

SPECTRUM OF LOCAL STATES OF HETEROPOLYMERS

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The well-known Lennard-Jones equation describing the spectrum of π -electrons in polyenes is extended to the case of heteropolyenes. The explicit form of the conditions (relating the alternation parameter, length of the heteropolyene and difference in Coulomb integrals for the heteroatom and carbon atom) which determine the appearance and disappearance of local states of π -electrons in heteropolyenes of the types $X-(CH)_{2N_d}-X$, $X^+-(CH)_{2N_d}-X^-$, and $X-(CH)_{2N_d}-CH_2$ is obtained. The spectrum of local states is also obtained in analytic form in the infinite-chain approximation. It is shown that the position of the intragap levels which determine the frequencies of the lowest dipole-allowed transitions in heteropolyenes is totally dependent on the above parameters, so that by varying them, one can change the position of the absorption and luminescence bands over a wide range. The results obtained can be used in a search for optically active compounds with specified properties.

The search for new materials based on organic compounds and having promising electrooptical properties is inconceivable without a detailed knowledge of the nature of the electronic structure of molecules, and for conjugated molecules, a knowledge of the π -electron structure.

It is well known that the simplest and most successfully parametrized Hamiltonian used to describe the π -electron structure of conjugated molecules is the Hückel Hamiltonian. This model has been elaborated in great detail for application to linear molecules with equal distances between the carbon atoms (see, for example, [1, 2]), and thus is oriented toward applications to polymethine dyes. Considerably less attention has been given in the literature to the case of heteropolyenes, where the C-C bond lengths alternate substantially. Thus, the single- and double-impurity problems in semi-infinite alternating chains in the Hückel approximation were studied by Kventsel' [3, 4]. This model can be applied to heteropolyenes of the types $X-(CH)_{2N_d}-X$, and $X-(CH)_{2N_d}-CH_2$. The results obtained in [3] in the solution of the single-impurity problem were extended to the case of finite-length molecules by Castano and Karadakov [5].

Primary attention in the above studies was given to local states of π electrons, the formation of which may lead to radical changes in the electrical and optical properties of heteropolyenes. Nevertheless, a number of questions pertaining to the pattern of formation of local states in heteropolyenes have remained unanswered. Essentially, only the case of local states in the $X-(CH)_{2N_d}-CH_2$ structure has been exhaustively described, and only on conditions that the terminal bonds of the heteropolyene remain double; see [3, 5]. These results are clearly insufficient for even a qualitative prediction of the position of local levels in other types of heteropolyenes. Moreover, the practically unstudied case of single terminal bonds certainly deserves no less attention, since, as was found by numerical calculations [6], it corresponds to the optimal geometry of heteropolyenes in the lowest dipole-allowed excited state and also of the ionic forms of heteropolyenes in the ground state.

This paper presents a detailed study of local levels in the π -electron spectrum of the main types of heteropolyenes with both double and single bonds between the terminal atoms and the main hydrocarbon chain.

SECULAR EQUATION

For the general model of a heteropolyene $X-(CH)_{2N_d}-Y$, the electronic structure in the Hückel approximation is described by the equation

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$$\sum_{j=1}^N H_{jj} A_j = E A_j \quad (1)$$

where A_j and E are the unknown coefficients of molecular orbitals (MO) and the energy of π -electron states, respectively, and the matrix elements of the Hamiltonian $H_{jj'} = H_{j'j} = \int \varphi_j H \varphi_{j'} dr$ (integration over the electron coordinates of the atoms j and j') are determined in a standard manner: $H_{jj} = \varepsilon_X, \varepsilon_Y$ ($\varepsilon_{X(Y)} = \alpha_{X(Y)} - \alpha_C$) for $j = 1, N = 2N_d + 2$ respectively, $H_{jj} = 0$ for $j \neq 1, N$; $H_{12} = \beta_X, H_{N-1N} = \beta_Y, H_{jj+1} = \beta \exp \eta$ for $j = 3, 5, \dots, N - 3$; $H_{j-1j} = \beta \exp(-\eta)$ for $j = 3, 5, \dots, N - 1$; $H_{j \neq j'} = 0$ for all the remaining values of j and j' . In this determination of the resonance integrals, the double bonds at the ends of the chain correspond to the case $\eta > 0$. Subsequently, the absolute value of the resonance integral $|\beta|$ is used as the energy unit.

The solution of Eq. (1) with an unperturbed Hamiltonian H^0 , i.e., for $H_{j \neq j} = 0$ and $\beta_X = \beta_Y = \beta$, is known [7]. (We note that the positive sign of the alternation parameter η in Eq. (1) corresponds to double terminal bonds of an unperturbed chain.) The explicit form of the Green's functions $G = (E - H^0)^{-1}$ can also be obtained [8]. Therefore, since the perturbation of the polyene chain may be local in character when the terminal atoms are replaced, the solution of the problem is conveniently carried out by use of the Lifshitz method [9].

By using the standard procedure of representing the solutions of systems of linear equations in terms of the Green's functions, one can show that the existence condition of nontrivial solutions of the system (1) is

$$\left(1 - \frac{\beta_X^2 G_{11}}{E - \varepsilon_X}\right) \left(1 - \frac{\beta_Y^2 G_{11}}{E - \varepsilon_Y}\right) - \frac{\beta_X^2 \beta_Y^2 G_{12}^2}{(E - \varepsilon_X)(E - \varepsilon_Y)} = 0, \quad (2)$$

where $G_{jj'}$ are the matrix elements of the Green's function in the strong-coupling representation. These matrix elements can be represented in explicit form as functions of the variable ξ [8], which is related to the energy of π -electron states as follows: $E = \pm \sqrt{2(\cosh(2\eta) + \cos \xi)}$. Thus, Eq. (2) constitutes a transcendental equation whose roots determine the energy spectrum for given values of parameters $N_d, \eta, \beta_{X(Y)}$ and $\varepsilon_{X(Y)}$ and which replaces the system of N th-order linear equations.

There are no fundamental difficulties in using the derived equations as the basis for an analysis of the spectrum of local states for a general model of heteropolyenes. However, to avoid cumbersome formulas, we will confine ourselves to examining the three main types of heteropolyenes, $X-(CH)_{2N_d}-X, X^+-(CH)_{2N_d}-X^-$ and $X-(CH)_{2N_d}-CH_2$. We will also consider the fact that as a rule, the chief role in the replacement of terminal atoms is played by perturbation of Coulombic integrals. Therefore, we will always assume below that $\beta_X = \beta_Y = \beta$. We note that an arbitrary heteropolyene may be regarded as an intermediate case of the above types of heteropolyenes. Consequently, the results obtained below give a representation of all the main trends of the influence of terminal heteroatoms on the π -electron spectrum.

Since the spectrum of local states of different types of heteropolyenes is distinguished by several characteristics, we will consider each of them separately.

HETEROPOLYENES OF THE TYPE $X-(CH)_{2N_d}-X$

Using the explicit form of the Green's functions [8] and assuming that $\varepsilon_{X(Y)} = \varepsilon$, we can reduce Eq. (2) to the form

$$\begin{aligned} \varepsilon^2 &= - \frac{\sin((N_d+2)\xi) + (\exp(-2\eta) - 2E\varepsilon)\sin((N_d+1)\xi)}{\sin((N_d+1)\xi) + \exp(2\eta)\sin(N_d\xi)} \Big|_{\eta \rightarrow 0} = \\ &= - \frac{\sin((N+1)\xi/2) - 2\varepsilon\sin(N\xi/2)}{\sin((N-1)\xi/2)}. \end{aligned} \quad (3)$$

From Eq. (3) it is easy to obtain secular equations for simpler models, equations which are widely used to interpret the electronic spectra of linear conjugated molecules. In particular, for $\varepsilon = 0$, we have from Eq. (3) the following well-known Lennard-Jones equation describing the spectrum of an ideal polyene [10]:

TABLE 1. Determination of Regions with Different Numbers of Intragap (In) and Extraband (Out) Local States in Heteropolyenes of Types $X-(CH)_{2N_d}-X$, $X^+-(CH)_{2N_d}-X^-$ and $X-(CH)_{2N_d}-CH_2$. The Region (R) I Corresponds to $|\varepsilon| < \varepsilon_1$, II - $\varepsilon_1 \leq |\varepsilon| < \varepsilon_2$, III - $\varepsilon_2 \leq |\varepsilon| < \varepsilon_3$, IV - $|\varepsilon| \geq \varepsilon_3$

Type $\eta > 0$	R	$2\eta < \ln \frac{N_d+1}{N_d}$		$2\eta > \ln \frac{N_d+1}{N_d}$		Determination of ε_i	
		in	out	in	out		
X—...—X	I	0	0	0	0	$\varepsilon_1 = e^{-\eta}$	
	II	1	1	1	1	$\varepsilon_2 = e^{-\eta} + 2(2N_d \cosh \eta + e^{-\eta})^{-1}$	
	III	1	2	1	2	$\varepsilon_3 = e^{-\eta} + 2(2N_d \sinh \eta - e^{-\eta})^{-1} $	
	IV	0	2	2	2		
X ⁺ —...—X ⁻	I	0	0	0	0	$\varepsilon_1 = e^{-\eta} \sqrt{1 + 2e^{-\eta}(2N_d \cosh \eta + e^{-\eta})^{-1}}$	
	II	0	2	0	2	$\varepsilon_2 = e^{-\eta} \sqrt{1 + 2e^{-\eta}(2N_d \sinh \eta - e^{-\eta})^{-1}}$	
	III	0	2	2	2		
X—...—CH ₂	I	0	0	0	0	$\varepsilon_1 = e^{-\eta} + (2(N_d + 1) \cosh \eta)^{-1}$	
	II	0	1	0	1	$\varepsilon_2 = e^{-\eta} + (2(N_d + 1) \sinh \eta)^{-1}$	
	III	1	1	1	1		

Type $\eta < 0$	R	$4 \eta < \ln \frac{N_d+2}{N_d+1}$ (a)		$\ln \frac{N_d+2}{N_d+1} < 4 \eta < 2 \ln \frac{N_d+2}{N_d+1}$ (b)		$2 \eta > \ln \frac{N_d+2}{N_d+1}$ (c)		Determination of ε_i	
		in	out	in	out	in	out		
X—...—X	I	0	0	0	0	2	0	$\varepsilon_1 = e^{ \eta } - 2(2N_d \sinh \eta + e^{ \eta })^{-1} $	
	II	1	0	1	0	1	0	$\varepsilon_2 = e^{ \eta }$	
	III	0	1	0	1	0	1	$\varepsilon_3 = e^{ \eta } + 2(2N_d \cosh \eta + e^{ \eta })^{-1}$	
	IV	0	2	0	2	0	2		
X ⁺ —...—X ⁻	I	0	0	0	0	2	0	$\varepsilon_1 = e^{ \eta } \sqrt{1 + 2e^{\eta}(2N_d \sinh \eta - e^{ \eta })^{-1}}$	
	II	0	0	0	0	0	0	$\varepsilon_2 = e^{ \eta } \sqrt{1 + 2e^{\eta}(2N_d \cosh \eta + e^{ \eta })^{-1}}$	
	III	0	2	0	2	0	2		
X—...—CH ₂	I	0	0	0	0	2	0	$\varepsilon_1 = e^{ \eta } + (2(N_d + 1) \cosh \eta)^{-1}$ (a)	
	II	0	1	1	0	1	0	$\varepsilon_1 = -e^{ \eta } + (2(N_d + 1) \sinh \eta)^{-1}$ (b)	
	III	1	1	1	1	1	1	$\varepsilon_1 = e^{ \eta } - (2(N_d + 1) \sinh \eta)^{-1}$ (c)	
								$\varepsilon_2 = -e^{ \eta } + (2(N_d + 1) \sinh \eta)^{-1}$ (a)	
								$\varepsilon_2 = e^{ \eta } + (2(N_d + 1) \cosh \eta)^{-1}$ (b)	
								$\varepsilon_2 = e^{ \eta } + (2(N_d + 1) \cosh \eta)^{-1}$ (c)	

$$\sin((N_d + 1)\xi) / \sin((N_d + 2)\xi) = -\exp(2\eta). \quad (4)$$

In the limit $|\varepsilon| \rightarrow \infty$, it follows from Eq. (3) that in addition to two levels with infinite energy, there exist $2N_d$ levels with finite energy, the position of which is determined from Eq. (4), where $N_d + 1$ should be replaced by N_d , and η should be replaced by $-\eta$. In the case of a chain with nonalternating bonds, $\eta = 0$, and instead of Eq. (3), we have

$$\begin{aligned}\cos((N+1)\xi/4)/\cos((N-1)\xi/4) &= \varepsilon, \\ \sin((N+1)\xi/4)/\sin((N-1)\xi/4) &= \varepsilon.\end{aligned}\tag{5}$$

Results of an analysis of the solutions of Eq. (3) which determine the local levels of the system are shown in Table 1 for positive and negative values of the alternation parameter. It is evident that a change in the number of local states in the spectrum takes place at three critical values of perturbation ε_i , $i = 1, 2, 3$, which determine four regions of $|\varepsilon|$ values to which correspond different numbers of local states inside the gap $|E| < 2 \sinh |\eta|$ and outside the bands $|E| > 2 \cosh \eta$. The ε_i values depend on the number of double bonds N_d , on the magnitude and sign of the alternation parameter η , and on the relationship between these parameters (the determinations of $\varepsilon^{(i)}$ are given in Table 1).

For $\eta > 0$ and, in addition, $2\eta > \ln((N_d + 1)/N_d)$ in region I (see Table 1), no local states exist; in region II, there is one intragap and one extraband local state; in region III, there is one more extraband local state, and in region IV, the heteropolyene spectrum has two intragap and two extraband states. If however $2\eta < \ln((N_d + 1)/N_d)$, the situation is distinguished only by the fact that in region IV there exist only two extraband local states. Thus, when the latter condition holds, for any perturbation of terminal atoms that is as large as desired, no more than one intragap local state can arise. This property of the spectrum of symmetric heteropolyenes was first pointed out by Kventzel [4]. It is also of interest to note that perturbation of terminal atoms may give rise to two, three, or four local levels. The presence of only one local level in the spectrum of this type of heteropolyenes is impossible.

We note that in [4], the conditions of appearance of intragap local states (only for $\eta > 0$) were obtained in a certain asymptotic limit. It is apparently for this reason that the corresponding results from the work cited are correct only in the limit $N_d \rightarrow \infty$, i.e., when $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \exp(-\eta)$.

In the case $\eta < 0$ (which was not considered in [4]), on the basis of Eq. (3), it can be shown that when the condition

$$2|\eta| > \ln((N_d + 2)/(N_d + 1))\tag{6}$$

holds and $|\varepsilon| < \varepsilon_1$, the spectrum of symmetric heteropolyenes has two intragap levels; when $|\varepsilon| = \varepsilon_1$, one of these levels disappears (i.e., the state corresponding to either the lowest unoccupied MO (LUMO), if $\varepsilon > 0$, or highest occupied MO (HOMO), if $\varepsilon < 0$, is converted from a local to a band state); when $|\varepsilon| = \varepsilon_2$, the disappearance of the second intraband state takes place simultaneously with the appearance of an extraband local state. Finally, when $|\varepsilon| = \varepsilon_3$, a second extraband state appears (see Table 1).

When the opposite of inequality (6) holds, no local states exist in region I. Only an intragap state appears at $|\varepsilon| = \varepsilon_1$, which when $|\varepsilon| = \varepsilon_2$ again converts to a band state. The behavior of the extraband local states remains qualitatively the same, so that in the case of negative values of the alternation parameter, the spectrum of a symmetric heteropolyene may show the presence of one local state, two local states, or no local state.

HETEROPOLYENES OF THE TYPE $X^+ - (CH)_{2N_d} - X^-$

In this case, the π -electron spectrum is given by the equation

$$\begin{aligned}\varepsilon^2 &= \exp(-2\eta) \times \\ &\times \frac{\exp\eta \sin((N_d + 2)\xi) + \exp(-\eta) \sin((N_d + 1)\xi)}{\exp(-\eta) \sin((N_d + 1)\xi) + \exp\eta \sin(N_d \xi)} \Big|_{\eta=0} \\ &= \frac{\sin((N+1)\xi/2)}{\sin((N-1)\xi/2)}.\end{aligned}\tag{7}$$

As is evident from Table 1, the existence conditions and pattern of appearance of local states in the spectrum of this type of heteropolyenes differ appreciably from those discussed above. Thus, when $2\eta < \ln((N_d + 1)/N_d)$ and the alternation parameter is positive, the appearance of intragap local states is completely impossible no matter how large the perturbation of the terminal atoms. If, however, the condition $4|\eta| < \ln((N_d + 2)/(N_d + 1))$ holds, then outside the dependence on the sign of η and at any values of $|\varepsilon|$, the π -electron spectrum of the structure $X^+ - (CH)_{2N_d} - X^-$ contains no intragap local states. It is also

TABLE 2. Energy of MO Closest to the Fermi Level

Type	State	Energy, u. $ \beta $			
		$\eta > 0$		$\eta < 0$	
		$\epsilon > 0$	$\epsilon < 0$	$\epsilon > 0$	$\epsilon < 0$
$X-(CH)_{2N_d-2}-X$	LUMO+1	$2\sinh \eta$	E_n^+	$2\sinh \eta $	$2\sinh \eta $
	LUMO	$2\sinh \eta$	E_n^+	E_n^+	$-E_n^+$
	HOMO	$-E_n^+$	$-2\sinh \eta$	E_n^+	$-E_n^+$
	HOMO-1	$-E_n^+$	$-2\sinh \eta$	$-2\sinh \eta $	$-2\sinh \eta $
$X^+-(CH)_{2N_d-2}-X^-$	LUMO+1	$2\sinh \eta$	$2\sinh \eta$	$2\sinh \eta $	$2\sinh \eta $
	LUMO	E_n^+	E_n^+	E_n^+	E_n^+
	HOMO	$-E_n^+$	$-E_n^+$	$-E_n^+$	$-E_n^+$
	HOMO-1	$-2\sinh \eta$	$-2\sinh \eta$	$-2\sinh \eta $	$-2\sinh \eta $
$X-(CH)_{2N_d-2}-CH_2$	LUMO+1	$2\sinh \eta$	$2\sinh \eta$	$2\sinh \eta $	$2\sinh \eta $
	LUMO	$2\sinh \eta$	E_n^+	E_n^+	0
	HOMO	$-E_n^+$	$-2\sinh \eta$	0	$-E_n^+$
	HOMO-1	$-2\sinh \eta$	$-2\sinh \eta$	$-2\sinh \eta $	$-2\sinh \eta $
$H_2C-(CH)_{2N_d-2}-CH_2$	LUMO+1	$2\sinh \eta$		$2\sinh \eta $	
	LUMO	$2\sinh \eta$		0	
	HOMO	$-2\sinh \eta$		0	
	HOMO-1	$-2\sinh \eta$		$-2\sinh \eta $	

useful to emphasize that in this case, in contrast to symmetric heteropolymers, as the magnitude of the perturbation $|\epsilon|$ changes, in contrast to symmetric heteropolymers, the transformation of the states corresponding to HOMO and LUMO from band to local states or vice versa takes place simultaneously. Thus, the presence in the spectrum of $X^+-(CH)_{2N_d}-X^-$ of intragap local states signifies that both indicated states are local (in a symmetric heteropolymer, at least one of them is a band state). Since the properties of local and band states differ very substantially, it may be expected that the optical properties of the indicated heteropolymers, which in many ways are determined precisely by HOMO and LUMO, will also be substantially different.

HETEROPOLYMERES OF THE $X^+-(CH)_{2N_d}-CH_2$

The spectrum of local states for this type of heteropolymers is determined by the equation

$$\begin{aligned} \epsilon &= \frac{\exp(-2\eta) \sin((N_d+1)\xi) + \sin((N_d+2)\xi)}{E \sin((N_d+1)\xi)} \Big|_{\eta=0} \\ &= \pm \frac{\sin((N+1)\xi/2)}{\sin(N\xi/2)} \end{aligned} \quad (8)$$

and for $\eta > 0$ was studied fairly closely in [3, 5]. We will therefore mention here the most significant characteristics of this spectrum, which pertain only to the case of negative values of the alternation parameter. A complete list of the conditions determining the appearance of local states, their number, and position (inside the gap and/or outside the bands) is given in Table 1.

Let us note first of all that in contrast to the types of heteropolyenes discussed above, for which the determination of the regions with different numbers of local states (i.e., determination of the critical values of $|\varepsilon|$) depend on the ratio of η to N_d , in the case under consideration this dependence holds only when $\eta < 0$. In [3], this important fact was overlooked. As follows from Table 1, not only the determination of the critical values of $|\varepsilon|$, but also the order of appearance (as $|\varepsilon|$ increases) of the intragap and extraband states in the π -electron spectrum depends on this ratio. Namely, if the condition $4|\eta| > \ln((N_d + 2)/(N_d + 1))$ holds, the intragap state for $|\varepsilon| = \varepsilon_1$ initially appears. Conversely, when the inequality $4|\eta| < \ln((N_d + 2)/(N_d + 1))$ holds, the extraband state arises first in the spectrum of local states. It should be emphasized that outside the dependence on the magnitude ($\eta \neq 0$) and sign of η , when $|\varepsilon| > \varepsilon_2$, there is always one intragap and one extraband state in the spectrum of $X-(CH)_{2N_d}-CH_2$. This fact is emphasized, since in [3] it was erroneously concluded that in the case of negative values of η , there exists one and only one local state for any perturbation.

SPECTRUM OF LOCAL STATES IN THE ASYMPTOTIC LIMIT

The study of this limit is of great interest, since the position of the local levels can be obtained in analytic form (as was done in [3] for heteropolyenes of the type $X-(CH)_{2N_d}-CH_2$).

Using (3), (7), and (8), one can show that in the limit $N_d \rightarrow \infty$, all three equations have the same solutions for $\delta = i\xi$ and $\delta' = i(\pi - \xi)$:

$$\begin{aligned} 2 \exp \delta &= \sqrt{(\varepsilon^2 - \exp(-2\eta))^2 + 4\varepsilon^2 \exp(2\eta)} - \\ &\quad - \exp(-2\eta) + \varepsilon^2, \\ 2 \exp \delta' &= \sqrt{(\varepsilon^2 - \exp(-2\eta))^2 + 4\varepsilon^2 \exp(2\eta)} + \\ &\quad + \exp(-2\eta) - \varepsilon^2. \end{aligned} \quad (9)$$

This does not mean, however, that the number and position of local levels in different types of heteropolyenes will also be the same. The positions of the intragap levels in the asymptotic limit are shown in Table 2, which gives the energies of four MO closest to the Fermi level in the ideal polyene ($E_F = 0$). The symbol E_{in}^∞ was introduced for the quantity $E_{in}^\infty = (2\cosh(2\eta) - 2 \cosh[\ln(1/2)(\sqrt{(\varepsilon^2 - \exp(-2\eta))^2 + 4\varepsilon^2 \exp(2\eta)} + \exp(-2\eta) - \varepsilon^2)])^{1/2}$. The existence conditions of the intragap π -electron states in this limit converge to $|\varepsilon| > \exp(-\eta)$ if $\eta > 0$ and $|2\varepsilon| < \exp(|\eta|)$ if $\eta < 0$.

The position of the extraband levels which exist when $|\varepsilon| > \exp(-\eta)$ is determined by the quantity $E_{out}^\infty = (2 \cosh(2\eta) + 2 \cosh[\ln(1/2)(\sqrt{(\varepsilon^2 - \exp(-2\eta))^2 + 4\varepsilon^2 \exp(2\eta)} - \exp(-2\eta) + \varepsilon^2)])^{1/2}$. In $X-(CH)_{2N_d}-X$, it is the doubly degenerate level with energy E_{out}^∞ ($|\varepsilon| > 0$) or $-E_{out}^\infty$ ($|\varepsilon| < 0$); in $X^+-(CH)_{2N_d}-X^-$ the energy of the two extraband levels is $\pm E_{out}^\infty$; the position of the extraband (nondegenerate) level in $X-(CH)_{2N_d}-CH_2$ is the same as in a symmetric polyene.

APPLICATION OF THEORY

As an illustration of possible applications of the results obtained above, we will consider the change in the frequency of the lowest dipole-allowed transition as a function of the perturbation parameter ε and of the state (neutral or ionic) in a symmetric substitution of the terminal carbon atoms in hexatriene ($N_d = 2$). The dependence of the position of the π -electron levels on ε in this system, calculated in accordance with Eq. (3) for $\eta \approx 0.13$ (experimental value of the alternation parameter in the neutral form of the molecule [11]) and $\eta \approx -0.13$ (postulated value of this parameter in its ionic forms [6]) is shown in Fig. 1a and b, respectively.

It is evident that the distance between the $(N/2)$ th and $(N/2 + 1)$ th levels, i.e., between the HOMO and LUMO levels, which determines the frequencies ν , ν^{++} and ν^{--} of the relevant transition in the neutral, dicationic and dianionic forms of the given heteropolyene, depends substantially on ε . Thus, if for $\varepsilon = 0$, $\nu = 1.25$ in units of $|\beta| = 30305$ cm (this value practically coincides with the experimental value [11]), and $\nu^{++} = \nu^{--} = 0.96$, then for $\varepsilon = -1$ (substitution with nitrogen atoms) or -2 (substitution with oxygen atoms), the indicated frequencies shift by the following amounts: $\Delta\nu = 0.08(0.11)$;

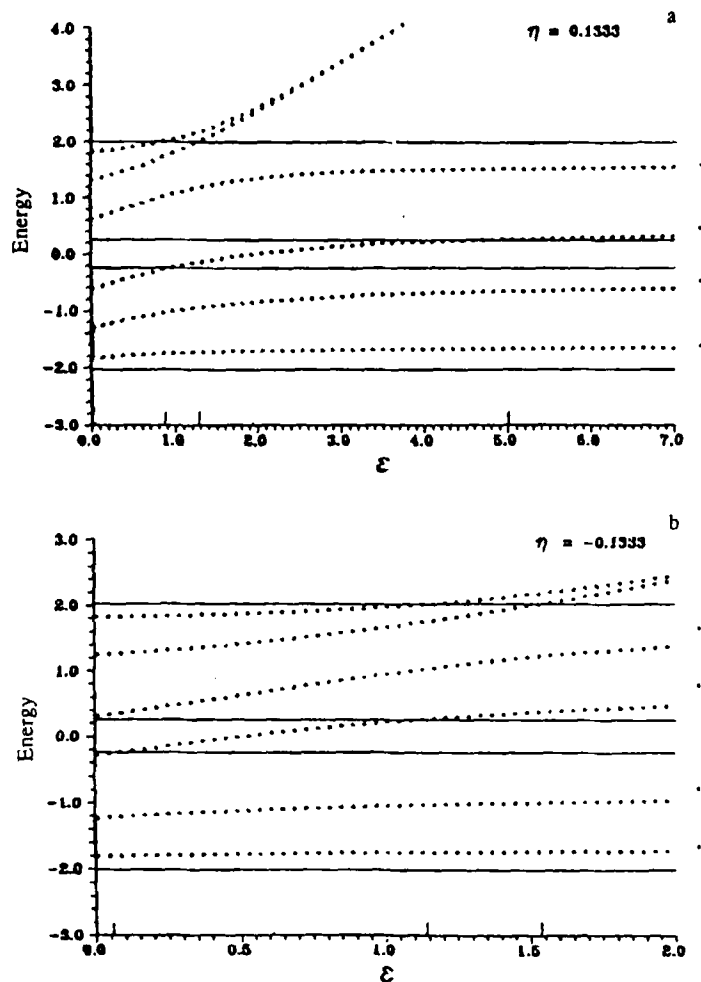


Fig. 1. Dependence of the position of π -electron levels on ε in hexatriene in a symmetric perturbation of terminal carbon atoms: a) $\eta = 0.1333$ (short bonds on the ends of the molecule); b) $\eta = -0.1333$ (long bonds on the ends of the molecule). The edges of the spectrum of the band states are shown by continuous horizontal lines for the values ($|E| = 0.2674$ and 2.0178). The points on the right correspond to the positions of the π -electron levels in the limit $\varepsilon \rightarrow \infty$. Vertical dashes on the ε axis denote the critical values of the perturbation (see determination of ε_i , $i = 1, 2, 3$, in Table 1); from left to right: $\varepsilon_1 = 0.87$ (a), 0.05 (b); $\varepsilon_2 = 1.28$ (a), 1.14 (b); $\varepsilon_3 = 5.0$ (a), 0.51 (b). The illustrated curves correspond to positive perturbation values. The spectrum for $\varepsilon < 0$ is obtained by specular reflection of the positions of the levels relative to the ε axis.

$\Delta\nu_{1(2)} = -0.22(0.1)$ and $\Delta\nu_{1(2)} = 0.34(0.5)$ (the subscript corresponds to the value of $|\varepsilon|$). Let us emphasize that both the large absolute value of the frequency shift and the nonmonotonicity of its dependence on $|\varepsilon|$ in the case of ν are determined by the "participation" of the local state in the determination of the transition frequency. Using the data of Table 1, one can easily see, for example, that in the determination of ν , the LUMO level corresponds to the local intragap state.

Thus, variation of the terminal atoms of the heteropolyene and of its charge (the latter can be changed by an appropriate selection of the solvent) is an effective method of modifying the absorption spectrum of this class of compounds. Additional possibilities in this regard are provided by changing the type of substitution. The secular equations (3), (7) and (8) obtained in this work as well as the existence conditions of local states in the main types of heteropolyenes make it possible to carry out a rapid determination of the parameters of the heteropolyene which are necessary to obtain the frequency of the absorption maximum in the specified portion of the spectrum. In the next publication, we hope to discuss in more detail the expected manifestation of the effects of heterosubstitution in the absorption of neutral and charged forms of polyenes.

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