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Studies of the Energy Spectrum of α, ω-Substituted Polymethine Chains.
II. Polymethine Chains With Odd Number of Methine Groups

Nikolay Tyutyulkov**, Fritz Dietz

University of Leipzig, Chair of Physical Chemistry "Wilhelm Ostwald" 701 Leipzig, DDR

Jürgen Fabian, Achim Melhorn

Technical University of Dresden, Section Chemistry, 8027 Dresden, DDR

Alia Tadjer

Institute of Organic Chemistry, Academy of Sciences, 1113 Sofia, Bulgaria

The analysis of the experimental data for the energy of the longest wavelength optical transitions $\Delta\varepsilon_{n,\mathrm{opt}}$ of substituted polymethines $X \overset{\cdot\cdot}{-} (\mathrm{CH})_{2n+1} \overset{\cdot\cdot}{-} X$ shows that in the asymptotic case $(n \to \infty)$ $\Delta\varepsilon_{\infty,\mathrm{opt}}$ does not tend to zero, as it follows from the empirically established correlations, but has a finite, non-zero value. It is shown that the energy gap of odd polymethines is the same as that of the even polymethines – the polyenes ($\Delta E_{\infty} \sim 2$ eV). The substituents ($X \in$ N, O, B) are responsible for the appearance of levels in the gap. These, depending on the substituent character, are vacant ($X \equiv$ B) or occupied ($X \equiv$ N, O). The transition from or to such a level determines the longest wavelength optical transition energy of polymethines.

Key words: Polymethines, α, ω-substituted – Polymethines, energy spectrum of ~.

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** Permanent address: Institute of Organic Chemistry, Academy of Sciences, 1113 Sofia, Bulgaria.

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1. Introduction

According to the empirical rules established by König [1], Brooker [2] and Platt [3] the wavelength of symmetrical α, ω-disubstituted polymethines (I and II)

$$[\geq N \overset{\cdots}{-} (CH)_{2n+1} \overset{\cdots}{-} N \leq]^+ \qquad (I)$$

$$[O \overset{\cdots}{-} (CH)_{2n+1} \overset{\cdots}{-} O]^- \qquad (II)$$

$$[\geq B \overset{\cdots}{-} (CH)_{2n+1} \overset{\cdots}{-} B \leq]^- \qquad (III)$$

$$[CH_2 \overset{\cdots}{-} (CH)_{2n+1} \overset{\cdots}{-} CH_2]^+ \qquad (IV)$$

depends on the vynil groups number (n) by the linear relation:

$$\lambda_n = a + bn. \qquad (1)$$

The above correlation holds also for the carbocations (IV), where [4] $\lambda_n(\text{Å}) = 655n + 3305$. There are no experimental data for the diboron-polymethines (III), but the calculated ones by means of the PPP method for the first members follow an equation of type (1), too (see Table 1).

Eq. (1) is a particular case of the generalized formula of Dähne and Radeglia [5]

$$\lambda_n = k(n+q)^p \qquad (2)$$

where k, q and p are parameters depending on the system's type. This formula (2) includes not only the linear relation (1) ($p = 1$), but also the rule of Lewis and Calvin [6] ($p = \frac{1}{2}$), defined for polyenes $CH_2 \overset{\cdots}{-} (CH)_{2n} \overset{\cdots}{-} CH_2$.

Table 1. Experimental energies $\Delta\varepsilon_n$ (eV) for the longest wavelength singlet-singlet ($\pi \rightarrow \pi^*$) transition of: polymethinecyanines (I) [7], polymethineoxonoles (II) [7], diboron-polymethines (III)[a] and carbocations (IV) [4] and the extrapolated values for infinite ($n \rightarrow \infty$) chains

$$X \overset{\cdots}{-} (CH)_{2n+1} \overset{\cdots}{-} X$$

n	$\Delta\varepsilon_n$(I)	$\Delta\varepsilon_n$(II)	$\Delta\varepsilon_n$(III)	$\Delta\varepsilon_n$(IV)
0	5.53	4.64	3.95	4.07
1	3.97	3.42	3.05	3.13
2	2.98	2.73	2.54	2.67
3	2.39	2.26	2.18	2.31
4	1.98	1.93	1.93	2.04
5	1.69	—	—	1.83
6	1.46	—	—	—
∞[b]	1.06	1.14	1.36	1.10
∞[c]	1.18	1.31	1.23	0.92

[a] The results for $\Delta\varepsilon_n$ (III) are calculated by means of the PPP method with geometry and parametrization cited in Refs. [9, 10].
[b] The extrapolation done applying the Pade approximation [8].
[c] Values obtained using Eq. (3).

The above empirical correlations have the same asymptotic behaviour – $n \to \infty$ results in $\lambda \to \infty$. This leads to the conclusion that for both the basic classes of π-electron systems – polyenes and polymethines – the gap tends to zero. Such a conclusion, based on the formal extrapolation of Eqs. (1) and (2), contradicts a number of other facts showing that both the longest wavelength transition energy $\Delta\varepsilon_{\infty,\mathrm{opt}}$ and the energy gap ΔE_∞ of these systems are non-zero.

The theoretical and the experimental researches [11–15] show that the gap of polyenes and their α, ω-disubstituted derivatives [16] is different from zero and amounts about ≈ 2 eV.

This result shows that both the rule of Lewis and Calvin [6] and Eq. (2) are valid for relatively small number of vinyl groups (n).

The application of the Pade approximation [8] gives for all the polymethines (see Table 1) finite, non-zero values for the longest wavelength transition energy when $n \to \infty$. Non-zero values for $\Delta\varepsilon_{\infty,\mathrm{opt}}$ are obtained also using the empirical correlations [17] between the transition energies calculated by means of the HMO method $\Delta\varepsilon_n(\mathrm{HMO})$ and those found experimentally $\Delta\varepsilon_n(\exp)$:

$$\begin{aligned}\Delta\varepsilon_n(\exp) &= c + d \cdot \Delta\varepsilon_n(\mathrm{HMO})\\ &= \Delta\varepsilon_{\infty,\mathrm{opt}} + d \cdot \Delta\varepsilon_n(\mathrm{HMO}).\end{aligned}$$

The values for $\Delta\varepsilon_{\infty,\mathrm{opt}}$ of polymethines, calculated using the above equation, are presented in Table 1. The MO energies for systems I, II and IV are obtained from the analytical expressions with parameters cited in Ref. [18, 19]; the MO energies of the oxonoles are obtained with the parameters $\alpha_{\ddot{\mathrm{O}}} = \alpha_{\mathrm{C}} + 2\beta_{\mathrm{CC}}$; $\beta_{\mathrm{C}\ddot{\mathrm{O}}} = \beta_{\mathrm{CC}}$.

For the carbocations (IV) Eq. (1) holds up to $n \leq 6$. However, the Pade approximation, respectively Eq. (3) (see Table 1), and the theoretical studies [20] show that λ_∞ tends not to infinity but for $n \to \infty$ the longest wavelength transition energy $\Delta\varepsilon_{\infty,\mathrm{opt}}$ is about ≈ 1 eV.

The above considerations taken into account, give the reasons to a suggestion that the functional relationship between the wavelength and the number of the vinyl groups $\lambda = \lambda(n)$ for linear systems: polyenes, polymethines and their derivatives, could be approximated by a linear correlation of type (1) or (2) only for low values of n. Actually, the expression of function λ (n) is more complicated and for high values of n $\lambda(\infty)$ tends to the finite value λ_∞ (Fig. 1).

A simple model function fulfilling the above conditions and allowing the determination of λ_n is the function

$$\lambda_n = \lambda_\infty - (\lambda_\infty - \lambda_k)(1 + \mathrm{tgh}\, ak - \mathrm{tgh}\, an). \tag{4}$$

If k – the value of n for which the experimental quantity λ_k is determined – is equal to zero ($k = 0$), Eq. (4) turns into

$$\lambda_n = \lambda_\infty - (\lambda_\infty - \lambda_0)(1 - \mathrm{tgh}\, an). \tag{4a}$$

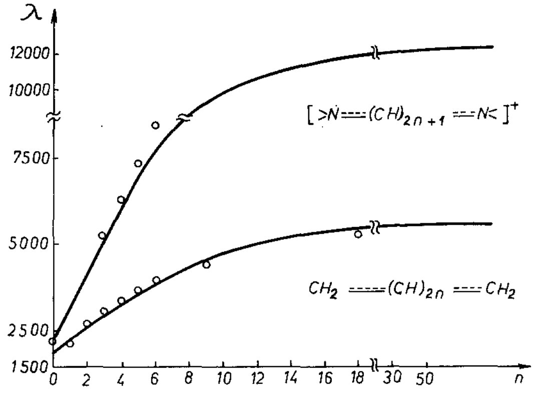


Fig. 1. Experimental (○○○○) [7, 21] and calculated (———) by means of Eq. (4a) values for the longest wavelength transition energies of even polyenes and polymethinecyanines

The parameter a, found empirically, amounts to $a = 0, 10$ for polyenes and carbocations (IV); for oxonoles $a = 0, 15$ and for polymethinecyanines (I) $a = 0, 10–0, 12$. The experimental data and the values of λ_n calculated by means of Eq. (4a) for polyenes and polymethine-cyanines are collected in Table 2.

Although Eq. (4) leads to satisfactory results for λ_n, one can hardly say that it expreses the optimal functional relationship of the longest wavelength transition energy and the number of vinyl groups in a linear molecular system. It should only be considered as a quantitative illustration of the statement that the longest

Table 2. Experimental and calculated by means of formula (4a) values of wavelength for the longest wavelength transition of even polyenes [21] $CH_2 \overset{\cdots}{=} (CH)_{2n} \overset{\cdots}{=} CH_2$, polymethinecyanines (I) [7], polymethineoxonoles (II) [7], and carbocations (IV) [4]

	Polyenes		Cyanines		Carbocations		Oxonoles	
n	λ_n^{exp}	λ_n^{calc}	λ_n^{exp}	λ_n^{calc}	λ_n^{exp}	λ_n^{calc}	λ_n^{exp}	λ_n^{calc}
0	1834[b]	1834	2200[b]	2200	3047[b]	3047	2672[b]	2672
1	2170	2200	3130	3147[c] (3335)[d]	3962	3867	3626	3687
2	2680	2560	4160	4075 (4437)	4644	4671	4572	4657
3	3040	2905	5190	4968 (5480)	5368	5443	5487	5547
4	3340	3231	6250	5809 (6440)	6078	6172	6472	6332
5	3640	3533	7345	6590 (7302)	6776	6848	—	7000
6	3900	3808	8480	7302 (8060)	—	7465	—	7553
9	4470	4467	—	—	—	—	—	—
∞[a]	5511	5511	11700	11700	11273	11273	9487	9487

[a] Values calculated applying the Pade approximation [8] (see Table 1).

[b] Values used for determining of λ_0.

[c] Values calculated for $a = 0.10$.

[d] Values calculated for $a = 0.12$.

wavelength transtion energy of an infinite linear system λ_∞ has a non-zero, finite value.

The theoretical research and argumentation of this statement, together with the working out of a method for quantitative evaluation of the optical properties of substituted polyenes and polymethines, is the purpose of the present study.

The finite, non-zero value of $\Delta\varepsilon_{\infty,\mathrm{opt}}$ could be interpreted qualitatively as follows: The polymethines containing an infinite (very high) number of methine groups ($n \to \infty$) might be considered as one-dimensional crystals. Taken for sure the non-zero gap to be characteristic for the energy spectrum of infinite polyenes, the substituted polyene (the polymethine, respectively) can be treated as a polyene one-dimensional crystal doped with one or two "impurity" atoms. This results in the appearance of new levels located in the gap. These particular levels define the optical properties of the one-dimensional systems in question.

2. Energy Gap of Unsubstituted Polyenes

In π-electron approximation, taking into account the long distance Coulomb electron interaction, the presence of a non-zero gap in the energy spectrum of the one-particle excitations for polyenes is determined mainly by the electron correlation [22]. The geometrical factor – the alternation in the C—C bond lengths – is conditioned by the electron-phonone interaction [23, 24].

The band structure of even polyene can be described simply in adiabatical approximation, in the framework of the extended Hartree–Fock method, applying the Hubbard approximation [25] for the electron interaction. In these approximations the energy gap of an arbitrary alternant homonuclear system [26], the polyenes in this number [27, 28], can be expressed simply by a correlational (Δ_{corr}) and a geometrical (Δ_{geom}) component

$$\begin{aligned}\Delta E_\infty &= \sqrt{\Delta_{\mathrm{corr}}^2 + \Delta_{\mathrm{geom}}^2}\\ &= \sqrt{4\gamma^2\delta^2 + 4(\beta_s - \beta_d)^2}.\end{aligned}$$

In the above equation γ is the one-center Coulomb integral and δ, the correlational correction, defined by the condition [26–28]

$$\delta = \sum_k^n \frac{\delta\gamma}{\sqrt{\delta^2\gamma^2 + e^2(\omega_k)}} \xrightarrow{n\to\infty} \frac{\gamma}{\pi}\int_0^{\pi/2} \frac{\delta\, d\omega_k}{\sqrt{\delta^2\gamma^2 + e^2(\omega_k)}} \tag{6}$$

where $e(\omega_k)$ are the terms for the MO energies of the polyene.

In Hubbard approximation the relative share of these two factors, the correlational and the geometrical, can not be determined; it depends on the geometry (type of alternation) and on the parametrisation. For the cases with strong alternation Eq. (6) allows only trivial solutions $\delta = 0$. Thus $\Delta_{\mathrm{corr}} = 0$ and the gap is defined only by the bondlength alternation $\Delta E_\infty = \Delta_{\mathrm{geom}} = 2|\beta_s - \beta_d|$, i.e. the gap is defined only by the geometrical factor [29–33].

The lack of alternation ($\beta_s = \beta_d = \beta_0$) makes the gap dependant only on the electron correlation [34, 35]

$$\Delta E_\infty = \Delta_{\rm corr} = 2\delta\gamma. \tag{7}$$

The problem for the appearance of "impurity" levels in the gap, as a result of a substitution in the polyene chain, could be treated as in the general case – $\Delta_{\rm corr} \neq 0$ and $\Delta_{\rm geom} \neq 0$ – so in the two extreme cases: lack of alternation ($\Delta_{\rm geom} = 0$) or absence of correlational correction ($\Delta_{\rm corr} = 0$). It will be shown that the three approaches lead to qualitatively equivalent results for the location of the impurity levels in the gap. A quantitative correspondence can be achieved just using an appropriate parametrisation, too.

The appearance of a local level in the case of monosubstituted polyene chains, the gap being defined only in terms of the electron correlation ($\Delta_{\rm geom} = 0$), is treated in a study of Ukrainsky and Kwentsel [37], (see also Ref. 38, 39).

3. Monosubstituted Polymethines

Let us denote the bonding and the antibonding MOs of an even polyene ($N = 2n$ AOs) by ψ_k and $\psi_{\bar{k}}$

$$\psi_{k(\bar{k}))} = \sum_{\mu} c_{k(\bar{k})\mu} \varphi_\mu.$$

In the AMO approximation [40–42] of the extended Hartree–Fock method the AMOs of a polyene can be represented as follows (as the energy expressions and the results for the orbitals with spin α (↑) or β (↓) are equal, the representation below is done only for AMOs with spin α (↑)):

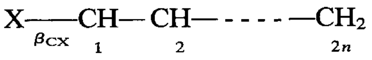
$$\text{BMO:} \quad \phi_k = \sin\theta_k \psi_k + \cos\theta_k \psi_{\bar{k}}$$

$$\text{ABMO:} \quad \phi_{\bar{k}} = \cos\theta_k \psi_k + \sin\theta_k \psi_{\bar{k}}$$

$$\sin 2\theta_k = \frac{\delta\gamma}{\sqrt{\delta^2\gamma^2 + e^2(\omega_k)}} = \frac{\delta\gamma}{E_k}; \qquad \cos 2\theta_k = \frac{\pm e(\omega_k)}{E(\omega_k)}. \tag{8}$$

In expression (8) the sign "+" refers to BMOs, while "−" to ABMOs.

If the AMOs of a monosubstituted polyene



$$\underset{\beta_{\rm CX}}{\text{X}\text{——}}\underset{1}{\text{CH}}\text{—}\underset{2}{\text{CH}}\text{—}\text{-----}\text{—}\underset{2n}{\text{CH}_2}$$

are constructed as

$$\chi_p = c_x \varphi_x + \sum_k^n a_k \phi_k + \sum_{\bar{k}}^n a_{\bar{k}} \phi_{\bar{k}}$$

in Hubbard approximation the matrix elements d_{kx} (see Eq. (Ia) in Appendix I) are equal to [40]

$$\alpha_x = \langle \varphi_x | H | \varphi_x \rangle = \alpha_c + h\beta_0 = h\beta_0$$

$$d_{kx} = \langle \varphi_x | H | \phi_k \rangle = c_{k1}\beta_{cx}(\sin\theta_k + \cos\theta_k)$$
$$= c_{k1}\eta_x\beta_0(\sin\theta_k + \cos\theta_k)$$
$$d_{\bar{k}x} = \langle \varphi_x | H | \phi_{\bar{k}} \rangle = c_{k1}\eta_x\beta_0(\sin\theta_k + \cos\theta_k).$$

The introduction of the above expressions turns Eq. (Ia) (Appendix I) into

$$(\alpha_x - E) + \beta_{cx}^2 \sum_k^n \frac{c_{k1}^2(1+\sin 2\theta_k)}{E+E_k} + \beta_{cx}^2 \sum_k^n \frac{c_{k1}^2(1+\sin 2\theta_k)}{E-E_k} = 0.$$

Using the expressions for E_k (8) and c_{k1} (Appendix II) in the case $n \to \infty$, the above equation transforms into

$$h\beta_0 - E + \eta_x^2\beta_0^2 \frac{4E}{\pi} \int_0^{\pi/2} \frac{\sin^2 \operatorname{arctg} \dfrac{\sin\omega_k}{e(\omega_k) - \cos\omega_k}}{E^2 - [\delta^2\gamma^2 + (\beta_s - \beta_d)^2 + 4\beta_s\beta_d \cos^2\omega_k]}$$
$$\times \left(1 + \frac{\delta\gamma}{\sqrt{\delta^2\gamma^2 + (\beta_s - \beta_d)^2 + 4\beta_s\beta_d\cos^2\omega_k}}\right) \mathrm{d}\omega_k = 0$$
$$e(\omega_k) = \sqrt{(1-t)^2 + 4t\cos^2\omega_k}; \qquad t = \beta_s/\beta_d. \tag{9}$$

If the relation between the resonance integrals and the interatomic distance is accepted to be [33] $\beta(R) = \beta_0 \exp \alpha(R_0 - R)$ and the energy gap is expressed in terms of Eq. (5), Eq. (9) leads to

$$h\beta_0 - E + \eta_x^2\beta_0^2 \frac{4E}{\pi} \int_0^{\pi/2} \frac{\sin^2 \operatorname{arctg} \dfrac{\sin\omega_k}{e(\omega_k) - \cos\omega_k}}{E^2 - (\frac{1}{4}\Delta E_\infty^2 + 4\beta_0^2\cos^2\omega_k)}$$
$$\times \left(1 + \frac{\delta\gamma}{\sqrt{\frac{1}{4}\Delta E_\infty^2 + 4\beta_0^2\cos^2\omega_k}}\right) \mathrm{d}\omega_k = h\beta_0 - E + F_1(E) = 0. \tag{10}$$

When $\delta = 0$ ($\Delta E_\infty = \Delta_{\text{geom}}$), Eq. (10) corresponds to the bond alternation model; if $t = 1$ ($\Delta E_\infty = \Delta_{\text{corr}}$), Eq. (10) corresponds to the model where the gap is determined only by the electron correlation. In Table 3 are represented the values of function $F_1(E)$ for different quantities of the parameters.

The roots of Eq. (10) within the interval $-|\beta_s - \beta_d| < E < |\beta_s - \beta_d|$, defining the position of the impurity level in the gap, are determined by the crossing point of the line $E - h_x\beta_0[\beta_0 < 0]$ and the function $F_1(E)$.

Figure 2 shows the graph of function $F_1(E)$. The position of the impurity level in the gap depends on the substituent atom, i.e. on the value of parameter h_x. If $h_x = 0$, i.e. the substituent is a carbon atom, the impurity level is in the middle of the gap. This means, that the transition from a polyene with $N = 2n$ AOs to a polymethine with $N = 2n+1$ AOs is accompanied with an appearance of a level in the middle of the gap, determining the optical properties of the polymethine. In the case of carbocations this level is vacant, and in that of carboanions – occupied (see Fig. 3). In both cases the longest wavelength transition energy would be equal to halfwidth the gap $\Delta\varepsilon_{\infty,\text{opt}} = \frac{1}{2}\Delta E_\infty$.

Table 3. Dependance of function $F_1(E)$ on parameters t and δ_γ Eq. (10). For the relation between the resonance integrals and the interatomic distance is used the formula [33]: $\beta(R)=\beta(R_0)\ \exp \alpha(R_0-R)$; $\alpha=3.2195$; the calculations are performed with $\gamma=5.4$ eV [34], $\Delta E_\infty=2.25$ eV [11].

E	$\beta_0=-3.39$ eV $t=0.719$ $\delta\gamma=0$	$t=1$ $\delta\gamma=1.125$	$\beta_0=-2.43$ eV $t=0.879$ $\delta\gamma=1.081$	$t=0.632$ $\delta\gamma=0$
0.0	0.000	0.000	0.000	0.000
0.1	0.256	0.297	0.297	0.173
0.2	0.519	0.604	0.603	0.350
0.3	0.797	0.930	0.929	0.540
0.4	1.098	1.289	1.287	0.745
0.5	1.440	1.699	1.695	0.981
0.6	1.841	2.187	2.181	1.260
0.7	2.338	2.802	2.792	1.610
0.8	3.003	3.634	3.614	2.083
0.9	4.000	4.901	4.864	2.800
1.0	5.920	7.358	7.282	4.198
1.1	20.804	21.719	21.369	16.353

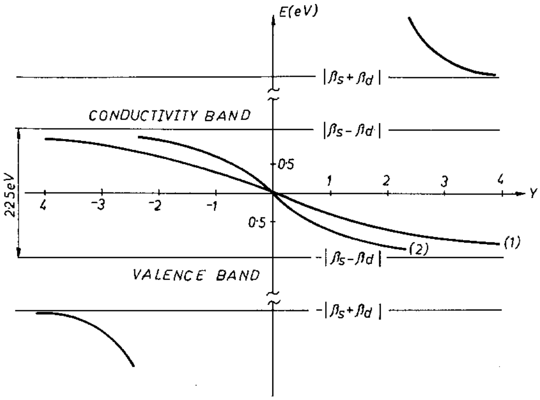


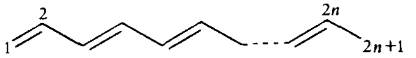
Fig. 2. Graph of function $y=F_1(E)$ (Eq. (10)). The results are obtained for the model with bondlength alternation $\Delta_{\text{corr}}=0$; $\beta_0=3.39$ eV; $\Delta E_\infty=2.25$ eV [11]; (1) $\eta_x=1.0$, (2) $\eta_x=0.7$

Assuming that ΔE_∞ of polyenes is equal to 2.25 eV [11], the calculated value for the transition energy of unsubstituted polymethines $\Delta\varepsilon_{\infty,\text{opt}}=1.125$ eV coincides with the experimental one (see Table 1).

4. Disubstituted Polyenes

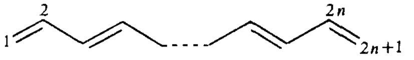
The band structure of symmetrical ($X=Y$) α, ω-disubstituted even polyenes was already treated in the first communication [16], where the problem is solved by means of the direct application of the AMO method formalism to infinite systems. For this reason here will be considered only the odd α, ω-disubstituted polyenes, including the systems I, II, III, which are of particular interest for the present study.

The position of the levels in the gap depends materially on the choice of alternation model for the unsubstituted odd polyene. The results for a substituted non-symmetrical $(2n+1)$-polymethine with bond alternation of type



(A)

differ from those for a symmetrical (C_{2v} group) one



(B)

Assuming the presence of bond alternation, the symmetrical model is adequate to the real system, so model (B) will be treated below. In order to simplify the formalism, we shall consider the extreme case without correlational correction ($\delta_\gamma = 0$).

The MOs of a substituted symmetrical polymethine with $2n+1=4m+3$ AOs could be written as

$$\phi_l(A_2) = c(\varphi_x + \varphi_x') + \sum_{k=0}^{n} C_{l,2n+1}\psi_{2k+1} \tag{11}$$

$$\phi_l(B_1) = c(\varphi_x - \varphi_x') + \sum_{k=1}^{n} c_{l,2k}\psi_{2k}. \tag{11a}$$

In the case of polymethines with $4m+1$ AOs the nonbonding MO belongs to the irreducible representation B_1.

It follows from the above expressions for the MOs that the problem for the symmetrical disubstituted odd polymethines turns into two effective problems: for a monosubstituted even polymethine and for a monosubstituted odd one. The equations corresponding to the MOs (11) and (11a) are Eqs. (Ib) and (Ic) (Appendix I).

Eq. (Ib), corresponding to the irreducible representation A_2 (Eq. (11)) leads to ($\delta\gamma = 0$)

$$E\left\{(h\beta_0 - E) + \eta_x^2\beta_0^2\frac{2E}{\pi}\int_0^{\pi}\frac{\sin^2 \operatorname{arctg}\dfrac{\sin\omega_k}{e(\omega_k)-\cos\omega_k}}{E^2-[\frac{1}{4}\Delta E_\infty^2 + 4\beta_0^2\cos^2\omega_k]}\,\mathrm{d}\omega_k\right\} + \eta_x^2\beta_0^2 c_{1,n+1}^2 = 0. \tag{12}$$

If $n\to\infty$, $c_{1,n+1}\to 0$ and Eq. (12) has a root $E=0$. The other equation (11a), corresponding to the representation B_1 is

$$h\beta_0 - E + \eta_x^2\beta_0^2\frac{2E}{\pi}\int_0^{\pi}\frac{\sin^2 \operatorname{arctg}\dfrac{\sin\omega_k}{e(\omega_k)-\cos\omega_k}}{E^2-[\frac{1}{4}\Delta E_\infty^2 + 4\beta_0^2\cos^2\omega_k]}\,\mathrm{d}\omega_k = 0 \tag{12a}$$

The roots of (12) and (12a), defining the position of the impurity levels in the gap, depend on the value of parameter h. In all cases Eq. (12) has a root $E=0$.

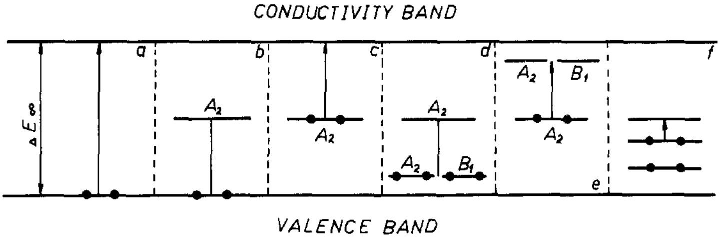


Fig. 3. Position of the levels in the gap and scheme of the electron transitions of disubstituted odd polyenes with $N=4m+3$ AOs. In the case of polymethines with $N=4m+1$ AOs the non-bonding MO belongs to the irreducible representation B_1.

a. even, unsubstituted polyene
b. carbocation of an unsubstituted odd polymethine
c. carboanion of an unsubstituted odd polymethine
d. symmetrical disubstituted odd polymethine

$h_x > 0 \quad (X \in \mathrm{N}, \mathrm{O})$

e. symmetrical disubstituted odd polymethine

$h_x < 0 \quad (X = \mathrm{B})$

f. asymmetrical ($X \neq Y$) disubstituted odd polymethine

$h_x > 0; \quad h_y > 0 \quad (X \equiv \mathrm{N},\ Y \equiv \mathrm{O})$.

The results, by using *d-*, *e- and f-*, are obtained using model B for the unsubstituted odd polyene

When the substituent is an atom with greater electronegativity than the carbon atom – N or O, $h > 0$. In this case Eqns. (12, 12a) have two equal roots, corresponding to two degenerate levels situated below the Fermi level, i.e. in the semigap to the bottom of the gap (Fig. 3). For substituents N (polymethinecyanines) or O (oxonoles) with $2n+1$ AOs, the number of π-electrons is $2n+2$. As the number of π-electrons in the valence band is equal to $2n-2$, the degenerate MOs in the gap are occupied.

Using the parameters (see Table 3 and Fig. 2) $\beta_0 = 3.39$ eV, $t = 0.7188$, $\Delta E_\infty = 2.25$ eV, the value $h_{\ddot{N}} = 1.5$ [43] accepted in the method of Hückel can be taken for h_N and the graphical solution of Eqs. (12, 12a) give the values $E_1 = 0$ and $E_2 = E_3 = -0.7$ eV ($\eta_{CN} = 1$) or $E_1 = 0$, $E_2 = E_3 = -0.9$ eV ($\eta_{CN} = 0.72$). Thus, for the transition energies $\Delta\varepsilon_{\infty,\mathrm{opt}}$ we have the values: 0.7 eV ($\eta_{CN} = 1$) or 0.9 eV ($\eta_{CN} = 0.72$). If $h_{\ddot{O}}$ is assumed to be equal to 2 [43], the respective transition energies are: 0.8 eV ($\eta_{C\ddot{O}} = 1$) or 1.0 eV ($\eta_{C\ddot{O}} = 0.72$).

The obtained values are in qualitative agreement with the extrapolated values for the longest wavelength transition energies of polymethinecyanines (I) and oxonoles (II) (see Table 1). In the framework of the models used, it is impossible to obtain for the longest wavelength optical transition energy values larger than halfwidth the gap.

An essential fact in all the cases treated is the non-zero longest wavelength transition energy.

When the electronegativity of the substituent atom is lower than that of the carbon atom ($h < 0$ as it is for the diboronpolymethines), except the root $E = 0$, Eqs. (12, 12a) have two equal roots, corresponding to two degenerate levels, situated above the Fermi level (Fig. 3e). A system of this type with $2n+1$ AOs possesses $2n$ π-electrons, so the non-bonding MO is occupied.

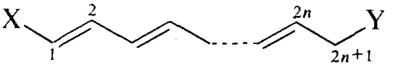
The results for symmetrical disubstituted polyenes obtained by means of the AMO formalism in the case $\Delta_{\mathrm{corr}} \neq 0$ and $\Delta_{\mathrm{geom}} \neq 0$ are qualitatively the same.

A typical example for asymmetrical α, ω-disubstituted polyenes are the merocyanines

$$R_2N\overset{\cdots}{-}(CH\overset{\cdots}{-}CH)_n\overset{\cdots}{-}CH\overset{\cdots}{-}O.$$

Due to the very strong influence of the solvent on the position of the longest wavelength optical ($\pi \rightarrow \pi^*$) transition [5], the evaluation of $\Delta\varepsilon_{\infty,\mathrm{opt}}$ by means of an extrapolation of the experimental data $\Delta\varepsilon_n$ leads to quite different and, therefore, unreliable quantities.

Equation (Ia) (Appendix I) in the case



turns into ($n \rightarrow \infty$)

$$\begin{aligned}
&\left(1-\frac{\alpha_x}{E}\right)\left(1-\frac{\alpha_Y}{E}\right)+(\alpha_y-E)\eta_x^2\beta_0^2\int_0^{\pi/2}\frac{2c_1^2(\omega_k)}{E^2-E^2(\omega_k)}\,\mathrm{d}\omega_k\\
&\quad+(\alpha_x-E)\eta_y^2\beta_0^2\int_0^{\pi/2}\frac{2c_N^2(\omega_k)}{E^2-E^2(\omega_k)}\,\mathrm{d}\omega_k\\
&\quad+\eta_x^2\eta_y^2\beta_0^4\left\{\int_0^{\pi/2}\frac{2c_1^2(\omega_k)}{E^2-E^2(\omega_k)}\,\mathrm{d}\omega_k\right\}\left\{\int_0^{\pi/2}\frac{2c_N^2(\omega_k)}{E^2-E^2(\omega_k)}\,\mathrm{d}\omega_k\right\}\\
&\quad-\eta_x^2\eta_y^2\beta_0^4\left\{\int_0^{\pi/2}\frac{2c_1(\omega_k)c_N(\omega_k)}{E^2-E^2(\omega_k)}\,\mathrm{d}\omega_k\right\}^2\\
&\quad=\left(1-\frac{\alpha_x}{E}\right)\left(1-\frac{\alpha_y}{E}\right)+F_1(E)=0.
\end{aligned}\tag{13}$$

In the derivation of the above Eq. (13) the coefficients of the NBMOs are neglected

$$\eta^2\beta_0^2c_{1(N),n+1}^2 \xrightarrow{n\rightarrow\infty} 0.$$

The analysis of Eq. (13) shows that it has two different roots $E_2 \neq E_3 \neq 0$, situated below ($h_{x,y} > 0$), above ($h_{x,y} < 0$) or on both sides ($h_x < 0$, $h_y > 0$) of the NBMO (Fig. 3f).

The applied formalism makes it hard to examine the character of the impurity states in the gap, i.e. to decide to what extent these are localised round a definite AO [44].

Starting from general considerations [44, 45] and grounding on the studies of Ukrainsky and Kwentsel [37] in the treatment of monosubstituted polyenes, one may expect the levels in the gap to be localized. For example, the NBMO of odd polyenes is localized.

The analytic solution, using the method of the finite differences [20], of the problem for polymethines with $2n+1=4m+3$ AOs results in the following expressions for the orbital coefficients

$$c_{2l}=0, \qquad c_{2l+1}=\frac{1}{\sqrt{2}}(-s)^{l}\sqrt{\frac{s^{2}-1}{s^{2l}+1}}$$

$$s=\beta_{d}/\beta_{s} \quad (\beta_{d}\neq\beta_{s}); \qquad l=0,1,2,\ldots,n,$$

i.e. the modulus of the orbital coefficient is a monotone function.

In the general case of substituted polymethines, the method developed by Lifschitz [46] and generalized by Koutecky [47] (see also Refs. 38, 39, 45) could give us an analytical solution of the problem for the orbital coefficients. As the character of such a study does not correspond to the problem treated here, the results of this research will be reported further [48].

It is interesting to note, that the substitution of small molecules with regular structure (polyenes, anulenes, etc.) also results in the appearance of levels with a local character in the gap.

Appendix I

Let us denote by $\psi_k=\sum_{\mu} c_{k\mu}\varphi_{\mu}$ the MOs of an arbitrary unsubstituted system and by φ_x and φ_y – the AOs of the substituents X and Y, connected with the system. Representing the MOs of the substituted system by means of the LCMO method

$$\phi_l=c_{lx}\varphi_x+c_{ly}\varphi_y+\sum_{k} c_{lk}\psi_k$$

and introducing

$$\langle\varphi_x|H|\varphi_x\rangle=\alpha_x \qquad \langle\varphi_y|H|\varphi_y\rangle=\alpha_y$$

$$\langle\varphi_x|H|\varphi_y\rangle=0 \qquad \langle\psi_k|H|\psi_k\rangle=E_k$$

$$\langle\varphi_x|H|\psi_k\rangle=d_{xk}=c_{kp}\beta_{px}=c_{kp}\eta_x\beta_0$$

$$\langle\varphi_y|H|\psi_k\rangle=d_{yk}=c_{kq}\beta_{qy}=c_{kq}\eta_y\beta_0$$

(the indices p and q mark the atoms connected with the substituents X and Y) the energy matrix is

$$\begin{pmatrix} \alpha_x-E & 0 & d_{x1} & d_{x2} & \cdots & d_{xN} \\ 0 & \alpha_y-E & d_{y1} & d_{y2} & \cdots & d_{yN} \\ d_{x1} & d_{y1} & E_1-E & 0 & \cdots & 0 \\ d_{x2} & d_{y2} & 0 & E_2-E & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ d_{xN} & d_{yN} & 0 & 0 & \cdots & E_N-E \end{pmatrix}$$

The secular determinant, corresponding to the energy matrix, leads to the equation

$$(\alpha_x-E)(\alpha_y-E)+(\alpha_x-E)\sum_k \frac{d_{yk}^2}{E-E_k}+(\alpha_y-E)\sum_k \frac{d_{xk}^2}{E-E}$$

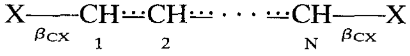
$$+\sum_k \sum_{l\neq k} \frac{d_{xk}^2 d_{yk}^2 - d_{xk}d_{yk}d_{xl}d_{yl}}{(E-E_k)(E-E_l)} = (\alpha_x-E)(\alpha_y-E)+F(E)=0. \qquad \text{(Ia)}$$

Eq. (Ia) could be also obtained using the one-partical classical function of Green [46, 47, 49].

Eq. (Ia) is a general one – it refers to arbitrary systems. Its use is expedient for systems with familiar analytical form of the orbital coefficients and the energies, in this number many one-dimensional systems as polyenes, etc.

For high values of N the sums in Eq. (Ia) turn into integrals, easy for numerical calculation. The roots, corresponding to levels in the gap, could be found graphically as crossing points of the curves $F(E)$ and $(\alpha_x-E)(\alpha_y-E)$.

In the case of symmetrical α, ω-disubstituted polyenes ($X = Y$)



$$\underset{\beta_{CX}}{\text{X}\text{——}}\underset{1}{\text{CH}}\cdots\underset{2}{\text{CH}}\cdots\;\cdots\;\cdots\underset{N}{\text{CH}}\underset{\beta_{CX}}{\text{——X}}$$

$\alpha_x = \alpha_y = \alpha$

$d_{kx} = d_{ky} = 2c_{k1}\beta_{cx} = 2c_{k1}\eta_x\beta_0$

Eq. (Ia) could be separated into

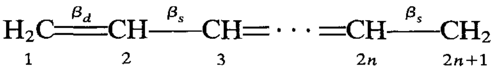
$$(\alpha-E)+2\eta_x^2\beta_0^2 \sum_k \frac{c_{2k+1,1}^2}{E-E_k}=0 \qquad \text{(Ib)}$$

$$(\alpha-E)+2\eta_x^2\beta_0^2 \sum_k \frac{c_{2k,1}^2}{E-E_k}=0. \qquad \text{(Ic)}$$

The summation in Eq. (Ib) is over the MOs belonging to the irreducible representation B_g for even polyenes, respectively to B_1 for odd ones. Analogous is the situation with Eq. (Ic), where in dependance of the methine groups number, the summation is over MOs belonging respectively to the irreducible representations A_u and A_2.

Appendix II

In Hückel approximation the energies of a polyene with $N = 2n + 1$ AOs



$$\underset{1}{H_2C}\overset{\beta_d}{=\!=}\underset{2}{CH}\overset{\beta_s}{-}\underset{3}{CH}=\cdots=\underset{2n}{CH}\overset{\beta_s}{-}\underset{2n+1}{CH_2}$$

are [33, 36]

$$e(\omega_k) = \pm\sqrt{(\beta_s - \beta_d)^2 + 4\beta_s\beta_d \cos^2 \omega_k}. \tag{IIa}$$

For sake of simplicity the Coulomb integral of the carbon atom is accepted to be $\alpha_C = 0$.

When $n \gg 1$

$$0 \le \omega_k \le \pi/2.$$

If the orbital coefficients of the polyene are [16]

$$c_{k\mu} = A_k \sin(\omega_k \mu + \varphi)$$

taking into account the boundary conditions

$$c_{k1}[\alpha_c - e(\omega_k)] + c_{k2}\beta_d = 0$$

$$c_{k,2n+1}[\alpha_c - e(\omega_k)] + c_{k,2n}\beta_s = 0$$

or

$$e(\omega_k)\sin(\omega_k + \varphi) \pm \beta_d \sin(2\omega_k + \varphi) = 0$$

$$e(\omega_k)\sin[(2n+1)\omega_k + \varphi] \pm \beta_s \sin(2n\omega_k + \varphi) = 0$$

(sign "+" refers to the bonding MOs and "−" to the antibonding ones) is obtained

$$\omega_k + \varphi = \operatorname{arctg}\frac{\beta_d \sin \omega_k}{e(\omega_k) - \beta_d \cos \omega_k}$$

$$(2n+1)\omega_k + \varphi = \operatorname{arctg}\frac{\beta_s \sin \omega_k}{e(\omega_k) - \beta_s \cos \omega_k}.$$

For the orbital coefficients c_{k1} and $c_{k,2n+1}$ we have respectively

$$c_{k1} = \sqrt{\frac{2}{N}} \sin \operatorname{arctg}\frac{\beta_d \sin \omega_k}{e(\omega_k) - \beta_d \sin \omega_k}$$

$$c_{k,2n+1} = \sqrt{\frac{2}{N}} \sin \operatorname{arctg}\frac{\beta_s \sin \omega_k}{e(\omega_k) - \beta_s \sin \omega_k}. \tag{IIb}$$

In the case of even polyenes ($N = 2n$), $c_{k,2n} = (-1)^{k+1} c_{k1}$.

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