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

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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.

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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.
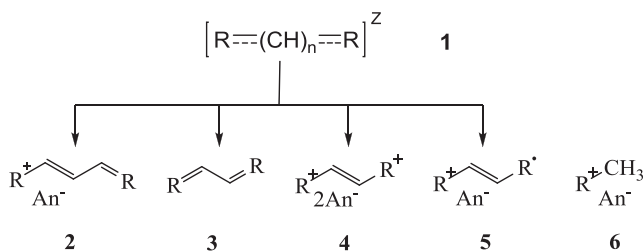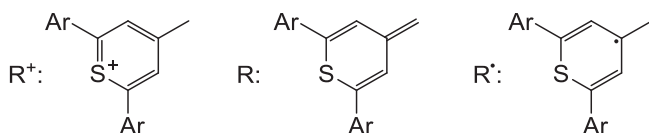
2. Results and discussion

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:

$$\left[R \!=\!=\! (CH)_n \!=\!=\! R \right]^Z \quad \mathbf{1}$$

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 oxidized 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**. Calculated 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