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Electronic properties of polymethine systems. 11. Absorption spectra and nature of electron transitions in cationic oxystyryl and their neutral derivatives

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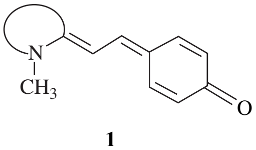
Abstract

Complex quantum-chemical and spectral study of the features of the electron transitions and absorption spectra of the both oxystyryls and related merocyanines containing the pyridinium, quinolinium, indolium and benz[*c*,*d*]indolium end residues has been performed. It was shown that the relative long wavelength absorption of the neutral merocyanines, in comparison with the cationic dyes, is caused by considerable redistribution of the electron density within the chromophore upon excitation, not by equalizing of the carbon–carbon bond lengths as it was predicted in the framework of the conception "cyanine limit". The opposite sign change of the dipole momentum in the excited state in the cationic and neutral dyes depends noticeably on the basicity of the donor end groups and causes the opposite solvatochromism which increases additionally the distance between the absorption bands of these dyes of the different types.

Keywords: Merocyanines; Oxystyryls; Electron structure; "Cyanine limit"; Absorption spectra; Quantum-chemical calculation

1. Introduction

Merocyanine **1** are typical high polarizable donor–acceptor molecules which can be considered as neutral derivatives of cationic oxystyryls **2**.



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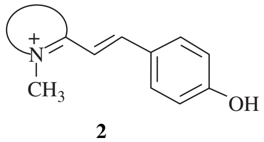

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Notwithstanding that these two related types of the linear conjugated systems differ from each other insignificantly in the chemical constitution, first of all, by a number of atoms bonded by σ-bonds and by hybridization of the oxygen atom, they exhibit the electron–structural similarity: oxystyryls **2** and merocyanine **1** contain the same number of the π-electrons. However, there is a principal distinction between π-electron systems of the compound **1** and **2** which is connected with a total charge: oxystyryls **2** are charged conjugated systems while merocyanine **1** are neutral molecules. It causes the sharp difference in the electron structure and spectral properties, in particular, in shape and position of the long wavelength absorption band [1,2]. In the contrast to the neutral cyanine bases absorbing in the shorter spectral region than the corresponding cationic cyanine [3], the absorption band is shifted bathochromically from charged oxystyryls **2** to their neutral merocyanines **1** [1,2].

As donor–acceptor π-electron molecules, the compounds **1** are well-known highly sensitive sensors on the solvent polarity [4] as well as they are used as the suitable model for the wide quantum-chemical study of the

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solvatochromism [5,6]. The theoretical model was based on the fact that **1** similarly to other types of the merocyanines consist of an electron donor residue (D) and an electron-acceptor group (A) linked by the polymethine chain, so that their highly polarizable π-electron structure can be described in terms of the resonance between a neutral form **3** and a charge-separated form **4**:

$$\underset{\mathbf{3}}{\mathrm{D-(CH=CH)}_n\mathrm{-A}} \leftrightarrow \underset{\mathbf{4}}{\mathrm{D^+=(CH-CH)}_n\mathrm{=A^-}}$$

The contribution of each resonance form depends self-evidently on solvent polarity. It was postulated that by providing the equal weights of two forms, there arises the so called cyanine-like structure which is, first of all, characterized by the minimum bond length alternation and the maximum in the wavelength of the first absorption band [6].

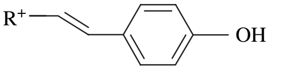
The growing interest in the merocyanines in the last two decades is connected with use of these compounds as non-linear optical materials (see review [7] and references therein). It was found that the higher hyper-polarizibilities, β_o and χ_o, are unambiguously determined by the donor and acceptor strengths of the terminals groups or, more correctly, by difference in the dipole moments in the excited (μ_e) and ground (μ_g) states: $\Delta\mu = \mu_e - \mu_g$, which, in turn, depends on the alternation of the lengths of the carbon–carbon bonds in the conjugated chain, so called parameter BLA [7,8]. Increasing of the BLA upon the increasing of the difference in the donor strength and acceptor strength causes the growth of the second hyperpolarizibility, β_o, but only to the crucial magnitude; thereafter parameter β_o decreases because of the decreasing of the overlap of the ground and excited state functions, $<\Psi_g|\Psi_e>$, and hence decreasing of the transition momentum, μ_{ge} [7].

Also, it was found in the framework of the topological (Hückel) approximation [8] that the BLA value can be both negative and positive, depending on the donor and acceptor strengths of the end residues (or Coulomb and resonance integrals of the terminal heteroatoms in the model donor–acceptor conjugated molecule). Providing the fixed difference in the electron donor–acceptor ability, BLA = 0 and "cyanine limit" can be reached. However, investigations in the approximations taking correctly into consideration an electron interaction have shown that the merocyanines could exhibit some features in the dependence of the electron structure on the nature of the end groups [6]. So, cyanine-like structure (BLA = 0) is not reached in the merocyanine $(H_3C)_2N-(CH=CH)_2-CH=O$, even in the extremely polar media. In contrast, in the meroform of the pyridoxystyryl, the charge-separated resonance structure prevails and parameter BLA is negligible which leads to the inversion of the solvatochromism, as compared with the merocyanines [6].

One can assume that properties of the meroforms should strongly depend on the donor strength of the nitrogen-containing end residue, as well as on the extending of the π-electron system of the total chromophore at the conjugation with own π-system of the end group. In this paper, we present the results of the quantum-chemical and spectroscopic study of the oxystyryls **5** and merocyanine **6** with the various heterocyclic donor residues which simulate decrease of the donor strength regularly.

2. Objects and methodology

The formulae of the oxystyryls **5** and their neutral derivatives, merocyanines **6**, investigated are following:



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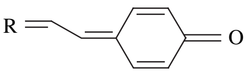
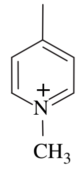


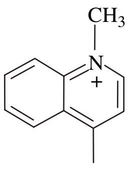
6

where R is end group. In present article, the following heterocyclic residues were used as end groups:

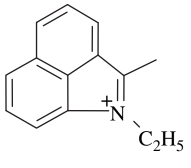
R⁺:



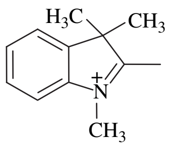
5-Py



5-Qu

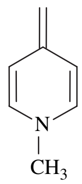


5-BIn

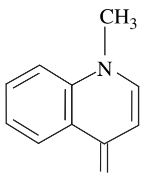


5-In

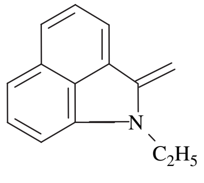
R :



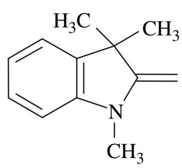
6-Py



6-Qu



6-BIn



6-In

Synthesis of dyes: 4-[(*E*)-2-(4-hydroxyphenyl)vinyl]-1-methylpyridinium (**5-Py**), 4-[(*E*)-2-(4-hydroxyphenyl)-vinyl]-1-methylquinolinium (**5-Qu**), 2-[(*E*)-2-(4-hydroxyphenyl)vinyl]-1-methylbenzo[*c*,*d*]indolium (**5-BIn**), 2-[(*E*)-2-(4-hydroxyphenyl)vinyl]-1,3,3-trimethyl-3*H*-indolium (**5-In**) were described earlier [9]. Absorption spectra were recorded on a spectrophotometer Shimadzu UV3100. Spectral grade acetonitrile was mainly used as a solvent for spectral measurements.

To study the electron structure and to interpret the nature of electron transitions, quantum-chemical calculations were performed. The equilibrium geometry of dye molecules in the ground state was mainly optimized in the semi-empirical AM1 approximation, only the compounds **5-Py** and **6-Py** as where as one the simplest classical merocyanines were calculated also in the non-empirical ab initio approximation. The electron transition characteristics were calculated by ZINDO/S methods, using all π-electron single excited configurations. The crucial parameter, overlap weight factor (OWF), was varied over a wide range taking into consideration simultaneously both the considerable bond length alternation in the chain and somewhat the equalizing of the lengths of bonds in the end groups, however, it was difficult if not impossible to obtain the well correlation between the calculated and experimental data. Only upon the different OWF values for cations (0.400) and neutral dyes (0.585), the acceptable results were found which could be carefully used for analysis of the nature of the electron transitions in the both types of the compounds, **5** and **6**, with the low and high basic donor end residues. Although, it is to be particularly noted that we have tried to understand, first of all, the nature of the electron transition, not to obtain the best correlation between the spectral and calculated data.

3. Molecular geometry and electron structure

In the beginning, we will consider the equilibrium geometries of the dye **5-Py** containing the most basic pyridinium residue and its neutral derivatives **6-Py** and will compare, first of all, the BLA in the polymethine chain. The calculation in ab initio approximation with the large basis set, STO 6-31G**, gives the considerable alternation of the bond lengths for the both oxystyryl cation and neutral meroform, but the order of the positions of the long and short bonds is opposite in two types of the related conjugated systems as it is seen from Fig. 1.

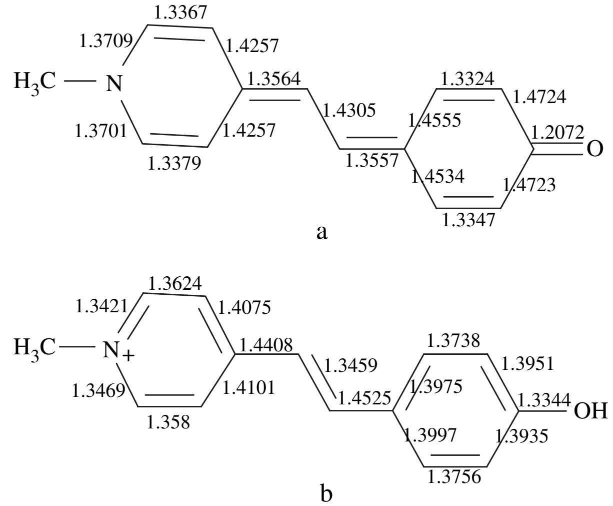


Fig. 1. Bond lengths (Å) in the merocyanine **6-Py** (a) and cation dye **5-Py** (b), calculated in the ab initio approximation.

In the same time, the difference in the lengths of neigbouring bonds in the chain middle of the corresponding merocyanine cation **7** with the equivalent chromophore length is essentially smaller: 1.408 Å, 1.386 Å, and 1.410 Å, while the lengths of the corresponding bonds in the chain middle of the neutral merocyanine **8** are nearly to that in the meroform **6-Py**: 1.335 Å, 1.449 Å, and 1.334 Å.

$(H_3C)_2N^+ = CH - (CH = CH)_4 - O^-$ $(H_3C)_2N - (CH = CH)_4 - CH = O$

7 **8**

Similar results were obtained also in the semi-empirical approximation. It is more convenient to characterize quantitatively a degree of the bond alternation by the special parameter, Δl_ν, which is calculated by following expression [10]:

$$\Delta l_\nu = (-l)^\nu (l_\nu - l_{\nu+1}) \quad (1)$$

The calculated function Δl_ν for the CC-bond along the chromophore in the compounds **5-Py**, **6-Py** as well as **7** and **8** are presented in the Fig. 2 (for the dyes **5-Py** and **6-Py**, we have used the average magnitudes for the topologically equivalent positions in the both rings). One can see from Fig. 2a that in merocyanine **8** and corresponding cation **7**, the alternation of the bond lengths is regular along whole chain; only the phase (the order of the disposition of the longer and shorter bonds) is opposite for dye cation **7** and neutral dye molecule **8**. Also, the ab initio method gives the larger BLA values for the neutral system and the higher degree of the bond equalizing for the cation. Meanwhile, the amplitudes Δl_ν in the chromophore middle of the pyridostyryl **5-Py** and its meroform **6-Py** follow form Fig. 2b to be essentially, in the contrast to equalizing of the bond lengths in the chromophore ends of the cation **5-Py**, i.e. in the branched parts (6-membered rings); also, the phase of the alternation is opposite compared with the open chain.

The appreciable distinction between the protonated form **7** and merocyanine **8** with open chain and the corresponding compounds **5-Py** and **6-Py** can be

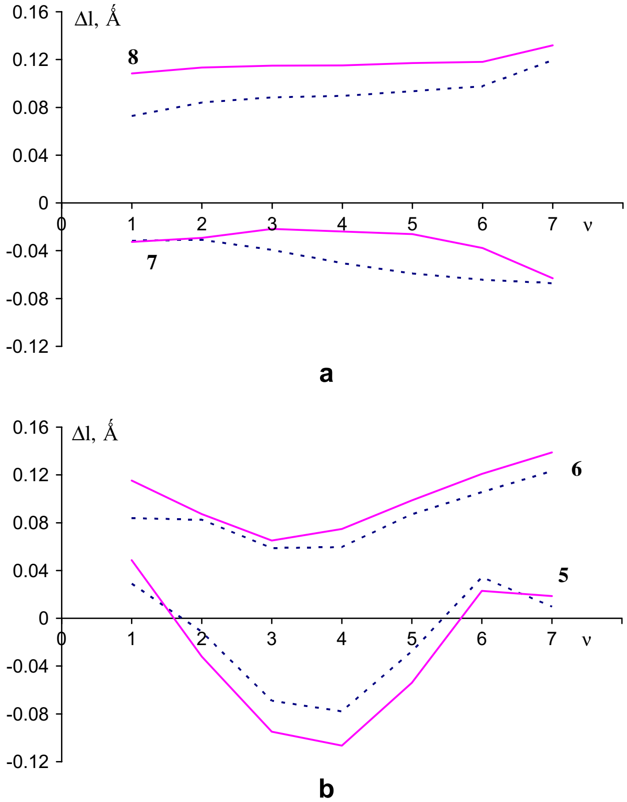


Fig. 2. Bond length alternation Δl_ν in the dye cations and merocyanines: the pair of the simplest dye (a) and dyes with the complex end residues (b). —, Ab initio, – – –, AM1.

connected with the considerable decreasing of the donor strength in the oxyphenyl residue in the cationic dyes and by the increasing the acceptor strength of the corresponding end group in the neutral donor–acceptor molecule. According to Brooker's conception of the basicity of the heterocycles in the polymethine dyes [11], the additional stabilization of the corresponding resonance structure is due to two Kekule structures for the benzene ring. Then, the basicity is connected with an ability of the heterocyclic residues as end groups to transfer an excess of the π-electron density to the chain. On the other hand, in the topological model of the quasi-long polymethines [12], the electron donor ability (basicity) of the end groups was proposed to estimate quantitatively by their topological index Φ_o, which can be calculated theoretically using the topological (or adjacency) matrix of an end group. For the molecules with stable closed electron shell, the parameter Φ_o magnitude is usually positive and falls within interval: $0° \leq \Phi_o \leq 90°$. Calculated indices for the heterocycles used as end groups in the studied dyes are as follows: Φ_o: **Py**, 76°; **Qu**, 66°; **BIn**, 45°; **In**, 40°; and **Ox**, 4°.

Now, taking into consideration the basic properties of the studied heterocyclic residues, we will try to consider the bond alternation in the chromophore of the dyes **5** and **6**, including the CC-bond in the chain and in the hydroxyphenyl residue. However, Fig. 3 shows the negligibly low sensitivity of the BLA in the open chain to the basicity of the donor group. Although, there exist some regular increase in the difference in the lengths of the first two CC-bonds in the series: **In**, **BIn**, **Qu**, **Py**, in an accordance with the increasing of the topological index Φ_o. This tendency can see from Fig. 3 to manifest itself more pronounced in the ionic systems than in the neutral molecules **6**.

Similarly, the bond lengths and the atomic charges in the chromophore of the both types of the molecules can be studied. Since we are going to compare charge distribution not only in the ground state, but also in the excited state, the calculations were performed in the "spectroscopic" approximation, ZINDO/S, using the molecular geometry optimized in the AM1 approximations. By analogy with Eq. (1), the alternation of the charges along the chromophore was proposed to be characterized by following parameter [13]:

$$\Delta q_\mu = (-l)^\mu \left(q_\mu - q_{\mu+1}\right) \tag{2}$$

where q_μ is the electron density at the μ-th atom. The calculated magnitudes of Δq_μ for the dyes investigated are presented in Fig. 4. One can see that there exists a comparative high alternation of the atomic charges (or the electron densities at the carbon atoms) practically along the whole chromophore, except in the atoms in the phenyl ring where charges in the ground state are rather equalized. In spite of the fact that the alternation amplitudes, Δq_μ, for the neutral molecules **6** are usually smaller than for the corresponding cations **5**, nevertheless, the total picture of the charge distribution in the chromophore of the merocyanines **6** resembles quantitatively the alternation of the atomic charges, even by a sign or phase.

Also, Fig. 4 demonstrates some dependence of the charge alternation in the open chain on the basicity of the donor terminal group. The amplitude Δq_μ in the ground state decreases regularly when the parameter Φ_o increases: **In**, **BIn**, **Qu**, and **Py**; although the influences

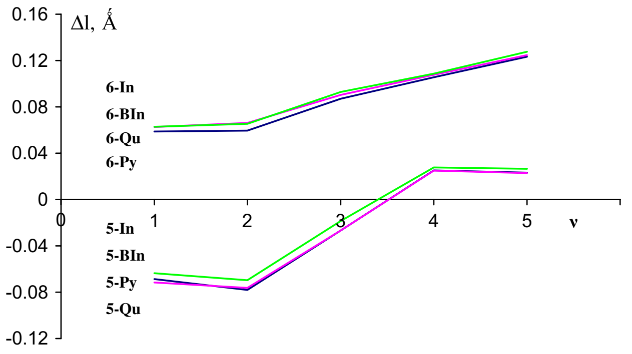


Fig. 3. Bond length alternation Δl_ν in the dye cations **5** and neutral merocyanines **6**.

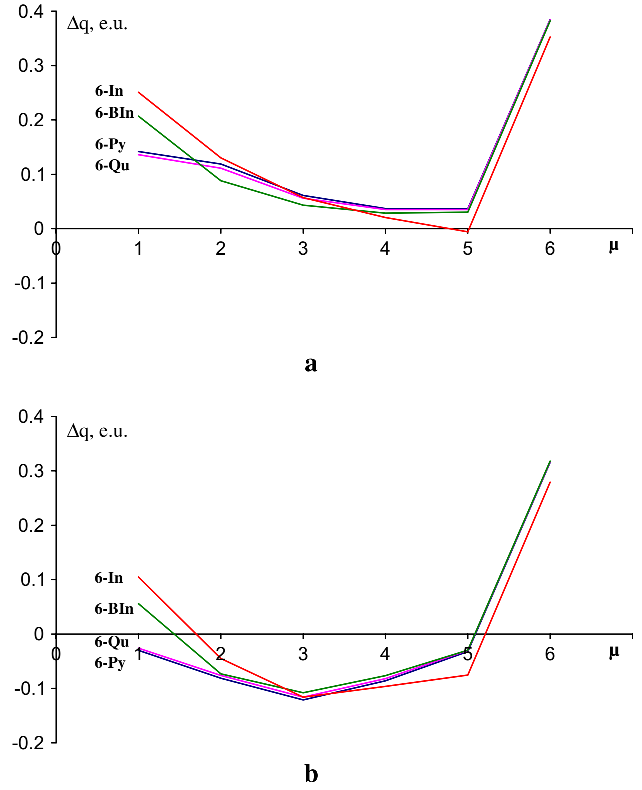


Fig. 4. Charge alternation in the ground state Δq_μ in the dye cations **5** (a) and neutral merocyanines **6** (b).

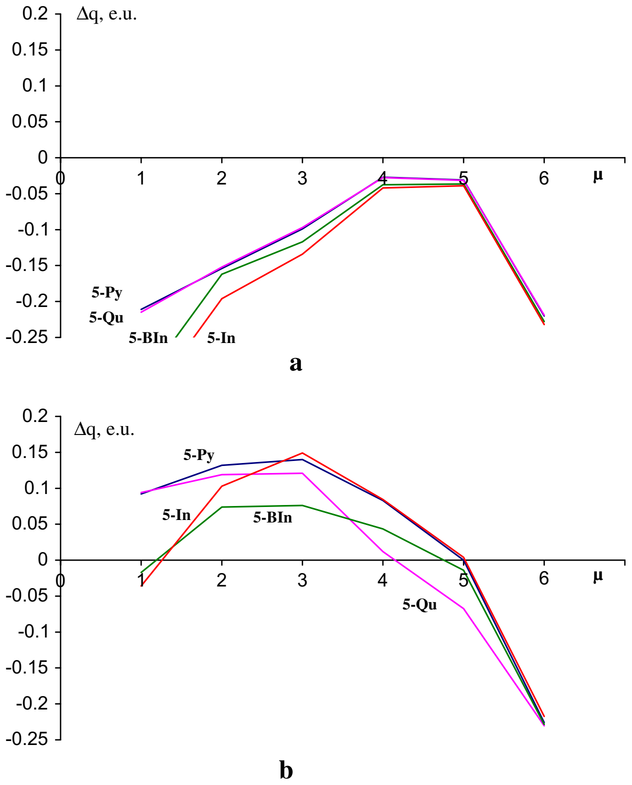


Fig. 5. Charge alternation in the exited state Δq_μ^* in the dye cations **5** (a) and neutral merocyanines **6** (b).

of the quinoline and pyridine residues are closely similar. Unlike to the chain, oxyphenyl residue is practically insensitive to the change of the constitution of the donor end group.

Going to the first excited state upon the same molecular geometry (Frank–Condon excited state) is accompanied by the substantial redistribution in the electron densities at the atoms in each type of the dye molecules (Fig. 5), so that reversion of the charge waves occur (the function Δq_μ changes its sign) in the chromophore middle, while the charge distribution at the atoms in the acceptor end group remains qualitatively the same. Whereas, in the chain near to the donor group, the sign of the value Δq_μ depends on the basicity of the heterocyclic residue: $\Delta q_\mu < 0$ for the low basic indolenine (**In**) and benz[*c*,*d*]indolenine (**BIn**) groups, while $\Delta q_\mu > 0$ for dye derivatives of the high basic pyridine (**Py**) and quinoline (**Qu**). This regularity holds good for both the cations **5** and neutral forms **6**.

Thus, because of the essential alternation of the charges along chromophore, the neutral donor–acceptor bases oxystyryls **6** somewhat resemble the cyanine dyes with their appreciable and characteristic wave of the electron density in the polymethine chain [14]. However, on the other hand, it was shown above (Figs. 2 and 3) that the merocyanines **6** exhibit the considerable bond length alternation that is inherent for typical polyenes [7] and cannot confirm the so called "cyanine limit" with its necessary condition: BLA → 0.

It would appear reasonable that the distinguishability in the charge distribution in dyes in the both ground and excited states should lead to a considerable difference in the dipole moments on the basicity (or donor strength) of donor terminal group. The calculated (ZINDO/S approximation) moments are presented in Table 1. One can see that the state dipole moments for the donor–acceptor conjugated molecules **6** are larger than that for

Table 1
Dipole moments (μ_i, *D*) in ground (S_0) and excited (S_1) states

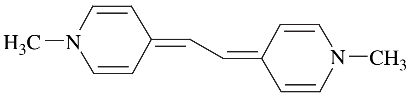
Dye	μ (S_0), *D*	μ (S_1), *D*	$\Delta\mu$ (S_1–S_0), *D*	$\Delta\mu$ (S_0), *D*	$\Delta\mu$ (S_1), *D*	$\delta\Delta\mu$, *D*
Cationic dyes						
5-Py	11.72	2.22	−9.50			
5-Qu	8.55	4.65	−3.90			
5-BIn	3.44	3.84	0.40			
5-In	0.86	0.36	−0.50			
Neutral dyes						
6-Py	13.10	19.67	6.57	−1.38	−17.45	16.07
6-Qu	12.33	17.77	5.44	−3.78	−13.12	9.34
6-BIn	9.74	16.54	6.80	−6.30	−12.7	6.40
6-In	10.25	16.91	6.66	−9.39	−16.55	7.16

Remarks: $\Delta\mu$ (S_1–S_0) = μ (S_1) – μ (S_0); $\Delta\mu$ (S_0) = μ (S_0) [neutral] – μ (S_0) [cation]; $\Delta\mu$ (S_1) = μ (S_1) [neutral] – μ (S_1) [cation]; $\delta\Delta\mu$ = $\Delta\mu$ (S_0) – $\Delta\mu$ (S_1).

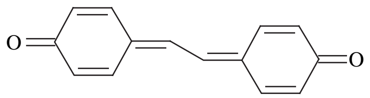
the corresponding cationic dyes **5**, especially, in the excited state.

Also, the magnitudes of the dipole moments in the grounds state depend on the basicity of the donor residues **Py**, **Qu**, **BIn**, and **In**, more obviously in the cationic dyes **5** and not strongly in the neutral systems **6** (larger in the dyes with high basic pyridinium and quonolinium nuclei and smaller in the dyes **6-BIn** and **6-In**). In the excited state, similar tendency is valid, except in the dye **5-Py** with its considerable change of the state dipole momentum from 11.72D in the ground state to 2.22D in the excited state, so that $\Delta\mu = 9.50D$ is the largest value amongst all dyes studied. Besides, the calculations show that increasing of the donor strength leads to the essential decreasing of the difference of the dipole moments for the cationic and neutral dyes, $\Delta\mu_o = \mu_o$ [neutral] $- \mu_o$ [cation], up to 1.38D in the ground states while similar value $\Delta\mu^*$ for the excited state is not so sensitive to the basicity of the end group R.

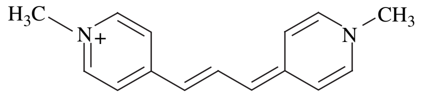
Now, we will consider the positions of the frontier MOs of the merocyanines and compare them with the electron levels of the corresponding symmetrical conjugated systems. For example, the pyridoxystyryl **6-Py** can be treated as a derivative of the both symmetrical parent neutral polyenes **11**, **12** and symmetrical parent polymethine dyes: the cation **13** and the anion **14**.



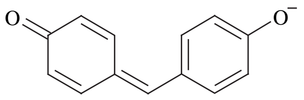
11 (Pe-Py)



12 (Pe-Oxo)



13 (Pm-Py)



14 (Pm-Oxo)

The calculated energies of the lowest unoccupied and highest occupied levels (in the ZINDO/S approximation) are depicted in Fig. 6. One can see that energy of the HOMO for the merocyanine **6-Py** is close to the average out the HOMO energies for the neutral polyenes **11**, **12** as well as to the average out the corresponding levels for the ionic dyes **13**, **14**. In just the same way, the position of the LUMO of the merocyanine **6-Py** corresponds to the lowest vacant levels of the related compounds **11**, **12** and **13**, **14**. Additionally, it is interesting to note that the midgap of the merocyanine (−4.41 eV) is close to the average out the LUMO energy of the anionic dye **14** and HOMO energy of the cationic dye **13** (−4.60 eV) as well as to the corresponding value for the polyenes **11**, **12** (−4.34 eV). Consequently, we could again re-state that merocyanines **6** should resemble somewhat to both neutral polyenes and ionic cyanine dyes.

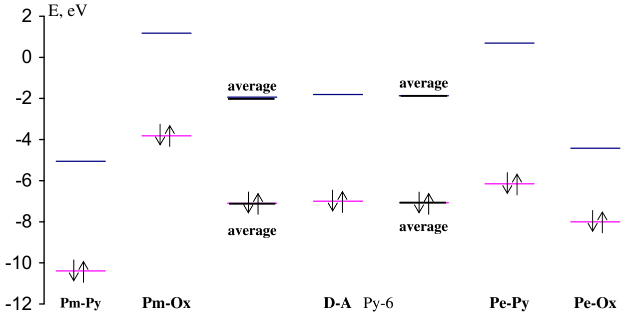


Fig. 6. Frontier electron levels for the ionic polymethine dyes **13**, **14** and neutral polyenes **11**, **12** as well as the average values (ZINDO/S).

The positions of the frontier and near levels for the other meroforms **6** and related oxystyryl cations **5** are presented in Fig. 7. One can easily see that going from the neutral molecules **6** to the cationic dyes **5** is accompanied by the considerable shift down of the energy gap. The influence of the donor groups is not regular in both cyanine cations and neutral merocianines; it is obvious that we would take into consideration not only the basicity (or parameter Φ_o) of end groups, but also an effective length of their extended π-electron systems.

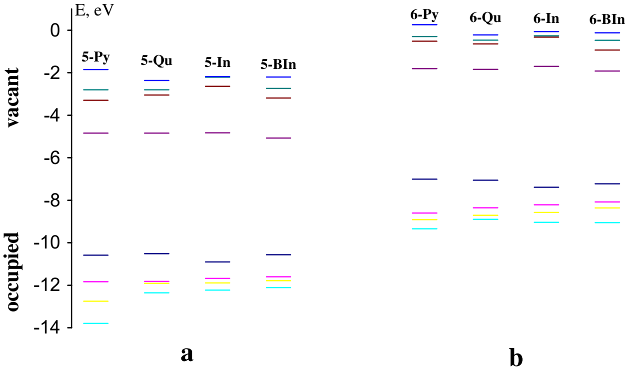


Fig. 7. Electron levels of the dye cations **5** (a) and neutral merocyanines **6** (b).

In the same time, the calculations show that energy gaps are somewhat smaller in the neutral meroforms than in the cationic dyes. This should manifest itself most efficiently in the absorption spectra.

4. Electron transitions and absorption spectra

The measured spectra of the dyes studied in the acetonitrile are presented in Fig. 8. One can see, first of all, that there are significant changes in the shape and position of the long wavelength band upon going from one type of the π-electron system to another. The cationic oxystyryls **5** exhibit the comparative narrow spectral bands without the vibronical structure. They absorb in the shorter spectral region, in comparison with the symmetrical cyanine or even with unsymmetrical styryls with their high degree of the asymmetry [11,15,16] that is caused by the extreme low basicity of the hydroxyphenyl residue ($\Phi_o = 4°$) and hence the high BLA along the chromophore. Consequently, the absorption maximum of the oxystyryl **5-Py** with the most basic pyridinium end group (λ_{max} 383 nm) seen from Fig. 8a is shifted maximum hypsochromically amongst the dyes investigated by us. Decreasing the donor strength of end group in the dye **5-In** leads naturally to the bathochromic shift of the spectral band (at 45 nm). Spectral band of the quino-styryl **5-Qu** (λ_{max} 425 nm) is located practically at the same wavelength where is band maximum of the dye **5-In**, although the quinolinium residue is more basic ($\Phi_o = 66°$); but at the same time, its effective length [13] ($L = 3.23$) exceeds this parameter for the indolium end group ($L = 2.76$). Introduction of the benzo[*c*,*d*]indolium residue with its essentially larger effective length ($L = 6.50$) causes the considerable bathochromic shift of the band maximum (λ_{max} 513 nm).

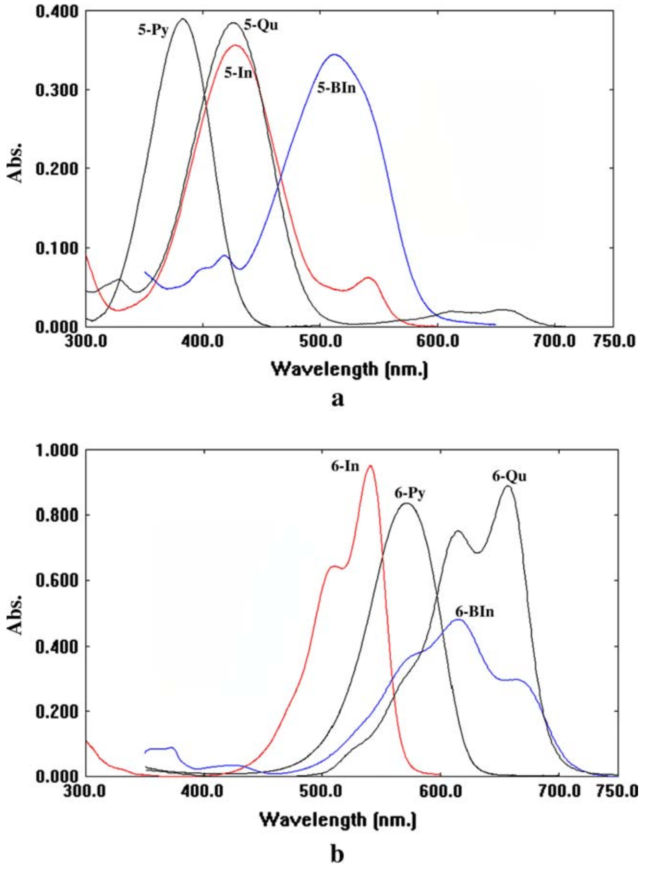


Fig. 8. Absorption spectra of the dye cations **5** (a) and neutral merocyanines **6** (b): solvent – acetonitrile, concentration 1×10^{-5} m/l.

In contrast to the neutral cyanine bases which absorb at the shorter wavelengths than the corresponding cationic dyes [15], going from the cations **5** to their neutral meroforms **6** is markedly accompanied by the substantially opposite, bathochromic, shift (compare Fig. 8a and b). Also, we have performed the quantum-chemical calculation of the wavelength of the electron transition which is shown Table 2. It was difficult to obtain the good agreement between the calculated wavelengths of the electron transitions and positions of the spectral bands which are besides highly sensitive to the solvent polarity. Moreover, such wide and non-regular disagreement between the quantum-chemical results and spectral data can be additionally connected with the fact that the solvatochromism is opposite for the ionic and neutral dyes. And in turn, the magnitude of the solvent effect depends appreciably on the change of the state dipole momentum upon excitation, $\Delta\mu = \mu(S_1) - \mu(S_0)$, which is not quite taken into consideration in the calculation. Then, as the first approximation, one can reasonably suppose that the divergence between the calculated and experimental wavelengths, $\Delta\lambda = \lambda^{exp} - \lambda_{max}$, should be in accordance with the value $\Delta\mu$. Really, for the cationic dyes **5-Py**,

Table 2
Calculated (λ^{calc}) and experimental (λ_{max}) wavelengths of the first transition for the dyes **5** and **6**

Dye	Calculated data		Experimental data		$\Delta\lambda$ (nm)	$\delta\Delta\nu$ (cm^{-1})
	λ^{calc} (nm)	$\Delta\nu^{calc}$ (cm^{-1})	λ_{max} (nm)	$\Delta\nu_{max}$ (cm^{-1})		
Cationic dyes						
5-Py	423		383		40	
5-Qu	438		425		13	
5-BIn	478		513		−35	
5-In	420		427		7	
Neutral dyes						
5-Py	518	4300	571	8600	−53	4300
5-Qu	523	3700	656	8300	−133	4600
5-BIn	501	900	662	4400	−161	3500
5-In	457	900	540	4800	−83	3900

Remarks: $\Delta\nu = \nu$ [neutral] $- \nu$ [cation]; $\Delta\lambda = \lambda^{calc} - \lambda_{max}$; $\delta\Delta\nu = \Delta\nu_{max} - \Delta\nu^{calc}$.

5-Qu, and **5-In**, the magnitudes $\Delta\lambda$ as seen from Table 2 decrease regularly, similarly to decreasing of the change dipole moments: $\Delta\mu = -9.50, -3.90, -0.50D$, while the calculations give higher value of λ^{exp} (478 nm) than the experimental maximum ($\lambda_{\text{max}} = 427$ nm) for dye **5-BIn**, in contrast to other cations which accords well with the opposite sign of the value $\Delta\mu$ ($+0.40D$).

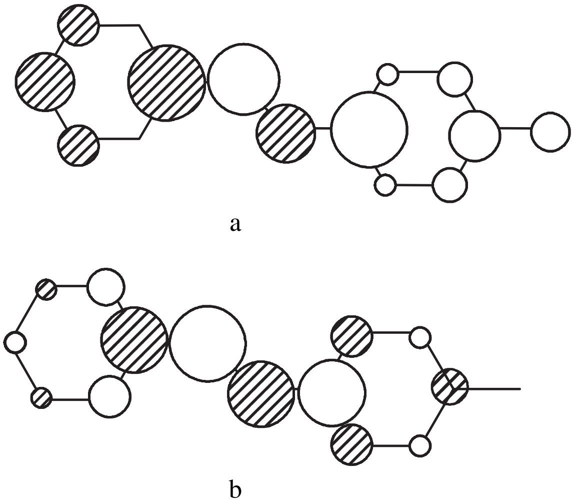
The similar correlation between the differences of the calculated and spectral data, $\Delta\lambda$, and the differences $\Delta\mu$ seen from Table 2 is worse for the neutral dyes **6**. The somewhat better correspondence was found for the spectral effects upon going from the cationic dyes **5** to the neutral dyes **6**. The larger differences between the calculated and spectral values $\delta\Delta\nu = \Delta\nu^{\text{calc}} - \Delta\nu_{\text{max}}$ are obtained for the pairs of the dyes **5-Py** → **6-Py** (4300 cm^{-1}) and **5-Qu** → **6-Qu** (3700 cm^{-1}) which exhibit the larger differences $\delta\Delta\mu$: 16.07D and 9.34D while the effects $\delta\Delta\nu$ for the dye pairs of the dyes with the lower values $\delta\Delta\mu$: **5-BIn** → **6-BIn** and **5-In** → **6-In**, are accordingly smaller (compare the corresponding values in Table 2).

It is seen from spectra in Fig. 8 and from Table 2 that the magnitudes of the spectral effects depend unambiguously on the basic properties of the donor end groups. So, for the pair of the cationic and corresponding neutral dyes with middle basic residues, the differences between their band maxima are following: $\approx$4800 cm^{-1} (**5-In** → **6-In**) and $\approx$4400 cm^{-1} (**5-BIn** → **6-BIn**). In the meantime, the shifts of the absorption band in the pair of the dyes containing the high basic end groups are larger approximately twice: $\approx$8600 cm^{-1} (**5-Py** → **6-Py**) and $\approx$8300 cm^{-1} (**5-Qu** → **6-Qu**).

Meanwhile, the calculated magnitudes of the change of the transition energy (or the frequency, $\Delta\nu$) from the dye cations **5** to the corresponding neutral merocyanine **6** seen in Table 2 are considerably smaller, although they are also essentially larger for the compounds with the high basic end groups, in comparison with the lower basic indolium and benzo[*c*,*d*]indolium residues.

Also, Fig. 8 shows that the shape of the spectral bands undergoes an essential change in the neutral dyes **6**, in comparison with the absorption bands of the corresponding cations **5**. Except the merocyanine **6-Py** with the extreme high basic pyridine residue, the vibronic structure appears, especially, in the benzo[*c*,*d*]indomerocyanine **6-BIn** when the second vibronic maximum is most intensive and additional third maximum manifests itself as a short wavelength shoulder. Nevertheless, for comparison of the spectral effects, we used the long wavelength shoulder (662 nm) which corresponds to the $0 \rightarrow 0'$ vibronic transition, similar to the spectral bands in the other dyes.

To understand the nature of the electron transitions, it was earlier proposed to use diagrams of the electron density upon excitation [7]. Such diagrams are plotted correspondingly to the differences:


a

b

Fig. 9. Schemes of the electron transition redistribution upon exentation (δq_μ) in the cationic dyes **5** (a) and neutral merocyanines **6** (b); ○, au electron density decreases; ▨, au electron density increases.

$$\delta q_\mu = q_\mu^* - q_\mu^0 \tag{3}$$

where q_μ^* and q_μ^0 are the electron densities at the μ-th atom in the excited and ground states. Fig. 9 shows the redistribution of the π-electron density in the cationic pyridoxystyl **5-Py** and its bases **6-Py**. In the middle of the both chromophores (Fig. 9a and b), the pictures of the change of the electron densities are reasonably similar and resemble quantitatively the diagrams for the typical cyanine dyes, where the excitation causes the transferring of the electron densities from the atoms in the odd positions in the polymethine chain to the atoms in the even positions [7]. An additional transfer of the electron density from rest of the atoms in the hydroxyphenyl residue to the pyridinium cycle in the cation **5-Py** is connected undoubtedly with the high degree of the asymmetry in the chemical constitution and hence the electron structure of the chromophore of the dye **5-Py**.

Unlike to the cationic dye, the alternation of the electron density redistribution at the neighbouring atoms (by sign) seen from Fig. 9b extend over not only the chromophore middle (open chain), but over the both cycles, although the values δq_μ are essentially smaller. Consequently, the nature of the electron transition in the neutral donor–acceptor merocyanine **6-Py** is more similar to the polymethine type electron transitions than in the highly asymmetric cationic dyes **5-Py**, where the polymethine type transition is mixed with the charge transfer electron transition (compare Fig. 9a and b). The electron density redistribution in the main chromophore of the other dyes is similar and is practically insensitive to the topology of the donor end group.

5. Conclusion

The donor–acceptor merocyanines **6** do not exhibit any equalizing of the carbon–carbon bond lengths in their chromophores, contrary to the expectations in the framework of the conception of the "cyanine limit". We would suggest that the relative long wavelength absorption of these neutral π-system appears to be caused by the considerable alternation of the atomic charges in the main part of the chromophore and by also the considerable redistribution of the electron density upon excitation, similarly to the typical cyanine dyes. The opposite solvatochromism for the cationic and neutral dyes increases additionally the difference in the positions of the long wavelength maxima of the corresponding dyes in the series **5** and **6**.

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Further reading

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