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Electronic properties of polymethine systems. 12. Solitonic nature of charge distribution in the excited state

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Abstract

The electron density distribution in the excited state as compared with the ground state of the ionic polymethine dyes containing both the simplest terminal groups and carbo- and heterocyclic residues are considered. It is found that the charge waves in the excited state are of solitonic nature, however, excitation causes the considerable change in their shape. The dimension of the soliton becomes significantly shorter in excited state than in the ground state; the wave shape and width are highly sensitive to donor strength of terminal groups. In the asymmetrical form, the solitonic wave is shifted to the polymethine chain center.

Keywords: Polymethine dyes; Electron structure; Excited state; Soliton; Symmetry breaking; Quantum-chemical calculation

1. Introduction

Cyanine dyes representing a special type of the charged π-electron organic compounds are well-known due to the broad use of them as light converters [1–6]. They exhibit high intensive and narrow absorption and fluorescence long wavelength bands which can cover the UV, visible and near IR spectral regions up to about 1600 nm by lengthening the polymethine chain or by introduction of specific terminal groups with their extended π-electron systems [7]. Because of their comparatively simple constitution of the chromophore and hence adequate and reliable interpretation of the electron spectra, cyanine dyes have proved to be available systems for the development and testing of new theories of colour or, more correctly, electron transitions in conjugated molecules [7–12].

Many unique spectroscopic properties and features of the electron structure of the cyanine dyes, especially, with the long polymethine chain can be correctly interpreted by only involving conception of solitons or charge waves and geometrical defects in the charged π-electron systems; i.e. it was found that a total charge (positive or negative) is not delocalized uniformly along the whole linear chromophore but it is distributed at carbon atoms as a wave of the electron density [13–17]. The quantum-chemical calculations show that the charge wave in the linear conjugated molecules is of finite length, approximately 15–17 carbon atoms for unsubstituted polymethine chain [14,15,18,19]. Since the polymethine chain is non-rigid π-electron system (in the contrast to, for example, a crystal), the wave of the partial charges raises to the corresponding rearrangement of the molecular geometry, primarily, the C–C bond lengths. It was established that the equilibrium C–C bond lengths are practically, equalized in that chain segment where the soliton is located [14,18,19].

In the unsubstituted cationic and anionic polymethines in the ground state, centers of the charge and

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geometrical solitons are located in the chain center. However, introduction of terminal amino- or dimethylamino-groups or pyridinium, thiapyrylium, benzothiazolium, indolenium and other residues (typical cyanine dyes) can affect substantially the location and shape of the solitonic waves. If the dimension of the soliton turns out to be shorter than the length of the conjugated chain, the wave center is shifted to one of the end groups, i.e. symmetry breaking occurs which manifests itself for example in the absorption spectra [20–22]. Based on the spectral and quantum-chemical data, it was assumed that near IR cyanine dyes with long chromophore may exist simultaneously in two charge-isomer forms with symmetrical and asymmetrical disposition of the solitonic wave maximum [22].

Excitation of cyanine dyes by light quantum is known to lead to substantial redistribution of the electron densities at the atoms in the chromophore (see, for example [6] and references therein). Earlier, we have shown that dimension and location of the soliton can change in the excited state in the thia-, pyridocyanines and their heteroanalogues [21–23]. This paper presents the results of the systematic quantum-chemical study on the dependence of the shape, dimension and location of the charge wave in the first excited state in the cyanine dyes containing both the simple terminal groups and complex residues with the extended π-electron system.

2. Objects and methodology

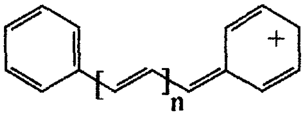
As the simplest model polymethine dyes, we have investigated the linear conjugated cationic and anionic compounds: the unsubstituted polymethines **1** as well as so-called streptocyanines **2** and malocyanines **3** with the heteroatomic end groups.

$$H_2C^+{-}(CH{=}CH)_n{-}CH{=}CH_2 \qquad \mathbf{1}\,(Pm-C)$$

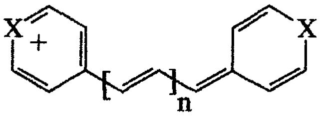
$$(CH_3)_2N^+{=}CH{-}(CH{=}CH)_n{-}N(CH_3)_2 \qquad \mathbf{2}\,(Str)$$

$$(NC)_2C^-{-}(CH{=}CH)_n{-}CH{=}C(CN)_2 \qquad \mathbf{3}\,(Mal)$$

Also, we have studied the electron structure in the cationic α,ω-diphenylpolymethines **4** as well as in the related well-known pyridocyanines and heteroanalogues **5** in their excited states.



4



X = NCH$_3$, O, S **5**

The dyes **4** and their heteroanalogues **5**, are suitable models for the investigation of the dependence of the electron structure of the chromophore on the electron donor properties of the end groups by changing only the nature of the heteroatoms X in the cations providing practically the same topology of the terminal residues. Although the experimentally investigated pyrido-($X = NCH_s$), pyrylo-($X = O$) and thiapyrylocyanines ($X = S$) contain, as a rule, the substituents CH_3, $C(CH_3)_3$, Ph, Th in the positions 2 and 6 [21,24], however, such modification in the chemical constitution does not lead to principal qualitative changes in the electron density distribution in the main chromophore.

In this paper, we will consider only the Frank-Condon electron transitions with the unchanged molecular geometry that corresponds to absorption spectra, and hence will assume that the location of the geometrical solitons remains the same as in the ground state. Meanwhile the changes in the electron occupation at the atoms and changes in the bond orders upon excitation could be appreciable.

It was mentioned above that the ionic polymethine dyes including cyanines are characterized by the considerable alternation in the electron densities at the atoms (π-centers) in the chromophore chain. The alternation degree was proposed to estimate quantitatively by the following parameter [15]:

$$\Delta q_\mu = (-1)^\mu (q_\mu - q_{\mu+1}) \qquad (1)$$

where μ is the number of atoms in the π-system and q_μ is the electron density at the μ-th atom.

As more simple value, the magnitude $|\Delta q_\mu|$ is often used [15,18]:

$$|\Delta q_\mu| = |q_\mu - q_{\mu+1}| \qquad (2)$$

Parameter Δq_μ was called the "bond ionicity" and could be treated as a vector Δq_μ directed from the atom with an electron deficiency to the atom with an excess of electron density along the bond between these atoms [15].

Similarly, the amplitude of the alternation of the bond lengths, l_ν, can be quantitatively estimated by the corresponding value $|\Delta l_\nu|$ [14,18]:

$$|\Delta l_\nu| = |l_\nu - l_{\nu+1}| \qquad (3)$$

where ν is the number of the bond in the chain.

The maximum of the $|\Delta q_\mu|$-function corresponds to the position of the charge wave (charge soliton) center while the minimum of the $|\Delta l_\nu|$-function gives the