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Dyes and Pigments 71 (2006) 19–27

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

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Received 27 April 2005; accepted 18 May 2005

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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0143-7208/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2005.05.014

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

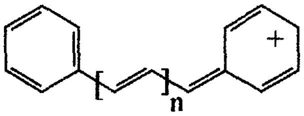
As the simplest model polymethine dyes, we have investigated the linear conjugated cationic and anionic compounds: the unsubstituted polymethines **1** as well as so-called streptocyanines **2** and malocyanines **3** with the heteroatomic end groups.

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

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

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

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.



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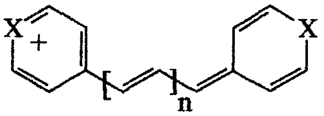

$X = NCH_3$, O, S **5**

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]:

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

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]:

$$|\Delta q_\mu| = |q_\mu - q_{\mu+1}| \tag{2}$$

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]:

$$|\Delta l_\nu| = |l_\nu - l_{\nu+1}| \tag{3}$$

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 position of the geometrical soliton. In the ground state, in the global energy minimum, the locations of both solitons coincide [18]. In the excited state, the mobile charge soliton, of course, could be instantly shifted from its position in the ground state whereas the location of the geometrical soliton in the excited state should depend on the vibronical relaxation which is a long-run process. Here, the location of only the charge wave is studied.

Taking into consideration that the calculation in the framework of both the non-empirical ab initio and semi-empirical AM1 approximations give similar shape of the solitonic waves of the atomic charges and C–C bond lengths in the linear conjugated molecules [14,15], we have used the AM1 method for the numerous systematic calculations of the equilibrium molecular geometry in the ground state and charge distribution in both the ground and excited states for the vinylogous serii of the polymethine dyes **1–4**. Only, the symmetry breaking in the streptocyanines **2** was tested by both the methods: ab initio and AM1. The packages HyperChem and MOPAC were used; the procedure of the molecular geometry optimization was stopped when the energy gradient of 0.1 kcal/mol was achieved. Upon calculation of the excited state, the configurational space has included 4 highest occupied MOs and 4 lowest vacant MOs.

We have found that the direct optimization of the molecular geometry with the relatively long polymethine chain leads to unsymmetrical form as the more stable. The symmetrical form can be obtained provided the optimization procedure starts from the equilibrium molecular geometry of the corresponding neutral radical (which is symmetric, by definition as a neutral conjugated molecule) and is cut off before a soliton begins to move (energy gradient should be higher than 1–2 kcal/mol). Also, it was shown that the equilibrium geometries of the cationic polymethine dyes and their neutral radicals coincide closely enough so that the main characteristic, wavelength of the electron transition in the dyes calculated upon two different molecular geometries (ionic dye and neutral radical) differ between each other only by 10–20 nm which is essentially lower than the accuracy of the AM1 approximation [23]. And consequently, we have used the equilibrium geometries of the corresponding radicals as a geometry for symmetrical form of the cationic long dyes.

3. Symmetrical form

In the simplest unsubstituted polymethine cations **1**, the charge wave center was shown earlier to be located just in the chain center, while the shape of the charge soliton in the streptocyanines **2** with the electron donor dimethylamino-residues as end groups suffers essential distortion and its maximum disappears [18,19,23]. Fig. 1a–d presents the charge distribution, q_μ, and function Δq_μ (1) for the polymethine **1** and streptocyanines **2** with the same number of vinylene groups, $n = 7$. One can see that in the ground state, the amplitude of the charge alternation at both the chain ends in the streptocyanine **2** is even higher than in the chain middle (Fig. 1b and d), in contrast to the corresponding unsubstituted polymethine **1** (Fig. 1a and c). Such spreading of the charge wave in the substituted conjugated systems is found to be accompanied by considerable equalizing of the lengths of the C–C bonds near to the terminal groups which can lead to the symmetrical breaking in the dyes with enough long chains [18,23].

Excitation of the dye cation from the ground state to excited state upon light absorption causes considerable redistribution of the charges at carbon atoms which is clearly seen from Fig. 1. In the chain middle, the electron densities are transferred from the atoms in the odd position to the neighbouring atoms so that “bond ionicities” vectors Δq_μ^* in the excited state reverse their directions. However, at both the chain ends, the directions of the vectors Δq_μ^* and Δq_μ^0 coincide, only the amplitude of the charge alternation in the excited state, $|\Delta q_\mu^*|$, becomes somewhat smaller when compared with the ground state. Meanwhile the $|\Delta q_\mu^*|$ values in the excited state for the pair of the atoms nearest to the end groups in unsubstituted polymethine **1** ($n = 7$) are close to the $|\Delta q_\mu|$ values in the ground state.

These features of the charge distribution in the chain middle and in the chain ends in the excited state when compared with ground state clearly indicate that there is a special segment in the total chromophore where the charge wave changes its shape upon excitation. At both boundaries of this segment, the charges at the neighbouring atoms are very close, so that the function $|\Delta q_\mu^*|$ reaches its minimum, as one can see from the $|\Delta q_\mu^*|$ values for the vinylogous series of the dyes **1** and **2** presented in Fig. 2. In the unsubstituted polymethines **1** (Fig. 1a), the positions of the two minima, $|\Delta q_\mu^*|_{\min}$, do not depend on the number of the vinylene groups, n, in the conjugated chain.

We would propose to consider the charge wave in the central segment of the chain, where vector Δq_μ^* changes its direction to opposite, as a soliton in the excited state. Consequently, the distance between two minima of the function $|\Delta q_\mu^*|$ can be taken as a dimension of this wave. One can see immediately from Fig. 2a that the calculated dimension of the “excited soliton” for the unsubstituted polymethines **1** is considerably shorter than the charge wave in the ground state (15–17 carbon atoms [13,14,18–20,23]). Unlike the unsubstituted polymethines **1**, lengthening of the chain of the streptocyanines **2** seen from Fig. 2b causes widening of the curves $|\Delta q_\mu^*|$ nearly to both the minimum points so that the outer boundaries of the soliton in the excited state tend to spread.

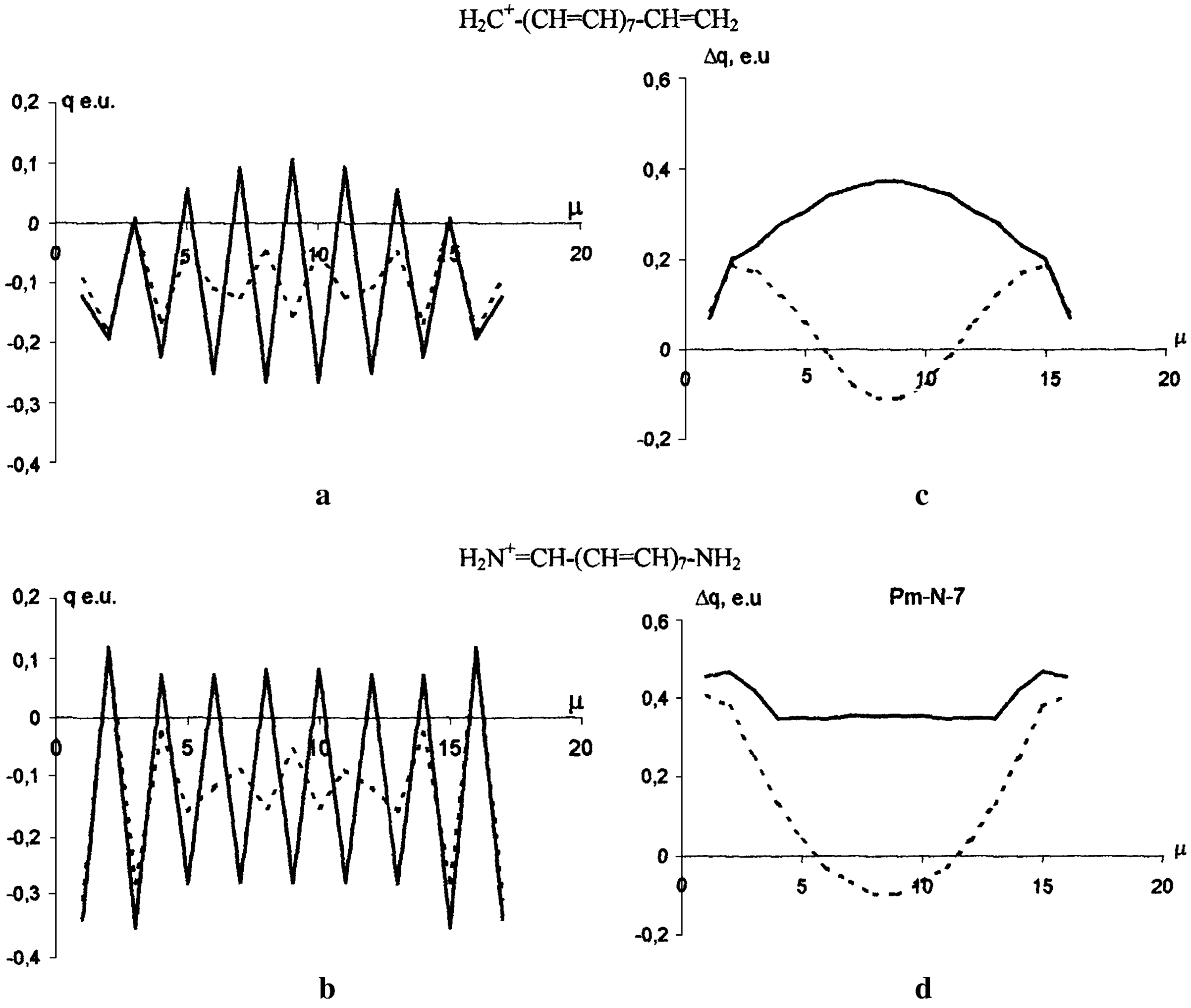

Fig. 1. Charge distribution q (a, b) and charge alternation Δq (c, d) in the unsubstituted polymethine **1**, $n = 7$ (a, c) and in the streptocyanine **3**, $n = 7$ (b, d); — ground state, - - - excited state.

The similar picture is observed also for dyes **4** and **5** containing more complexed terminal residues. One can see from Fig. 3a that excitation to the higher vinylogous in the series of the α,ω-diphenylpolymethines **4** is accompanied, first, by the increase in the minimum amplitude $|\Delta q^*_\mu|$ ($n = 3,4$); thereafter ($n = 5$) $|\Delta q^*_\mu|$ values became equalized along the large segment of chain; and the last ($n = 6$), the calculation shows the function $|\Delta q^*_\mu|$ to have single minimum, in contrast to the unsubstituted polymethines **1** with their two minima, independent of the number of the vinylene groups in the chain (compare with Fig. 2a).

Replacement of the phenyl residues by the donor heterocyclic end groups, for example, pyridinium residues, leads to somewhat increase in the soliton dimension (Fig. 3b) which can be explained by the decrease in the alternation in the bond lengths at both the chain ends.

A contraction in the dimension of the soliton and hence an appearance of two minima in the charge alternation function $|\Delta q^*_\mu|$ should involve a decrease in stability of the symmetrical form of the dyes in the excited state. Consequently, we have suggested that there exist simultaneously two forms for those molecules which are symmetrical in the ground state: the first form with the symmetrically located soliton and the second form with asymmetrical location of the soliton in the chain. This suggestion was supported experimentally using the low-temperature time-resolved fluorescence spectra, where we have found two components with the different life-time and different maxima in the fluorescence spectra of the thiacarbocyanine and its derivatives with the bridges in the chain [25].

4. Asymmetrical form

The symmetry breaking and hence the optimized asymmetrical form of the cyanine cations can be obtained in both the non-empirical and semi-empirical

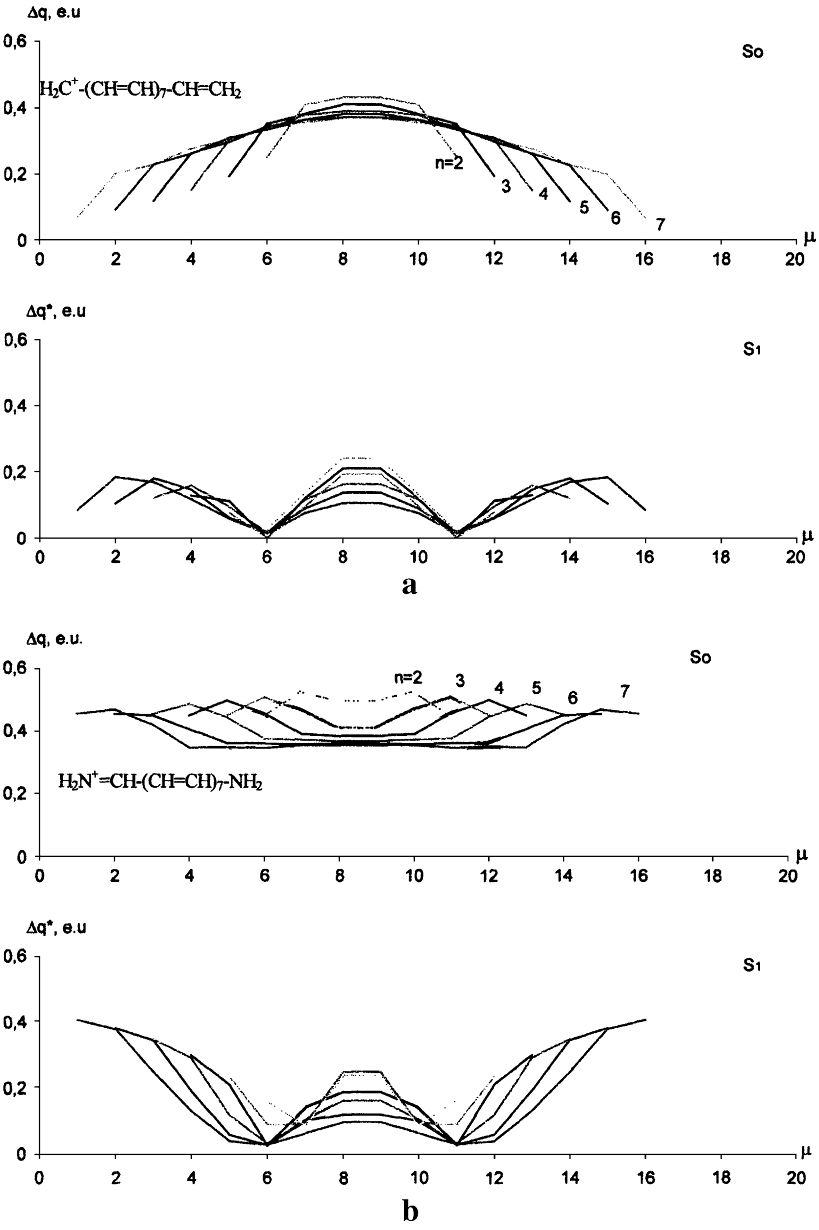

Fig. 2. Charge alternation in the ground state (S_0) and excited state (S_1) in the vinylogous series of the unsubstituted polymethine (a) and streptocyanines (b).

approximations. As a typical example, the positions of the "topological" soliton or the minimum of the function $|\Delta l_\nu|$ for the vinylogous series of the unsubstituted polymethines **1** and streptocyanines **2** calculated by the ab initio (STO 6-31G**) and AM1 methods are presented in Fig. 4. Both approximations give the same crucial number of vinylene groups, n_{cr}, in the chain of the vinylogous series of the streptocyanines when the symmetry in the equilibrium molecular geometry breaks, and the center of the topological soliton is shifted from the chain center (Fig. 4b), unlike the unsubstituted polymethine cations **1** with the same position of the $|\Delta l_\nu|$ minimum in the chain center, independent of the number of the vinylene groups, n, in the chain. One can see from Fig. 4b that subsequent lengthening of the chromophore is accompanied by regular shift of the soliton to one of the end groups, although its locations obtained at the different approximations do not coincide. At the same time, no symmetry breaking occurs in the unsubstituted polymethine cations **1** which is shown to be connected with the fact that the alternation amplitude of C–C bonds at both the chain ends increases regularly upon lengthening of the chromophore. In contrast to the unsubstituted polymethines **1**, the dimethylamino-residues as end groups in the streptocyanines **2** cause considerable equalizing of the bond lengths at the chain ends. This decrease in the bond length alternation nearly to the end residues resembles the bond length equalizing in the location of the charge and hence "topological" solitons. As a result, the soliton can move along the chain and transfer to one of the end groups upon enough lengthening of the charged π-conjugated system.

Here, we will calculate the charge distribution in both the ground and excited states and transferring of the charge wave upon excitation in the series of the dyes not only with the simplest terminal groups, but also with end residues containing the own extended π-electron system, and hence will use only the semi-empirical AM1 approximation below.

It was shown earlier that the AM1 calculation gives the symmetry breaking for the well-known thia-, pyrido- and thiapyrylocyanines upon shortening of the length of the polymethine chain [19,23]. In the just same way, the symmetry breaking was found [19] to appear in the anionic malocyanines **3**. The AM1 calculation gave $n_{cr} = 7$ for these dyes. It is to be noticed that, similar to the cationic polymethines **1**, the corresponding anionic unsubstituted polymethines, $H_2C^-{-}(CH{=}CH)_n{-}CH{=}CH_2$, do not exhibit symmetry breaking upon an arbitrary length of the chain, similar to the series of the cationic analogs **1** [19].

The shifting of the solitonic charge wave from the chain center occurring upon symmetry breaking should cause self-evidently the essential change in the soliton

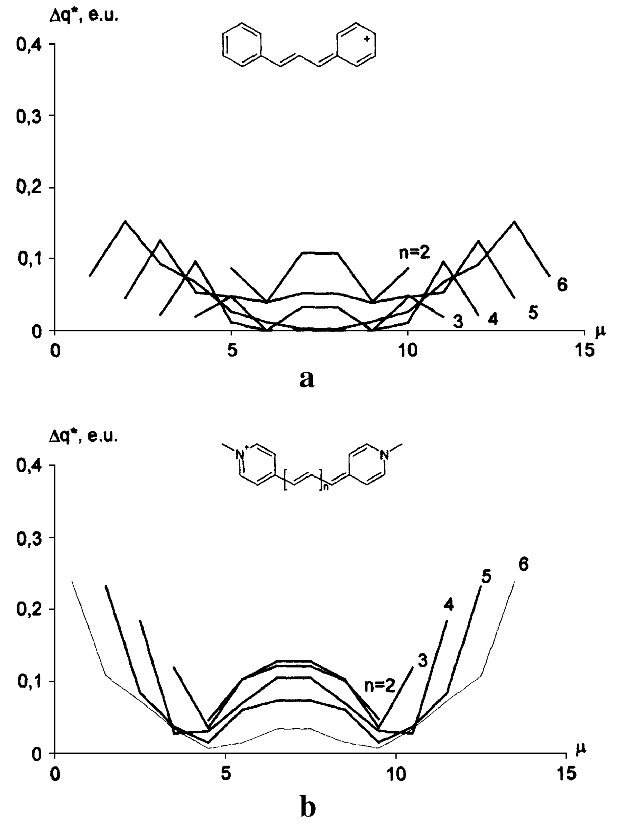

Fig. 3. Charge alternation Δ*q* in the excited state in the dyes **4** (a) and dyes **5** (b).

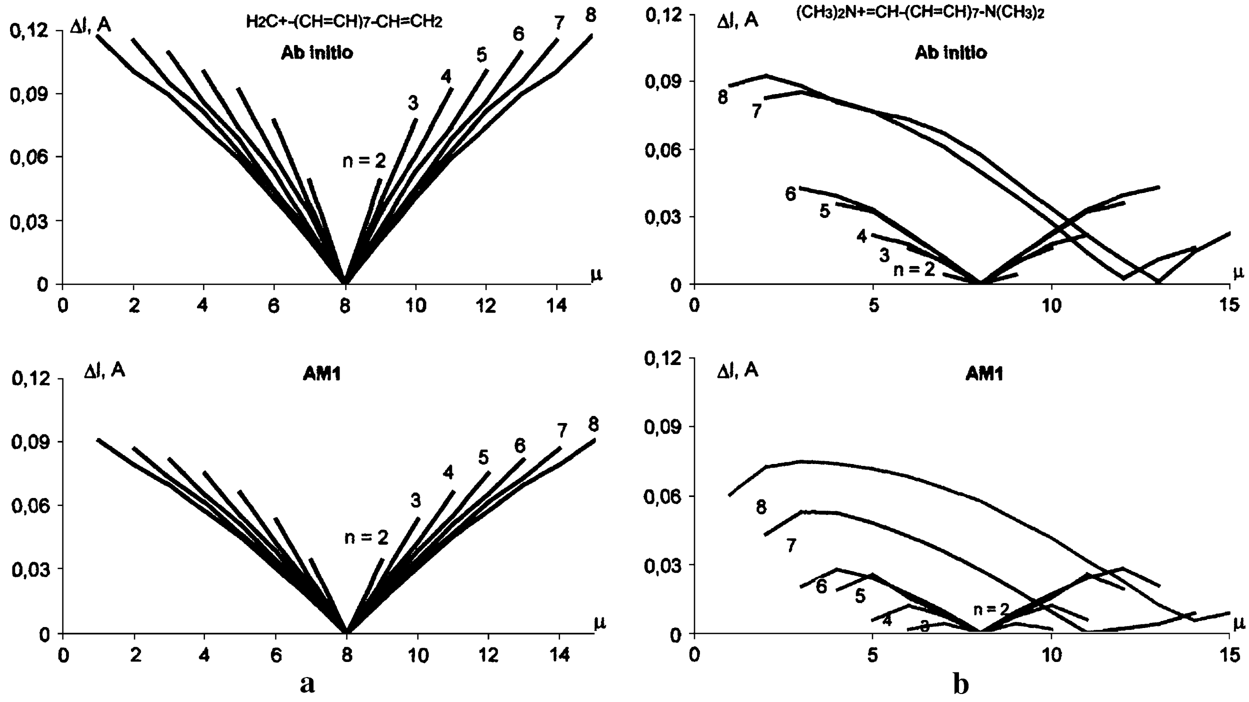

Fig. 4. Bond length alternation (Δl_v) in the ground state in the polymethines **1** (a) and streptocyanines **2** (b) calculated by the ab initio and AM1 approximations.

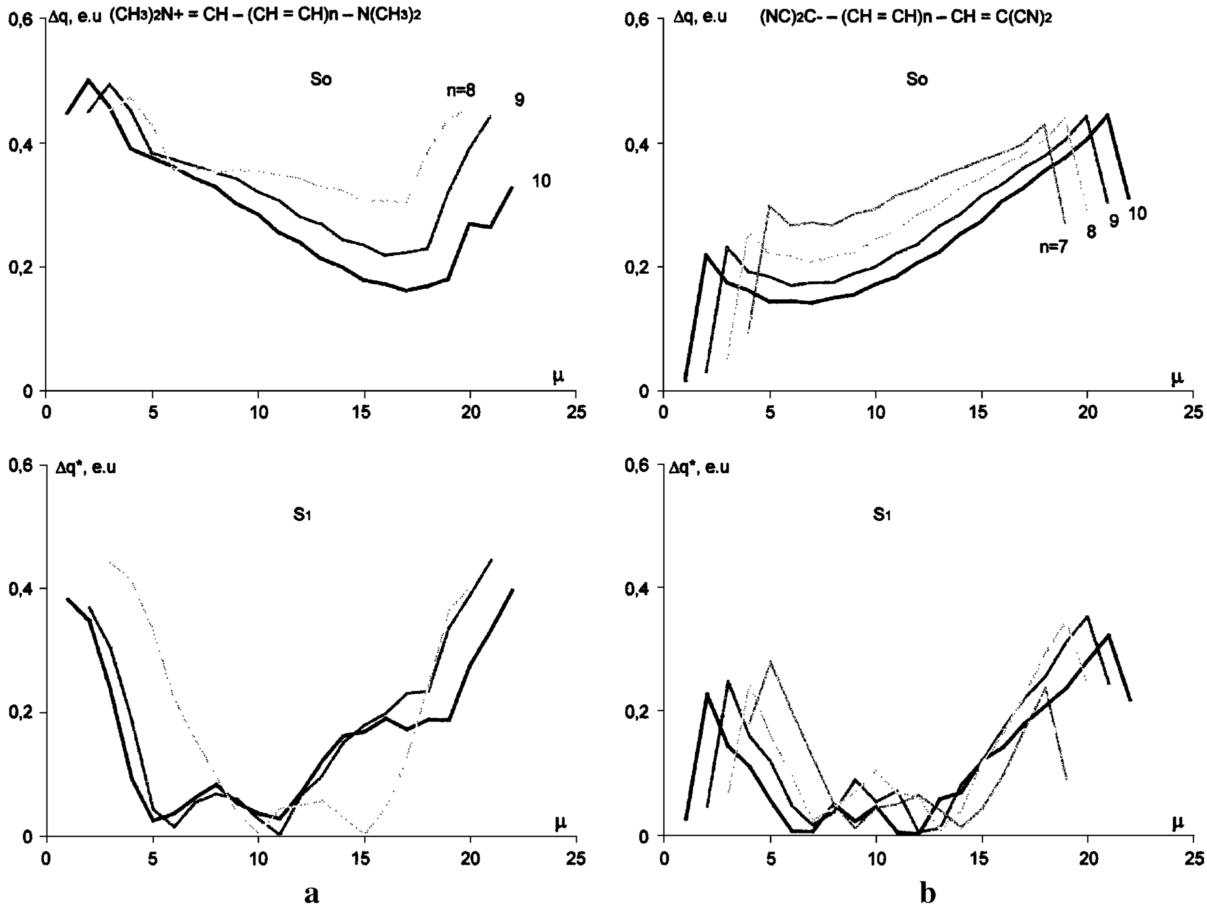

Fig. 5. Charge alternation Δq in the ground (S_0) and excited state (S_1) in the asymmetrical forms of the streptocyanines **2** (a) and malocyanines **3** (b).

shape in the excited state. We have shown earlier that the electron density in the first excited state of the asymmetrical form of the higher vinylogous of the thia-, pyrido- and thiacyanines is distributed along the chromophore more symmetrically than in the ground state [21,22]. Now, we will study in detail the dependence of the position of the soliton in the excited state (or maximum of the function $|\Delta q^*_\mu|$) in the asymmetrical form on the number of the vinylene groups in the chain as well as on the basicity of the end residues.

In Fig. 5, the calculated $|\Delta q^*_\mu|$ values for the simplest cationic streptocyanines **2** and anionic malocyanines **3** providing $n > n_{cr}$ are presented. One can see that the shape of the charge wave in the excited state somewhat resembles the function $|\Delta q^*_\mu|$ for the unsubstituted polymethine **1** (Fig. 2a) or even the symmetrical form of the streptocyanines **2** (Fig. 2b), only the solitonic waves are shifted from the chain middle. Existence of the well-defined "excited soliton" (although asymmetrical) with its two specific pronounced quasi-minima is inherent for both the cationic streptocyanines **2** and anionic malocyanines **3**. Comparing with the charge waves in the ground state, we can conclude that the excitation leads to the essential "symmetrization" of the electron density distribution in the chromophore. The lengthening of the polymethine chain seen from Fig. 5 is accompanied by the regular shift of the charge wave from the chromophore center. Also, the function $|\Delta q^*_\mu|$ becomes irregular, unlike the relatively smooth curves for the symmetrical form (compare with Figs. 2 and 3). One would expect that the vibronic relaxation in the excited state will lead to smoothing out the shape of the charge wave (more correctly, the function $|\Delta q^*_\mu|$), in contrast to the Frank-Condon excited state.

The influence of the donor strength of the end groups on the location of the soliton in the excited state can be examined in the pyridocyanines and their heteroanalogues **5**. Fig. 6 presents the charge alternation along the polymethine chain in both the ground and excited states in the asymmetrical form of the dyes **5**. Although the functions $|\Delta q^*_\mu|$ are not smooth, especially in the higher vinylogous, nonetheless some regularities can be established. So, for the shortest unsymmetrical forms of each series of the dyes **5** (X = O, $n = 6$; X = NCH_3, $n = 5$ and X = S, $n = 4$), the calculations show two pronounced quasi-minima for the function $|\Delta q^*_\mu|$; the distance between them and shift from the chain center

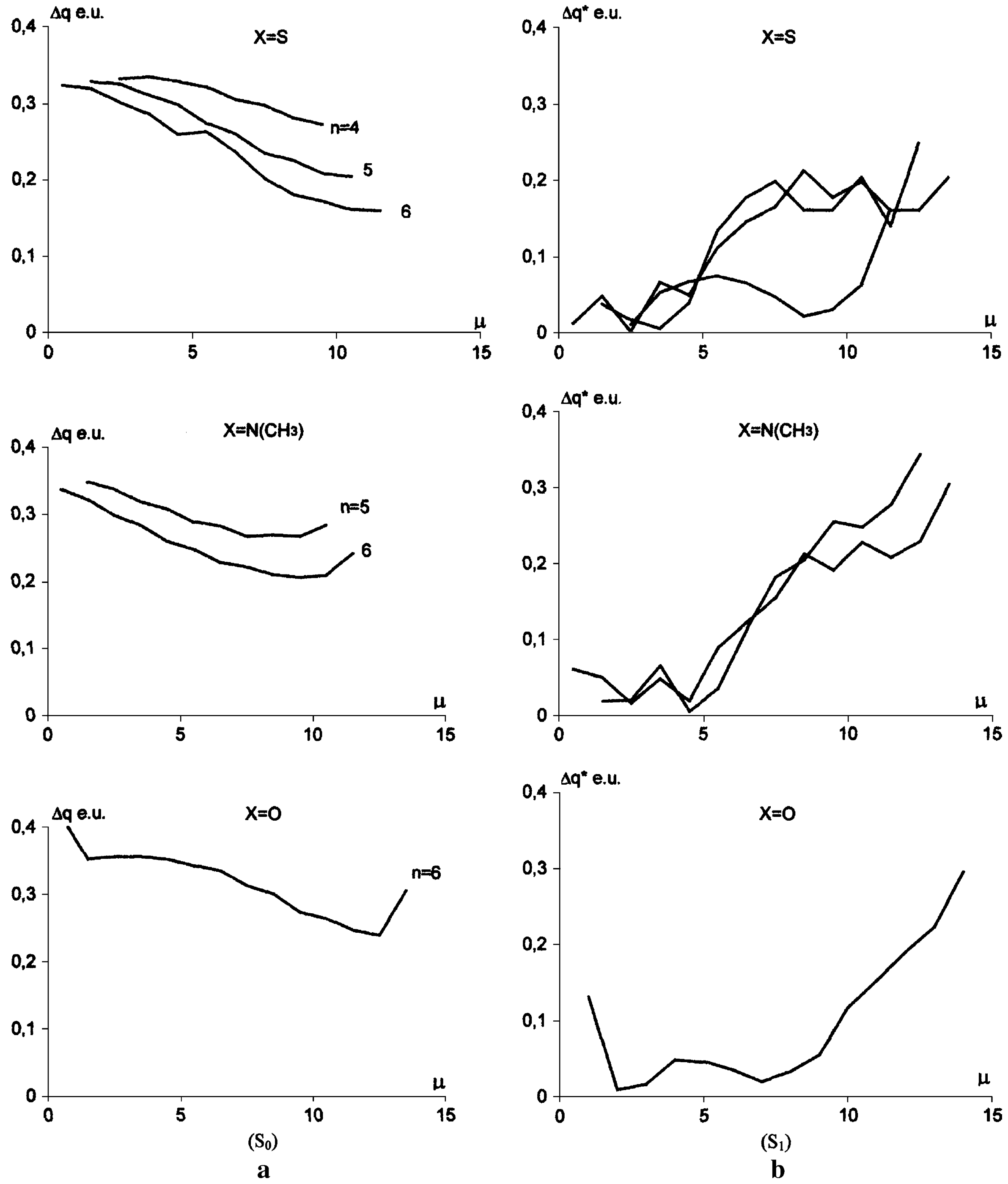

Fig. 6. Charge alternation Δq in the ground (S_0) and excited state (S_1) in the asymmetrical forms of the dyes **5**: X = S, NCH_3, O.

depend unambiguously on the basicity of the heterocyclic end residues. The next introduction of the vinylene groups in the polymethine chain leads to the growing distortion in the original shape of the solitonic wave, as compared with the excited state of the unsubstituted polymethines **1** (Fig. 2a). Again, one can suggest that the relaxation of the molecular geometry of the asymmetrical form should tend the function $|\Delta q^*_\mu|$ to become more smooth.

5. Conclusion

Thus, our quantum-chemical investigation shows that the excitation of the ionic polymethine dyes causes considerable change in the shape of the charge wave; its dimension becomes significantly smaller and depends on the basicity of the terminal groups. In the asymmetrical form, the "excited soliton" proves to be shifted to the chromophore center when compared with the location of the charge wave in the ground state; the chain lengthening causes the distortion of the smooth shape of the charge wave in the excited state for the asymmetrical form of the cyanine dyes.

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