non polar solvents on the electronic spectrum of molecules which exhibit zero dipole moment both in Ψ_G and in Ψ_I or on systems where excitation from Ψ_G to Ψ_I is not even accompanied by a charge redistribution—such as in alternant π-electron systems[6]—have received little attention from the experimental side.[7] There exists by now a comprehensive theory of such solvent effects,[8] from which specific predictions have been derived which still await experimental verification.

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This is one of the occasions, still rare at the moment, where the results of theoretical organic chemistry precede—and indeed suggest—the work of the experimentalist.

In this paper we shall first review briefly the relevant theoretical aspects of dispersive interaction between non-polar solvents and non-polar solutes and we extend the results in a crudely simplified manner to mixed solvents. We shall then derive a series of predictions which will subsequently be verified experimentally under conditions suggested by the theoretical treatment.

General theory

We now review in a very much simplified manner those parts of the theory of dispersive interaction which are relevant to this paper. For a more critical derivation the reader is referred to the review papers quoted above, especially those of Liptay.[2]

The solute molecules M with which we are going to be concerned are carotenoids, i.e. long chain polyenes which deviate considerably from the spherical molecules or "point"-molecules usually assumed in theoretical derivations. We shall distinguish between those solvent molecules L which are either:

(a) inside a solvation shell of volume V and in *van der Waals* contact with M; or
(b) at a distance larger than R from the centre of M, such that from their point of view M may be considered as a "point"-molecule; or
(c) in an intermediate range between the boundary of V and the sphere of radius R (cf. Fig. 1).

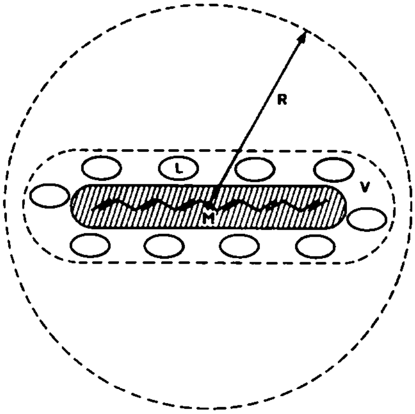


Fig. 1 Solute molecule M and solvation shell (schematic representation).

From a purely heuristic point of view, which in the final analysis may well prove to be an unrealistic approximation (cf. acknowledgement), we postulate that only the interaction of M with the r molecules L_j ($j = 1, 2, \ldots r$) inside V will contribute to those changes in solvent effects in which we are interested. Therefore, we shall concern ourselves primarily with those solvent molecules which occupy positions inside V. Also, for the sake of an argument we restrict the number of electronic states of M and of the molecules L_j to two each: namely to the ground state Ψ_G of energy ε_G and the electronically excited state Ψ_I of energy ε_I for M and to the ground state Φ_{jG} of energy E_G and the electronically excited state Φ_{jI} of energy E_I for L_j.

Ψ_G and Ψ_I are defined as

$$\Psi_G = \|1\bar{1}2\bar{2}\ldots m\bar{m}\| \tag{1}$$

$$\Psi_I = (1/\sqrt{2})\ \{\|1\bar{1}2\bar{2}\ldots m\,\overline{m+1}\| + \|1\bar{1}2\bar{2}\ldots m+1\,\bar{m}\|\} \tag{2}$$

m being the quantum number of the topmost orbital ψ_m occupied in the ground state. The other symbols have their usual meaning.[9] If M is a carotenoid then $\varepsilon_I - \varepsilon_G$ will refer to a $\pi \rightarrow \pi^*$ excitation and in a zero differential overlap approximation there will be no change in the charge order q_μ going from Ψ_G to Ψ_I. This will eliminate all first order interactions with charges and/or local dipoles of the solvent molecules L_j and thus prevent first order effects due to the reaction field as discussed above.

The ground and electronic excited states of a solvent molecule L_j are defined in analogy to (1) and (2), with the added simplifying restriction that only two molecular orbitals ϕ_{j1} and ϕ_{j2} are assigned to each L_j:

$$\Phi_{jG} = \|1_j\bar{1}_j\| \tag{3}$$

$$\Phi_{jI} = (1/\sqrt{2})\ \{\|1_j\bar{2}_j\| + \|2_j\bar{1}_j\|\} \tag{4}$$

The total energy of the non interacting aggregate is therefore $\varepsilon_G + rE_G$ when all molecules are in their respective groundstates and $\varepsilon_I + \mathrm{r}E_G$ or $\varepsilon_G + (r-1)E_G + E_I$ when either M or one of the L_j has been electronically excited.

The interaction of M with L_j will be described by a perturbation hamiltonian which is of the coulombic type, i.e. a sum of terms of the form e^2/r_{st} where r_{st} is the distance of electron s in M to electron t in L_j. As shown for instance by Longuet-Higgins and Murrell,[10] the matrix element of interaction can be expressed in terms of the one-electron molecular orbitals ψ_m, ψ_{m+1}, ϕ_{j1} and ϕ_{j2} as follows:

$$x_j = 2\langle\psi_m^{(1)}\phi_{j1}^{(2)}|G|\psi_{m+1}^{(1)}\phi_{j2}^{(2)}\rangle \tag{5}$$

This is twice the coulombic interaction of the one-electron transition densities $\psi_m \cdot \psi_{m+1}$ of M and $\phi_{j1} \cdot \phi_{j2}$ of L_j.

For a qualitative discussion it is sometimes useful to think of x_j as the dipole–dipole interaction of the transition moments $\vec{\mu_M}$ and $\vec{\mu_j}$ associated with the excitations $\Psi_G \rightarrow \Psi_I$ and $\Phi_{jG} \rightarrow \Phi_{jI}$ respectively. Defining $\mu_M = |\vec{\mu_M}|$ and $\mu_L = |\vec{\mu_j}|$ we obtain, using a point-dipole approximation:

$$x_j \approx \frac{\mu_M \mu_L}{R_j^3} F \tag{6}$$

In (6) R_j is the distance of the two point-dipole centers and F a function which depends on the relative orientation of $\vec{\mu_M}$ and $\vec{\mu_j}$.

The effect of the solvent molecules L_j on the transition energy $\Delta\varepsilon$ of M is given by second order perturbation theory as

$$\Delta\varepsilon' = \Delta\varepsilon + \delta\varepsilon = \Delta\varepsilon + (\Delta\varepsilon - \Delta E)^{-1} \sum_{j=1}^{r} x_j^2. \tag{7}$$

As $\Delta E > \Delta\varepsilon$, we find that $\delta\varepsilon$ is *negative* and $\Delta\varepsilon' < \Delta\varepsilon$. This corresponds to a *bathochromic* shift of the transition of the solute molecule M.

This shift is associated with a change in the transition moment from $\vec{\mu}_M$ to $\vec{\mu}'_M$ which can be obtained directly according to the expression

$$\begin{aligned} \vec{\mu}'_M &= \vec{\mu}_M + \delta\vec{\mu}_M \\ &= \vec{\mu}_M + (\Delta\varepsilon - \Delta E)^{-1} \sum_{j=1}^{r} x_j \vec{\mu}_j \end{aligned} \tag{8}$$

The corresponding influence on the absorption intensity as measured by the change in the oscillator strength from f to f' is calculated as

$$f'/f = (\mu'_M/\mu_M)^2 \tag{9}$$

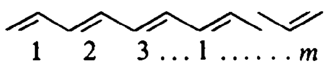
Note that in formulae (5) to (9) we have assumed a fixed position and orientation of the solvent molecule L_j with respect to the solute molecule M and that the approximation (6) is only applicable under rather stringent conditions, which are not valid if L_j is inside the solvation shell V.

To obtain an estimate of the observable changes in band position and intensity we have to average over all positions and all orientations which the solvent molecules L_j can assume relative to M. We shall first discuss *first order effects*.

It has been shown by Liptay[2] that for a spherically symmetrical model, i.e. a spherical solute molecule M surrounded by a succession of spherical shells of solvent molecules L_j, the averaging process yields a finite, negative value for $\delta\varepsilon$ (formula (7)) but a *zero* contribution $\delta\vec{\mu}_M$ to the transition moment $\vec{\mu}_M$ (formula (8)), if *only first order* effects are taken into account. Furthermore, the contribution to $\delta\varepsilon$ of the successive shells dies out quickly with increasing radius of the shell (approximately as r^{-4}). Hence, as far as our problem is concerned, all those molecules L, which are outside the sphere of radius R (cf. Fig. 1) may be neglected. (See however the remark below, concerning *second* order effects.)

In the polyenic molecules M under discussion in this paper, the shell of solvent molecules L_j which are in *van der Waals* contact with M is far from spherical. As a consequence we should obtain first order effects both for $\delta\varepsilon$ and for $\delta\vec{\mu}_M$.

Consider a polyene M having m double bonds in the all-*trans* configuration and all of its single bonds in *s-trans*-conformation



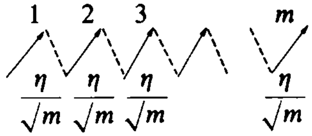
One could use Hückel molecular orbitals ψ_m and ψ_{m+1} of the polyene π-system to define the transition density $\psi_m\psi_{m+1}$ and thus the transition moment $\vec{\mu}_M$ of M which, according to (5), will in turn yield the interaction term x_j. However, it is well known that the Hückel orbitals exaggerate electron delocalization[12] and it is for this reason that we are going to redefine Ψ_I of the polyene in terms of Simpson's independent system treatment.[13] In this procedure one assigns a locally excited state λ_l to each of the m double bonds of M.[9, 13] The locally excited states interact by an energy delocalization mechanism and we shall assume that this is only operative between linked double bonds l and $l + 1$ or l and $l - 1$ respectively. For the lowest electronically excited state of a polyene of m double bonds, the result of such a treatment is

$$\Psi_I = \sqrt{\left(\frac{2}{m+1}\right)} \sum_{l=1}^{m} \left(\sin \frac{\pi l}{m+1}\right) \lambda_l ; \quad \Delta\varepsilon = \Delta\varepsilon_0 + 2\gamma \cos \frac{\pi}{m+1} \tag{9}$$

Here $\Delta\varepsilon_0$ is the transition energy for an isolated double bond and γ can be thought of as the coulombic interaction of the transition moments $\vec{\eta}_l$ and $\vec{\eta}_{l+1}$ or $\vec{\eta}_l$ and $\vec{\eta}_{l-1}$ of two consecutive, linked double bonds. It is a negative quantity. In view of the uncertainties which will enter our argument when we consider the interaction of M with the solvent we may without loss of significance replace (9) for large values of m by the approximation

$$\Psi_I \approx \sqrt{\left(\frac{1}{m}\right)} \sum_{l=1}^{m} \lambda_l \tag{10}$$

This gives equal weight to all locally excited states λ_l, rather than accentuating those towards the middle of the chain. The transition density corresponding to the transition from Ψ_G to Ψ_I can then be visualized as the alignment of m transition moments, each one of the size $|\vec{\eta}_l|/\sqrt{m} = \eta/\sqrt{m}$ where η, the absolute value of the transition moments $\vec{\eta}_l$, is the same for all double bonds.



The energy which approximates $\Delta\varepsilon$ is obtained from (10) as

$$\Delta\varepsilon \approx \Delta\varepsilon_0 + 2\gamma \left(1 - \frac{1}{m}\right) \tag{11}$$

Finally the approximate transition moment $\vec{\mu}_M$ for an all-*trans* configuration in which all the individual moments $\vec{\eta}_l$ of the bonds are parallel is

$$\vec{\mu}_M \approx \frac{1}{\sqrt{m}} \sum_{l=1}^{m} \vec{\eta}_l = \sqrt{m} \quad \vec{\eta} \tag{12}$$

From (12) one predicts that the oscillator strength f_M is essentially a linear function of the number of double bonds, a conclusion which is well borne out by the experimental observation[14–16]:

$$f_M \propto \mu_M^2 = m\eta^2 \tag{13}$$

Let us now surround the polyene chain with solvent molecules L_j which do interact according to the model discussed above. The maximal number r of solvent molecules in the solvation shell of volume V (cf. Fig. 1) will be proportional to m, the number of double bonds in the polyene M, i.e. $r = Am$, where A is a proportionality factor.

Space filling models suggest that the factor A is of the order of 1 to 2 (e.g. for carbon sulfide as a solvent) depending on the packing arrangement in the volume V. We are now making the assumption that a given solvent molecule L_j interacts mainly with the partial transition moments $\eta/\sqrt{m}$ of the π-bonds in its immediate vicinity. This will yield according to (6) to an expression of the type

$$x_j \approx \frac{B}{\sqrt{m}} \mu_L \eta \tag{14}$$

The constant B is obtained by averaging over all relative orientations of the solvent molecule L_j. From (7) follows that

$$\delta\varepsilon \approx (\Delta\varepsilon - \Delta E)^{-1} AB^2 \mu_L^2 \eta^2 \tag{15}$$

In contrast to the case of a spherical solute molecule M surrounded by spherically symmetrical shells of solvent molecules L, the first order effect on $\vec{\mu}'_M$ will no longer vanish and an expression of the following type is obtained for $\vec{\mu}'_M$:

$$\vec{\mu}'_M \approx \rightleftharpoons m(\vec{\eta} + (\Delta\varepsilon - \Delta E)^{-1} BA\mu_L \eta \vec{\mu}_L) \tag{16}$$

or for the ratio of the oscillator strengths f'_M and f_M

$$f'_M/f_M \approx \frac{|\vec{\eta} + (\Delta\varepsilon - \Delta\varepsilon)^{-1} BA\mu_L \eta \vec{\mu}_L|^2}{\eta^2} \tag{17}$$

It should be realised that the second term in the denominator of (17) is small compared to $\vec{\eta}$. Therefore one finds on expansion that the ratio f'_M/f_M of the oscillator strengths is essentially linear in A

$$f'_M/f_M \approx 1 - A\,.\,\text{constant} \tag{18}$$

The minus sign stems from the fact that $\Delta\varepsilon < \Delta E$.

All the above formulae refer to changes in the electronic spectrum of a polyene molecule M which are due to the dispersive interaction with a solvent and which are defined relative to the spectrum of M in the gas phase. However, they will also be valid for such changes as occur when a weakly interacting solvent is replaced by one exhibiting a stronger coupling. The only difference will be one of size: The observable effects should now be smaller, being only the difference in dispersive interaction from one solvent to another. With this in mind, the most important predictions to be derived from (15) and (18) are the following:

(1) For large polyenes we expect that the replacement of a weak interacting solvent by one which gives rise to greater dispersive coupling with the double bonds of the polyene will yield a *bathochromic shift* $\delta\varepsilon$, *the size of which is largely independent of the length of the polyene*, e.g. of the number m of double bonds.

(2) The bathochromic shift is accompanied by a *decrease* of the oscillator strength f_M. *The relative decrease* f'_M/f_M *is again independent of* m, and should therefore be the same for all polyenes.

Further predictions can now be made concerning the dependence of the effects on compositions, if mixed solvents are used. Consider a binary mixture of solvent molecules L_j and K_i, where the latter shall exhibit greater dispersive coupling with the solute molecule M than the former. This may be due to one or a number of causes: $\mu_K > \mu_L$, $A_K > A_L$, $|\Delta\varepsilon - \Delta E_K| < |\Delta\varepsilon - \Delta E_L|$ etc.

The changes $\Delta\varepsilon$ and the ratio f'_M/f_M—which have to be taken relative to the values $\Delta\varepsilon$ and f_M observed when M is dissolved in pure L—depend on the number of molecules K_i in the solvation shell V. Let us assume that the volume fractions of L and K in the mixture are v_L and v_K respectively, then all we have to do in a crude, first approximation is to replace A in formulae (15) to (18) by

$$A = av_K \tag{20}$$

It is immediately apparent that both $\delta\varepsilon$ (formula (15)) and f'_M/f_M (formulae (17) and (18)) become linear functions of v_K. However, this will be true only if there is no preferential solvation of M by solvent molecules of type K relative to the solvation by L molecules. In other words the volume fraction v_K inside the solvation shell V must be the same as in the bulk solvent.

In addition to the predictions 1 and 2 we expect the following dependence on solvent composition if a binary mixed solvent is used where v_K is the volume fraction of the component K which gives rise to stronger dispersive interaction with the solute molecule M.

(3) The *bathochromic shift* $\delta\varepsilon$ observed when the solvent L is replaced by the solvent K *is a linear function of* v_K.

(4) *The decrease in oscillator strength* f_M observed when the solvent L is replaced by the solvent K *is a linear function of* v_K.

The above treatment relies on the assumption that the major contribution comes from those solvent molecules which are in *van der Waals* contact with M. The solvent molecules in the intermediate range, i.e. outside of V but inside the sphere of radius R (cf. figure 1) will yield small negative contribution to $\delta\varepsilon$ and presumably small if not negligible contributions to the decrease of $\tilde{\mu}_M$.

It has been pointed out by Liptay[2, 17] that the second order effects, which have been neglected in our discussion, will also yield the above predictions (1. to 4.) for the changes induced in the electronic spectra as a function of solvent or of mixed solvent composition. The bathochromic shift can be written as a function of the refractive index n of the solvent or solvent mixture:

$$\delta\varepsilon \propto -\frac{n^2 - 1}{2n_2 + 1} \tag{21}$$

This relationship has been verified previously by Le Rosen and Reid,[18] who have investigated the spectroscopic behaviour of lycopene in a series of seventeen solvents. Also, the decrease in intensity which accompanies the bathochromic displacement of the absorption bands in the electronic spectra of non-polar solutes in non-polar solvents is again predicted by Liptay to be a linear, decreasing function of $(n^2 - 1)/(2n^2 + 1)$ if only second order effects are operative.[17] (So far this prediction had not been verified experimentally). The model which underlies this treatment assumes spherical symmetry both for M and the surrounding solvent shells.

It is difficult to decide at this stage whether one or the other of the two mechanisms (i.e. first or second order) dominates the situation in the case of long chain polyenes, or whether both contribute equally towards the observed effects. Experimental and theoretical studies are under way to allow a decision.

It is obvious that large solvent effects on the electronic spectra of a non-polar solute dissolved in a given non-polar solvent will be observed only in cases where the following conditions are fulfilled: (1) The transition moments of the solute molecule M and the solvent molecule L_j must be large, in particular that of M. (2) Other things being equal, the number r of solvent molecules in the solvation shell V must be large.

Among the readily available hydrocarbons with alternant π-electron systems—and only to these can the theory developed in the preceding paragraphs be validly applied—we find that only polyenes satisfy the conditions (1) and (2) in an optimal way. The long-wave absorption band of these compounds shows an extinction coefficient $\varepsilon \approx 10^5$ if their number of double bonds exceeds 7, that is higher by a factor of ten than for example the L_a-band of acenes[14] with the same number of π-centres. Furthermore, their linear extension yields a considerably larger solvation volume V than their more compactly built aromatic counterparts. Finally the well defined first absorption band of the polyenes, assigned by Platt to their ${}^1A \rightarrow {}^1B^0$ transition[15] (corresponding to $\Psi_G \rightarrow \Psi_I$) is well separated from the higher energy transitions (the next in energy, ${}^1A \rightarrow {}^1C$ being a forbidden one in the all *s-trans* conformation) and thus ideally suited for this type of investigation.

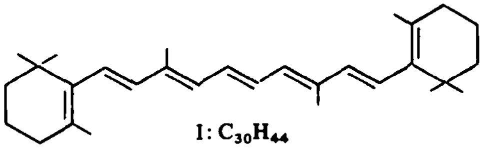
Experimental results

Under the experimental conditions reported below (see Experimental Part) we have investigated the solvent dependence of the ${}^1A \rightarrow {}^1B^0$ band of the electronic spectra of the carotenoid hydrocarbons I to IV listed in Table 1 both in pure and in mixed binary solvents. In addition we have included the polyene derivatives VII to X, in which the functional groups can be considered as minor perturbations of the polyenic π-electron system. The relevant literature references are summarized in Ref.[19]

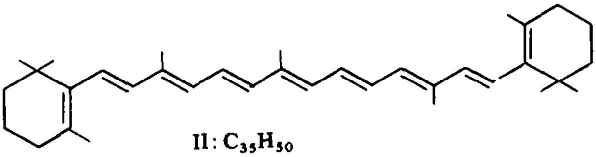
Table 1. List of compounds; m = number of double bonds. (In compounds VIII to X this includes the carbonyl group)

Compound		m.p.	Form	m
C_{30}-Polyene	$C_{30}H_{44}$	147–148°	I	7
C_{35}-Polyene	$C_{35}H_{50}$	156–156·5°	II	9
β-Carotene (C_{40})	$C_{40}H_{56}$	179·5–180°	III	11
Lycopene (C_{40})	$C_{40}H_{56}$		IV	11
C_{45}-Polyene	$C_{45}H_{62}$	176·5–177°	V	13
C_{50}-Polyene	$C_{50}H_{68}$	158–158·5°	VI	15
Vitamin A-acetate	$C_{22}H_{32}O_2$	60°	VII	5
Vitamin A-aldehyde	$C_{20}H_{28}O$	63°	VIII	6
C_{25}-apo-Carotenal	$C_{25}H_{34}O$	105°	IX	8
C_{30}-apo-Carotenal	$C_{30}H_{40}O$	137·5–138°	X	10

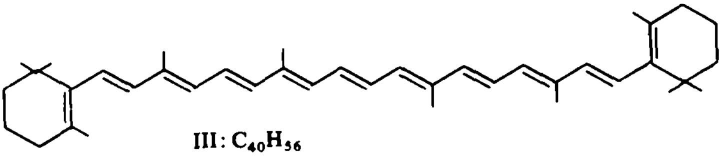
The list of pure and mixed solvents used in this investigation is given in the Experimental (Tables 7 and 8). From the point of view of testing the predictions derived from our simplified model the most important results are those referring to the binary solvent system hexane/carbon disulfide. While hexane (solvent L) is of course transparent in the spectral region investigated—its longwave transition occurring above 58,000 cm^{-1} ($\sim$170 nm)[20]—carbon disulfide (solvent K) exhibits a characteristic spectrum[21] with a first low intensity band at 32,000 cm^{-1} ($\sim$300 nm) which is followed by an intense transition at 48,000 cm^{-1} ($\sim$210 nm) as shown in Fig. 8. (It should be pointed out that in view of the extreme volatility of this solvent, the extinction



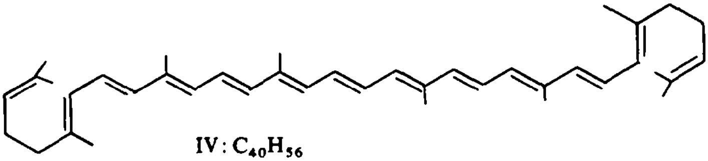
I: $C_{30}H_{44}$



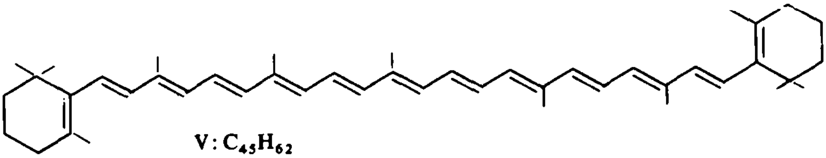
II: $C_{35}H_{50}$



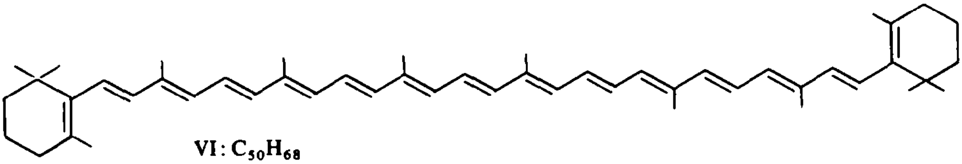
III: $C_{40}H_{56}$



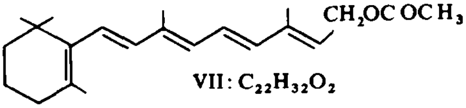
IV: $C_{40}H_{56}$



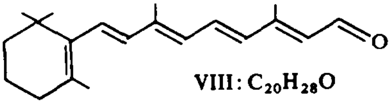
V: $C_{45}H_{62}$



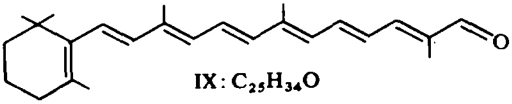
VI: $C_{50}H_{68}$



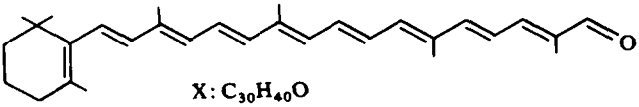
VII: $C_{22}H_{32}O_2$



VIII: $C_{20}H_{28}O$



IX: $C_{25}H_{34}O$



X: $C_{30}H_{40}O$

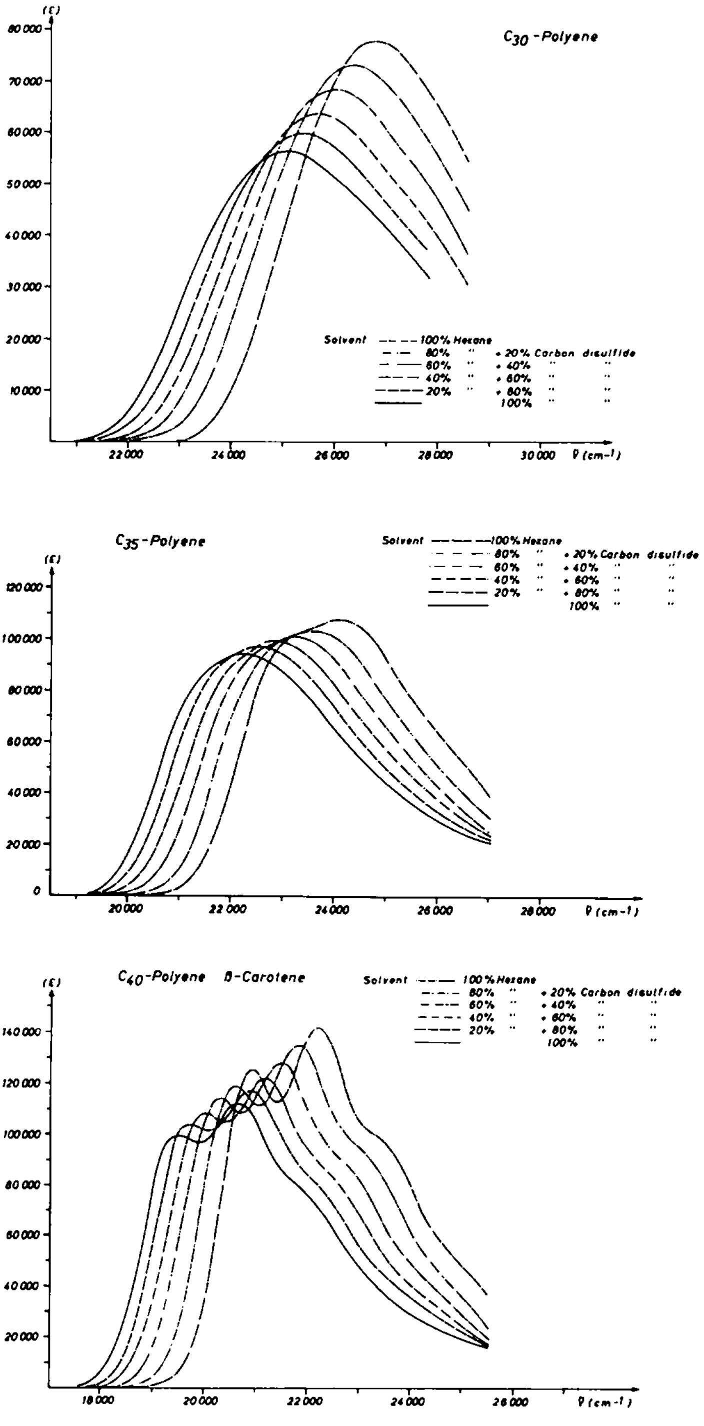


FIG. 2 Dependence of position and intensity of the $^1A \rightarrow {}^1B^0$ band of the hydrocarbons I to III on the composition of the binary mixed solvent hexane/carbon disulfide

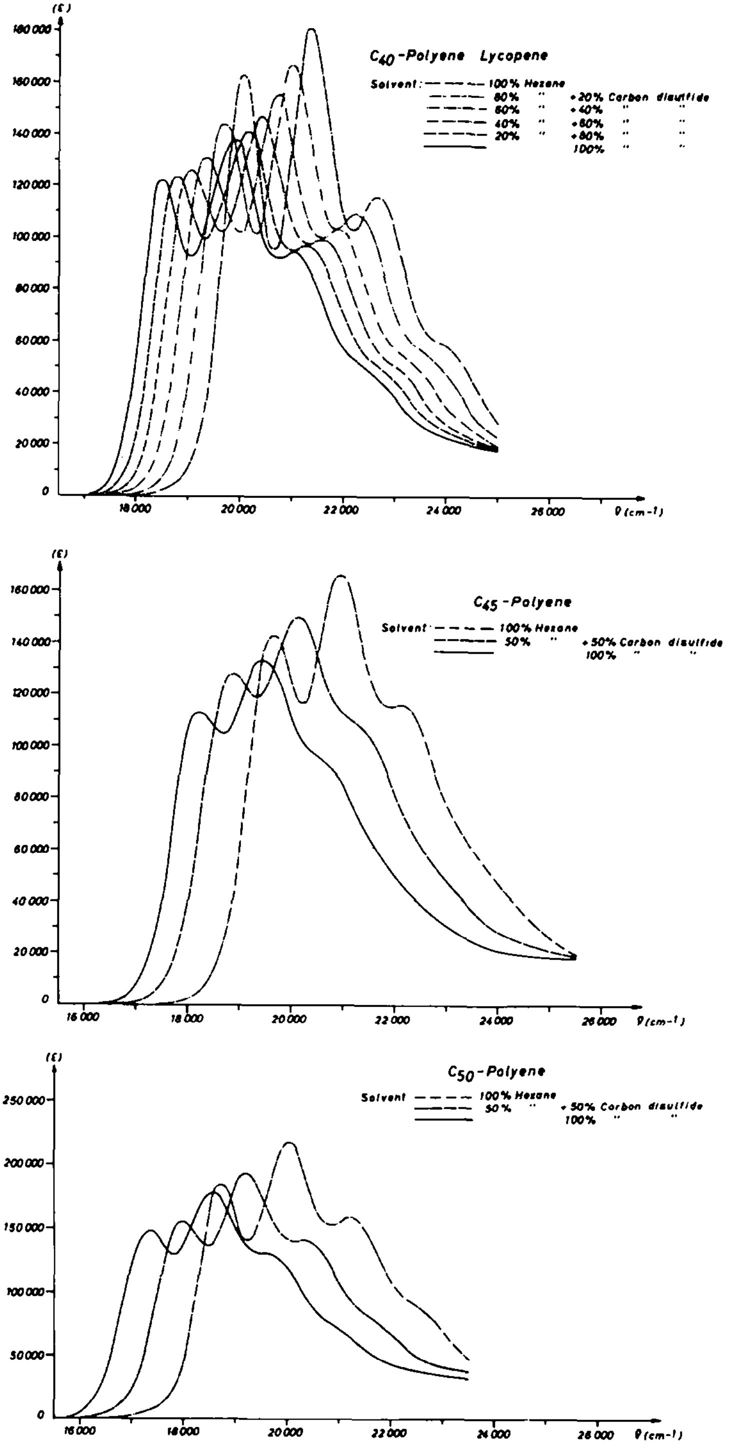


FIG. 3 Dependence of position and intensity of the $^1A \rightarrow {}^1B^0$ band of the hydrocarbons IV to VI on the composition of the binary mixed solvent hexane/carbon disulfide

coefficient given may be affected with a systematic error in excess of the usual 1 to 2 per cent valid for the ε-values quoted for the other compounds in this paper.)

Figs. 2 and 3 show the electronic spectra i.e. their $^1A \rightarrow {}^1B^0$ bands, of the hydrocarbons I to VI in the mixed solvent L/K = hexane/carbon disulfide as a function of its composition expressed in volume percent $v_L = v_{\text{hexane}}$, $v_K = v_{\text{carbon disulfide}}$ ($v_L + v_K = 100$ Vol.-percent). The relevant data are collected in Table 2.

TABLE 2. I: C_{30}-POLYENE

Solvent	$\tilde{\nu}$ (cm^{-1})	ε ($l \cdot Mol^{-1} \cdot cm^{-1}$)
Hexane	26,800	78,000
80% Hexane + 20% Carbon disulfide	26,400	74,000
60% Hexane + 40% Carbon disulfide	26,100	69,000
40% Hexane + 60% Carbon disulfide	25,700	64,000
20% Hexane + 80% Carbon disulfide	25,400	60,000
Carbon disulfide	25,100	57,000
Cyclohexane	26,600	78,000
Benzene	26,100	75,000
Carbon tetrachloride	26,100	70,000
Dioxane	26,500	78,000
Acetone	26,500	93,000
Dimethylformamide	26,200	85,000

TABLE 2. II: C_{35}-POLYENE

Solvent	$\tilde{\nu}$ (cm^{-1})	ε ($l \cdot Mol^{-1} \cdot cm^{-1}$)
Hexane	24,200	105,000
80% Hexane + 20% Carbon disulfide	23,600	103,000
60% Hexane + 40% Carbon disulfide	23,200	100,000
40% Hexane + 60% Carbon disulfide	22,900	99,000
20% Hexane + 80% Carbon disulfide	22,600	96,000
Carbon disulfide	22,300	95,000
Cyclohexane	23,900	113,000
Benzene	23,300	113,000
Carbon tetrachloride	23,400	110,000
Dioxane	23,500	101,000
Acetone	23,800	108,000
Dimethylformamide	23 400	112 000

TABLE 2. III: C_{40}-POLYENE: β-CAROTENE

Solvent	$\tilde{\nu}$ (cm^{-1})	ε ($l \cdot Mol^{-1} \cdot cm^{-1}$)
Hexane	20,900	126,000
	22,200	142,000
95% Hexan + 5% Carbon disulfide	20,900	122,000
	22,100	139,000
90% Hexan + 10% Carbon disulfide	20,800	120,000
	22,000	137,000
85% Hexan + 15% Carbon disulfide	20,700	119,000
	21,900	135,000

TABLE 2: III—*continued*

Solvent	$\tilde{\nu}$(cm^{-1})	ε(l·Mol^{-1}·cm^{-1})
80% Hexan + 20% Carbon disulfide	20,600	118,000
	21,800	134,000
60% Hexan + 40% Carbon disulfide	20,300	113,000
	21,500	127,000
40% Hexan + 60% Carbon disulfide	20,000	109,000
	21,200	122,000
20% Hexan + 80% Carbon disulfide	19,800	104,000
	20,900	118,000
Carbon disulfide	19,600	100,000
	20,700	112,000
Cyclohexane	20,700	126,000
	22,000	145,000
95% Cyclohexan + 5% Carbon disulfide	20,600	123,000
	21,900	142,000
90% Cyclohexan + 10% Carbon disulfide	20,500	120,000
	21,800	141,000
85% Cyclohexan + 15% Carbon disulfide	20,500	119,000
	21,700	138,000
80% Cyclohexan + 20% Carbon disulfide	20,400	118,000
	21,700	135,000
60% Cyclohexan + 40% Carbon disulfide	20,200	111,000
	21,400	127,000
40% Cyclohexan + 60% Carbon disulfide	20,000	107,000
	21,200	120,000
20% Cyclohexan + 80% Carbon disulfide	19,700	104,000
	20,900	116,000
Dimethylformamide	20,400	114,000
	21,600	130,000
95% Dimethylformamide + 5% Carbon disulfide	20,300	113,000
	21,600	127,000
90% Dimethylformamide + 10% Carbon disulfide	20,300	111,000
	21,500	126,000
85% Dimethylformamide + 15% Carbon disulfide	20,300	110,000
	21,400	125,000
80% Dimethylformamide + 20% Carbon disulfide	20,200	108,000
	21,300	122,000
60% Dimethylformamide + 40% Carbon disulfide	20,000	104,000
	21,200	118,000
40% Dimethylformamide + 60% Carbon disulfide	19,800	103,000
	21,000	115,000
20% Dimethylformamide + 80% Carbon disulfide	19,700	102,000
	20,800	114,000
Benzene	20,300	114,000
	21,500	132,000
Carbon tetrachloride	20,400	115,000
	21,600	134,000
Dioxane	20,500	118,000
	21,700	139,000
Acetone	20,700	125,000
	22,000	140,000

TABLE 2. IV: C_{40}-POLYENE: LYCOPENE

Solvent	$\tilde{\nu}$(cm^{-1})	ε (l·Mol^{-1}·cm^{-1})
Hexane	20,100	164,000
	21,400	180,000
	22,600	117,000
80% Hexane + 20% Carbon disulfide	19,700	145,000
	21,000	168,000
	22,300	110,000
60% Hexane + 40% Carbon disulfide	19,300	130,000
	20,700	153,000
	22,000	102,000
40% Hexane + 60% Carbon disulfide	19,000	126,000
	20,400	146,000
	21,600	99,000
20% Hexane + 80% Carbon disulfide	18,800	124,000
	20,200	142,000
	21,300	97,000
Carbon disulfide	18,500	122,000
	19,900	137,000
	21,100	93,000
Cyclohexane	19,800	149,000
	21,100	173,000
	22,400	113,000
80% Cyclohexane + 20% Carbon disulfide	19,500	136,000
	20,800	161,000
	22,100	107,000
60% Cyclohexane + 40% Carbon disulfide	19,200	129,000
	20,600	153,000
	21,800	102,000
40% Cyclohexane + 60% Carbon disulfide	19,000	125,000
	20,300	144,000
	21,500	99,000
20% Cyclohexane + 80% Carbon disulfide	18,700	124,000
	20,100	142,000
	21,300	97,000
Dimethylformamide	19,500	149,000
	20,900	173,000
	22,100	114,000
80% Dimethylformamide + 20% Carbon disulfide	19,300	137,000
	20,600	161,000
	21,800	107,000
60% Dimethylformamide + 40% Carbon disulfide	19,000	129,000
	20,400	150,000
	21,500	102,000
40% Dimethylformamide + 60% Carbon disulfide	18,900	126,000
	20,200	144,000
	21,400	99,000
20% Dimethylformamide + 80% Carbon disulfide	18,700	125,000
	20,000	141,000
	21,200	97,000
Benzene	19,300	138,000
	20,700	164,000
	22,000	106,000

TABLE 2. IV—*continued*

Solvent	$\tilde{\nu}$(cm^{-1})	ε(l·Mol^{-1}·cm^{-1})
Carbon tetrachloride	19,500	150,000
	20,800	175,000
	22,100	116,000
Dioxane	19,700	148,000
	21,000	172,000
	22,200	111,000
Acetone	19,500	153,000
	21,200	171,000
	22,500	111,000

TABLE 2. V: C_{45}-POLYENE

Solvent	$\tilde{\nu}$(cm^{-1})	ε(l·Mol^{-1}·cm^{-1})
Hexane	19,800	144,000
	21,000	166,000
50% Hexane + 50% Carbon disulfide	18,900	128,000
	20,100	150,000
Carbon disulfide	18,200	113,000
	19,500	133,000
Cyclohexane	19,400	140,000
	20,700	166,000
50% Cyclohexane + 50% Carbon disulfide	18,800	125,000
	20,100	148,000
Benzene	19,000	136,000
	20,300	163,000
Carbon tetrachloride	19,100	125,000
	20,400	150,000
Dioxane	19,200	142,000
	20,500	168,000
Acetone	19,500	147,000
	20,800	171,000
Dimethylformamide	19,200	127,000
	20,400	151,000

TABLE 2. VI: C_{50}-POLYENE

Solvent	$\tilde{\nu}$(cm^{-1})	ε(l·Mol^{-1}·cm^{-1})
Hexane	18,700	185,000
	20,000	216,000
50% Hexane + 50% Carbon disulfide	18,000	154,000
	19,200	191,000
Carbon disulfide	17,300	148,000
	18,600	180,000
Cyclohexane	18,600	171,000
	19,800	205,000

TABLE 2. VI—*continued*

Solvent	$\tilde{\nu}$(cm^{-1})	ε(l·Mol^{-1}·cm^{-1})
50% Cyclohexane + 50% Carbon disulfide	17,900	149,000
	19,100	186,000
Benzene	18,100	148,000
	19,300	180,000
Carbon tetrachloride	18,200	144,000
	19,400	175,000
Dioxane	18,300	171,000
	19,500	206,000
Acetone	18,600	185,000
	19,800	220,000
Dimethylformamide	18,200	146,000
	19,500	176,000

In addition, Table 2 contains the data for the spectra measured in a series of pure solvents and in the case of β-carotene (III) and lycopene (IV)—both C_{40}-polyenes—also for the mixed solvent systems L/K = cyclohexane/carbon disulfide and L/K = dimethylformamide/carbon disulfide. Finally, we have collected in Table 3 the corresponding results for the longwave $^1A \rightarrow {}^1B^0$ transition of the polyene derivatives VII to X.

TABLE 3. VII: VITAMIN A-ACETATE

Solvent	$\tilde{\nu}$ (cm^{-1})	ε(l·Mol^{-1}·cm^{-1})
Hexane	30,800	53,000
Carbon disulfide[a]	—	—
Cyclohexane	30,700	52,000
Benzene	30,000	52,000
Carbon tetrachloride	30,000	51,000
Dioxane	30,400	50,000
Dimethylformamide	30,200	53,000

[a] Absorption of the solvent covers the transition.

TABLE 3. VIII: VITAMIN A-ALDEHYDE

Solvent	$\tilde{\nu}$ (cm^{-1})	ε(l·Mol^{-1}·cm^{-1})
Hexane	27,300	50,000
Carbon disulfide	25,600	38,000
Cyclohexane	27,000	48,000
Benzene	26,300	44,000
Carbon tetrachloride	26,400	49,000
Dioxane	26,700	46,000
Acetone	26,900	48,000
Dimethylformamide	26,300	46,000
Methanol	26,500	30,000

TABLE 3. IX: C_{25}-APO-CAROTENAL

Solvent	$\tilde{\nu}$ (cm^{-1})	ε (l·Mol^{-1}·cm^{-1})
Hexane	24,300	76,000
50% Hexane + 50% Carbon disulfide	23,400	67,000
Carbon disulfide	22,300	60,000
Cyclohexane	24,000	73,000
50% Cyclohexane + 50% Carbon disulfide	23,100	65,000
Benzene	23,400	67,000
Carbon tetrachlordie	23,600	71,000
Dioxane	23,500	72,000
Acetone	23,900	70,000
Dimethylformamide	23,300	70,000

TABLE 3. X: C_{30}-APO-CAROTENAL

Solvent	$\tilde{\nu}$ (cm^{-1})	ε (l·Mol^{-1}·cm^{-1})
Hexane	20,900	100,000
	22,100	123,000
50% Hexane + 50% Carbon disulfide	21,100	93,000
Carbon disulfide	20,500	85,000
Cyclohexane	20,700	94,000
	21,900	117,000
50% Cyclohexane + 50% Carbon disulfide	21,000	90,000
Benzene	21,500	104,000
Carbon tetrachlordie	21,500	108,000
Dioxane	21,700	113,000
Acetone	22,100	117,000
Dimethylformamide	21,400	99,000
Methanol	21,900	110,000

Discussion of the results

We shall now show that the data presented in the previous section verify the predictions 1 to 4.

Prediction 1 namely that substitution of the solvent L = hexane by K = carbon-disulfide (or by any other solvent with higher n) is accompanied by a bathochromic shift, is well borne out by Figs 2 and 3 and the data in Tables 2 and 3. As shown in Table 4 for the pair of solvents hexane/carbon disulfide, the shift $\delta\tilde{\nu} = \delta\varepsilon/hc$ of the $^1A \rightarrow {}^1B^u$ band is largely independent of the number m of conjugated double bonds in the solute molecule M. This is even the case for such systems where one of the terminal carbon-carbon double bonds has been replaced by a carbonyl group. The mean shift $\delta\tilde{\nu}$ for the polyenes is -1570 cm^{-1}, if measured at the band-maximum or at the highest fine structure maximum. The corresponding mean shift for the systems with a terminal carbonyl group is -1770 cm^{-1}. However, the difference of 200 cm^{-1} is not significant.

TABLE 4. SHIFTS $\delta\tilde{\nu}$ OF THE $^1A \rightarrow {}^1B^0$ TRANSITION OF THE SOLUTE MOLECULES I TO X ON REPLACEMENT OF HEXANE BY CARBONDISULFIDE AS SOLVENT

m = number of conjugated double bonds (including C=O-bonds in the cases marked *). Values $\tilde{\nu}$ not marked by a superscript refer to the band maximum or the most intense of the fine structure maxima of the band.

m	Compound	Location of band maxima $\tilde{\nu}$ in		$\delta\tilde{\nu}$
		Hexane	Carbon disulfide	
5	VII	30,800	[a]	[a]
6*	VIII	27,300	25,600	−1700
7	I	26,800	25,100	−1700
8*	IX	24,300	22,300	−2000
9	II	24,200	22,300	−1900
10*	X	22,100	20,500	−1600
11	III	20,900[b]	19,600[b]	−1300[b]
		22,200	20,700	−1500
11	IV	20,100[b]	18,500[b]	−1600[b]
		21,400	19,900	−1500
13	V	19,800[b]	18,200[b]	−1600[b]
		21,000	19,500	−1500
15	VI	18,700[b]	17,300[b]	−1400[b]
		20,000	18,600	−1400

[a] Band obliterated by the absorption of the solvent.

[b] These values refer to the longwave fine structure maximum of the band.

The verification of prediction 3, is shown in Fig. 4, where the dependence of the $^1A \rightarrow {}^1B^0$ band location on the composition of the mixed solvent system hexane/carbondisulfide is shown for β-carotene (III) and lycopene (IV). The abscissa is calibrated in volume percent carbon disulfide (v_K). Similar plots are obtained for the other polyenic hydrocarbons.

The functions $\tilde{\nu} = f(v_K)$ are practically linear in v_K, with only a small—albeit significant—quadratic term, which extends over the whole range. In contrast, the analogous plot of $\tilde{\nu}$ *vs* v_K for Vitamin *A*-aldehyde (X) shown in Fig. 5 exhibits a significant higher order term in the region $0 < v_K < 20\%$, which seems to indicate that this polar molecule is prone to selective solvation in the ground state.

The predictions 2 and 4 concerning the behaviour of the integrated absorption intensities when one solvent L is substituted by another solvent K showing stronger dispersive interaction with the solute molecule M are even better borne out than those pertaining to the band shifts $\delta\tilde{\nu}$. In Table 5 we have listed the ratios f'_M/f_M of the oscillator strength (resulting from the integral intensities of the $^1A \rightarrow {}^1B^0$ bands given in the Experimental Table 9) as a function of solvent composition. The data refer again to the system hexane/carbon disulfide and the abscissa is calibrated in volume percent carbon disulfide (v_K). We note that prediction 2 is fulfilled i.e. the ratio f'_M/f_M is smaller than one (for v_K = 100 per cent) and almost independent of m, the number of conjugated double bonds in the solute molecule M. The range of the ratios is very narrow, extending only from 0·77 (in I) to 0·84 (in II).

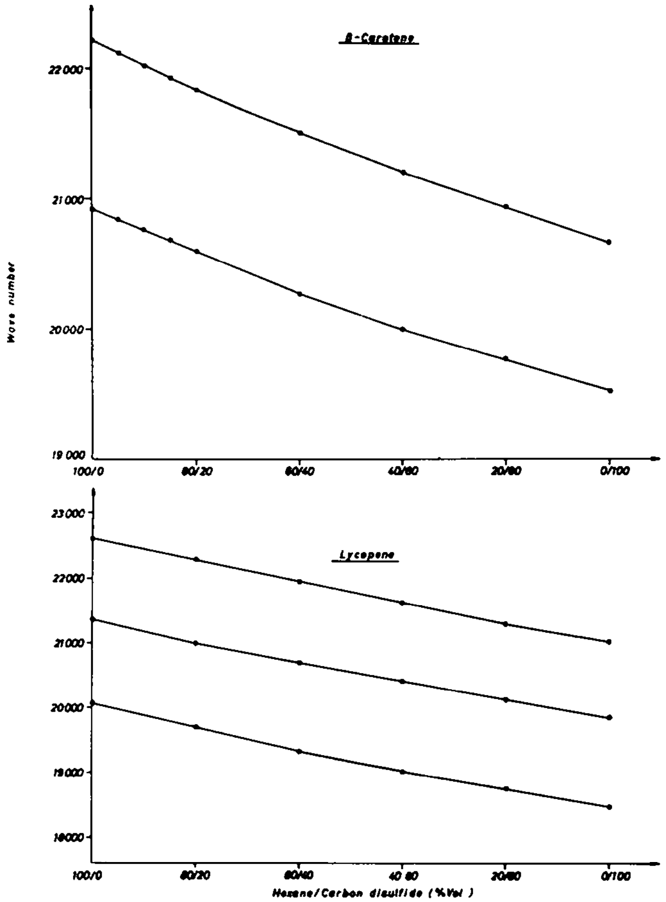


FIG. 4 Shift of the $^1A \rightarrow {}^1B^0$ band of β-Carotene (III) and of Lycopene (IV) as a function of the volume per cent ratio $v_L/v_K = v_{\text{hexane}}\ v_{\text{carbon disulfide}}$

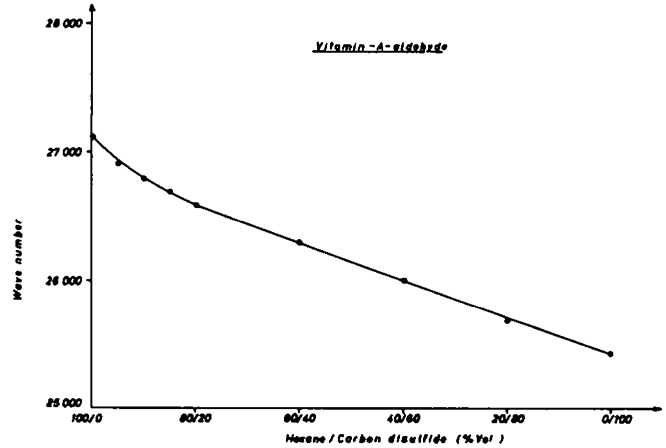


FIG. 5 Shift of the $^1A \rightarrow {}^1B^0$ band of Vitamin A-aldehyde (VIII) as a function of the volume per cent ratio $v_L/v_K = v_{\text{hexane}}/v_{\text{carbon disulfide}}$

TABLE 5. DEPENDENCE OF THE OSCILLATOR-STRENGTH RATIO ON SOLVENT COMPOSITION

Solvent mixture: hexane/carbon disulfide, ν_{hexane} and $\nu_{\text{carbon disulfide}}$ in volume per cent. m = number of conjugated double bonds.

Compound	v_{hexane}	$v_{\text{carbon disulfide}}$	Oscillator-strength ratio f'_M/f_M
C_{30}-Polyene (I)	100	0	1·00
$m = 7$	80	20	0·96
	60	40	0·91
	40	60	0·86
	20	80	0·81
	0	100	0·77
C_{35}-Polyene (II)	100	0	1·00
$m = 9$	80	20	0·94
	60	40	0·91
	40	60	0·88
	20	80	0·86
	0	100	0·84
β-Carotene (III)	100	0	1·00
$m = 11$	80	20	0·96
	60	40	0·92
	40	60	0·87
	20	80	0·84
	0	100	0·80
Lycopene (IV)	100	0	1·00
$m = 11$	80	20	0·97
	60	40	0·92
	40	60	0·89
	20	80	0·86
	0	100	0·83
C_{45}-Polyene (V)	100	0	1·00
$m = 13$	50	50	0·94
	0	100	0·82
C_{50}-Polyene (VI)	100	0	1·00
$m = 15$	50	50	0·89
	0	100	0·83

TABLE 6. TEMPERATURE DEPENDENCE OF $\delta\tilde{\nu}$ AND f'_M/f_M FOR THE $^1A \rightarrow {}^1B^0$ BAND OF β-CAROTENE DISSOLVED IN HEXANE OR CARBON DISULFIDE

Temp. °C	Band position $\tilde{\nu}$ (cm^{-1})		$\delta\tilde{\nu}$	f'_M/f_M
	Hexane	Carbon disulfide		
22°	22,250	20,680	−1570	0·78
−50°	21,900	20,320	−1580	0·82
−90°	21,750	20,100	−1650	0·83

Furthermore, as shown in Fig. 6 for β-carotene (III) and lycopene (IV), the dependence of f'_M/f_M on v_K is strictly linear inside the limits of error. This verifies prediction 4.

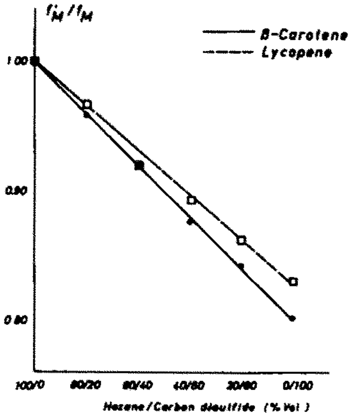


FIG. 6 Dependence of the oscillator-strength ratio f'_M/f_M of the ${}^1A \rightarrow {}^1B^u$ transition on solvent composition.

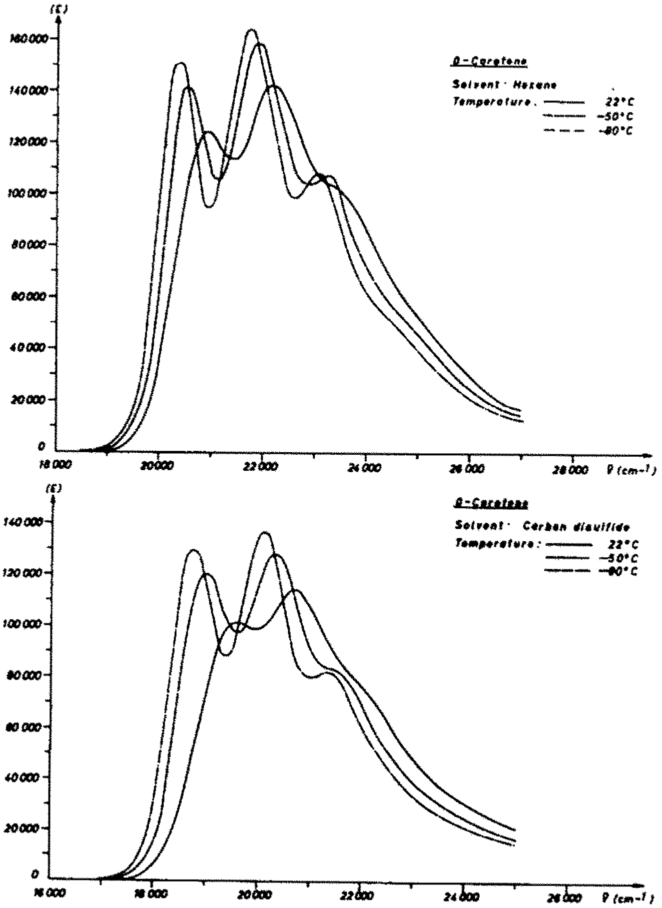


FIG. 7 Temperature dependence of the ${}^1A \rightarrow {}^1B^0$ band of β-Carotene (III) dissolved in hexane or carbon disulfide

Fig. 7 shows the change of the $^1A \rightarrow {}^1B^0$ band shape on cooling, for solutions of β-carotene (III) in hexane or carbon disulfide. (The relevant data are summarized in Table 9).

As can be seen, our conclusions will not be affected in principle if the experiments are carried out at lower temperatures. This is also evident from the shifts $\delta\tilde{\nu}$ and the oscillator strength ratios f'_M/f_M given in Table 6.

The verification of the predictions **1** to **4** deduced from our model has been only on the qualitative side, as far as the size of the effects is concerned. The question arises whether the observed shifts $\delta\tilde{\nu}$ and the intensity reduction measured by the ratio f'_M/f_M are of the correct order of magnitude. For the following reasons this is rather difficult to assess. First of all we observe only the differences between the spectra recorded in two solvents instead of the differences between the spectra measured in a given solvent and in the gas phase. Secondly it is very difficult to guess how sensitive the predictions depend on the various assumptions concerning the packing of the solvent molecules in the solvation shell or the neglect of interaction terms with higher locally excited states. One can only expect to obtain the correct orders of magnitude and that the observed shifts $\delta\tilde{\nu}$ and ratios f'_M/f_M are compatible in terms of the model. One of the parameters on which the size of the predicted effects depends most critically is the mean distance R_j of the solvent molecule L_j to the nearest double bond(s) of M. (c.f. formula (6)). Unfortunately this value is not uniquely defined. However, a crude calculation will show that the shift $\delta\varepsilon = -1600\ \text{cm}^{-1}$ and the ratio $f'_M/f_M = 0{\cdot}8$ found experimentally for the carotenoids will require mean values R_j of 1·6 Å and 2·4 Å respectively for the computation of coupling terms x_j of corresponding magnitude.

EXPERIMENTAL

Compounds. With the exception of IV the compounds I to X have been synthesized according to the procedures described,[19] which are based on the well known Wittig reaction.[21] All compounds have been recrystallized from pet. ether (I, VII, VIII, IX) or mixtures of benzene/MeOH (III), benzene/EtOH (II) or CH_2Cl_2/MeOH (V, VI, X). Their m.ps are given in Table 1. A sample of pure IV has been kindly provided by Dr. O. Isler (Hoffmann-La Roche S.A., Basel), whose help is gratefully acknowledged.

Solvents. All solvents used (Table 7) were spectroscopic grade. In particular, the CS_2 obtained from E. Merk (Darmstadt) corresponded to their "Uvasol" grade. The solvents have been further purified according to standard procedure,[22] their purity checked by spectroscopic means, degassed and saturated with O_2 free N_2. The handling and weighing of the compounds as well as the preparation of the soln has been carried out under pure N_2 to prevent oxidation of the rather delicate polyenes.

TABLE 7. REFRACTIVE INDEX n_D OF THE SOLVENTS AT 25°C

Solvent	n_D
Hexane	1·3738
Carbon disulfide	1·6233
Cyclohexane	1·4235
Benzene	1·4982
Carbon tetrachloride	1·4579
Dioxane	1·4202
Acetone	1·3567
Dimethylformamide	1·4282
Methanol	1·3272

Table 8 contains the refractive indices of the binary mixed solvents used in this investigation.

Spectroscopic investigation. The measurements have been carried out on a spectrophotometer Perkin-Elmer Spectracord 4000 A and a spectrophotometer Zeiss PMQ II. Relative values for the oscillator strengths f_M and f'_M are given in Table 9. These are expressed in arbitrary planimeter units and refer to the area bordered by the abscissa $\varepsilon = 0$ and the curve $\varepsilon = f(\tilde{\nu})$ between the two ordinates listed in the fourth

TABLE 8. REFRACTIVE INDICES n_D OF THE BINARY MIXED SOLVENTS CARBON DISULFIDE/HEXANE, CARBON DISULFIDE/CYCLOHEXANE AND CARBON DISULFIDE/DIMETHYLFORMAMIDE AT 25°C

Volume per cent $v_{\text{carbon disulfide}}$	Carbon disulfide mixed with Hexane n_D	Cyclohexane n_D	Dimethylformamide n_D
0	1·3738	1·4235	1·4282
5	1·3849	1·4322	1·4365
10	1·3963	1·4408	1·4447
15	1·4074	1·4498	1·4533
20	1·4195	1·4592	1·4622
40	1·4680	1·4970	1·4977
60	1·5168	1·5376	1·5367
80	1·5705	1·5794	1·5772
100	1·6233	1·6233	1·6233

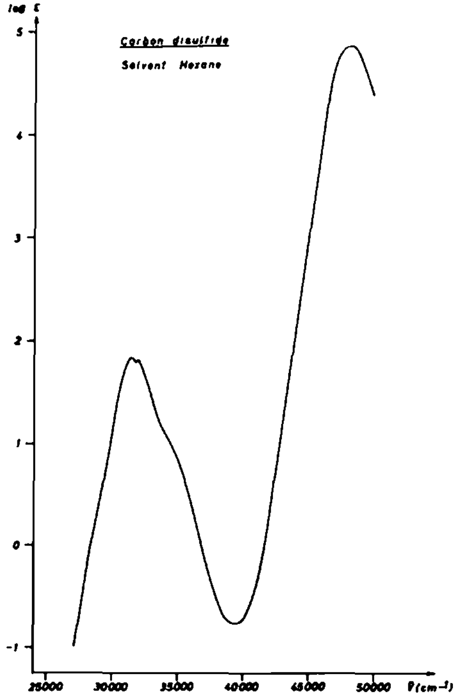


FIG. 8 Electronic spectrum of carbon disulfide dissolved in hexane.

Table 9. Relative oscillator strengths of the $^1A \rightarrow {}^1B^0$ transition of the polyenes I to VI

Low temperature spectra of β-carotene (III) and lycopene (IV) in hexane and carbon disulfide. v_H = volume per cent hexane, v_C = volume per cent carbon disulfide. $\tilde{\nu}$ = position of band maximum or of highest fine structure maximum (in cm^{-1}). t = temperature at which spectrum was recorded.

Compounds	Solvent composition v_H/v_C	$\tilde{\nu}$	Range of integration (cm^{-1})	Relative oscillator strength in planimetric units
C_{30}-Polyene (I)	100/ 0	26,800	22,800–29,550	5785
	80/ 20	26,350	22,000–28,100	5563
	60/ 40	26,000	21,700–27,750	5249
	40/ 60	25,700	21,450–27,450	4940
	20/ 80	25,400	21,200–27,150	4668
	0/100	25,100	21,000–26,850	4435
C_{35}-Polyene (II)	100/ 0	24,125	20,350–27,100	4766
	80/ 20	23,625	19,950–26,600	4500
	60/ 40	23,150	19,650–26,150	4340
	40/ 60	22,750	19,450–25,750	4203
	20/ 80	22,450	19,250–25,500	4109
	0/100	22,200	19,000–25,225	4003
β-Carotene (III)	100/ 0	22,250	18,750–25,525	5786
	80/ 20	21,880	18,500–25,150	5560
	60/ 40	21,500	18,250–24,800	5360
	40/ 60	21,175	18,000–24,500	5068
	20/ 80	20,900	17,750–24,200	4863
	0/100	20,680	17,500–23,950	4645
t = 22°C	100/ 0	22,250	18,900–26,600	6361
= −50°C	100/ 0	21,900	18,850–26,370	6420
= −90°C	100/ 0	21,750	18,800–26,250	6327
t = 22°C	0/100	20,680	17,500–24,900	4966
= −50°C	0/100	20,320	17,250–24,550	5264
= −90°C	0/100	20,100	17,000–24,350	5256
Lycopene (IV)	100/ 0	21,300	18,000–24,860	6291
	80/ 20	21,000	17,750–24,500	6081
	60/ 40	20,740	17,500–24,200	5770
	40/ 60	20,400	17,350–23,900	5597
	20/ 80	20,150	17,200–23,650	5431
	0/100	19,890	17,100–23,400	5230
t = 22°C	100/ 0	21,300	18,150–25,750	5555
= −50°C	100/ 0	21,050	18,000–25,550	5643
= −90°C	100/ 0	20,950	17,850–25,450	5383
C_{45}-Polyene (V)	100/ 0	20,950	17,500–25,500	6838
	50/ 50	20,150	16,550–24,700	6449
	0/100	19,430	16,200–23,970	5601
C_{50}-Polyene (VI)	100/ 0	20,025	16,750–23,500	4180
	50/ 50	19,175	16,100–22,650	3741
	0/100	18,575	15,700–22,050	3477

column of Table 9. To ensure reliable values for f_M and f'_M the shortwave cutoff has been taken at a fixed distance from the position of the band maximum for each compound. As these distances are not the same for all polyenes, the f-values so obtained should be used with caution if oscillator strength of two different compounds are compared. However, they should be quite reliable for one compound dissolved in various solvents or mixtures.

For the data referring to the spectra recorded at lower temps the volume contraction of the solvent has been taken into account. The following expansion coefficients have been used: $\gamma(\text{Hexane}) = 1{\cdot}35 \,.\, 10^{-3}$; $\gamma(CS_2) = 1{\cdot}20 \,.\, 10^{-3}$.

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