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Nature of the lowest electron transitions in the linear conjugated systems derivatives of 2,6-diphenylthiapyrylium: Cationic trimethinecyanine, neutral ethylene, its dication and cation-radical

M.O. Kudinova [a], D.O. Melnyk [b],*, O.D. Kachkovsky [a], O.I. Tolmachev [a]

[a] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 5 Murmanska Str., 03660 Kyiv, Ukraine
[b] Ivano-Frankivsk National Medical University, 2 Galytska Str., 76000 Ivano-Frankivsk, Ukraine

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ABSTRACT

A series of linear conjugated systems of different types containing the 2,6-diphenylthiapyrylium residues as terminal groups have been synthesized and investigated by the combined spectral and quantum-chemical methods. The analysis of calculated by ab initio and semi-empirical methods of their molecular geometry and electron structure, and nature of the lowest electron transitions has shown that four types, cationic cyanine, neutral polyene, polyene-dication and cationic polyene-radical differ fundamentally each other by the charge distribution and alternation of bond lengths along π-electron system, as well as by nature of their lowest electron transitions and hence of shapes of the absorption bands. It was established the cyanine-like similarity of the "middle" high intensive and narrow spectral band for the cationic polyene-radical and cyanine dye, whereas the polyene with the close electron shell exhibit the comparatively wide longwavelength bands.

1. Introduction

Cationic polymethine dyes are the most well-known among the linear conjugated systems containing pyrylium and thiapyrylium residues as terminal groups. They have been synthesized for more than half century, but wide investigation of them is continued so as their application permanently extends [1–7]. Besides traditional using of polymethine dyes as photosensitizers in photography, fluorescence probes, initiators for polymerization, active and passive components for tunable lasers, media exploring excited-state absorption, non-linear optical materials, etc. [8–12]. It have invited further wide investigation of the electron structure of different types of the conjugated molecules, particularly of the higher excited states. Earlier we were studied in details the nature of the electron transitions in the cationic pyrylocyanines and their heteroanalogues and have established that comparatively deep color, in comparison with the corresponding neutral α,ω-disubstituted polyenes, was connected with the appearance of the so-called solitonic level (level of the positive charge or impurity level) in the energy gap [13,14]. In the same time, it is known that polyene-dications absorb the light at considerably longer wavelength, 400–500 nm, in contrast to cationic polyene-radical, absorbing in the longerwavelengths [3,6]. Also, many spectral bands of different intensities are observed in the visible and NIR spectral region, whereas the only single typical separated highly intensive, so-called "cyanine-like" spectral band appears in the spectrum of the corresponding cation-polymethine.

On the other hand, it was established that the lowest electron transitions in the linear conjugated systems with the comparatively short polymethine chain and with the complex terminal groups containing their own extended π-electron system, depend on the topology of the terminal residues; moreover, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions could be considered as splitting transitions from the donor orbitals to the solitonic MO [15]. One could suppose that the relative location of the "local" levels of the complex thiapyrylium terminal groups should significantly depend on the total charge of the conjugated system and hence should influence principally on the nature of the first and higher electron transitions.

The present paper concerns with the features of the generation of the frontier and nearest molecular orbitals and with features of the lowest electron transitions in four stable types of the symmetrical linear conjugated systems containing the thiapyrylium residues as symmetrical terminal groups. The main goal is to understand the cause of the similarity of the electron structure of the thiapyrylocarbocyanine cation with even number of the methine groups in the polymethine chain and related polyenic cation-radical with odd number of the π-centers in the chain.

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* Corresponding author.
E-mail address: melnyk_dm@ukr.net (D.O. Melnyk).

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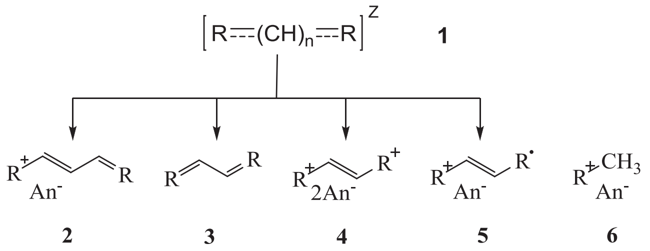
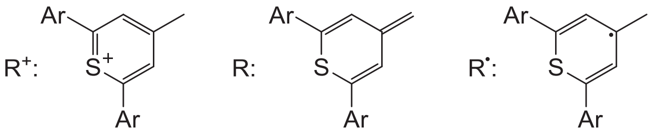
2. Results and discussion

2.1. Conjugated systems

The linear conjugated systems **1** (pyrylcarbocyanine **2**, neutral polyene **3**, its dication **4** and cation-radical **5**) as well as initial salt **6** studied are described by following formulae:



Here An = ClO_4 except **4a** (An = Br) and **6a** (An = BF_4);
R^+, R and $R^\cdot$ are the terminal groups:



Here Ar = C_6H_5 (for compounds **2**–**6**), Ar = C_6H_4–C_2H_5–p (for compounds **2a**–**6a**).

2.2. Synthesis

The synthesis of the compounds **2** and **6** is described in the papers [1,2]; the dyes **2a** and **6a** were obtained similarly. The polyenes **3** (**3a**) were obtained by heating of the corresponding salts **6** (**6a**) in pyridine [5,6]. Then, they were oxidated in the dications **4** (**4a**) by $CuClO_4$ in acetonytryl or by Br_2 in CH_2Cl_2. The solutions of the cation-radicals **5** (**5a**) were obtained by mixed of the equimolar solutions of the neutral polyene **3** (**3a**) and dication **4** (**4a**). An existence of the radical particles was confirmed by the EPR spectrum presented in the Fig. 1.

2.3. Optimized molecular geometry

The optimization of the molecular geometry performed by the ab initio method (STO 6-31G**) has shown that both the neutral molecule **2** and the ions **3–6** are practically planar, as it is typical for the π-electron systems. Only the phenyl substituents in the thiapyrylium residue are twisted slightly, at 15–17° relatively to the molecular plane, what is in a good accordance with the experimental data obtained by NMR spectroscopy for the salt **6** [2]. Here, we will suppose that the main chromophore includes the internal polymethine chain and both heterocycles, whereas the four phenyl substituents disturb relatively small the charge distribution at atoms and molecular geometry of the main chromophore system. The calculated optimized lengths of carbon–carbon bonds in the main chromophore (terminated by two sulfur atoms) for the various types of the linear conjugated systems derivatives of the thiapyrylium are presented in Fig. 2. It should be noted that the carbon–carbon bond lengths in all phenyl residues in all types of the linear systems **2–5** and salt **6** are practically equalized and are approximately 1.39–1.40 Å. One can see from Fig. 2 that the all carbon–carbon bonds are maximum equalized in the monocationic polymethine dye **2**. It accords with the theoretical conception about the solitonic-like shape of the charge distribution and maximum equalizing of the molecular geometry in the center of the charge wave in the linear conjugated monoions [16]. In contrast, the bond lengths in the neutral polyene **3** and dication **4** are seen from Fig. 2 to differ considerably, the order of the alternation of the lengths of the neighboring bonds being opposite in the compounds **3** and **4**. Meanwhile, the alternation of the bond lengths along the chromophore of the cationic polyene-radical **5** is lower than in other two types of the polyenes, **3** and **4**; however, the alternation degree is somewhat higher, in comparison with polymethine dye **2**. Also, the calculation gives the symmetry breaking in the chromophore of the cation-radical **5.** This is connected with the slight shift of the waves of the charge and spin density from the center.

2.4. Charge distribution

Similarly to the bond lengths in the polymethine chain, the various types of the linear conjugated systems **1** differ principally each other by the distribution of the electron density at the carbon atoms. It is well-known that the charges at the neighboring atoms alternate considerably in the chromophore of the polymethine cation/anion, whereas the electron density is equalized in the neutral polyenes [16,17].

Here we will analyze the charge distribution calculated by ZINDO/S method. Other methods have given the considerable polarization of the C-H bonds, so that the calculated charge at the hydrogen atom can reach as much as 0.146 (AM1) or even 0.167 (ab initio), while ZINDO/S gives only 0.02–0.04. The fulfilled calculations have shown that the electron distribution at the atoms in the phenyl substituents is practically independent on the type of the linear system; the atomic charges are practically equalized, in contrast to the distribution of the electron density along the main chromophore. The calculated charges at the atoms in the cationic pyrylotrimethine **2** in Fig. 3 show that the considerable alternation of the electron density extends within both terminal heterocycles. In the polyenes with closed electron shell, neutral compound **3** and dication **4**, the alternation of the charges is lower. The minimum of the charge alternation is obtained for the cationic polyene-radical **5.** It is to be noted that the charge distribution is unsymmetric. Also, Fig. 4 shows the symmetry breaking for the alternation of the spin densities at atoms calculated by the following formulas:

$$\Delta\rho = (-1)^{\mu}(\rho_{\mu} - \rho_{\mu+1}), \tag{1}$$

where $\rho_\mu = q_\mu(\alpha) - q_\mu(\beta)$ is a difference of the densities of α- and β-electrons at the μth atom. The Fig. 4 demonstrates that phases of the wave of the electron densities of the opposite spin are also opposite, both waves being intersected at one of the central atom, but not at the middle of the central bond; hence this leads to the symmetry breaking in the electron density distribution and equilibrium molecular geometry.

2.5. Positions of electron levels and shapes of molecular orbitals

Before starting the analysis of the nature of electron transitions related to the spectral bands to understand the reasons of the significant difference let us examine the position of the frontier and nearest electron levels and shape of the corresponding MOs in the conjugated systems of the neutral molecule **3** and ions **2**, **4–6**. **C**alculated data are presented in Figs. 2 and 3. Firstly, one can see from Fig. 5a that the lowest unoccupied MO (LUMO) is totally and uniformly delocalized along the whole molecule, whereas the highest occupied MO (HOMO) and next MO, HOMO-1, extends practically only over the open polymethine chain and

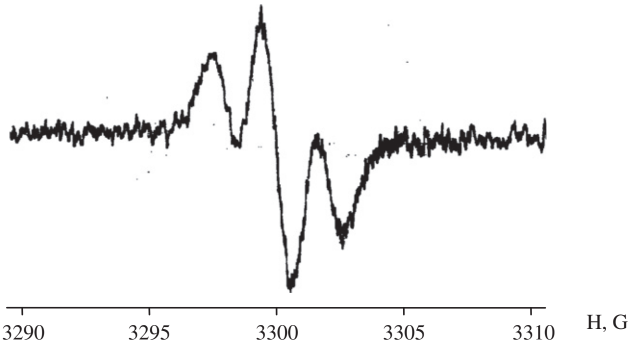


Fig. 1. EPR spectrum of the cation-radical **5**.

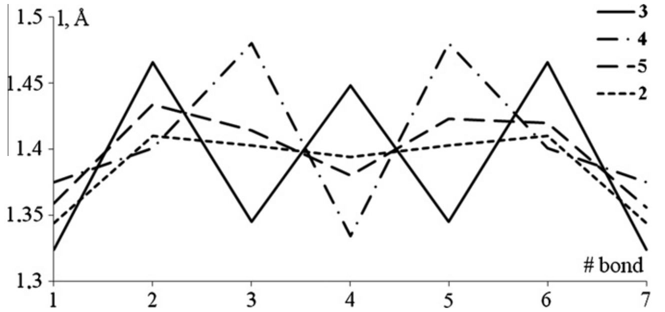


Fig. 2. Carbon–carbon bond lengths in main chromophore of the compounds **2–5**; for sake convenience, bond in the cycles are considered as equivalent; two central bonds in polymethine dye **2** are presented by one point.

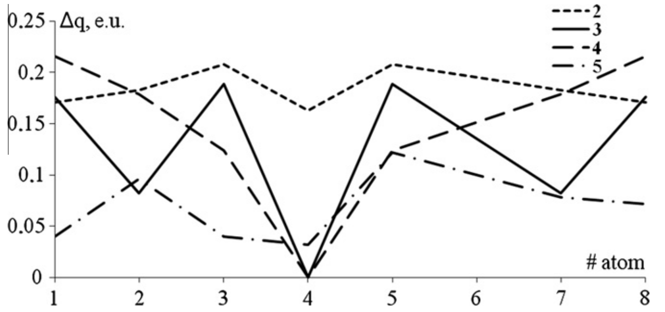


Fig. 3. Alternation of charges at carbon atoms in main chromophore of the compounds **2–5**; for sake convenience, value Δq_μ for two pair of central atoms in polymethine **2** are presented by one point.

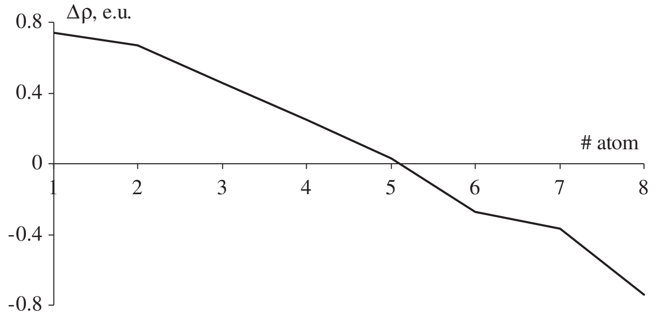


Fig. 4. Alternation of spin densities at carbon atoms in main chromophore of cation-radical **5**.

both heterocyclic rings, excepting all four phenyl substituents. It should be to noted the next two vacant orbitals, LUMO + 1 and LUMO + 2 are local MOs and do not extend over the polymethine chain. Both orbitals have their molecular node at the atom connected with the chain, similar to the HOMO in the initial salt **6** (compare with Fig. 6a); hence, they do not conjugate with the rest of the π-electron system and remain degenerated MOs.

Removing of one electron from the collective system of the neutral polyene **3**, i.e. going to the cationic polyene-radical **5** is accompanied by considerable shifting down of the energy gap, as it is seen from Fig. 5b. Similarly to the neutral molecule **3**, the LUMO in the radical **5** for the both α-electron is totally and uniformly delocalized along the whole conjugated system, while two next α-spin-orbitals, LUMO + 1 and LUMO + 2, are local. In contrast, both lowest vacant β-MOs are totally delocalized, whereas both highest occupied β-MOs are seen from Fig. 5b to be local, although they are not degenerated. Also, going to the cation-polyene causes extending of the delocalization of the highest occupied α-MOs over the phenyl substituents. In the same time, the calculation without taking into consideration the spin of the electron (RHF version) gives delocalization of the single occupied MO (SOMO) to be only over the chain and both heterocycles (Fig. 6c), similarly to the HOMO in both the neutral molecules (Fig. 5a) and the cationic polymethine dye **2** (Fig. 6b). One can see in Fig. 6c that the highest double occupied MO and LUMO are delocalized, including the phenyl substituents, whereas the HOMO-1 is local.

Next going to the polyenic dication **4** leads to the further shifting of the electron levels down, so that the lowest vacant level is positioned below the highest occupied level in the neutral polyene **3** (compare Fig. 5c and a). Two lowest vacant orbitals, LUMO and LUMO + 1, are totally delocalized, whereas the two next MO are local. In contrast to vacant MOs, both carbon atoms of such short chain in the dication of the ethylene **4** do no take part in the occupied MOs, because of the absence of the own π-electrons. This is responsible for the specific nature of the lowest electron transitions in the polyene dications, as it was established by us earlier for the ethylene-dication containing flavilium residues [13,14].

At last, we consider the frontier and the nearest MOs in the polymethine dye **2**. One can see from comparing Fig. 6b with the Fig. 5b that the energy gap in both cations, **2** and **5**, is situated approximately close. Both HOMO-1 and HOMO-2 are degenerated local orbitals; their shapes are practically the same as the HOMO in the initial cationic salt **6** (Fig. 6a). Because the MO nodes at the atom connecting with the polymethine chain, this MO does not conjugate with the rest of the π-system. The LUMO as well LUMO + 1 are seen from Fig. 6b to be delocalized over the whole molecule.

In the simplest scheme, in the RHF approximation, the position of the single occupied MO in the radical could be treated as producing of the additional level in the energy gap of the virtual system with closed electron shell, i.e. with double occupied orbitals (Fig. 6c). Such model enables to treat more simple and illustrative the electron transitions.

2.6. Electron transitions and absorption spectra

The measured absorption spectra of the compounds **2–6** solutions in the same region (UV, visible and near IR) are presented in Fig. 7 and in Table 1. The simplest spectrum is observed for the cationic polymethine dye **2**; the high-intensive and comparatively narrow spectral band in the longwavelength part and more intensive and wider band in the UV region. Comparing the spectra of the dye **2** and salt **6**, one can see that the position of the second spectral band of the trimethincyanine coincides approximately with the position of the corresponding initial salt. It is seen from Table 2 that the first band is connected practically only with the

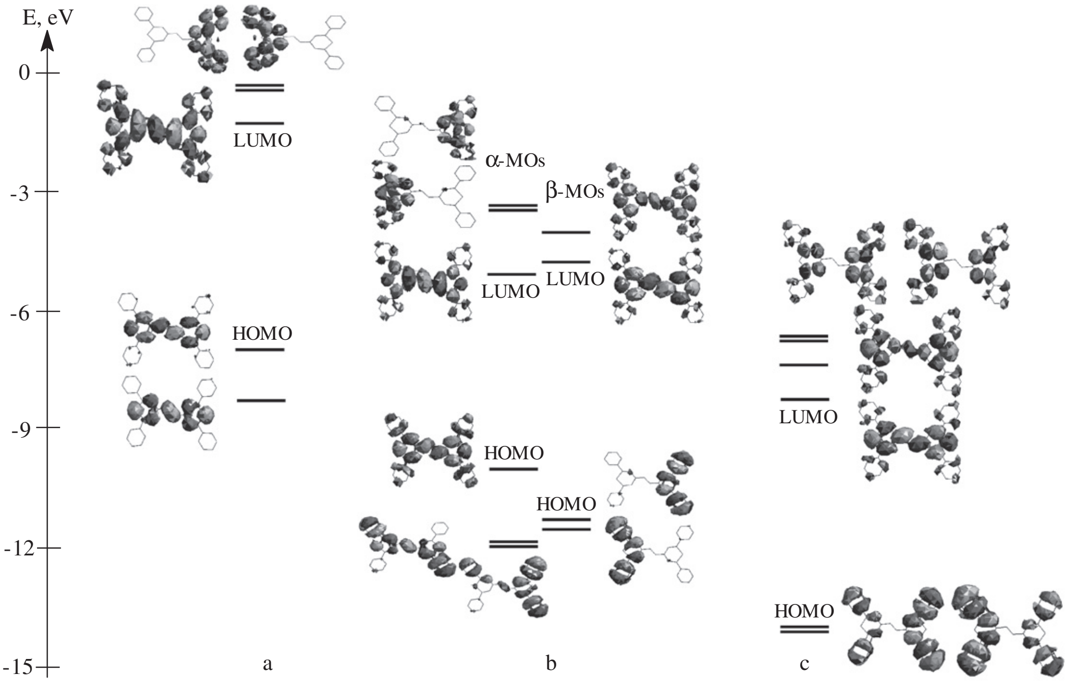


Fig. 5. Positions of the levels and shape of the MOs in neutral polyene **3** (a) [AM1 approximation, RHF version], cationic radical-polyene **5** (b) [UHF], polyene dication **4** (c) [RHF].

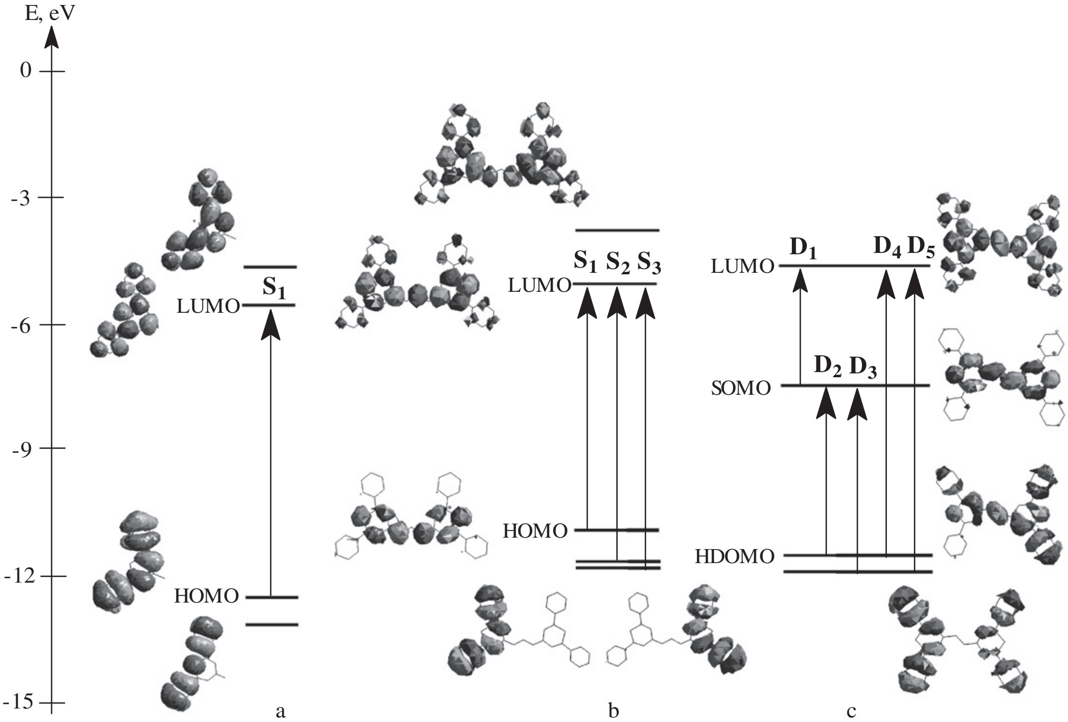


Fig. 6. Scheme of electron transitions in cationic systems: salt **6** (a), polymethine dye **2** (b) and radical-polyene **5** (c); AM1 approximation, RHF version.

electron transition between the antisymmetrical and symmetrical the frontier MOs. Because of fact that the frontier MOs taking part into this transition are of opposite symmetry, the first transition is antisymmetrical, $A_1 \rightarrow B_1$, and is polarized along the polymethine chain; hence its transition dipole momentum is comparative large: $f_1 = 1.876$.

The second and the third electron transitions are seen from Fig. 6b to involve practically degenerated local MOs as well as the LUMO. The calculation shows that both transitions are allowed and are polarized perpendicular to the polymethine chromophore. Data in Table 2 show that the splitting of these local transitions is negligible.

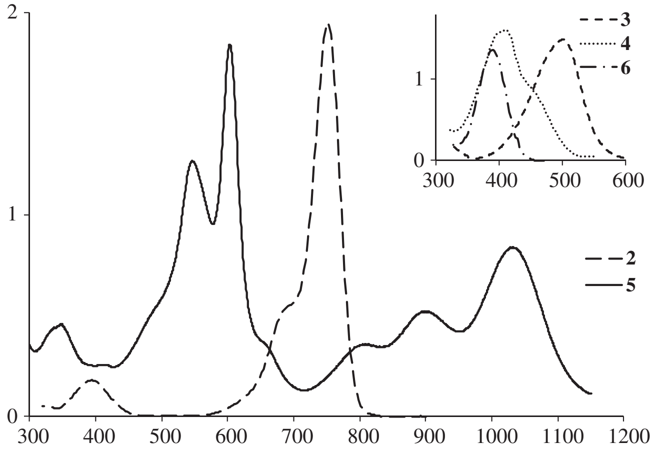


Fig. 7. Absorption spectra of the compounds **2**–**6**.

Table 1
Spectral properties of compounds **2** (**2a**)–**6** (**6a**) in acetonitryl.

Compound	λ_{max}, nm ($\varepsilon \times 10^{-4}$)
2	752 (19.5); 394 (1.8)
2a	760 (20.72); 413 (2.11)
3	500 (7.45)
3a	504 (–); 513[a] (4.66)
4	409 (3.31)
4a	474 (2.62); 411 (3.53)
5	1031 (4.19); 904 (2.6); 813 (1.79); 603 (9.2); 546 (6.32); 347 (2.28);
5a	1040 (–); 908 (–); 817 (–); 605 (–); 556 (–); 364 (–);
6	390 (1.695)
6a	415 (2.32)

[a] In toluene.

Here we should note that the calculated energies of the first and, especially, higher transitions for the cationic linear conjugated systems disagree with the spectral data. It is well-known that there is a serious problem concerning the correlation between the calculated and experimental energies simultaneously for both the first and the higher electron transitions. The parameter OWF (Overlap Weight Factor) in the semi-empirical method ZINDO/S is connected indirectly with the of the electron-electron repulsion $\gamma_{\mu\nu}$ in the integrals J_{ij} and K_{ij} in the transition energy: $\Delta E(S_0 \rightarrow S_p) = \varepsilon_j - \varepsilon_i + 2K_{ij} - J_{ij}$. The standard Mataga–Nishimoto's formulas, $\gamma_{\mu\nu} = a/(1 + R_{\mu\nu})$, where a is constant and $R_{\mu\nu}$ is the distance between the μ-th and ν-th atoms overestimates the electron interaction if the atoms are removed to a great distance from each other [18]. Then, using the same OWF for both totally delocalized and local MOs leads to the too low energies of the higher electron transitions. In this paper, we have used different methods for the comparative estimation of the energies of the first and higher electron transitions, optimistically supposing that divergence between the experimental and experimental transition energies is no so considerable to establish correctly the order of the transitions of the different types: delocalized or local. The central and largest part of our work was to find the nature of the first and higher transitions in the dyes **1–6**, and hence to explain correctly the main reason for the considerable difference between their spectra. Similar methodology was proposed by one of us in the previous work [19].

Practically, the generation of the calculated transitions $|S_0 \rightarrow S_2>$ and $|S_0 \rightarrow S_3>$ indicates that both transitions correspond to the same observed spectral band with the maximum 400 nm. It was shown above, that the local HOMO-1 and HOMO-2 with their nodes at the carbon atom connected with the chain in the dye **2** are practically the same as the highest occupied orbital of the salt **6**. At the same time, the LUMO in both compounds, **2** and **6**, is the solitonic or charge level [20]. Taking into consideration that the salt is an electron-balanced π-system (n π-electrons are delocalized at n π-centers), in contrast to the electron – excessive π-system of the dye **3** ($n + 1$ π-electrons and n π-centers), then going from the salt to the corresponding trimethinecyanine should be slightly accompanied by shifting of the energy gap up, what is in a good agreement with the direct calculation (compare Fig. 6a and b). As a result, the distance between local levels and solitonic level should be close in the both dye **2** and corresponding salt **5**; the observed spectra confirm this conclusion. The similar nature of the short-wavelength spectral band in the spectra of the thiapyrylocyanines (as well as of their heteroanalogues) and of the first band in the spectra of the corresponding salts was additionally confirmed by the spectral and quantum-chemical investigations of the vinylogues series of these dyes: the lengthening of the polymethine chain leads to regular batochromic shift of the longwavelength band at 120–130 nm, whereas the position of the shortwavelength band remains practically the same and coincides with the position of the first spectral band of the corresponding salt [7,21].

Going from the polymethine dye **2** to the related polyenic conjugated systems **3** and **4** with the closed electron shell is seen from Fig. 7 to be accompanied by the significantly hypsochromic shift of the absorption band. This spectral phenomenon, i.e. the considerable distinction in the energy gaps upon comparing two types of

Table 2
Calculated data of compounds **2**–**6** (AM1 approximation).

Dye	Transition	λ (nm)	f	Symmetry	Main configuration, $T_{p,i\rightarrow j}$
6 (salt)	$S_0 \rightarrow S_1$	398	0.722	B_1	$\vert S_1> = 0.96 \vert H \rightarrow L>$
	$S_0 \rightarrow S_2$	338	0.145	A_1	$\vert S_2> = 0.89 \vert H\text{-}1 \rightarrow L> + 0.45 \vert H \rightarrow L + 1>$
3 (**Pe-Tprl**)	$S_0 \rightarrow S_1$	509	1.899	B_u	$\vert S_1> = 0.99 \vert H \rightarrow L>$
	$S_0 \rightarrow S_2$	404	0.017	A_g (Loc+)	$\vert S_2> = 0.86 \vert H \rightarrow L + 1>$
	$S_0 \rightarrow S_3$	402	0.069	B_u (Loc−)	$\vert S_3> = 0.81 \vert H \rightarrow L + 2>$
4 (**Pe-DC-Prl**)	$S_0 \rightarrow S_1$	422	0.005	A_g (Loc+)	$\vert S_1> = 0.55 \vert H \rightarrow L + 1 > -0.74 \vert H\text{-}1 \rightarrow L>$
	$S_0 \rightarrow S_2$	415	1.082	B_u (Loc−)	$\vert S_2> = 0.74 \vert H \rightarrow L > -0.55 \vert H\text{ -}1 \rightarrow L + 1>$
	$S_0 \rightarrow S_3$	352	0.049	A_g (Loc+)	$\vert S_3> = 0.81 \vert H\text{-}2 \rightarrow L> + 0.45 \vert H\text{-}3 \rightarrow L + 1>$
	$S_0 \rightarrow S_4$	351	0.005	B_u (Loc−)	$\vert S_4> = 0.81 \vert H\text{-}3 \rightarrow L> + 0.45 \vert H\text{ -}2 \rightarrow L + 1>$
2 (**Pm-Prl**)	$S_0 \rightarrow S_1$	566 (747)	1.876 (1.218)	B_u	$\vert S_1> = 0.99 \vert H \rightarrow L>$
	$S_0 \rightarrow S_2$	339 (561)	0.149 (0.381)	A_g (Loc+)	$\vert S_2> = 0.83 \vert H\text{-}2 \rightarrow L>$
	$S_0 \rightarrow S_3$	337 (554)	0.049 (0.387)	B_u (Loc−)	$\vert S_3> = 0.81 \vert H\text{-}1 \rightarrow L>$
5 (**Pe-R-Prl**)	$D_0 \rightarrow D_1$	1235 (1308)	0.282 (0.358)	B_u	$\vert D_1> \in \vert SOMO \rightarrow LUMO>$
	$D_0 \rightarrow D_2$	541 (787)	0.008 (0.010)	A_g	$\vert D_2> \in \vert HDOMO \rightarrow SOMO>$
	$D_0 \rightarrow D_3$	428 (600)	1.670 (0.387)	B_u	$\vert D_3> \in \vert HDOMO \rightarrow LUMO>$
	$D_0 \rightarrow D_4$	408 (580)	0.001 (0.006)	A_g	$\vert D_4> \in \vert HDOMO\text{-}1 \rightarrow LUMO>$

Comments. Data in brackets are obtained by ZINDO/S methods (OWF = 0.3).

the linear conjugated system with the same terminal groups, polymethinic and polyenic, is explained in the framework of the Daehne's triad theory by the considerable alternation of the lengths of the carbon–carbon bonds along the chromophore [17], what agrees with the results of our calculations discussed above. The calculated characteristics for the neutral molecule **3** the polyene-dication **4** are presented in Table 2.

One can see that three first electron transitions are described practically by single configuration with the jump of electron from the HOMO to the LUMO, LUMO + 1 and LUMO + 2, correspondingly. Because of the local type of the LUMO + 1 and LUMO + 2, the second and third transitions prove to be degenerated; their oscillator strengths are too low these transitions to be observed in the absorption spectra. Then, the comparatively wide spectral band with maximum at 500 nm corresponds only to the first electron transition. However, the intensity of this band is appreciably lower, in comparison with the longwavelength absorption band of the cationic polymethine dye; so, the extinctions are as follows: $\varepsilon = 7.45 \times 10^{-4}$ (polyene **3**), $\varepsilon = 19.50 \times 10^{-4}$ (polymethine **2**),

In contrast to the neutral disubstituted-ethylene **3** with its delocalized HOMO and HOMO-1 (Fig. 5a), the two highest occupied orbitals in the polyene-dication **4** are seen from Fig. 6c to be degenerated and are local. On the other hand, both lowest vacant orbitals are solitonic MOs and hence should be considered as coupled orbitals. Consequently, the two lowest transitions prove to be the mixed local transitions, as it is seen from calculated data collected in the Table 2. The first transition is forbidden, while the second transition is allowed. The performed calculation gives the similar mixing of the next configurations involving the pair degenerate orbitas: HOMO-2 and HOMO-3 (Table 2). It should be noted that increasing of the number of the single excited configurations upon calculations by the configurational interaction methods leads to the regular increasing of oscillator strengths of the allowed third transition, f_3, whereas the value f_2 decreases. Then, we can suppose, that band maxima at 410 nm in the absorption spectra of the dication **4** correspond to the $S_0 \rightarrow S_3$ transition, while the shoulder in the right side of the main spectral band (what is shifted approximately at 50–70 nm) is connected with the $S_0 \rightarrow S_2$ transition. The calculation gives the distance between these transitions, which close to experimental data.

At last, let us consider the absorption spectrum and, correspondingly, the nature of the electron transitions in the conjugated system **5** with the open electron shell. Here, we are restricted only by the qualitative analysis of the relationships between the observed maxima in the visible and near IR regions, as well as by comparing of the absorption spectra of the two cationic systems: the radical **5** with the open electron and polymethine dye **2** with the closed shell.

Firstly, some spectral maxima are observed in the spectra of the radical **5** positioned more bathochrhromically, in comparison with the longwavelength spectral band of the dye **2** with the same total charge.

Secondly, the comparative narrow and more intensive band with the typical cyanine-like vibronical maximum at the short-wavelength shoulder is observed in the spectrum of the radical **5**, which is positioned approximatively in the same spectral region, as the first band in the spectrum of the dye **2** (see the corresponding curves in Fig. 7).

To interpret the observed spectrum, we use the simplified scheme of the electron levels transitions obtained by calculation in the restricted HF approximation, presented in Fig. 6c. In such model, it is convenient to treat the change in the electronic structure upon going from the π-system of the polymethine-cation **2** to the π-system of the polyene-cation **5** as an appearance of the additional single occupied level (SOMO) in the energy gap. The two new electron configurations with lower energies, connected with the SOMO (HDOMO → SOMO and SOMO → LUMO) are generated, as it is shown in the Fig. 7. These configurations with the same MO should interact substantially, so that two lowest doublet states are described by the following mixture:

$$|D_0 \rightarrow D_1 >\sim |\mathrm{HDOMO} \rightarrow \mathrm{SOMO} > +|\mathrm{SOMO} \rightarrow \mathrm{LUMO} >$$

$$|D_0 \rightarrow D_2 >\sim |\mathrm{HDOMO} \rightarrow \mathrm{SOMO} > -|\mathrm{SOMO} \rightarrow \mathrm{LUMO} >$$

We suppose that the $|D_0 \rightarrow D_1>$ and $|D_0 \rightarrow D_1>$ are just these electron transitions which correspond to the two additional spectral bands in the spectra of the polyene-radical positioned bathochromically, in comparison with the main intensive cyanine-like spectral band, what is observed experimentally (Fig. 7). However, one can see from the Table 2 that the calculations by the AM1 or ZINDO/S methods using the MOs obtained in RHF approximation as basis set for the building the configurations give too low energies of both transitions.

In contrast, the energy of the third transition with the comparatively large oscillator strength, $|D_0 \rightarrow D_3>$, is too high in the AM1 approximation. The ZINDO/S with the same parameter OWF using for the polymethine dye **2** results in the close wavelength of this transition. Consequently, we can propose that the intensive cyanine-like spectral band at 603 nm with the largest extinction, $\varepsilon = 9.21 \times 10^{-4}$, is evidently connected with the $|D_0 \rightarrow D_3>$ transition. Similarly to the first electron transition in the cationic polymethine dye **2**, this transition in the cationic polyene-radical involves one of the splitting donor MO as a starting orbital and solitonic orbital (orbital of the hole or positive charge) as a final MO. As a result, the longwavelength spectral band in the spectrum of the polymethine **2** and high intensive and selective band in the spectrum of the radical **5** are of the same cyanine-like nature.

Of course, the better correlation between calculated and spectral data can be reached by the methods using the spin-orbital (UHR approximation) what involves considerable difficulties upon the constructing the configurational interaction. Here, we have attempted only to connect the observed bands with different intensities in the spectrum cationic polyene-radical **5** with the possible electron transition, as well as to explain the cyanine-like similarity of the intensive spectral band at 603 nm with longwavelength band in the spectra of the cationic compounds of the another type of the linear conjugated system with the same terminal groups.

3. Experimental section

UV/Vis absorption spectra of acetonytryl solutions were recorded on a Shimadzu UV-3100 spectrophotometer. All NMR measurements were carried out on Varian GEMINI 2000 spectrometer with 1H and 13C frequencies of 400.07 and 100.61 MHz, respectively at 293 K. Tetramethylsilane was used as standard for δ scale calibrating. 1H NMR spectra were recorded with spectral width 8000 Hz and numbers of points 32000.

4,4′-(Ethandilyden)-bis[2,6-diphenyl)-4H-thiapyran] 3 and its ethyl-substituted analogue **3a** was obtained similarly to [3–5]. ^{1}H NMR (in $CDCl_2$): **3a** 1.245 (t, 6H, 2× CH_3, J 7.5 Hz); 1.252(т, 6H, 2× CH_3, J 7.5 Hz); 2.688 (c-wide., 8H, 4× CH_2); 6.757 (c, 2H, H-chain); 7.040–7.499 (м, 16H, H-aromatic., 4H, β′, β-H).

4,4′-{(1,2-vinylen)bis[2,6-di(p-ethylphenyl)thiapyrylium]} dibrom 4a ^{1}H NMR (in $CDCl_2$): 1.337 (т, 12H, 4× CH_3, J 7.8 Hz); 2.83 (q., 8H, 4× CH_2, J 7.8 Hz); 7.563 (d, 8H, H-aromatic., J 7.8 Hz); 8.0185 (d, 8H, H-aromatic., J 8.1); 8.851(c, 2H, H-chain); 9.207 (c, 4H, 2 β-H). $C_{44}H_{42}Br_2S_2$. Calcd.% Br 20.11. Found% Br 20.35;

2,6-(p-ethyl)phenyl-4-methylthiapyrylium tetraftorborat 6a $C_{22}H_{23}BF_4S$. Calcld.% C 65.12; H 5.67; F 18.64. Found% C 65.20; H 5.72; F 18.64.

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