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Electronic properties of polymethine systems 7: soliton symmetry breaking and spectral features of dyes with a long polymethine chain

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Abstract

The dependence of the position and shape of the absorption bands on the length of the polymethine chromophore is quantum-chemically and spectrally investigated for the vinylogous series of the following dyes: pyrido-, thia- and thiapyrylocyanines. It is established that the symmetry breaking occurs in the cyanines containing the comparatively long chain, 4–6 vinylene groups. It is assumed that in the ground state the near-infrared polymethine dyes with the long enough polymethine chain may exist in two charged forms with symmetrical and asymmetrical disposition of charge wave or soliton. The distortion in the electron density distribution and π-bond occupancies in the asymmetrical form leads to the drastic widening of the long wavelength spectral bands and, simultaneously, to considerable decreasing of the absorption band intensity. It is shown that the spectral effects caused by symmetry breaking are strongly sensitive to the solvent polarity.

Keywords: Thia- and thiapyrylocyanines; The long wavelength spectral bands; Quantum-chemical investigations; Soliton

1. Introduction

The widest field of application of polymethine dyes (PMDs) is based on their specific spectral properties [1–3]. They exhibit high intensive and comparatively narrow absorption and fluorescence bands, their maxima being easily shifted from UV to IR region by lengthening of the polymethine chain or by the introduction of terminal groups of effective length [4]. The largest longwave spectral region achieved to date is 1600 nm [5].

It is shown in numerous investigations (see, for example, review in Ref. [4] and the references therein) that comparatively short symmetrical PMDs (containing 0–4 vinylene groups in the chain) are characterized by the essential equalization of the equilibrium CC-bond lengths and appreciable alternation of the positive and negative charges at carbon atoms in the polymethine chromophore. This excitation leads to substantial change in the charge while π-bond orders remain practically unchanged. These features of the structure in the ground and excited states of PMDs make the first electron transition highly intensive, the intensity increasing regularly upon increasing the number of vinylene groups, *n*, in the polymethine chain [6,7]. Also, because of minimal changing of π-bond orders upon excitation, the absorption bands of the shorter PMDs are rather narrow, the band widths of typical polycarbocyanines being between 500 cm^{-1} and 1000 cm^{-1} in non-polar solvents [6].

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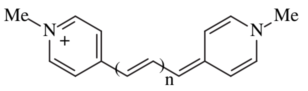
The spectra of polymethines absorbing in the near-IR region have been found to demonstrate a number of specific features, particularly their band intensity decreases regularly and the band width increases progressively. This spectral effect was explained traditionally by a specific solvent influence [8,9]. Other explanation of the drastic change in the absorption spectra of the pyridohexacarbocyanine was proposed by Tolbert and Zhao [10]. Based on the theoretical concept about the charged defects or soliton in doped conjugated polymers, it was assumed that such a substantial increasing of the spectral band width is connected with the symmetry breaking in the long PMDs. In fact, the quantum-chemical investigations have shown that the symmetry of the equilibrium geometry of polymethines containing more than 5–7 vinylene groups in the chromophore is broken [11–15]. As a result, the essential alternation of the CC-bond lengths occurs in a way similar to that in unsymmetrical PMDs which exhibit a comparatively wider spectral bands [16].

In the previous paper [17] we have established that the root-mean-square of the change in the π-bond orders upon excitation, δ (which correlates with spectral width), drastically increases when the number of vinylene groups in the chain exceeds 6–7. The present paper focuses in more detail on the quantum-chemical and spectral study of the features of the electronic structure and the equilibrium geometry and spectra of long polymethine dyes with complex residues.

2. Materials and quantum-chemical calculations

The polymethine dye ions studied quantum-chemically are as follows:



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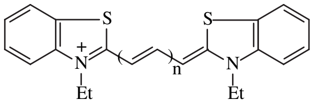

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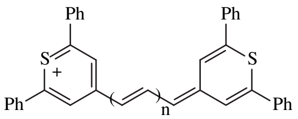

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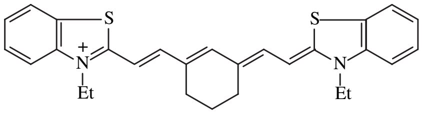

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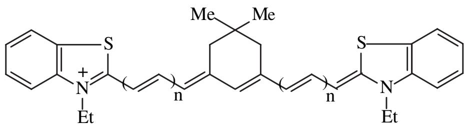

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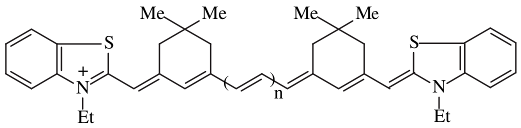

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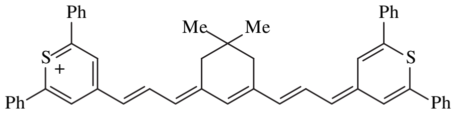

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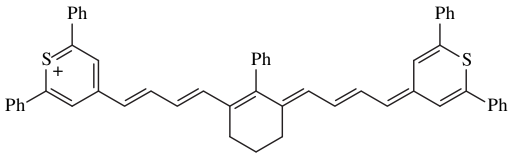

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The PMDs **2** (n = 1–3), **3** (n = 0–3), **4**, **5** (n = 0, 1), **6** (n = 1, 2), **7** and **8** were also investigated experimentally. The synthesis of **2** [18], **3** (n = 0, 1) [19], **3** (n = 2, 3) [20], **4**, **5** (n = 0, 1) [5,21], **6** [1,5], **7** [5] and **8** [5,21] is described earlier.

Absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100. Spectroscopy grade dichloromethane and dimethyl sulfoxide (Merck) were used as solvents.

The equilibrium geometry of dye molecules in the ground state was optimized by the AM1 approximation (with the gradient of 0.01 kcal/mol). The electron transition characteristics were calculated in the ZINDO/S approximation (with spectral parameterization) using 90 as the lowest singly excited configuration.

3. Spectral data

The absorption spectra of dyes **2–8** are presented in Figs. 1–4. The lengthening of the polymethine

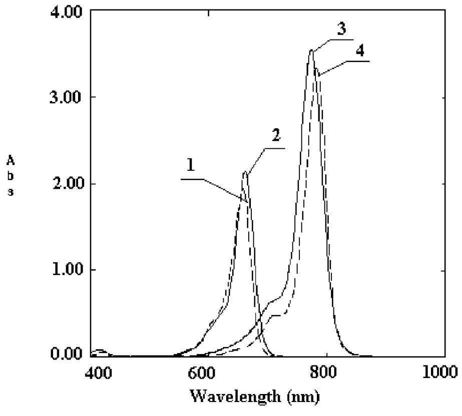

Fig. 1. Absorption spectra of thiacyanines in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/l): 1, dye **2** (n = 2); 2, dye **5** (n = 0); 3, dye **2** (n = 3); 4, dye **4**.

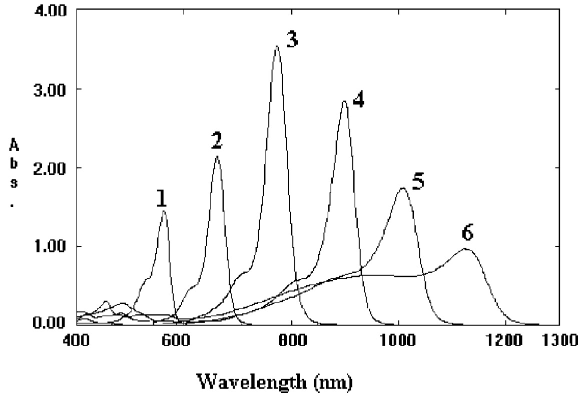

Fig. 2. Absorption spectra of thiacyanines in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/l): 1, dye **2** (n = 1); 2, dye **2** (n = 2); 3, dye **2** (n = 3); 4, dye **5** (n = 1); 5, dye **7** (n = 1); 6, dye **6** (n = 2).

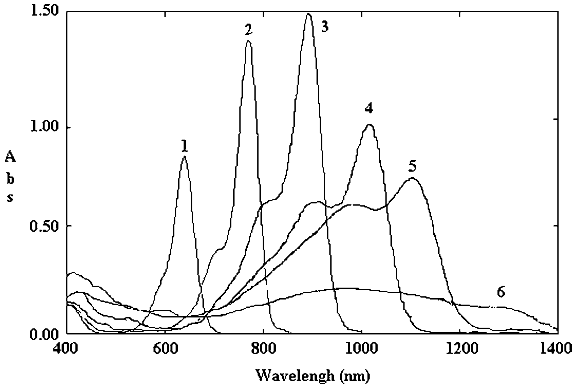

Fig. 4. Absorption spectra of thiapyrylocyanines in DMSO ($c = 8 \times 10^{-6}$ mol/l): 1, dye **3** (n = 0); 2, dye **3** (n = 1); 3, dye **3** (n = 2); 4, dye **3** (n = 3); 5, dye **7**; 6, dye **8**.

chromophore is known to usually reduce the stability of the dye molecules [20]. It is established that the introduction of polymethylene bridges into the chain results in substantive stabilization of molecules [5], the absorption spectra being changed only slightly. As an example the spectra of two pairs of PMDs containing the open chain and the chain with bridges as well as different number of vinylene groups (**2**, n = 2; **5**, n = 0; **2**, n = 3; and **4**) are shown in Fig. 1. These show that the spectra of dyes with the bridges are similar to those of the unsubstituted PMDs. Because of this, it is possible to compare spectral characteristics in the whole vinylogous series of the polycarbocyanines although the higher members are experimentally represented by the dyes with one or even two polymethylene bridges.

Figs. 2 and 3 present the absorption spectra of thiapolycarbocyanines **2** (n = 1–3) and their higher substituted vinylogs **4–6**; thiapyrylopolycarbocyanines **3** (n = 0–3) and dyes with bridges **7** and **8**. It is seen that the lengthening of the chromophore leads to a regular bathochromic shift of the band maxima. The spectral effect per vinylene group, V, is traditionally called the vinylene shift [22]. For thiacyanines (Fig. 2), the vinylene shift is approximately 105–115 nm while for 2,6-diphenylthiapyrylocyanines (Fig. 3) this is equal to 120–130 nm. The comparison of Figs. 2 and 3 shows that absorption band maxima of the PMDs with 2,6-phenylthiapyrylium residues are considerably shifted to longer wavelengths relative to the maxima of the thiacyanines with the same chain length. The influence of the topology of the end groups on the wavelength of the first transition can be estimated quantitatively by means of their effective length, L, the wavelength of the band maximum being defined by the relationship: $\lambda_{\max,n} = V(n + L)$. It was found earlier that for the 2,6-diphenylthiapyrylium end group the parameter $L = 6.04$ while for a benzothiazolium residue $L = 2.72$ [23].

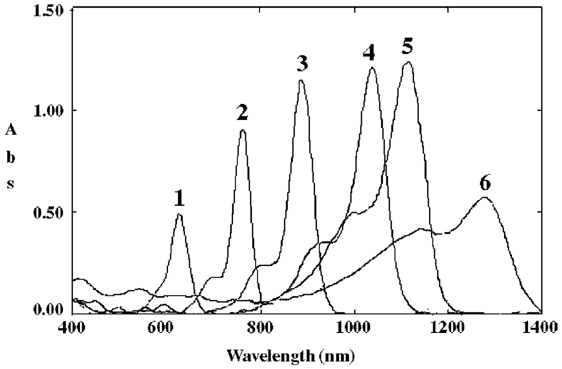

Fig. 3. Absorption spectra of thiapyrylocyanines in CH_2Cl_2 ($c = 4 \times 10^{-6}$ mol/l): 1, dye **3** (n = 0); 2, dye **3** (n = 1); 3, dye **3** (n = 2); 4, dye **3** (n = 3); 5, dye **7**; 6, dye **8**.

As evident from Figs. 2 and 3, short PMDs exhibit comparatively narrow spectral bands and their widths increase progressively in each series. However, the band intensities of the dyes with long polymethine chain decrease sharply, and the bands are strongly broadened. More drastic decrease in intensities and increase in width of the spectral bands of higher vinylogs are observed in the high-polarity solvent DMSO (Fig. 4).

There is no question that these spectral effects are associated with essential changes in the electronic structure in the ground and excited states occurring in the long PMDs in comparison with the short dyes.

4. Solitonic structure of polymethine chromophore

In Fig. 5, the charges at carbon atoms in chains of thiacyanines **2** are presented. The total positive charge in the dye ion is delocalized non-uniformly over the π-centers. It is distributed within the chromophore as a wave of alternating positive and negative partial charges, i.e. a soliton of the electron or hole type in PMD anions or PMD cations, respectively [10–15]. This is a typical picture for cyanine dyes connected with the

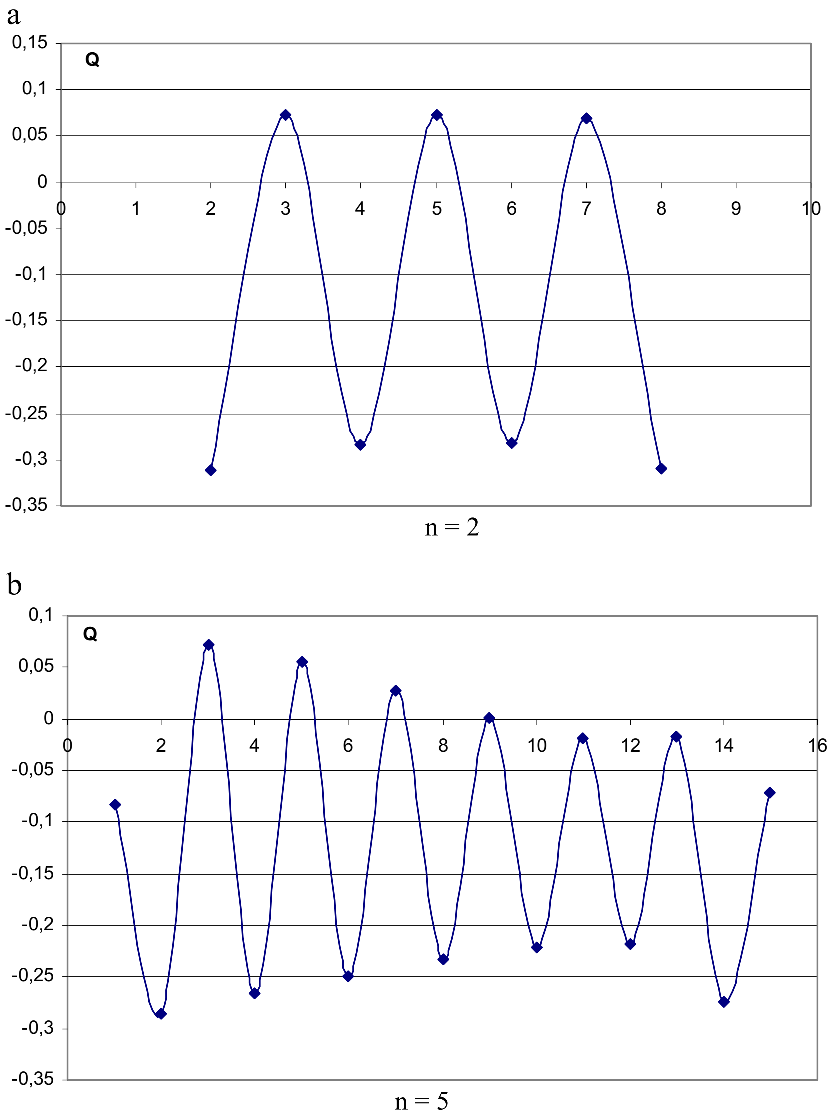

Fig. 5. The charges at the carbon atoms in the chain of the thiadicarbocyanine **2**, $n = 2$ (a) and thiapentacarbocyanine **2**, $n = 5$ (b).

fact that PMDs are charged one-dimensional π-electron systems with a closed electron shell.

It was found that the solitonic wave in the linear conjugated systems is of a finite size in length, approximately composed of 15–17 carbon atoms for the open unsubstituted polymethine chain [11–14]. As a result, there appears a chain section of the polyenic type structure with a relatively large amplitude of alternation of the CC-bond lengths with equalization of the electron density at the π-centers, in contrast to the solitonic section with maximally equalized CC-bond lengths and with maximum difference in the π-electron population at the neighboring carbon atoms [13,14].

In the MOLCAO method, as a version of the one-electron approximation, the soliton in the cations of PMDs should be placed on the lowest unoccupied MO (the hole soliton). The probability of its location at the *p*th π-center (a carbon atom) is determined by the coefficient squared of the corresponding MO, C_{ip}^2. The calculation on PMDs with simple end groups has shown that the position of the soliton in the long enough chromophore depends on the nature of the terminal residues [14,15]. In the case of an unsubstituted polymethine cation, the hole soliton is in the middle of the chain and its length amounts to 10 vinylene groups. If a PMD contains amino or oxy substituents as the nuclei, which cause a shift of the MO nodes as compared to the unsubstituted polymethine, the soliton is displaced to one of the end groups.

A similar shift of the LUMO to one of the ends of the polymethine chain is typical for cyanine cations containing terminal groups of middle basicity, for example, dyes **1–3** with pyridinium, benzothiazolium or thiapyrylium residues. Fig. 6 shows the localization of frontier MOs for two members of cyanine series **3** with a short ($n = 2$) and a comparatively longer ($n = 5$) chain. As can be

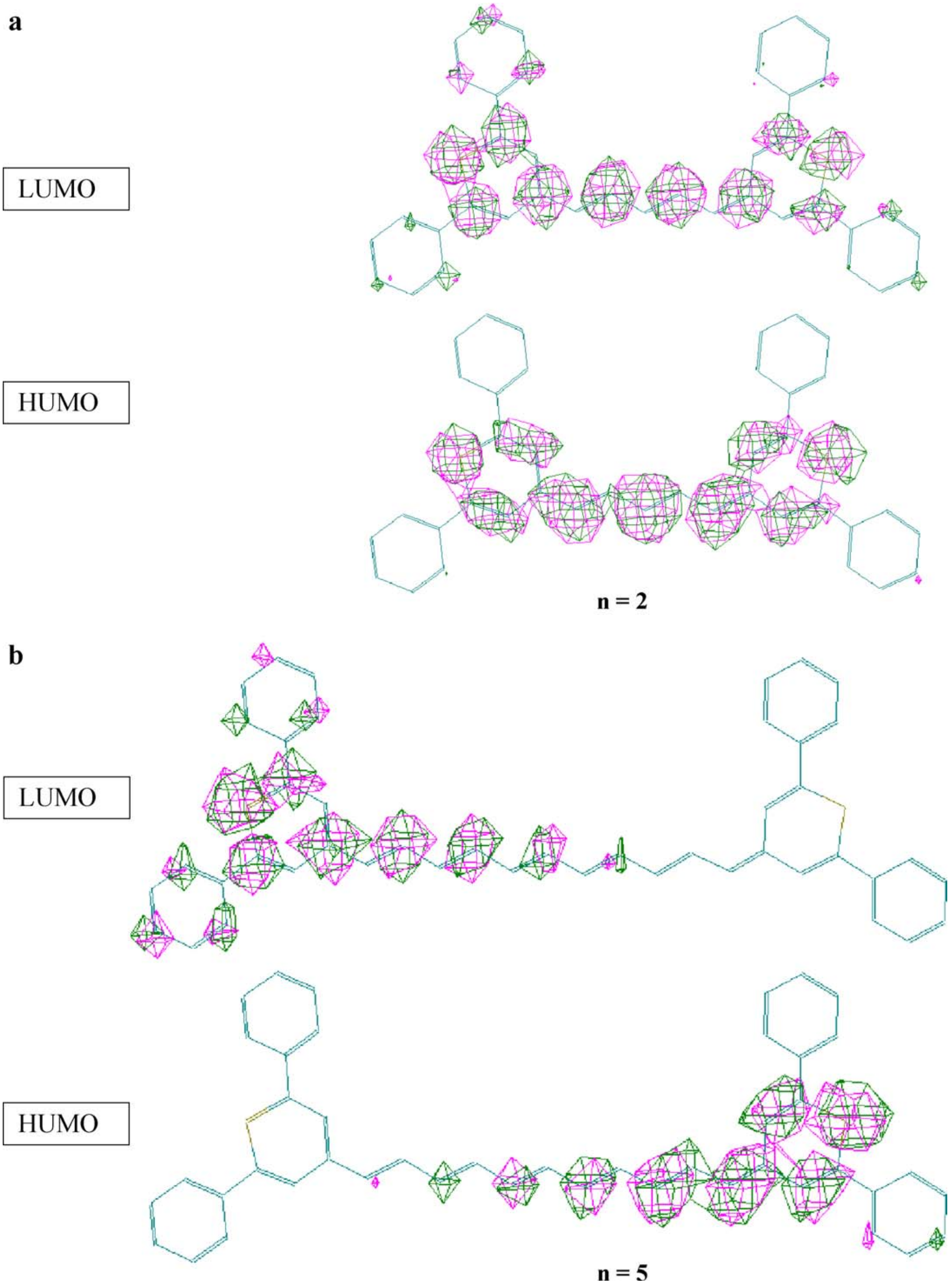

Fig. 6. Localization of the frontier MOs in the thiapyrylocyanines **3**.

seen, the LUMO is positioned symmetrically in the dicarbocyanine (Fig. 6a), but in the pentacarbocyanine (Fig. 6b) it is shifted to one of the terminal groups. It should be noted that the other frontier MO in long PMDs with a non-central displacement of the soliton is shifted to the opposite end of the chain (Fig. 6b).

It was proposed earlier [11–15] to describe the solitonic wave within linear conjugated systems by the amplitude of alternation of electron densities at the neighboring π-centers: $\Delta q = |q_\mu - q_{\mu+1}|$, where μ is the number of the π-center. The maximum of such a curve corresponds to the middle of the soliton [14,15]. Fig. 7 demonstrates the function $\Delta q = f(n)$ for the ground state of three polycarbocyanines in series **1**–**3**. It is easy to see that, as the number of vinylene groups in the chain is raised from 1–4 (or to 3 in thiapyrylocyanines **3**), the charge wave within the chromophore remains symmetrical, but the shape of the soliton changes

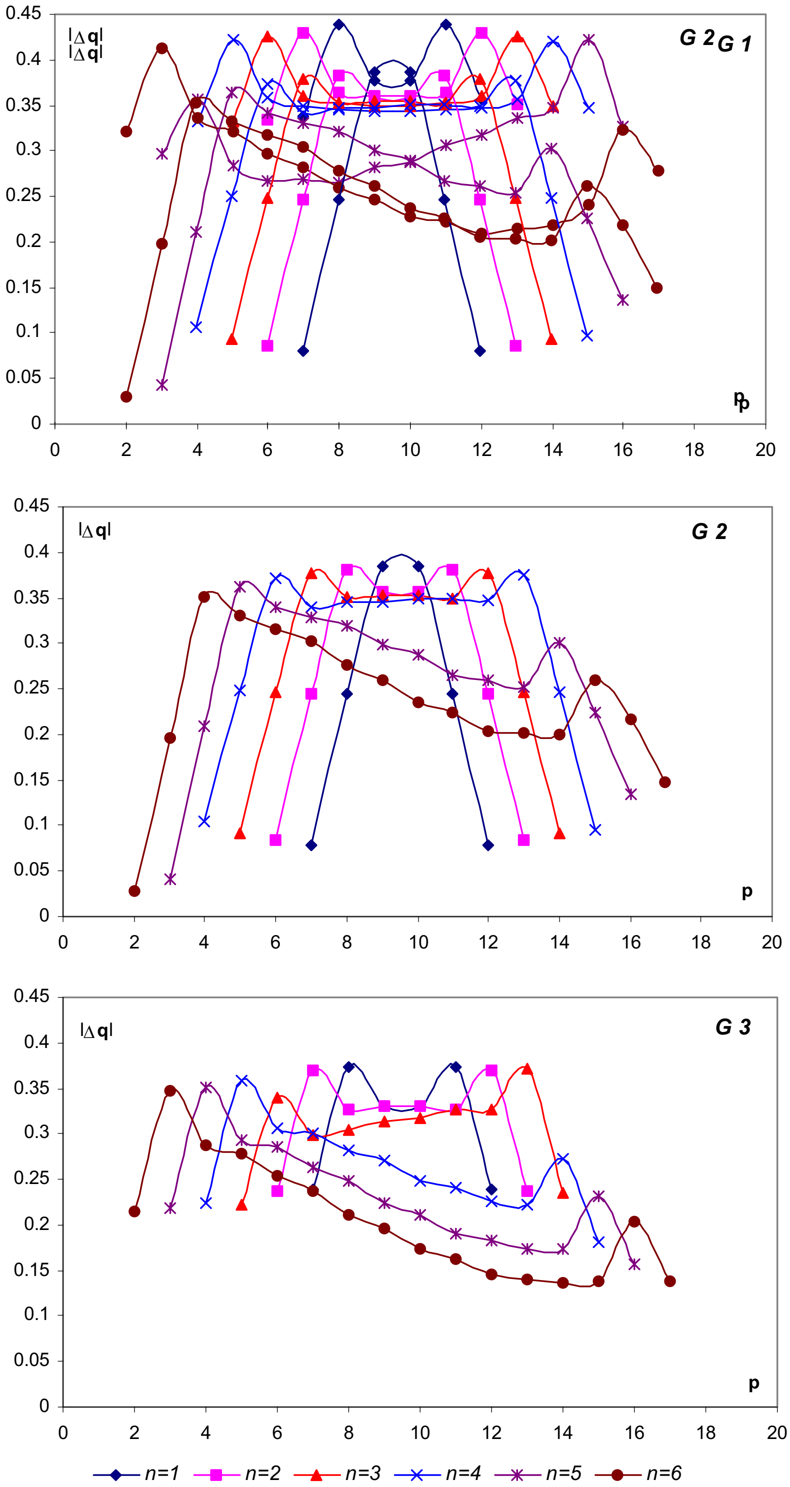

Fig. 7. Charge alternation ($\Delta q = |q_\mu - q_{\mu+1}|$) in the ground state vinylogous series of the dyes **1** (G1), **2** (G2) and **3** (G3).

sharply and becomes unsymmetrical on a further lengthening of the polymethine chain.

The analysis of the spectral and quantum-chemical data enabled us to assume that in the ground state the near-infrared polymethine dyes with the long enough polymethine chain may exist in two charged forms with symmetrical and asymmetrical disposition of charge density [24].

In the dyes with a relatively short polymethine chain, the charge or solitonic wave could exceed the dimension of the molecule. In this case only one symmetric charge wave can be detected. These PMDs show typical spectral

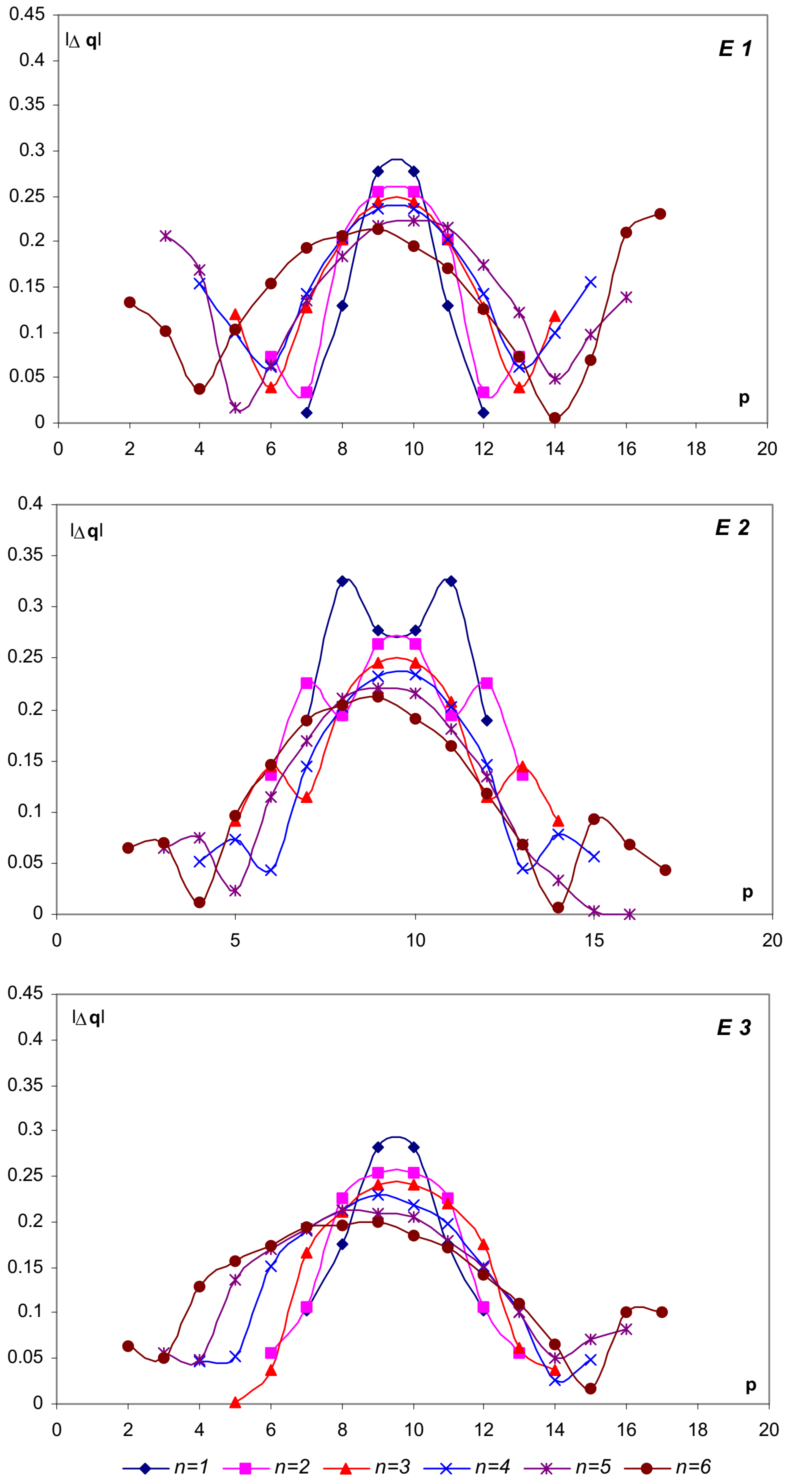

Fig. 8. Charge alternation ($\Delta q = |q_\mu - q_{\mu+1}|$) in the excited state vinylogous series of the dyes **1** (E1), **2** (E2) and **3** (E3).

behavior (narrow and intensive absorption bands, etc.). An increase of the length of the polymethine chain leads to the dramatic changes in the electron distribution and molecular geometry when the width of the charge wave becomes comparable to the length of the π-system. Then, both charge-isomer forms (symmetric and asymmetric) are responsible for the change in the spectral characteristics of IR-dyes.

We assume that the additional wide band shifted hypsochromically in the spectrum of the long dye is connected with an electron transition in the asymmetrical form while the long wavelength maximum or shoulder (in strong polar solvents) corresponds to the transition in the symmetrical form.

Similar to solitonic waves in the ground state, Fig. 8 gives the alternation of the electron densities in the excited state.

Both Figs. 7 and 8 show the dependence of the maximum and minimum of the solitonic wave amplitude, Δq, on basicity of the end groups which decreases regularly along the series pyridinium–benzothiazolium–2,6-diphenylthiapyrylium. This agrees with the known fact that the basicity of heterocyclic residues in the PMDs is determined by their ability to give up π-electrons to the polymethine chain [4,25]. In the excited state, the distance between two minimum values of the solitonic wave amplitude is shorter than that in the ground state (compare the corresponding curves in Figs. 7 and 8). This testifies that the dimension of the soliton in the excited state is smaller. The efficient lengthening of the chromophore also leads to breaking of symmetry of the electron density distribution in the excited state, although the degree of asymmetry in this case is smaller than that in the ground state.

Since PMD molecules are nonrigid π-systems (in contrast, for example, to crystals), the solitonic wave disturbs the equilibrium molecular geometry, primarily the CC-bond lengths. Because of this, the shift of the soliton to one of the end groups in the long dyes is accompanied by breaking of equality of the CC-bond lengths in equivalent positions of the polymethine chain, as demonstrated by the calculated data in Table 1.

Hence, the shift of the electron density wave and the breaking of symmetry of the molecular geometry are two main factors which cause the drastic change in the absorption spectra of the relatively long cyanine dyes.

5. The nature of electron transitions and absorption spectra

The displacement of the frontier MOs in the opposite parts of the unsymmetrical form of the long dye ions (Fig. 6b) should cause a change in the nature of the lowest electron transition between these orbitals as compared to typical electron transitions in cyanines with comparatively short polymethine chains. It was shown earlier that the first electron transition between the totally delocalized HOMO and LUMO is characterized by a substantial change of charges at the carbon atoms and is accompanied by a transfer of electron density from the π-centers in the odd positions of the polymethine chain to the atoms in the even positions [4,26]. Similar very intensive transitions can be referred to solitonic ones. On the contrary, the changes in magnitudes of the π-bond orders induced by the solitonic type transition are small.

It was established that the solvent polarity affects only little the maximum and intensity of the longwave absorption band which corresponds to solitonic transition in typical ionic cyanine dyes. Thus, for thiapyrylocyanines **3** with $n = 0$: λ_{max} 629 nm (ε 12.25×10^4) in CH_2Cl_2; λ_{max} 641 nm (ε 12.25×10^4) in o-$Cl_2C_6H_4$; λ_{max} 639 nm (ε 10.30×10^4) in DMSO; with $n = 1$: λ_{max} 762 nm (ε 22.85×10^4) in CH_2Cl_2; λ_{max} 779 nm (ε 23.97×10^4) in o-$Cl_2C_6H_4$; λ_{max} 770 nm (ε 17.20×10^4) in DMSO; with $n = 2$: λ_{max} 888 nm (ε 29.22×10^4) in CH_2Cl_2; λ_{max} 906 nm (ε 26.97×10^4) in o-$Cl_2C_6H_4$; λ_{max} 891 nm (ε 12.66×10^4) in DMSO.

The increase in solvent polarity in going from CH_2Cl_2 to o-$Cl_2C_6H_4$ does not cause an appreciable shift of the spectral band while the band intensity can rise

Table 1
Bond lengths in the polymethine chains of dyes **1–3** (Å)

Dye	n	C_μ–C_ν								Symmetry
		$C_{n'}$–$C_{n'-1}$	$C_{n'-1}$–$C_{n'-2}$	$C_{n'-2}$–$C_{n'-3}$	C_1'–C_0	C_0–C_1	C_{n-3}–C_{n-2}	C_{n-2}–C_{n-1}	C_{n-1}–C_n	
1	1	1.3961	–	–	1.3906	1.3907	–	–	1.3961	Symm.
	2	1.3946	1.3911	–	1.3917	1.3917	–	1.3910	1.3945	Symm.
	3	1.3927	1.3931	1.3903	1.3927	1.3927	1.3900	1.3934	1.3926	Symm.
	4	1.3937	1.3919	1.3916	1.3950	1.3863	1.3838	1.3991	1.3871	Symm.
	5	1.3698	1.4204	1.3627	1.4225	1.3661	1.4130	1.3741	1.4121	Asymm.
	6	1.3650	1.4268	1.3569	1.3570	1.4292	1.4189	1.3694	1.4169	Asymm.
2	1	1.4006			1.3899	1.3899			1.4006	Symm.
	2	1.3991	1.3906		1.3923	1.3904		1.3918	1.3987	Symm.
	3	1.3966	1.3934	1.3901	1.3923	1.3947	1.3877	1.3951	1.3956	Symm.
	4	1.3988	1.3911	1.3927	1.3988	1.3835	1.3788	1.4041	1.3871	Symm.
	5	1.4136	1.3769	1.4103	1.3665	1.4244	1.3607	1.4235	1.3712	Asymm.
	6	1.4170	1.3735	1.4146	1.4298	1.3578	1.3558	1.4298	1.3666	Asymm.
3	1	1.4021			1.3892	1.3926			1.3994	Symm.
	2	1.4016	1.3869		1.3960	1.3875		1.3947	1.3955	Symm.
	3	1.4143	1.3739	1.4111	1.3708	1.4145	1.3688	1.4134	1.3786	Asymm.
	4	1.4232	1.3664	1.4211	1.4258	1.3582	1.3584	1.4248	1.3702	Asymm.
	5	1.4274	1.3643	1.4259	1.3561	1.4347	1.3551	1.4305	1.3672	Asymm.
	6	1.4287	1.3628	1.4268	1.4357	1.3518	1.3533	1.4324	1.3661	Asymm.

For convenience, the carbon atoms are numbered in such a way that $\mu = 0$ for the central atom in the polymethine chain.

(for carbocyanine), decrease (for dicarbocyanine) or remain unchanged (for monomethinecyanine). It should be noted that the increase in maximum number of solvent molecules arranged about the chromophore as a result of lengthening of the chain in comparative short dye has an insignificant effect on the position of the band maximum: the bathochromic shift is equal to 12 nm ($n = 0$), 17 nm ($n = 1$) or 18 nm ($n = 2$). As a consequence, one can assume that a further increase in the number of vinylene groups, n, providing the solitonic nature of the first electron transition, should not lead to principal changes in the position, shape and width of the absorption bands in response to solvent effects. In contrast to this assumption, the spectra observed (Figs. 2 and 3) show a substantial decrease in the band intensity and a sharp increase in the band width. Moreover, the band shape of the long dyes ($n = 5$ for thiapyrylocyanines and $n = 6$ for thiacyanines) radically differs from usually narrow high-intensity bands for short cyanines, especially in the more polar solvent DMSO (Fig. 4).

Taking into consideration our assumption about two charged forms, we could explain these spectral features by increasing of number of the molecules in the asymmetrical form.

It was found [6] that the experimental band width of the polymethine dyes correlates with the quantum-chemical parameter δ which is calculated by the following equation:

$$\delta = \sqrt{\sum (p^{*}_{\mu\nu} - p^{\text{o}}_{\mu\nu})^2},$$

where $p^{*}_{\mu\nu}$ and $p^{\text{o}}_{\mu\nu}$ are π-bond orders in the excited and ground states, respectively. The summation runs for all π-bonds. As a rule, for dyes containing comparatively short chains, the parameter δ decreases slightly as the number of the vinylene groups increases. This is in agreement with the experimental data: the absorption bands of dicarbocyanines or even tricarbocyanines are somewhat narrower than the bands of carbocyanines [6]. The calculation data for the dyes investigated (Fig. 9) show abrupt jumps in the magnitude of the parameter δ in going from the tetracarbocyanine to the pentacarbocyaine for dyes with pyridinium and benzothiazolium residues (series **1** and **2**) whereas the sharp increase in the parameter δ for thiapyrylocyanines **3** is observed with $n = 2$–4. The examination of the frontier MOs localization shows that the first electron transition changes in nature as the chromophore length reaches

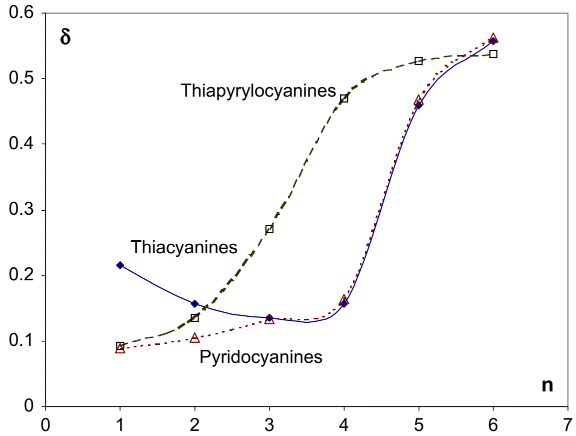

Fig. 9. The dependence of the parameter δ on the number of the vinylene groups, n, for the pyridocyanines **1**, thiacyanines **2** and thiapyrylocyanines **3**.

Table 2
Calculated data for dyes **1**–**3**

Dye	n	RHF geometry			UHF geometry		
		λ (nm)	f	V (nm)	λ (nm)	f	V (nm)
Pyridocyanines (**1**)	1	521	1.853		521	1.855	
	2	598	2.317	77	603	2.291	82
	3	672	2.716	74	681	2.687	78
	4	739	3.074	67	754	3.065	73
	5	772	2.932	33	830	3.372	76
	6	781	2.783	9	900	3.664	70
Thiacyanines (**2**)	1	490	1.420		492	1.415	
	2	547	1.903	57	550	1.898	58
	3	603	2.365	56	609	2.341	59
	4	660	2.743	57	671	2.749	62
	5	689	2.845	29	733	3.124	62
	6	709	2.898	20	796	3.454	63
Thiapyrylocyanines (**3**)	1	602	2.118		620	2.112	
	2	671	2.527	69	703	2.515	83
	3	727	2.756	56	773	2.943	70
	4	754	2.688	27	850	3.301	77
	5	761	2.607	7	904	3.605	54
	6	770	2.557	9	982	3.958	78

the values indicated above. Namely, the change in nature of the transition appears to be the main reason for the absorption bands of the long ionic dyes to become so wide: instead of the solitonic type transition with the electron redistribution between the atoms in the odd and even positions of the polymethine chromophore, there is realized the transition with the intramolecular transfer of the charge from one side of the dye molecule to the other. Such transitions (ICT transitions) are characterized by the widest and low-intensity spectral bands [27].

However, the change in the nature of the electron transition and, hence in the spectral band shape for the dyes with the long polymethine chain, has only little effect on the values of the observed vinylene shift, *V*. On the other hand, the calculations give the rough value of *V* providing the equilibrium geometry of the dye molecules optimized in the restricted and the unrestricted Hartree–Fock approximations (Table 2). Of course, the calculated vinylene shifts for cyanines **1–3** are lower than the experimental ones; it is a typical limitation of the semiempirical methods [28].

In addition, the ICT transitions are known to be more sensitive to solvent polarity [27]. It should be taken into consideration that the symmetry breaking in the unsymmetrical form of the long dye ions induces the appearance of a marked dipole in both the ground and excited states which clearly enhances the interaction between the dye and solvent molecules, especially in polar solvents, in contrast to a slight solvent effect for dyes with a short chain. Such an enhancement in the dye–solvent interaction (both specific and nonspecific or dispersed) brings about a rise in the spectral band width and distortion of the band shape.

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