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Low-temperature fluorescence of oxystyryls and some of their neutral derivatives

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Abstract

The features of the electron structures and molecular geometry in the excited state, as well as the time-resolved fluorescence spectra at room and low temperatures for the series of oxystyryls and some merocyanines are discussed. It is shown that the large Stock's shifts in the cationic oxystyryls containing the high basic terminal groups are mainly caused by solvation in the ground state, and not by the geometrical relaxation. Lowering of the temperature leads to the regular hypsochromic shift, and to the unusual widening of the spectral bands in the pyrido- and quinooxystyryls; the last effect is connected with the existence of an additional component which can be registered by time-resolved spectroscopy.

Keywords: Merocyanines; Oxystyryls; Electron structure; "Cyanine limit"; Low-temperature fluorescence spectra; Time-resolved spectroscopy; Stock's shift; Quantum-chemical calculation

1. Introduction

In our previous article [1], the features of the electron structure and molecular geometry as well as absorption spectra of the oxystyryls containing the donor groups with the regularly varied basicity were studied in detail. The state dipole moment was found from the calculation to be considerably decreased in the dyes with high basic pyridinium and quinolinium residues while the change of this parameter in the indo- and benzo[*c*,*d*]indooxystyryls are practically negligible. Also, it was shown that the magnitudes of the dipole moments depend, first at all, on the basicity of the donor end groups. For example, in the ground state, the dipole moment increases markedly in the series indo-, benz[*c*,*d*]indo-, quino- and pyridooxystyryl: 0.86, 3.44, 8.55 and 11.72 D (calculated in the AM1 approximation), respectively. It is in a good agreement with the experimental fact that the absorption spectra of the oxystyryls as extreme unsymmetrical cyanine dyes are highly sensitive to solvent polarity [2–4].

In the same time, it is well known [5,6] that the fluorescence spectra of the cyanine dyes depend usually far less on the nature of the solvents than on absorption bands because excitation leads to the significant redistribution of the charges at the atoms along the chromophore and hence are accompanied by the reorientation of the solvent polar molecules; as a result, in the relaxed excited state, the dye molecules remove their solvent shell. However, upon the low-temperature measurements, the mobility of the dye and solvent molecules are restricted; consequently, influence of the solvent polarity should manifest itself also on the fluorescence, similarly to the absorption spectra.

In this paper, we present the results of our investigation of the dependence of the fluorescence spectra upon the high and low temperatures on the basicity of the donor end group in the series of the oxystyryl dyes and two different neutral derivatives: oxystyryl base and merocyanine.

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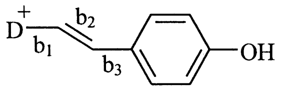
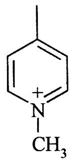
2. Objects and methodology

The oxystyryls studied can be presented by a general formulas:

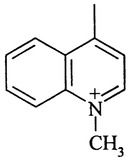


1

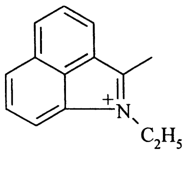
D$^+$:



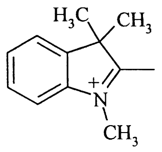
1-Py



1-Qu

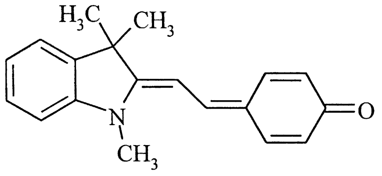


1-BIn

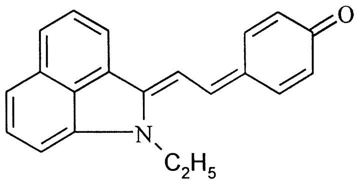


1-In

The merocyanines **2** which can be considered as derivatives of oxystyryls **1-BIn** and **1-In** were investigated.



2-In-m



2-BIn-m

The synthesis of all compounds was described earlier [7]. Spectral measurements were carried out in the comparatively high polar solvent, CH$_3$CN, while the isoenergetic point was studied in the water–pyridine mixture.

2.1. Absorption spectra

Absorption spectra were recorded on a spectrophotometer Shimadzu UV3100.

2.2. Fluorescence spectra

The fluorescence excitation spectra were measured with a Hitachi MPF-4 spectrophotometer. The stationary and time-resolved fluorescence spectra were recorded with an SPM-2 monochromator with a photoelectric attachment. The spectral slit width was 0.2–0.4 nm. The fluorescence was excited by a 337.1-nm pulsed nitrogen laser with a pulse repetition rate of 100 Hz, a pulse duration of 10 ns, and a pulse power of 5 kW. The time-resolved fluorescence spectra were recorded using a 0.1-ns gating system. The fluorescence kinetics and fluorescence spectra were recorded with different time delays t_d relative to the laser pulse maximum. To improve the time resolution, the fluorescence spectra were detected at the initial moment after excitation at the leading edge of the laser pulse (negative values of t_d). Because of a high steepness of the leading edge of the laser pulse, the duration of excitation of a sample under study for $t_d = -4$ ns was equal to 0.7 ns. The decay curves were analyzed by recording the shape $G(t)$ of the laser pulse and the fluorescence decay curves at different wavelengths. This ensured the determination of the lifetime τ of fluorescence with an accuracy not worse than 0.1 ns.

2.3. Quantum-chemical calculations

The equilibrium geometry of the dye molecules were obtained in the AM1 approximation; in the excited state, the configuration interaction includes all single and many electron promotions from three highest occupied orbitals to three lowest vacant MOs (MOPAC package). We supposed that the molecules in the so called "fluorescent" relaxed excited state remain planar; the short-lifetime twisting component is not fluorescent. The energies of the electron transitions were calculated in the "spectroscopic" ZINDO/S approximation (HyperChem package) using all π → π* single excited configurations. The transitions calculated upon the ground state molecular geometry correspond to the experimental data from the absorption spectra while the transitions upon the excited state geometry correspond to fluorescence spectra, in accordance with the Frank–Condon's rule [5]. In our calculation, the overlap weight factor (OWF) for the π–π bonds calibrate against the maxima of the fluorescence bands. It enables to estimate quantum-chemically the Stock's shift as $\Delta\lambda_s = \lambda$ (relaxed geometry) $- \lambda$ (ground geometry) or $\Delta\nu_s = \nu_{(gr)} - \nu_{(rel)}$.

3. Results and discussion

3.1. Change of the equilibrium geometry upon relaxation in the excited state

As a typical example, the calculated molecular geometries in both ground and relaxed "fluorescent" excited states for the pyridooxystyryl **1-Py** are presented in Fig. 1. One can see considerable alternation of the bond lengths along the chromophore in both states, the difference in the lengths of the neighboring bonds in the chain reaching 0.069 Å (b1–b2) or 0.078 Å (b2–b3) and hence being comparatively close to in the polyenes (0.099 Å in the AM1 approximation). The calculation has shown that the regular decreasing of the donor strength in the series **1-Py**, **1-Qu**, **1-In**, **1-BIn** influences negligibly on the bond lengths in the ground state (Fig. 2a). In contrast, the relaxed geometry (Fig. 2b) proves to depend considerably on the topology of the donor terminal group D. The alternation of the bond lengths in the excited state is seen from Table 1 to be less than that in ground state. It is to be noted that the relaxation in the excited state does not change the sign of the alternation: $\Delta 1 = 1_\nu - 1_{\nu+1}$ (where ν is a number of the bond), in contrast to the corresponding neutral merocyanines, $Py{=}CH{-}CH{=}C_6H_4{=}O$; 1.366, 1.424, 1.365 Å in the ground state and 1.459, 1.344, 1.431 Å in the relaxed excited state. As a result, the total change in the molecular geometry (bond lengths, first at all) should be less than that in the polyenes or the extreme unsymmetrical donor–acceptor systems [8]. It was established that the change in the lengths of all the bonds in the chromophore estimated by formula (1) corresponds to the Stock's shift, $\Delta\lambda_s$ [9].

$$\delta = \sqrt{\sum_\nu \left(l_\nu^* - l_\nu^0\right)^2} \qquad (1)$$

where l_ν^* and l_ν^0 are the lengths of the μ-th bond in the excited and ground states, respectively.

The calculated magnitudes of parameter δ as well as the wavelength of the electron transitions for the dyes studied are collected in Table 2. One can see the same tendencies of regular increasing simultaneously for values $\Delta\nu_s$ and δ in the oxystyryl series **1-Py**, **1-Qu**, **1-In** with the approximately close effective length of the donor group ($L = 2.73$, 3.23, 2.76, respectively [1]), except dye **1-BIn** containing the benzo[*c*,*d*] indolium residue with the relatively large effective length ($L = 6.50$). However, the calculated Stock's shifts for all oxystyryls were proved to be considerably less than the observed spectral values.

3.2. The room temperature fluorescence

The typical spectra including the absorption bands as well as fluorescence bands upon both high (300 K) and low (77 K) temperatures are presented in Fig. 3. Here, we have restricted only by consideration of the long-wavelength fluorescence bands. Although, it is to be mentioned that the excitation at $\lambda_{exc} = 337$ nm of dye **1-BIn** causes also an appearance of the additional spectral band in the short-wave length region, with a maximum at 410 nm at room temperature. To check, we have measured the fluorescence of the compound **1-BIn** upon excitation at $\lambda_{exc} = 532$ nm; the observed spectral band practically coincides with the long-wavelength band (with a maximum at 613 nm) as presented in Fig. 3b. We assume that this spectral phenomenon in the fluorescence of the dyes containing the benzo[*c*,*d*]indolenine residue with the extended π-electron system and with the 5-membered ring is likely to be of the same nature of the anti-Stock's fluorescence as the $S_2 \rightarrow S_0$ emission observed for the azulenes, pseudoazulenes [10] or even for the squarilium dye containing the azulene residues as terminal groups [11].

The shape of the spectral bands of quinooxystyryl **1-Qu** is similar to the absorption and fluorescence of dye **1-Py**. In contrast to the non-structural uniform shape of the spectral bands in the spectra of dyes **1-Py**, **1-Qu** and **1-BIn**, the appreciable vibronical structure manifests itself as two shoulders in the short- and long-wavelength parts of the fluorescence band at 300 K for the indooxystyryls **1-In** (Fig. 3c). It is reasonable to suggest that the band maxima at 529 nm corresponds to the 1 → 0 vibronical transition, while the 0 → 0 transition

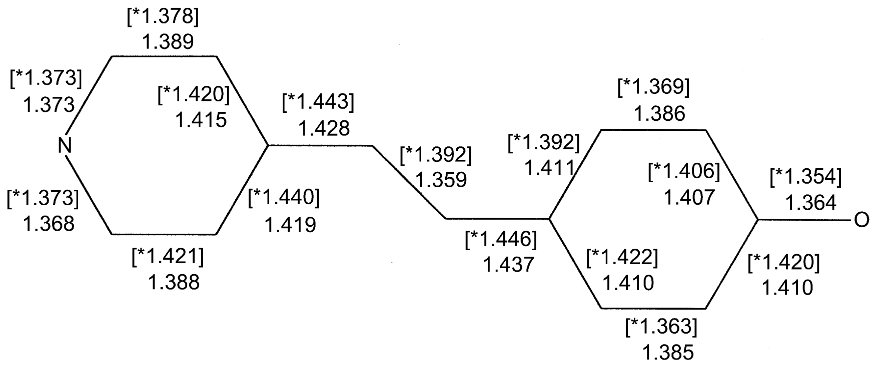


Fig. 1. Calculated bond lengths (in Å) in the ground state and the relaxed excited [*] state in the pyridooxystyryl **1-Py**.

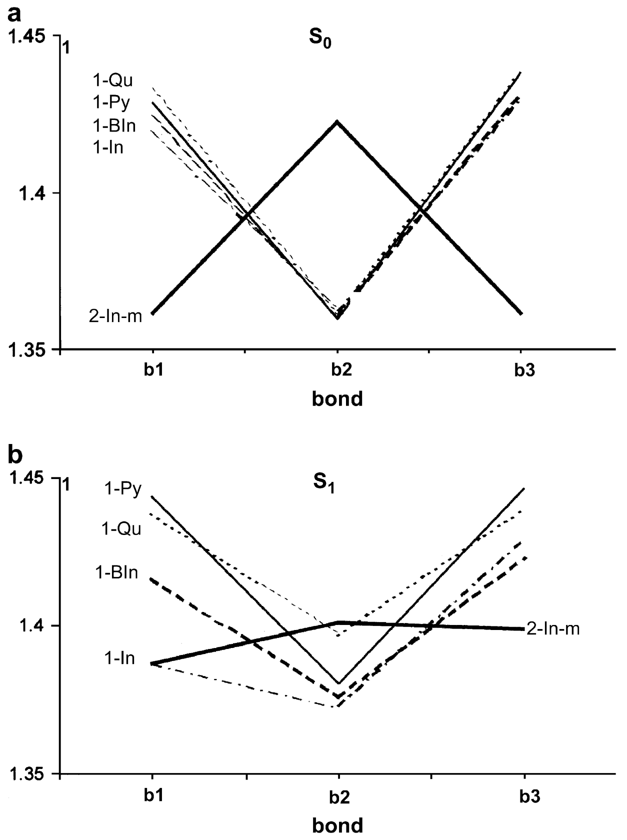


Fig. 2. Bond lengths (in Å) in ground state S_0 (a) and relaxed excited state S_1 (b) in the chain oxystyryls and merocyanine **2-In-m**.

should be positioned approximately 500 nm, in so far as the vibronical transition frequency for the linear conjugated system is equal to 1100–1300 cm^{-1} [5].

Table 1
Alternation bond lengths ($\Delta 1 = |1\nu - 1\nu + 1|$) (in Å) in the chain of dyes **1–3**

Dye	Bond numbers	State	
		Ground	Excited
1-Py	b1–b2	0.0694	0.0633
	b2–b3	0.0780	0.0656
1-Qu	b1–b2	0.0716	0.0416
	b2–b3	0.0759	0.0429
1-In	b1–b2	0.0572	0.0148
	b2–b3	0.0660	0.0568
1-BIn	b1–b2	0.0636	0.0402
	b2–b3	0.0695	0.0469
2-In	b1–b2	0.0608	0.0136
	b2–b3	0.0612	0.0023

Table 2
Calculated data of dyes **1–2** upon the ground state geometry (λ_{gr}) and relaxed excited state geometry (λ_{rel})

Dye	OWF	λ_{rel}	λ_{gr}	$\Delta\lambda$ (nm)	$\Delta\nu$ (cm^{-1})	δ
1-Py	0.50	491	481	10	423	0.0626
1-Qu	0.46	550	528	22	758	0.0800
1-In	0.50	531	486	45	1744	0.0870
1-BIn	0.47	609	575	34	971	0.0722
2-In-m	0.14 (5 × 1)	580	550	30	940	0.0669

OWF is overlap weight factor (ZINDO/S).

The measured maximum of the spectral curves is collected in Table 3. Comparing the data from Fig. 3 and Table 3 with the corresponding values in Table 2, one can easily see that experimental Stock's shifts ($\Delta\nu_s$ or $\Delta\lambda_s$) exceed significantly the calculated data which will not take into consideration the influence of the solvent. Also, the trends in the change of the spectral value $\Delta\nu_s$ in the series **1-Py**, **1-Qu**, **1-In**, **1-BIn** do not quite agree with this parameter obtained by quantum-chemical calculation. So, the spectra of the pyridooxystyryl **1-Py** show the maximum Stock's shift ($\Delta\nu_s = 6029$ cm^{-1}), while the calculation, in contrast, predicts the minimum parameter, $\Delta\nu_s = 423$ cm^{-1}. However, one should necessarily take into account the fact that the change of the state dipole moment upon excitation, $\Delta\mu = \mu^* - \mu^0 = 2.22 - 11.72 = -9.50$ D, was obtained just for the pyridooxystyryl **1-Py** containing the most basic pyridinium residue as a terminal group [1].

On the other hand, the calculation of dyes **1-In** and **1-BIn** with the end groups of the lower basicity gives the relative small magnitude of the parameter $\Delta\mu$ (−0.50 D and +0.40 D, respectively) which agrees qualitatively with the lower Stock's shifts for these compounds: 3180 cm^{-1} for dye **1-BIn** and especially, 0 → 0 transition for dye **1-In**, 3400 cm^{-1}. It is to be noticed that the values $\Delta\mu$ are calculated upon the same (ground state) equilibrium molecular geometry, whereas the relaxation in the excited state could cause the appreciable changes in the bond lengths, and hence the changes of the state dipole moments in the relaxed emission state. So, the calculation gives that the dipole moment decreases upon relaxation in the pyridooxystyryl **1-Py** (from 2.22 D to 1.71 D) and quinooxystyryl **1-Qu** (from 4.65 D to 3.94 D), while the relaxation is accompanied by increasing the state dipole moment in **1-In** (from 0.36 D to 6.50 D) and dye **1-BIn** (from 3.84 D to 4.28 D).

Finally, we propose that the comparatively large Stock's shifts in the strong unsymmetrical cationic dyes **1-Py** and **1-Qu** are caused not by the change in the molecular geometry upon relaxation in the excited state, but by the influence of the solvent in the ground state which vanishes in the emission state. Therefore, the solvation effect can be estimated, approximately, as a difference between experimental and calculated Stick's shifts: $\Delta\nu_{Solv} = \Delta\nu^{exp} - \Delta\nu_s^{theor}$. It is seen from Table 3 that this value for the oxystyryl with the lower basic benzo[*c*,*d*] indolium (**1-BIn**) and indolium (**1-In**) residues (2722 cm^{-1} and 2209 cm^{-1}) is substantially smaller than the spectral effects for the high basic dyes: 5606 cm^{-1} (**1-Py**) and 4721 cm^{-1} (**1-Qu**).

Then, the electron transitions may be illustrated by the following scheme, presented in Fig. 4. The excitation starts from the solvatic ground state (which is stabilized by solvation, in comparison with the "pure" ground state) to the solvatic excited state which is disposed higher than the "pure" excited state. The next relaxation to the emission state is accompanied by the change of the molecular geometry and reorientation of the solvent shell; both processes are most likely to proceed concurrently or simultaneously. Consequently, the final

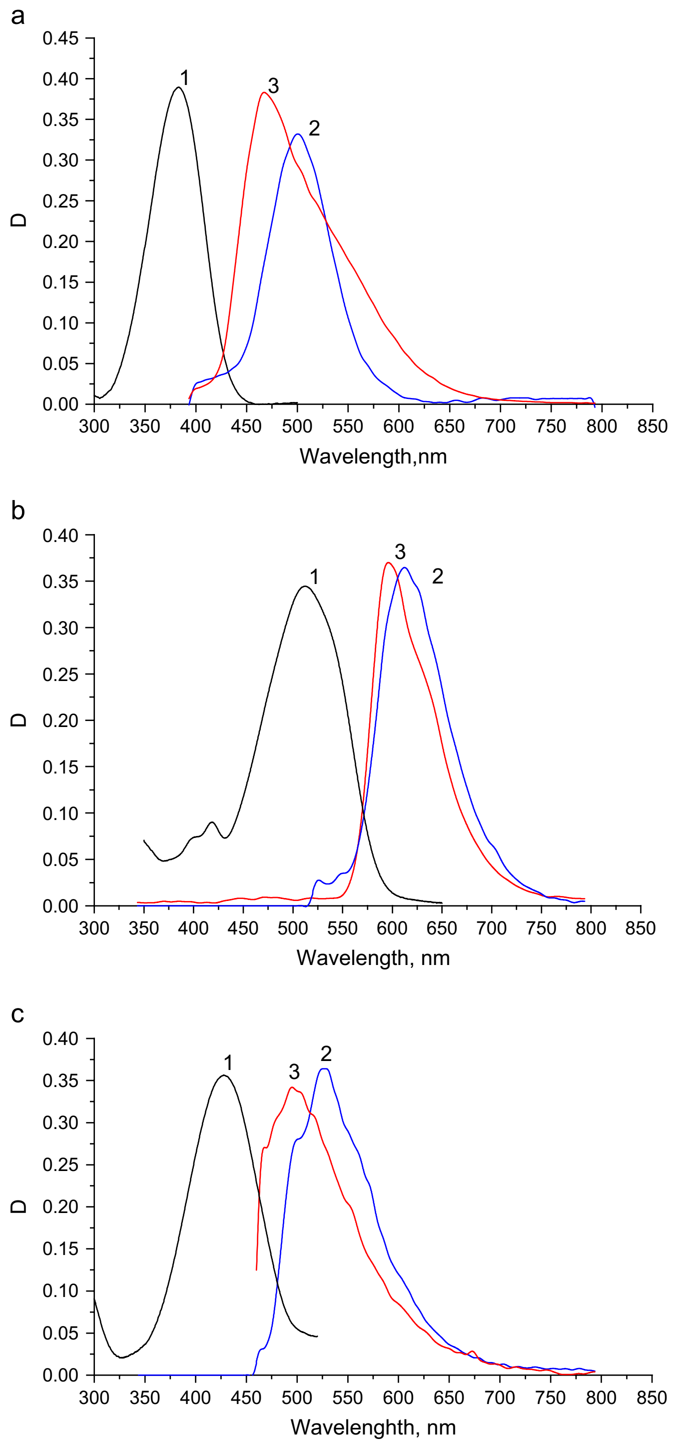


Fig. 3. Absorption and fluorescence spectra of cationic dyes: (a) **1-Py**, (b) **1-BIn**, (c) **1-In**; 1, absorption spectra; 2, fluorescence at 300 K; 3, fluorescence at 77 K.

emission state is unsolvatic; thereafter, the electron transits correspondingly to the unsolvatic ground state with the relaxed (in the excited state) molecular geometry, except, of course, the twisting short-lifetime component which is not considered here. Without doubt, the energies of solvation in the ground state and reorientation in the excited state depend on the degree of asymmetry of the oxystyryl molecules.

At last, it is to be noted that in the Fig. 4 is somewhat simplified, for convenience. In fact, the excitation at $\lambda_{exc} = 337$ nm causes the jump of an electron to the higher excited state; nevertheless, the emission occurs from the lowest excited state, according to the well-known Franck–Condon's rule [5] (this rule is disrupted for dye **1-BIn**).

3.3. Low-temperature fluorescence

Fig. 3 presents also the typical fluorescence spectra of the three dyes measured at low temperature, i.e. in the frozen matrix; the maxima of the fluorescence bands of all compounds studied are collected in Table 3. As would be expected, spectral bands obtained in the frozen solutions preventing reorientation of the dye and solvent molecules are regularly shifted into the short-wavelength region. Hence, the relaxed emission state of the oxystyryls fixed in the frozen matrix is disposed higher (Fig. 4b) than the emission state after the final relaxation upon the room temperature when all molecules are not restricted in their mobilities. Unfortunately, the correct quantum-chemical simulation of the relaxation of the molecular geometry and post-redistribution of the electron density are faced with difficulties; we would only assume that the ''solvatic'' relaxed state in the matrix is disposed slightly below the solvatic excited state upon the high temperature (compare the corresponding energy curves in Fig. 4a and b). One can see from Table 3 that the hypsochromic effects of the decreasing of the temperature, $\Delta\nu(H-L)$, for the high basic dyes, **1-Py** (1333 cm^{-1}), **1-Qu** (1367 cm^{-1}), are larger than for the dyes with the lower donor strength of the end group, **1-BIn** (522 cm^{-1}) and **1-In** (1258 cm^{-1} for the $0 \to 0$ transition).

3.4. Time-resolved spectroscopy

Another feature of the low-temperature fluorescence is connected with the shape of the spectral bands for some dyes. One can clearly see from Fig. 3a that the fluorescence at 77 K exhibits the wider spectral band, compared with the width of the fluorescence curves measured upon room temperature. This is in contrast with the width of the fluorescence curves measured upon room temperature. This is in contrast with the widely known experimentally and well-justified theoretically spectral phenomenon that bandwidth is usually narrowed down upon low temperature because of decreasing intensity of the vibronic interaction [5]. As a consequence, we have assumed that the observed increase of the fluorescence bandwidth is not of the homogeneity (vibronic structure), but is connected with the existence of an additional component which can be registered by time-resolved spectroscopy. The measured spectra (steady-state and time-resolved at two time interval) of pyridooxystyryl **1-Py** are presented in Fig. 5. The initial fluorescence bands are seen to be narrower (in comparison with the integral steady fluorescence); nevertheless, the band tail extends up to 600 nm and so on. In time, the intensity in the long-wavelength region regularly increases. By subtraction of the fluorescence curves obtained at two time

Table 3
Spectral data of dyes **1–2** (in CH_3CN) (HT and LT correspond to 300 K and 77 K, respectively)

Compound	λ_{max}^{abs} (nm)	λ_{max}^{fl} (nm) (CH_3CN)		Stock's shift		$\Delta\nu(L-H)$ (cm^{-1})	$\Delta\nu_s^{theor}-\Delta\nu_s^{exp}$
		HT	LT	$\Delta\lambda_s$ (nm)	$\Delta\nu_s$ (cm^{-1})		
1-Py	383	498	467	115	6029	1333	5606
1-Qu	425	554	515	129	5479	1367	4721
1-In	427	529	496	69	4516	1258	2722
		≈500[a]		≈73[a]	≈3400[a]	≈150[a]	≈1650[a]
1-BIn	513	613	594	100	3180	522	2209
2-In-m	540	582	564	42	1336	546	396

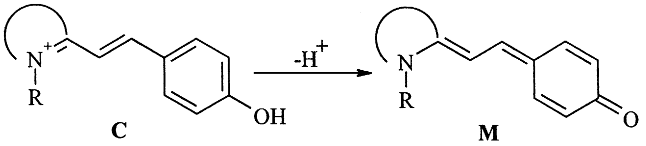
[a] Magnitude corresponds to 0′ → 0 vibronical transition.

intervals, the new wide spectral band, with the maximum at 530–540 nm, appears. Similar spectral effects have also been found in the low temperature time-resolved spectrum for the other high basic quinooxystyryl **1-Qu**. At the same time, the bandwidths of the dyes with the relative low donor strength, **1-In** and **1-BIn**, are changed only slightly upon going from the room temperature to 77 K.

Thus, in the frozen matrix, the dyes with the high dipole moments can also relax to an additional long-wavelength emission state, as is proposed in Fig. 4b. We would not discuss the nature of this component; it is not impossible that the later relaxation can lead to the unsymmetrical structure with the higher degree of asymmetry of the electron density distribution, in comparison with the ground state. While the distribution of the charges in the chromophore of dyes **1-In** and **1-BIn** was shown earlier [1] to be more equalized, and hence an appearance of any additional components upon relaxation is a little possible.

It is interesting to compare the effects in the fluorescence spectra of the cationic oxystyryls with the spectral features in the related neutral derivatives, merocyanines **2**, as we have studied earlier for absorption spectra [1].

The merocyanines **M** may be regarded as deprotonated neutral derivatives, in which the removal of the proton is accompanied by changing of coordination number of the oxygen atom (from 2 to 1).



The neutral compounds **2-In-m** and **2-BIn-m** are typical donor–acceptor conjugated molecules. So, we have shown earlier that the merocyanines constituted from one end group with the high donor strength and another residue with the acceptor strength absorb light deeper than the corresponding cationic oxystyrys [1]; in contrast, the absorption band maxima of the neutral cyanine bases containing the low basic *p*-alkoxyphenyl as a donor end group and heterocycles, desalkiled on the atom of nitrogen as another end group with low acceptor strength are considerably shifted to short-wavelength spectral region.

Here, we will consider in detail the fluorescence of two stable merocyanines **2-In-m** and **2-BIn-m**. Typical spectra of the compound **2-In-m** are presented in Fig. 6, while the absorption and fluorescence band maxima are collected altogether in Table 3.

First, let us consider the geometrical changes upon relaxation in the excited state, restricted by only the bond lengths in

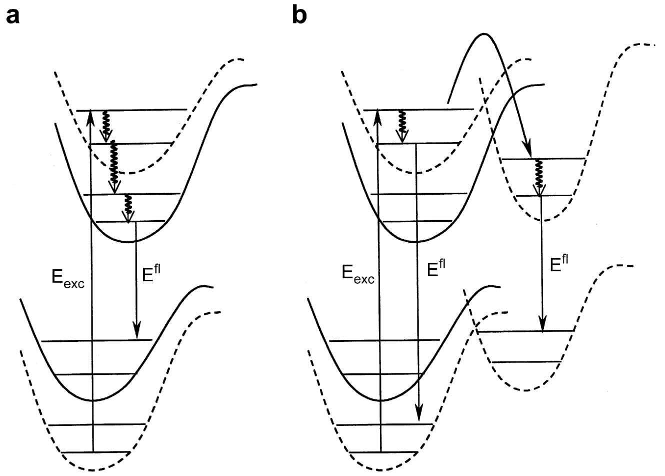


Fig. 4. Scheme of electron transitions upon (a) high and (b) low temperatures; curves (—— and - - - - -) correspond to pure and solvation electronic states, respectively.

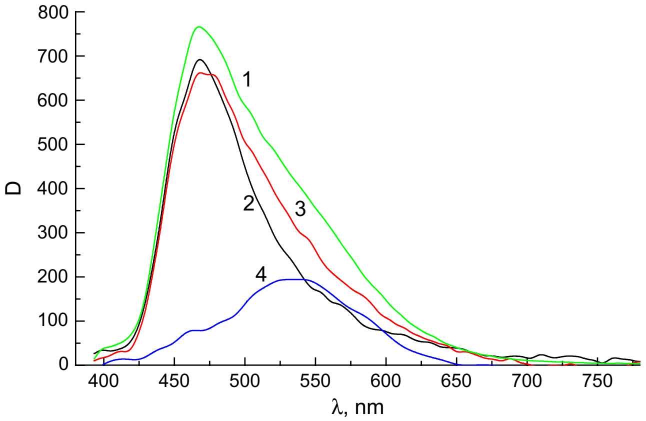


Fig. 5. Time-resolved spectra of **1-Py**; 1, steady; 2, $t_1 = -4$ ns; 3, $t_2 = 8$ ns; 4, $\lambda(t_2 - t_1)$.

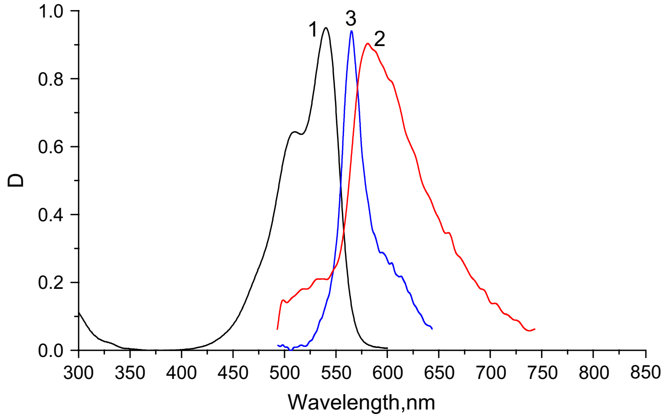


Fig. 6. Absorption and fluorescence spectra of merocyanine: **2-In-m**; 1, absorption spectra; 2, fluorescence at 300 K; 3, fluorescence at 77 K.

the chain. One can see from Fig. 2 and Table 1 that there is considerable alternation of the lengths of the neighboring bonds in the ground state, so that value Δ1 is close to that for bonds in the corresponding cationic dye **1-In**, but is opposite in sign. The relaxation is found from calculation (Fig. 2a) to lead to equalizing of the bond lengths, so that the lengths of all three bonds in the chain are close to the magnitude 1.4 Å which is a common length of the CC-bonds in the polymethine chain of the symmetrical cyanine dyes exhibiting the deep color [12]. As a result, the merocyanines also absorb light in the relative long-wavelength spectral region [1]; for example, going from the indooxystyryl **1-In** to its meroform **2** is accompanied by the bathochromic shift 113 nm (in CH_3CN), as one can see from Table 3. It is well known that merocyanines are polar highly sensitive sensors on the solvent polarity as well as they are used as the suitable model for the wide quantum-chemical study of the solvatochromism [13,14]. One way to estimate the polar sensitivity is to measure the change of the position of the band maximum and the intensity (extinction) of the spectral band for the merocyanine dye in the mixture of polar and non-polar solvents. It was proposed by Kiprianov [15] and then by Brooker [16] that the regular bathochromic shifting of the absorption band maximum upon increasing of the concentration of the relatively weak polar pyridine in the strong polar water and consequently decreasing of the solution polarities connected with the increasing of the contribution on neutral valence structure, whereas in the polar solvent, the zwitterionic structure with the separated charges becomes dominant; they have assumed that the point of the highest extinction corresponds to exact energetic equivalence of the valence structures of their merocyanine (conveniently called the "isoenergetic" point). Although Kiprianov–Brooker's assumption cannot now be regarded as correctly established, nevertheless, the "isoenergetic" point may be used as the simplest way to test the degree of merocyanine asymmetry depending on the basicity of the donor end group. We have carried out similar spectral investigation for the water–pyridine solutions of the merocyanines **2-In-m** and **2-BIn-m**; the results are presented in Fig. 7. It is to be noted that going from CH_3CN solvent to water causes the hypsochromic shift 19 nm for indomerocyanine **2-In-m**, while the corresponding spectral effects are somewhat smaller and regularly decreases in the low basic cationic dyes: 10 nm (**1-Py**), 11 nm (**1-Qu**) 6 nm (**1-In**) and 4 nm (**1-BIn**).

One can see from Fig. 7 that "isoenergertic" points for merocyanines **2-In-m** and **2-BIn-m** are reached upon the comparatively low concentration of the pyridine what could be interpreted as a predominance of the bipolar valence structure, not neutral. This may indicate the weak sensitivity of the merocyanines to solvent polarity, and hence the solvation effect in the spectra should be minimum.

Our calculation gives the parameter $\delta = 0.0669$ and Stock's shift $\Delta\nu_s^{calc} = 940\ \text{cm}^{-1}$ which are close to the corresponding values for oxystyryls **1-Qu** (758 cm^{-1}) and **1-BIn** (971 cm^{-1}) (Table 2). One can see from Fig. 7a and Table 3

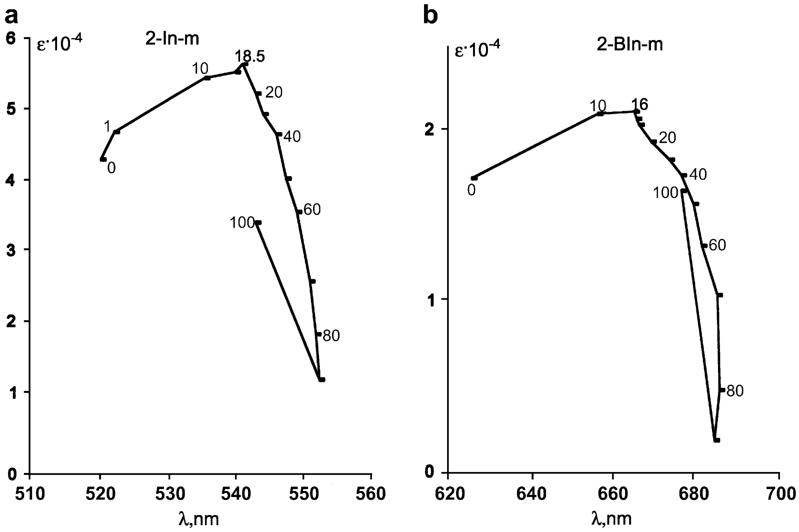


Fig. 7. Dependence of position of absorption band maximum (λ_{max}) and its extinction coefficient (ε) on the concentration of pyridine (numbers on the curve) in the water–pyridine mixture.

that the calculated value $\Delta\nu_s^{calc}$ is only slightly smaller than the experimental Stock's shift: 1336 cm^{-1}, so that "solvation" effect, 396 cm^{-1}, is negligible (taking into consideration an accuracy of the quantum-chemical simulation).

The relatively small hypsochromic shift is seen from Table 3 and Fig. 6 to be observed upon decreasing of the temperature: 546 cm^{-1} i.e. the influence of the solvatic shell on merocyanine on the fluorescence of the merocyanine **2-In-m** is non-appreciable, in comparison with the high basic oxystyryl **1-Py** or **1-Qu**. Fig. 6 also demonstrates the considerable narrowing of the spectral bandwidth at 77 K, in the rigorous agreement with the well-known theoretical postulation about decreasing of the vibronical interaction upon low temperature [5]. Although the distinct shoulder is observed on the long-wavelength tail of the fluorescence band at 77 K, we could not detect any additional component, so the relaxation was found by the femtosecond pump probe spectroscopy [17] to be finished too quickly, approximately 5–10 ps.

4. Conclusion

Thus, the simultaneous quantum-chemical and spectral study of the dyes propose that the large Stock's shifts in the fluorescence spectra of the cationic oxystyryls containing the high basic donor group are mainly caused by solvation in the ground state, and not by the significant geometrical relaxation; the influence of the solvent polarity decreases with the lowering of the basicity of the end groups (**1-In** and **1-BIn**). The appreciable dependence of the spectra on the solvent microenvironment remains at low temperature; the band maxima are shifted hypsochromically, the positions depending on the donor strength of the end groups. In contrast, the spectral properties of the neutral derivative, the merocyanines depend substantially less on polarity.

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