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Band Structure of Even and Ions of Odd Polyenes

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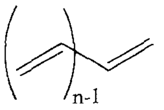
The analysis of experimental data for singlet transitions (ΔE_n) of even polyenes (I), cations (II) and anions (III) of odd polyenes show that for infinite chains $\Delta E_\infty(\mathrm{I})/\Delta E_\infty(\mathrm{II}) = \Delta E_\infty(\mathrm{I})/\Delta E_\infty(\mathrm{III}) = 2:1$. It is shown that the energy gap is equal for the three systems. In cases (II) and (III) there is a level (NBMO) in the gap which is vacant in (II) and occupied in (III). That is why the first optical transition in (II) and (III) depends on the semiwidth of the gap.

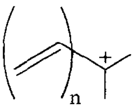
Key words: Polyenes, even, band structure of ~ – Polyenes, ions of odd, band structure of ~

1. Introduction

Even polyenes (I) and the cations of odd polyenes (II), the allylcarbenium cations,



I



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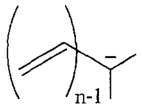


III

differ considerably in their spectral properties, not only for low values of n [1], but also in the asymptotic case when $n \to \infty$ (see Fig. 1 and Table 1). The energy gap $\Delta E_\infty(\mathrm{I})$ for even unsubstituted polyenes, equal to the energy of the longest-wavelength optical transition $\Delta E_{\infty,\mathrm{opt}}(\mathrm{I})$, is evaluated at 2.25 eV [6]. A similar value is obtained for the α-, ω-methyl substituted polyenes (see Table 1). In the paper of Sorensen, where spectra of allylcarbenium cations [3] are treated, the following dependence is given for the wavelengths of the longest-wavelength transition: $\lambda(\text{Å}) = 3305 + 655\,n$ (which is analogous to Broocker's rule for polymethyncyanines [7–9]). According to the above dependence, when $n \to \infty$,

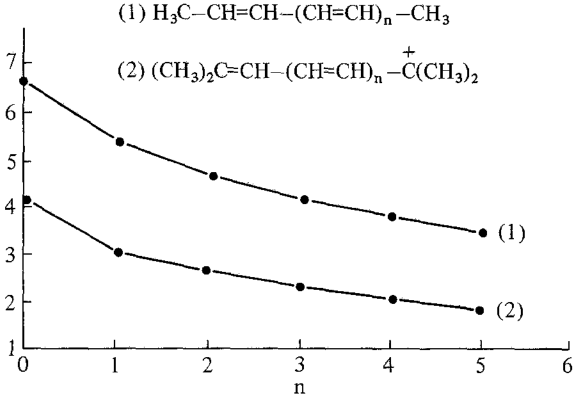


Fig. 1. Dependence of the energy of the longest-wavelength singlet transitions for even polyenes and cation of odd polyenes on the number of vinylene groups

$\lambda \rightarrow \infty$, i.e. the energy of the longest-wavelength transition $\Delta E_{\infty,\mathrm{opt}}(\mathrm{II}) \rightarrow 0$ respectively the energy gap $\Delta E_{\infty}(\mathrm{II}) \rightarrow 0$. However, the statistical treatment of the experimental data (see Table 1) gives a finite value for $\Delta E_{\infty,\mathrm{opt}}(\mathrm{II}) \sim 1$ eV. Hence, the ratio of the energies of the longest-wavelength transition for the two classes of polyenes is:

$$\Delta E_{\infty,\mathrm{opt}}(\mathrm{I}):\Delta E_{\infty,\mathrm{opt}}(\mathrm{II}) \approx 2{:}1 \tag{1}$$

Having in mind that the effects of the solvent and of the substituents were not taken into account when the asymptotic behaviour of $\Delta E_{\infty}(\mathrm{I})$ and $\Delta E_{\infty,\mathrm{opt}}(\mathrm{II})$ was being determined, the precising of ratio (1) would be unrealistic.

There are no experimental data for the optical transitions of the anions of odd polyenes (III). However, there are some data for the anions of odd α-, ω-diphenylpolyenes [4]. Their extrapolation (see Table 1) leads to values of $\Delta E_{\infty,\mathrm{opt}}(\mathrm{III})$ which are also of the order of 1 eV, as in case (II). In view of the fact that for large values of n the boundary effects may be neglected, we can consider that Eq. (1) is satisfied by the anions of odd polyenes too.

The existence of the energy gap in the spectrum of one-particle excitations in even polyenes, which coincides with the energy of the longest-wavelength optical transition, is determined by the geometry factor (the presence of alternation of the bond lengths) and the electron correlation [10–20].

Table 1. Experimental values of the longest-wavelength singlet transitions (in eV) for even I, cations of odd polyenes II and anions of odd α-, ω-diphenyl polyenes III

n	I[a]	II[b]	III[c]
0	6.76	4.07	2.47
1	5.46	3.13	2.32
2	4.71	2.67	2.18
3	4.14	2.31	2.07
4	3.80	2.04	1.96
5	3.52	1.83	–
∞	2.21[d]	1.10[d]	1.21[d]

[a] I: $H_3C{-}CH{=}CH{-}(CH{=}CH)_n{-}CH_3$, cf. Ref. [2].

[b] II: $(CH_3)_2C{=}CH{-}(CH{=}CH)_n{-}\overset{+}{C}(CH_3)_2$, cf. Ref. [3].

[c] III: $C_6H_5{-}\overset{-}{C}H{-}(CH{=}CH)_n{-}C_6H_5$, cf. Ref. [4].

[d] Values calculated by means of Pade approximation, cf. Ref. [5].

2. One-Electron Approximation

The purpose of the present paper is to determine the origin of the gap of the ions of odd polyenes, resp. to find a physical explanation of ratio (1).

In Hückel's approximation, the MO energies of a polyene with N atomic orbitals (AO), considering ideal geometry (equality of all resonance integrals), are given by the formula [21]:

$$e_k = \alpha + 2\beta \cos \frac{\pi}{N+1} k, \quad k = 1, 2, \ldots, N. \tag{2}$$

For odd polyenes ($N = 2n + 1$), the $(n + 1)$ st MO is nonbonding. The energy of the longest-wavelength transition for (II) and (III) is identical and equal to [4]:

$$\begin{aligned} \Delta E_{\mathrm{N,\,opt}}(\mathrm{II}) &= e_{n+1} - e_n = \Delta E_{\mathrm{N,\,opt}}(\mathrm{III}) \\ &= e_{n+2} - e_{n+1} = -2\beta \cos \frac{n\pi}{2n+2} \xrightarrow{n \to \infty} 0 \end{aligned} \tag{3}$$

The energy of the first transition for an isoelectronic even polyene ($N = 2n$) is equal to:

$$\Delta E_{\mathrm{N,\,opt}}(\mathrm{I}) = e_{n+1} - e_n = -4\beta \sin \frac{\pi}{4n+2} \xrightarrow{n \to \infty} 0 \tag{4}$$

When $n \to \infty$, the ratio of (4) to (3)

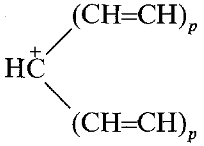
$$2 \lim_{n \to \infty} \frac{\sin \dfrac{\pi}{4n+2}}{\cos \dfrac{n\pi}{2n+2}} \longrightarrow 1 \tag{5}$$

Ratio (5) disagrees with (1) not only formally; according to (3) and (4): $\Delta E_{\infty}(\mathrm{I}) \equiv \Delta E_{\infty,\mathrm{opt}}(\mathrm{I}) \to \Delta E_{\infty,\mathrm{opt}}(\mathrm{II}) \to \Delta E_{\infty,\mathrm{opt}}(\mathrm{III}) \to 0$, while the experiment gives finite values for the energies of the optical transitions. There is bond order alternation both for even polyenes [21] and for ions of odd polyenes. The expression for the bond order of an odd polyene with N AO, obtained with all resonance integrals equal, is of the type (identical for cations and anions):

$$\begin{aligned} p_{\mu,\mu+1} &= \frac{2}{N+1} \left[\frac{\sin A}{2 \sin B} - \cos \frac{\pi}{4} (2\mu + 1) \frac{\sin (2\mu + 1)A}{\sin (2\mu + 1)B} \right] \\ A &= \frac{N-1}{N+1} \frac{\pi}{4}, \qquad B = \frac{\pi}{2N+2}. \end{aligned} \tag{6}$$

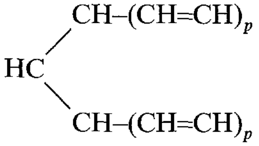
From the C_{2v} symmetry of all-*trans* configuration of the polymethyne chain and expression (6), it follows that the cations of odd polyenes can be divided in two classes:

$4p+1$ -polyenes ($p = 1, 2, 3,\ldots$)



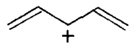
$$\overset{+}{\mathrm{HC}}\begin{matrix}\nearrow (\mathrm{CH{=}CH})_p\\ \searrow (\mathrm{CH{=}CH})_p\end{matrix}$$

$4p+3$ -polyenes $p = 0, 1, 2,\ldots$)

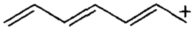


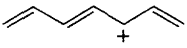
$$\mathrm{HC}\begin{matrix}\nearrow \mathrm{CH{-}(CH{=}CH)}_p\\ \searrow \mathrm{CH{-}(CH{=}CH)}_p\end{matrix}$$

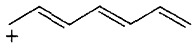
Completely analogous is the classification that can be made for the anions of odd polyenes, in which the alternation of bond orders is the same. This classification of the ions of odd polyenes is not formal. In the case of $4p+1$ polyenes (e.g. pentamethyn cation) there exists an ionic Kekule structure with the same C_{2v} symmetry



as the molecule. In the case of $4p+3$ polyenes (e.g. heptamethyn cation), none of Kekule's ionic formulae possesses C_{2v} symmetry, as can be seen from the following examples:







Quite similar is the situation for the linear polyacenes with an even and odd number of benzene rings, where a considerable difference exists in the stability of the Hartree–Fock solutions for finite values of n, as is shown in the work of Paldus and Čižek [22].

The MO of a polymethyn chain with $2n+1$ AO and C_{2v} symmetry

$$\begin{array}{l}
\mathrm{C{=}C{-}\cdots C{=}C{-\!\!-}C{-}\cdots C{-}C{-}C{-}\cdots C{=}C}\\
1\;\;2\quad 2l-1\;\;2l\quad 2l+1\quad n\;\;n+1\;\;n'\quad 2'\;\;1'
\end{array}$$

belong to the irreducible representations B_1 and A_2 and are of the type:

$$\Psi_k(B_1) = c_{n+1}\varphi_{n+1} + \sum_1^n c_{k\mu}(\varphi_\mu + \varphi'_\mu)$$

$$\Psi_k(A_2) = \sum_1^n c_{k\mu}(\varphi_\mu - \varphi'_\mu)$$

The secular equations for both classes of MO are:

$$c_{2l}(\alpha - e_k) + \beta_d c_{2l-1} + \beta_s c_{2l+1} = 0$$
$$c_{2l+1}(\alpha - e_k) + \beta_s c_{2l} + \beta_d c_{2l+2} = 0$$

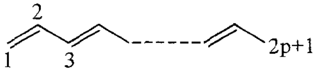
By means of the method of finite differences, from the above equations for MO energies (B_1 and A_2), one can easily obtain:

$$e_k = \alpha \pm \sqrt{\beta_s^2 + \beta_d^2 + 2\beta_s\beta_d \cos \omega_k}$$
$$\omega_k = \frac{4\pi}{2n+2} k \tag{7}$$

In order to determine the parameter k, from the secular equations, the boundary conditions and (7), we obtain the transcendental equation: $\beta_s \sin ik = \beta_d \sin jk$ (i and j are integers), which is identical to the equation derived by Lennard-Jones for even polyenes [23]. It is easily solved only in the case of $4p + 3$ polyenes for MO with A_2 symmetry, where ($4p + 3 = 2n + 1$):

$$k = 1, 2, \ldots, p.$$

In this case Eq. (7) coincides with the formula given by Rebane [24] for odd polyenes of the following structure:



For $4p + 3$ polyenes the nonbonding MO also belongs to the irreducible representation A_2. For this MO the orbital coefficients with even indices $c_{2l} = 0$ and those with odd indices:

$$c_{2l+1} = (-t)^l/\sqrt{2}\sqrt{\frac{t^2-1}{t^{2p+2}-1}}\ \sqrt{},\ t = \beta_d/\beta_s,\ (\beta_s \neq \beta_d) \tag{8}$$

From (8) and the condition for alternancy of the system, we obtain for the electron charge of the atoms the expression:

$$q_{2l} = 1 \qquad q_{2l+1} = 1 \mp \frac{t^{2l}}{2} \cdot \frac{t^2-1}{t^{2p+2}-1} \quad (l = 0, 1, 2, \ldots, p) \tag{9}$$

The minus sign related to cations and the plus sign to the anions.

In the case of $4p + 1$ polyenes the NBMO is with B_1 symmetry. This follows from the development of the secular determinant, and leads to a polynomial of the type $(\alpha - e) \cdot P_{2p}[(\alpha - e)^2]$, where $P_{2p}[(\alpha - e)^2]$ is a polynomial containing only even powers of $(\alpha - e)$.

The orbital coefficients of the NBMO are $c_{2l} = 0$, and:

$$c_{2l+1} = 1 \mp (-t)^l \sqrt{\frac{t^2-1}{t^{2p+2} + t^{2p} - 2}} \tag{10}$$

The charges respectively:

$$q_{2l} = 1 \qquad q_{2l+1} = 1 \mp t^{2l} \frac{t^2-1}{t^{2p+2} + t^{2p} - 2} \quad (l = 0, 1, 2, \ldots, p) \tag{11}$$

Depending on whether the alternation in the bond lengths is taken into account or not, the charge distribution in the ions of the odd polyenes differs considerably. The treatment of ideal geometry ($\beta_s = \beta_d$) gives for the electron charges of atoms with even indices [21]: $q_{2l} = 1$, and those of atoms with odd indices (for a polymethyn chain with $2n + 1$ AO):

$$q_{2l+1} = 1 \mp \frac{1}{n+1}$$

When the alternation is taken into account, the values of the electron charges alter monotonously with the change of 1 for both classes of polyenes. In the asymptotic case ($p \to \infty$) for $4p + 3$ polyenes

$$q_1 = 1, \qquad q_{2p+1} = 1 \mp \frac{t^2 - 1}{t^2} \tag{12}$$

and for $4p + 1$ polyenes

$$q_1 = 1, \qquad q_{2p+1} = 1 \mp \frac{t^2 - 1}{t^2 + 1} \tag{13}$$

For large values of p, the boundary effects can be neglected, hence ω_k in (7) for both types of polyenes alters in the interval

$$0 \leqslant \omega_k \leqslant \pi.$$

Consequently, the energy gap for both cases is identical and equal to:

$$\Delta E_\infty(\mathrm{I}) = \Delta E_\infty(\mathrm{II}) = \Delta E_\infty(\mathrm{III}) = 2|\beta_d - \beta_s| = \Delta_{\mathrm{geom}}$$

Since the odd polyenes also possess a NBMO, the energy of the longest-wavelength transition for ions of odd polyenes will be equal to the halfwidth of the gap

$$\Delta E_{\infty,\mathrm{opt}}(\mathrm{II}) = \Delta E_{\infty,\mathrm{opt}}(\mathrm{III}) = 1/2\Delta E_{\infty,\mathrm{opt}}(\mathrm{I}) = 1/2\Delta_{\mathrm{geom}} = |\beta_d - \beta_s| \tag{14}$$

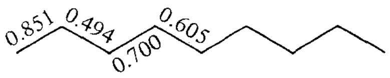
It is exactly twice less than the energy of the longest-wavelength transition for an even polyene [10], which is equal to the energy gap:

$$\Delta E_{\infty,\mathrm{opt}}(\mathrm{I}) = \Delta E_\infty(\mathrm{I}) = 2|\beta_d - \beta_s| = \Delta_{\mathrm{geom}} \tag{15}$$

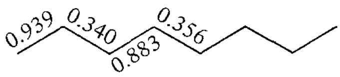
where the nonbonding MO is absent. From (14) and (15), it follows that (1) is satisfied:

$$\frac{\Delta E_{\infty,\mathrm{opt}}(\mathrm{I})}{\Delta E_{\infty,\mathrm{opt}}(\mathrm{II})} = 2/1 \tag{16}$$

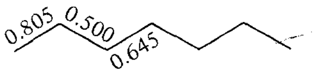
The geometry components of the energy gap satisfy Eq. (1) on condition that bond order alternation is equal for even and ions of odd polyenes. Equal or similar alternation for even and ions of odd polyenes is physically acceptable in the asymptotic case, taking into account not only the expressions for bond orders obtained by Hückel's method, but also the numerical values obtained by means of the PPP method [25, 26]. This can be seen from the molecular diagrams of the cations of nonamethyn:



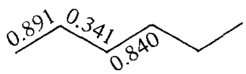
and octatetraene



The calculations have been done with the same parametrization as in paper [27]. The above molecular diagrams have been obtained without taking into account the configuration interaction. The molecular diagrams of the cations of heptamethyn:



and hexatriene



have been obtained (using the same parametrization) by means of the SCF-CI method, taking into account the electron correlation through the inclusion of all biexcited configurations. As can be seen from the molecular diagrams, bond order alternation is clearly marked both for even polyenes and for cations of odd polyenes. No firm conclusion about the geometry in the asymptotic case can be made on the basis of the bond order alternation of the short polyenes. The close values of bond orders for both classes of polyenes however, give us reason to suppose identical or similar geometry when $n \to \infty$, in both cases.

Ratio (1) can be satisfied including electron correlation too (see the text below), only if an identical or very similar bond order alternation is presumed.

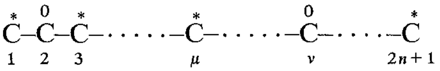
3. Influence of the Electron Correlation

However, the presence of an energy gap in the case of even polyenes cannot be explained by means of the geometry factor alone. A review of the studies on even polyenes [10–20] shows that with these, as with all quasi-monodimensional systems with delocalized electrons, the electron correlation plays an important part in determining the energy gap. If by Δ_{corr} we denote the factor determined by the electron correlation, then the width of the energy gap is given by the expression:

$$\Delta E_{\infty} = \sqrt{\Delta^2_{\text{corr}} + \Delta_{\text{geom}}} \qquad (17)$$

The above equation, derived at first for polyenes only [12, 17], is valid for any arbitrary homonuclear systems [28, 29] with a closed shell. It was derived on condition that the electron charge q of the atoms is equal to 1. This condition is not fulfilled for the ions of odd polyenes, but it can be shown, however, that Eq. (17) is valid for them too.

The effects of electron correlation can be taken into account by means of the extended Hartree–Fock method in the version of the alternant molecular orbitals (AMO) [30–32]. The MO of an odd polyene (cation) with $2n + 1$ AO:



$$\underset{1}{\overset{*}{\mathrm{C}}}-\underset{2}{\overset{0}{\mathrm{C}}}-\underset{3}{\overset{*}{\mathrm{C}}}-\cdots\cdots-\underset{\mu}{\overset{*}{\mathrm{C}}}-\cdots\cdots-\underset{\nu}{\overset{0}{\mathrm{C}}}-\cdots\cdots-\underset{2n+1}{\overset{*}{\mathrm{C}}}$$

can be expressed as follows:

bonding MO

$$\psi_k = \overset{*}{\sum} \overset{*}{c}_{k\mu}\overset{*}{\varphi}_\mu + \overset{0}{\sum} \overset{0}{c}_{k\nu}\overset{0}{\varphi}_\nu$$

antibonding MO

$$\psi_{\bar{k}} = \overset{*}{\sum} \overset{*}{c}_{\bar{k}\mu}\overset{*}{\varphi}_\mu - \overset{0}{\sum} \overset{0}{c}_{k\nu}\overset{0}{\varphi}_\nu$$

According to the AMO method the wave function of the polyene cation may be represented in the form:

$$\Phi = \frac{1}{\sqrt{2n!}} |\psi_1^\alpha \alpha \psi_2^\alpha \alpha \ldots \psi_n^\alpha \alpha \psi_1^\beta \beta \ldots \psi_n^\beta \beta| \tag{18}$$

where ψ_k^α and ψ_k^β are AMO with α (↑) and β(↓) spin:

$$\begin{aligned} \psi_k^\alpha &= \sin\theta_k \overset{*}{\sum} + \cos\theta_k \overset{0}{\sum} \\ \psi_k^\beta &= \cos\theta_k \overset{*}{\sum} - \sin\theta_k \overset{0}{\sum} \end{aligned} \tag{19}$$

The vacant NBMO is not included in expression (18).

The secular equations for AMO with α spin (the secular equations for AMO with β spin are analogous and their solution for the given system leads to the same result) will take the form:

$$\begin{aligned} &\sin\theta_k \overset{*}{c}_{k\mu}(\overset{*}{F}{}^\alpha_{\mu\mu} - E_k^\alpha) + \cos\theta_k \sum_\zeta c_{k\zeta}F^\alpha_{\mu\zeta} = 0 \\ &\sin\theta_k \sum_\zeta c_{k\zeta}F^\alpha_{\nu\zeta} + \cos\theta_k \overset{0}{c}_{k\nu}(\overset{0}{F}{}^\alpha_{\nu\nu} - E_k^\alpha) = 0 \end{aligned} \tag{20}$$

In PPP- [25, 26] and Hubbard approximation [33] the matrix elements of the HF-operator in the unrestricted HF method are [28]:

$$F^\sigma_{\mu\nu} = \beta_{\mu\nu}, \quad \sigma \in \alpha, \beta \tag{21}$$
(μ and ν are neighbours)

$$F^\alpha_{\mu\mu(\nu\nu)} = \alpha - \gamma P^\sigma_{\mu\mu(\nu\nu)} + {}^\gamma[P^\alpha_{\mu\mu(\nu\nu)} + P^\beta_{\mu\mu(\nu\nu)}] \tag{21a}$$

where

$$\begin{aligned}
\overset{*}{P}{}^{\alpha}_{\mu\mu} &= 2\sum_{k}^{n} \overset{*}{c}{}^{2}_{k\mu}\sin^2\theta_k = 1/2q_\mu - \sum_{k}^{n} \overset{*}{c}{}^{2}_{k\mu}\cos 2\theta_k = 1/2q_\mu - \delta_\mu \\
\overset{*}{P}{}^{\beta}_{\mu\mu} &= 1/2q_\mu + \delta_\mu \\
\overset{0}{P}{}^{\alpha}_{\nu\nu} &= 1/2q_\nu + \delta_\nu \\
\overset{0}{P}{}^{\beta}_{\nu\nu} &= 1/2q_\nu - \delta_\nu
\end{aligned} \tag{22}$$

Taking into consideration expressions (21) and (22), the secular equations (20) become (for simplicity the Coulomb integral of the C atom α is assumed to be 0):

$$\begin{aligned}
&\sin\theta_k\overset{*}{c}_{k\mu}(1/2q_\mu\gamma - \delta_\mu\gamma - E_k^\alpha) + \cos\theta_k \overset{0}{\sum_{\nu}} c_{k\nu}\beta_{\mu\nu} = 0 \\
&\sin\theta_k \sum_{\mu} \overset{*}{c}_{k\mu}\beta_{\mu\nu} + \cos\theta_k\overset{0}{c}_{k\nu}(1/2q_\nu\gamma + \delta_\nu\gamma - E_k^\alpha) = 0
\end{aligned} \tag{23}$$

where γ is the one centre Coulomb integral between the $2p_z$ AO of the C atom, $q_{\mu(\nu)}$ and $c_{\mu(\nu)}$ are the selfconsistent values of the electron charges and the coefficients of MO. If $\sin\theta_k = \cos\theta_k$, then $\delta_\mu = \delta_\nu = 0$ and the secular Eqs. (23) convert into the equations of the conventional HF method:

$$\begin{aligned}
&\overset{*}{c}_k(1/2q_\mu\gamma - e_k) + \overset{0}{\sum} c_{k\nu}\beta_{\mu\nu} = 0 \\
&\sum_{\mu} \overset{*}{c}_{k\mu}\beta_{\mu\nu} + \overset{0}{c}_{k\nu}(1/2q_\mu\gamma - e_k) = 0
\end{aligned} \tag{24}$$

In the above equations, the energies e_k do not coincide with the energies determined by means of (2) or (7). They depend on the geometry of the polymethyn chain, if a bond order alternation is assumed, expressed by the resonance integrals β_s and β_d in expression (21).

It follows from (23) and (24) that:

$$\begin{aligned}
&\sin\theta_k(1/2_\mu\gamma - \delta_\mu\gamma - E_k^\alpha) + \cos\theta_k(e_k - 1/2q_\mu\gamma) = 0 \\
&\sin\theta_k(e_k - 1/2_\nu\gamma) + \cos\theta_k(1/2q_\nu\gamma + \delta_\nu\gamma - E_k^\alpha) = 0
\end{aligned} \tag{25}$$

If in (25) a summation is carried out over all μ-, respectively ν-, and the following notations are introduced:

$$\begin{aligned}
&\overset{*}{f} = \frac{\gamma}{2n+2}\overset{*}{\sum_{\mu}} q_\mu, \quad \overset{0}{f} = \frac{\gamma}{2n}\overset{0}{\sum_{\nu}} q_\nu \\
&\overset{*}{\delta} = \frac{1}{n+1}\overset{*}{\sum_{\mu}}\delta_\mu \\
&\overset{0}{\delta} = \frac{1}{n}\overset{0}{\sum_{\nu}}\delta_\nu = \frac{1}{n}\sum_{k}^{n}\cos 2\theta_k - \frac{n+1}{n}\overset{*}{\delta}
\end{aligned} \tag{26}$$

the secular equations (25) take the form

$$\begin{aligned} &\sin\theta_k(\overset{*}{f} - \overset{*}{\delta}\gamma - E_k^{\alpha}) + \cos\theta_k\,(e_k - \overset{*}{f}) = 0 \\ &\sin\theta_k\,(e_k - \overset{0}{f}) + \cos\theta_k(\overset{0}{f} + \overset{0}{\delta}\gamma - E_k^{\alpha}) = 0 \end{aligned} \tag{27}$$

The solution of the above secular equations leads to the following expression for the AMO energies (the same for AMO with α and β spin):

$$E_k^{\alpha,\beta} = \frac{\overset{*}{f} + \overset{0}{f} + \overset{*}{\delta} - \overset{0}{\delta}}{2} \pm \sqrt{\left(\frac{\overset{*}{f} - \overset{0}{f}}{2} + \delta\gamma\right)^2 + (e_k - \overset{*}{f})\,(e_k - \overset{0}{f})} \tag{28}$$

where

$$\delta = \tfrac{1}{2}(\overset{*}{\delta} + \overset{0}{\delta})$$

The minus sign relates to the nonbonding, and the plus sign to the antibonding AMO.

For $n \gg 1$, (see Eqs. (26))

$$\delta = \frac{1}{2n}\sum_k^n \cos 2\theta_k \tag{29}$$

In Hückel's approximation, according to Eqs. (8–13)

$$\sum_\mu^{*} q_\mu - \sum_\nu^{0} q_\nu = 1$$

Hence, for $n \gg 1$:

$$\overset{0}{f} - \overset{0}{f} \to 0, \qquad \overset{*}{\delta} - \overset{0}{\delta} \to 0.$$

These conditions are fulfilled not only for ideal geometry of the polymethyn chain, but also when bond length alternation is present ($\beta_s \neq \beta_d$).

Under the above conditions, (28) becomes

$$E_k^{\alpha,\beta} = 1/2\gamma \pm \sqrt{\delta^2\gamma^2 + e_k^2}. \tag{30}$$

From (27) and (30) we obtain:

$$\cos 2\theta_k = \frac{\delta\gamma}{\sqrt{\delta^2\gamma^2 + e_k^2}} \tag{31}$$

Eqs. (30) and (31) coincide with the equations for even polyenes [12, 17]. The energy gap in both cases is equal to:

$$\Delta E_\infty = 2\sqrt{\delta^2\gamma^2 + e_n^2} \tag{32}$$

where e_n is the highest occupied MO. For ideal geometry ($\beta_s = \beta_d = \beta$) the energy gap $\Delta E_\infty = 2\delta\gamma$, i.e. it is determined by the electron correlation only. If $\beta_s \neq \beta_d$

then $e_n = |\beta_d - \beta_s|$ and

$$\Delta E_\infty = \sqrt{4\delta^2\gamma^2 + 4(\beta_s - \beta_d)^2} = \sqrt{\Delta^2_{\mathrm{corr}} + \Delta^2_{\mathrm{geom}}}$$

i.e. we obtain Eq. (17).

However, in the case of cations of odd polyenes, the longest-wavelength transition is determined by the transition of an electron from the n'th MO to the vacant NBMO (ψ_{n+1}); it will be equal to the halfwidth of the gap $\Delta E_{\infty,\mathrm{opt}}(\mathrm{II}) = 1/2\Delta E_\infty(\mathrm{II})$ (see Fig. 2), hence, Eq. (1) is satisfied.

For cations of odd polyenes one may expect an intensive transition with an energy to the gap, just as for even polyenes.

In the asymptotic case, one may expect the same properties for both anions and cations of odd polyenes. The nonbinding NBMO (ψ_{n+1}) of the anions is doubly occupied and the longest-wavelength transition will take place from the NBMO to the lowest antibonding MO. The treatment of cations of odd polyenes may be generalized for the anions too. In this case the wave function is expressed in the form:

$$\Phi = \frac{1}{\sqrt{(2n+2)!}} |\psi_1^\alpha \alpha \psi_2^\alpha \alpha \ldots \psi_n^\alpha \alpha \psi_1^\beta \beta \ldots \psi_n^\beta \beta \psi_{n+1}^\alpha \alpha \psi_{n+1}^\beta \beta| \qquad (33)$$

In expression (33) for NBMO (ψ_{n+1}), $\sin\theta_{n+1} = \cos\theta_{n+1}$, i.e. the correlation correction to NBMO is equal to 0 ($E_{n+1}^{\alpha,\beta} = e_{n+1}$). For $n \gg 1$ the matrix elements of the HF-operator [31, 32] are unchanged – their correction is of the order $1/n$ [28]. For the AMO energies, respectively the energy gap, the same expressions are obtained [30–32] as in the case of cations. In contrast, the longest-wavelength transition will be determined by the transition of an electron from NBMO to the lowest antibonding AMO, i.e. the transition energy will also be equal to the half-width of the gap (Fig. 2). It follows from here that Eq. (1) is satisfied too.

As in the case of cations, the similar bond order alternation of the even polyenes is a necessary condition for the fulfilment of Eq. (1).

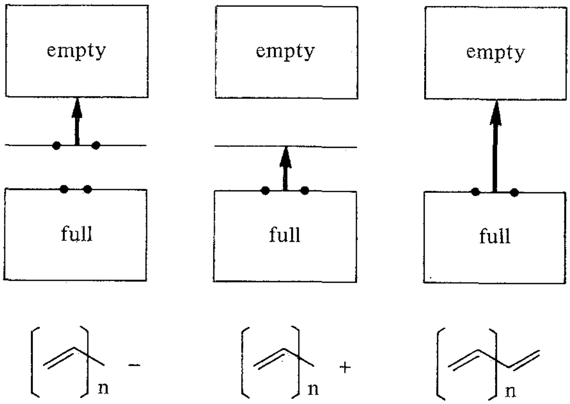


Fig. 2. Band structure and scheme of electron transitions corresponding to the longest-wavelength optical transition for even polyenes and ions of odd polyenes

The exact values of the ratios

$$\Delta E_{\infty,\,\mathrm{opt}}(\mathrm{I})/\Delta E_{\infty,\,\mathrm{opt}}(\mathrm{II})$$

probably deflect a little from the ratio 2:1. This can easily be explained by a certain difference in the bond order alternation of the even and the ions of odd polyenes.

4. Conclusion

The problem of the contribution of the correlation (Δ_{corr}) and geometry (Δ_{geom}) component of the energy gap, which is treated for even polyenes in papers [10–20], is not discussed here. A realistic, quantitative evaluation of the ratio $\Delta_{\mathrm{corr}}/\Delta_{\mathrm{geom}}$ in the framework of the above mentioned semiempirical approximations can be done if only we know the exact experimental bond order alternation in infinite polyenes (there are no such data), as well as the value of the ratio β_s/β_d. The detailed study of this problem is the subject of a separate research, and its results will be reported in a following communication.

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