Crown-containing styryl dyes
14.* Synthesis, luminescence, and complexation of the *trans*-isomers of chromogenic 15-crown-5-ethers

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Novel crown ether styryl dyes containing heterocyclic residues with various substituents were synthesized. The fluorescence and absorption spectra of the *trans*-isomers of crown ether styryl dyes and their complexes with metal cations were studied. Based on spectral data, the influence of the nature of a heterocyclic residue, the crown ether fragment, and the temperature on the fluorescence of dyes and their complexes with metal cations was elucidated.

Key words: crown ether styryl dyes; fluorescence spectra; complex formation.

The presence of intense absorption bands (AB) in the visible region and high quantum yields of fluorescence (φ_f) and *trans-cis*-photoisomerization (φ_{t-c}) of *trans*-isomers of styryl dyes allows one to use them in luminescent systems for recording information.[2] However, the thermal instability of nonfluorescent *cis*-isomers (they cannot be isolated and stored in an unchanged state) is a significant obstacle.

Earlier we studied conjugated reactions of photoisomerization and complexation of crown-containing styryl dyes (CSD).[3] We found that so-called "closed" complexes are formed, which contain an additional coordination bond between an anionic group of the *N*-sulfoalkyl substituent of the heterocyclic residue of a styryl dye in the *cis*-form and the metal cation located in the cavity of the crown ether moiety.[4] This results in a strong hypsochromic shift of the long-wave AB and, simultaneously, a pronounced increase in the thermal stability of the *cis*-form of the dye. The effects discovered allow us to consider CSD as promising elements in creating fluorescent photo-switching molecular devices.

One may assume that changing the nature of a heterocyclic moiety (or introduction of substituents, capable of interacting with a chromophore, into this moiety) and a crown ether fragment would influence considerably the luminescent properties of the *trans*-isomers of dyes of this type and their complexes with metal cations.

Therefore, we synthesized a series of styryl dyes (**1a—i**). Heterocyclic residues for dyes **1a—i** were chosen among the heterocycles with gradually increasing values of deviations[5] which relate the spectral characteristics of asymmetric styryl dyes with the electron-donating properties (basicity) of different heterocycles constituting the dyes.

The synthesis of indolenine styryl dyes **1a—i** was described by us previously.[6] Compound **1c** contains a crown ether fragment, and the benzene ring of dye **1b** contains two methoxy groups which reproduce, in general, the electron-donating influence of the crown ether substituent on the system of conjugated double bonds of the dye chromophore. However, unlike CSD **1c**, compound **1b** and the similar compound **1a** should not have a noticeable ability to form complexes with ions of alkali and alkaline-earth metals.

Earlier we briefly described, without reporting the procedure, the synthesis of compounds **1e** and **1h** (see Refs. 4 and 7, respectively). Perchlorate **1h** was obtained by an exchange reaction between the iodide ion of a dye and $HClO_4$ in MeOH. Styryl dyes **1e—i** were synthesized in up to 66 % yields by condensation of quaternary salts (**2e—h**) with 4-formylbenzo-15-crown-5 (**3c**) or 4-formylphenylaza-15-crown-5 (**3i**) in the presence of pyridine or in acetic anhydride.

Quaternary salts of heterocyclic bases **2d,e,g,h** were obtained by heating 2-methyl-5-phenylbenzooxazole (**4d**), 2-methylbenzothiazole (**4e**), 2-methylquinoline (**4g**), and 2-methyl-5-methoxybenzothiazole (**4h**), respectively, with ethyl iodide in a sealed tube (see Ref. 8).

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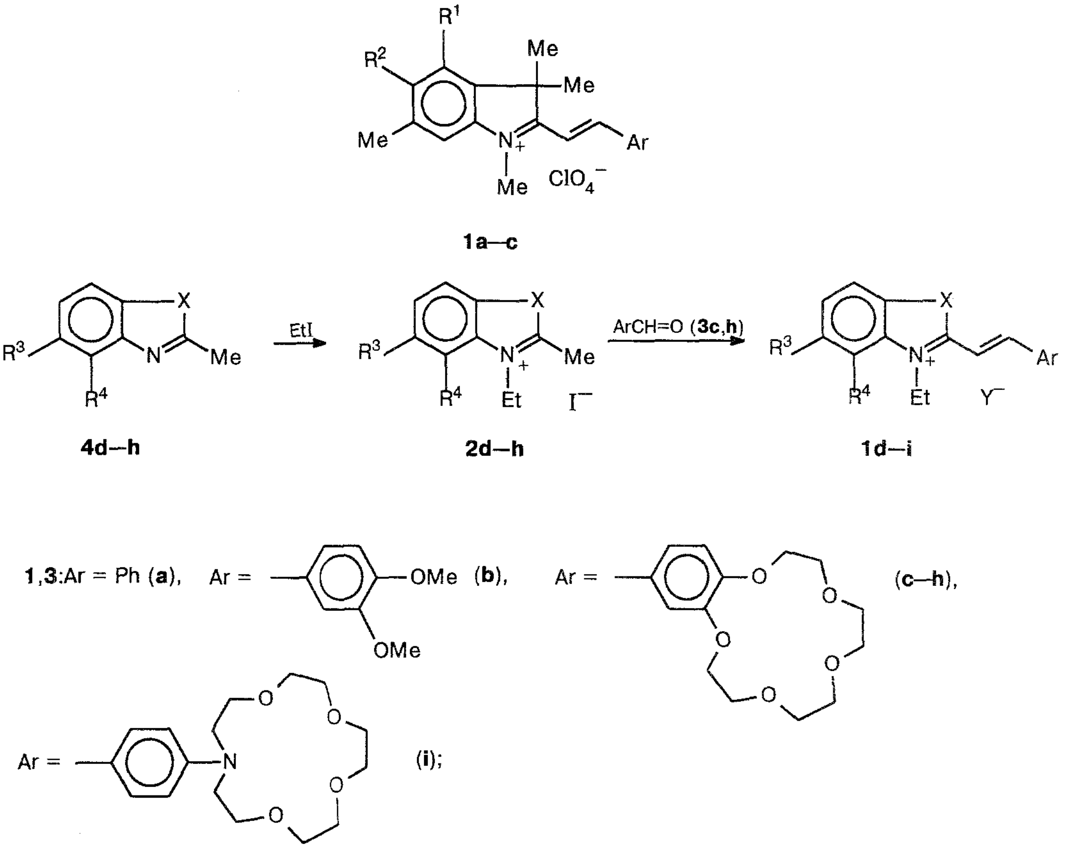
Scheme 1



1,2: R^1 = Me, R^2 = H (**a,b**); R^1 = H, R^2 = Me (**c**), R^3 = Ph (**d**), R^3 = H (**e,g,i**), R^3 = OMe (**h**),
$R^3 + R^4 = C_4H_4$ (**f**), R^4 = H (**d,e,g—i**)
1,2: X = O (**d**), X = S (**e,f,h**), X = CH=CH (**g,i**)
1: Y = ClO_4 (**d—h**), Y = I (**i**)

Quaternization of the sterically hindered 2-methylnaphto[1,2-*d*]thiazole (**4f**) was carried out by heating the starting base with ethyl toluenesulfonate[9] (Scheme 1).

The structure of compounds **1d—i** obtained was confirmed by ^{1}H NMR spectroscopy (see Experimental). The elemental analysis data are consistent with the proposed structures. According to the ^{1}H NMR data, all of the styryl dyes **1a—i** obtained exist in a *trans*-from. This conclusion can be made with confidence based on the high coupling constant ($^3J_{trans}$ = 15.4—16.0 Hz) for olefin protons in the compounds obtained.

The wavelengths of the maxima of the long-wave AB (λ_a) of dyes **1a—i** in EtOH at room temperature are given in Table 1 (hereinafter, all data are attributed to the *trans*-isomers of the dyes, unless stated otherwise). When $NaClO_4$ (0.01 *M*) is added, the absorption spectrum of crown ethers **1c—h** is shifted towards the shortwave region (10—14 nm at 293 K). The corresponding shifts of the AB of crown ether **1i** and dyes **1a** and **1b**, which do not contain a crown ether moiety, are less by an order of magnitude. The shifts of the AB for compounds **1c—h** are virtually unchanged, whereas those of **1i**, **1a**, and **1b** increase with increasing concentration of $NaClO_4$ from 0.01 to 0.1 mol L^{-1}. This fact indicates that the observed shift of the AB for **1c—h** results from the formation of complexes with Na^+ (**1c**Na^+—**1h**Na^+) rather than from the salt effect. The shift of the absorption spectrum of **1i**, **1a**, and **1b** in the presence of $NaClO_4$ may be due to the salt effect. The similar salt effect was observed for 3-aminofluorenone in MeCN (see Ref. 10). The opposite directions of the shift of the AB for **1a** and **1b** in the presence of $NaClO_4$ indicate that, in the case of **1b** and **1i**, formation of weak complexes **1b**Na^+ and **1i**Na^+ is also possible.

Styryl dyes **1a—i** have weak fluorescence in EtOH at 293 K. The fluorescence intensity increases significantly when the temperature is decreased. The corrected fluorescence spectra of dyes **1a—i** in EtOH at 173 K are given in Fig. 1, and the wavelengths of the maxima in the fluorescence spectra (λ_f) are presented in Table 1. An increase in the electron-donating ability of a heterocyclic residue of a dye results in shift of the AB and fluorescence spectrum to the long-wave region within the **1d—g,h** series and in an increase in φ_f within the **1c,e,f,h** series. Introduction of the indolenine moiety, which is the most electron-accepting among the

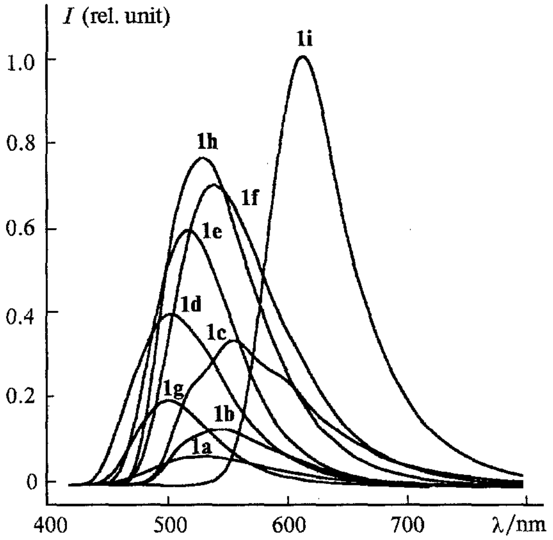


Fig. 1. Corrected fluorescence spectra of the CSD in EtOH at 173 K (**1a—f,h,i**) and at 77 K (**1g**). The areas under the fluorescence spectra of **1a—c,e,f,h,i** are proportional to φ_f. The spectrum of **1a** is increased 5 times.

heterocyclic residues studied, causes, contrary to expectations, the greatest long-wave shift of the AB and fluorescence of the dye. This may result from the fact that the five-membered indolenine ring, unlike the other heterocyclic residues of the dyes under study, is non-aromatic. The structure of the styryl substituent also has a significant effect on the spectral characteristics of the dyes. The introduction of a crown ether fragment (*cf.* **1b** and **1c**) or an increase in its electron-donating ability (*cf.* **1g** and **1i**) results in a long-wave shift of the absorption and fluorescence spectra, as well as in a significant increase in φ_f.

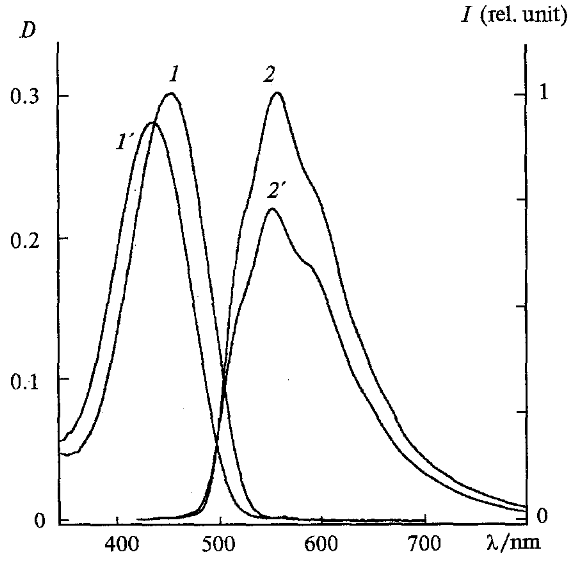


Fig. 2. Absorption spectra at 293 K (*1, 1′*) and fluorescence spectra at 173 K (*2, 2′*) of dye **1c** in EtOH. $NaClO_4$ concentration: 0 (*1, 2*) and 0.01 mol L^{-1} (*1′, 2′*).

Table 1. Spectral characteristics of *trans*-**1a—i** and *trans*-**1c—iNa$^+$** in EtOH

Compound	T /K	λ_a	$\Delta\lambda_a$	λ_f	$\Delta\lambda_f$	$\langle\lambda_f\rangle$	$\langle\Delta\lambda_f\rangle$	σ_f /nm	φ_f
1a	173	387^a		534		557		57	0.012
1a+Na$^+$	173	390^a	2.6	536	2.0	554	2.4	53	0.011
1b	173	447^a		545		571		52	0.102^c
1b+Na$^+$	173	447^a	0.6	541	3.9	569	−2.0	49	0.107
1c	290	451		562		595		63	0.0024^c
1cNa$^+$	290	434	−17	562	0.3	599	3.6	76	0.0020
1c	173	—		557		595		70	0.299
1cNa$^+$	173	—		552	−4.4	593	−2.3	69	0.218
1c	77	433		543		576		51	—
1cNa$^+$	77	432	−1.4	541	−1.7	576	0.1	54	—
1c	77	447^a		—		—		—	—
1cNa$^+$	77	443^a	−3.4	—		—		—	—
1d	173	420^a		504		—		—	—
1dNa$^+$	173	410^a	−10	499	−4.9	—		—	—
1e	173	432^a		519		537		42	0.375
1eNa$^+$	173	417^a	−15	515	−3.7	574	37	89	0.227
1f	293	442		555		576		52	—
1fNa$^+$	293	428	−14	537	−17	557	20	53	—
1f	173	—		541		570		55	0.554
1fNa$^+$	173	—		540	−1.3	611	41	88	0.183
1f	77	—		521		557		55	—
1fNa$^+$	77	—		522	1.3	578	18	62	—
1f	77	441^a		—		—		—	—
1fNa$^+$	77	442^a	1.1	—		—		—	—
1g	77	436^a		502		520		—	—
1gNa$^+$	77	416^a	−22	—		—		—	—
1g	77	429		502		520	40	—	—
1gNa$^+$	77	412	−17	579	77	571	51	63	—
1h	173	443^a		531		555		49	0.535
1hNa$^+$	173	428^a	−14	537	6.1	599	44	84	0.167
1i	173	531^a		615		638		51	0.644
1iNa$^+$	173	529^a	−1.4	616	0.69	639	−0.98	52	0.486

Note. All λ values are given in nm; $\Delta\lambda_{a,f} = \lambda_{a,f}^{complex} - \lambda_{a,f}^{ligand}$. * At 293 K. ** Fluorescence excitation spectrum, registration wavelengths were 542 (**1c**) and 500 (**1f**) nm. *** φ_f = 0.0015 for **1b** and φ_f = 0.002 for **1c** in H_2O at T = 295 K (see Ref. 3).

When $NaClO_4$ (0.01 *M*) is added, the maximum of the fluorescence spectrum of **1b**—**1e** and **1f** is shifted by 1—4 nm to the short-wave region, and the fluorescence maximum of **1a,h,i** is shifted by 1—6 nm to the long-wave region (Fig. 2, Table 1). The fluorescence spectra of **1e,f,h** are strongly widened in the presence of Na$^+$ ions. Widening is characterized by an increase in the dispersion of the fluorescence spectrum, $\sigma^2{}_f$. This may result from the existence, in the presence of Na$^+$ ions, of several fluorescent forms, which leads to a strong (40 nm) increase in the average fluorescence wavelength $\langle\lambda_f\rangle$ of **1e,f,h**. The fluorescence excitation spectra of **1f** and its complex with Na$^+$ ion in solid glassy solutions in EtOH at 77 K (Fig. 3) do not depend on recording

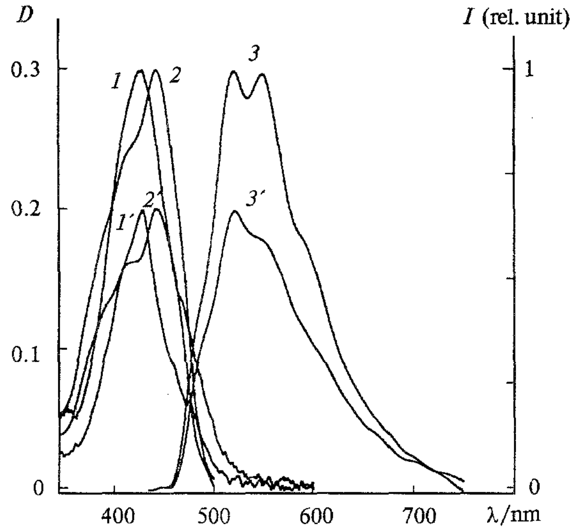
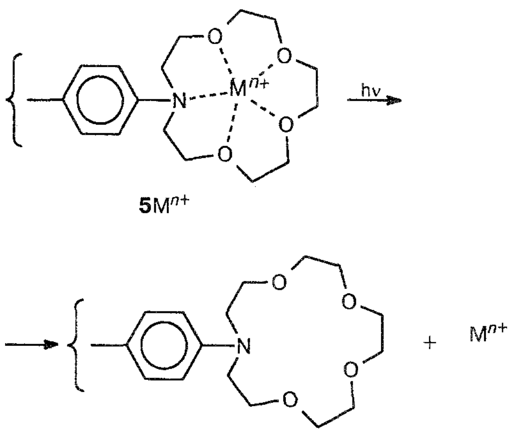


Fig. 3. Absorption spectra (*1, 1′*) and fluorescence excitation (*2, 2′*) and emission (*3, 3′*) spectra of dye **1f** in EtOH at 77 K. $NaClO_4$ concentration: 0 (*1, 2,* and *3*) and 0.01 mol L^{-1} (*1′, 2′*, and *3′*). Wavelength of fluorescence registration was 500 nm (*2, 2′*); wavelength of fluorescence excitation was 420 nm (*3, 3′*).

wavelength, which indicates that either the fluorescent forms of **1f**Na^+ have practically similar absorption spectra, or these forms appear as a result of relaxation in an excited state. In the case of **1c**, we do not observe widening of the fluorescence spectrum due to the complex formation. Therefore, the changes in λ_f and $\langle\lambda_f\rangle$ in the presence of $NaClO_4$ are equal in sign and close in the absolute value. The complex of dye **1g** with Na^+ has double-band fluorescence. The fluorescence excitation spectra of these two bands at 77 K are different, which probably results from the existence of a mixture of conformers in the ground state. Compound **1d** is unstable in EtOH and decolorizes rather quickly (1 h), which prevented us from determining the φ_f of the dye.

The addition of $NaClO_4$ to solutions of most of the dyes results in fluorescence quenching (see Table 1). Compounds **1a** and **1b** are the only exceptions. The decrease in φ_f can not be explained by a change in φ_{t-c} since complexation of CSD, as a rule, does not lead to a significant increase in φ_{t-c} and, hence, to a decrease in φ_f (see Ref. 11). The formation of a coordination bond between Na^+ and the oxygen atom at the *para*-position relative to the central double bond results in a decrease in its conjugation with the π-system of the molecule. It is known[12] that the introduction of a methoxy group into a chromophore conjugation chain usually leads to an increase in φ_f. Therefore, one might expect that complex formation with Na^+ ion would have the opposite effect, *i.e.*, a decrease in φ_f; this is just what we observe in the experiment. Within the framework of this assumption, one may explain the absence of noticeable changes in φ_f for **1a** and **1b**, which do not form complexes.

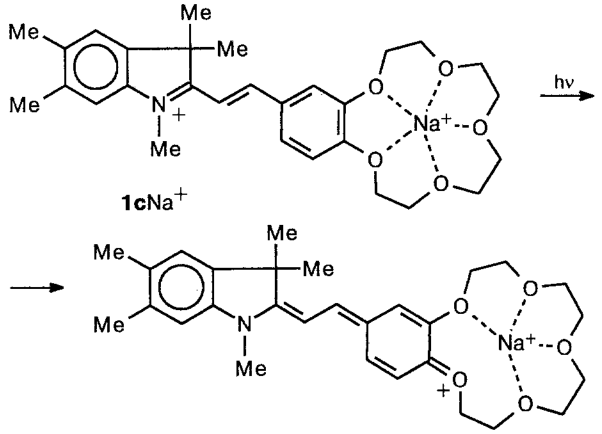
The fluorescence spectrum of **1c** in EtOH at room temperature is a wide structureless band, whose maximum practically does not change in the presence of 0.01 *M* $NaClO_4$. On the other hand, the absorption spectrum of **1c** in the presence of 0.01 *M* $NaClO_4$ is significantly shifted toward the short-wave region (Table 1). A similar phenomenon was recently[13] observed for crown ether complexes based on merocyanine dye DCM (**5**), whose structure involves a styryl group, with Li^+ and Ca^{2+} ions. The authors of this work proposed that the total elimination of metal ion from the complex occurs in excited state:



5M^{n+}

5

The small shift of the fluorescence spectrum of dye **1c** upon complex formation in comparison with the similar shift of the absorption spectrum could be due to a change in coordination of the metal ion and the position of the ion in the macroheterocycle. When passing to the first excited state of dye **1c**, the electron density at the oxygen atom, which is involved in the structure of the chromophore and is located in the *para*-position relative to the central double bond, is decreased, weakening the bond between the metal ion and the oxygen atom. This results in a change of the equilibrium position of the metal ion in the macroheterocycle. Since the energy of the donor-acceptor interaction is quickly decreased with increasing distance between the donor and the acceptor, even a small increase in the distance leads to a significant weakening of the bond between the metal and the oxygen atom, an increase in the degree of conjugation of its unshared electrons with the rest of the chromophore, and a decrease in the transition energy. As a result, the metal ion in the excited state in a complex with **1c** is bonded mainly with four oxygen atoms from the five in the 15-crown-5 fragment:



1cNa$^+$

The absence of agreement between the shifts of the absorption and fluorescence maxima may result from the influence of the metal ion on the Stoke's shift of a fluorescence spectrum ($\Delta\lambda_s = \lambda_f - \lambda_a$). The Stoke's shift is high (>100 nm for **1** in EtOH at 173 K and 157 nm for **5** in MeCN)[13], which indicates a significant change of the equilibrium structure, a molecule not bonded to the metal ion, or its environment upon excitation. Therefore, since $\Delta\lambda_a$ and $\Delta\lambda_f$ are small in comparison with $\Delta\lambda_s$, and $\Delta\lambda_a - \Delta\lambda_f = \Delta\lambda_s - \Delta\lambda_s^+$, where $\Delta\lambda_s^+$ is related to the complex with the metal ion, even a weak influence of the metal ion on $\Delta\lambda_s$ should lead to substantial differences in $\Delta\lambda_f$ and $\Delta\lambda_a$. In any case, it is difficult to agree with the viewpoint of the authors[12] who observed the similar spectral effects upon complex formation of **5** and proposed that rupture of all coordination bonds of the metal with the ligand and elimination of the metal cation from the complex with the macrocyclic ligand occur. The difference between the fluorescence excitation spectra of the system in the presence and in the absence of the salt may serve as evidence for a change in the type of coordination of the metal ion in the macro heterocycle in excited state. However, a very low intensity of fluorescence of dye **1c** at 293 K does not allow us to measure the fluorescence excitation spectra with a sufficient accuracy. To check the possibility of elimination of a metal cation from a complex with CSD, we studied the absorption, fluorescence emission, and fluorescence excitation spectra of dyes **1c,f** in solid glassy EtOH at 77 K. Under these conditions, the fluorescence of compounds **1c,f** is rather effective, which permitted us to measure the fluorescence excitation and emission spectra with a sufficiently high spectral resolution. The photodissociation of complexes **1c**Na$^+$ and **1f**Na$^+$ in a solid solution becomes impossible, which should result in close values of shifts of the absorption, fluorescence emission, and fluorescence excitation spectra. Under these conditions the spectra significantly change their shape in the presence of Na$^+$ ions (see Fig. 3), which indicates the formation of complexes of CSD with the Na$^+$ ion. However, the small spectral shift for compounds **1c,f** in the presence of Na$^+$ ions (see Table 1) does not allow us to make a final conclusion about the possibility of photodissociation of the complexes of CSD with metal ions. This problem requires additional studies.

Thus, we synthesized novel crown ether styryl dyes containing heterocyclic residues with different substituents. The data obtained reveal the regularities of the influence of the nature of the heterocyclic residue, substituents in this residue, and the temperature of the medium on the fluorescence of ionophores of the styryl series. This creates a basis for the directed control of their fluorescent parameters and their capability of complex formation by a synthetic method.

Experimental

MeCN was distilled over $KMnO_4$ and twice over P_2O_5 to eliminate admixtures and water. EtOH was purified by boiling with 2,4-dinitrophenylhydrazine and conc. HCl for 8 h followed by fractional distillation. Absorption spectra were measured on a Shimadzu UV-3100 spectrophotomete; fluorescence spectra were recorded on a Alumin-2M spectrofluorimeter. Electron fluorescence spectra were corrected for the spectral dependence of the sensitivity of the spectrofluorimeter recording system. The quantum yield of fluorescence φ_f was determined by comparison of the areas under the corrected fluorescence spectrum of the dye under study with that of quinine sulfate in 1 *N* H_2SO_4 (φ_f = 0.546)[15] using the SPECTR program on a PC-AT computer. The measurements were carried out at 296—77 K. Solutions of dyes were prepared in darkness to prevent *trans-cis*-photoisomerization and were kept for 1 h to complete complex formation with $NaClO_4$. The completeness of the reaction was monitored with the absorption spectra.

^{1}H NMR spectra were obtained on a Bruker WM-400SY spectrometer using DMSO-d_6 as a solvent and $SiMe_4$ as an internal standard. The purity of compounds was controlled by HPLC chromatography on a Milikhrom chromatograph (2×64 mm column, Separon C18, 5 μm, detection at 230 nm). The dyes were analyzed using a MeCN—H_2O (85 : 15) mixture as the eluent. The dyes give one peak with retention volume 140—160 μL.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-5-phenyl-(3-ethylbenzoxazolium perchlorate (1d). 4-Formylbenzo-15-crown-5 (**3c**) (0.8 g, 2.75 mmol) was added to a solution of 2-methyl-5-phenyl-3-ethylbenzoxazolium iodide (**4d**) (0.9 g, 2.45 mmol) in acetic anhydride (30 mL), and the mixture was refluxed for 4 h. The reaction mixture was evaporated *in vacuo*; the residue was dissolved in MeOH. Then a solution of 57 % $HClO_4$ (1 mL, 7.5 mmol) was added, and the mixture was cooled. The precipitate formed was filtered and recrystallized from MeOH to give 0.23 g (15 %) of **1d**, m.p. 164—166 °C. ^{1}H NMR, δ: 1.57 (t, 3 H, Me, J_{MeCH_2} = 7.3 Hz); 3.64 (br. s, 8 H, 4 CH_2O); 3.83 (m, 4 H, 2 CH_2O); 4.21 (m, 4 H, 2 CH_2O); 4.79 (q, 2 H, CH_2N, J_{CH_2Me} = 7.3 Hz); 7.15 (d, 1 H, HC(5′), $J_{C(5')C(6')}$ = 8.4 Hz); 7.47 (m, 1 H, Ph); 7.56 (m, 2 H, Ph); 7.64 (d, 1 H, α-CH, ^3J_t = 15.7 Hz); 7.67 (d, 1 H, HC(6′), $J_{C(6')C(5')}$ = 8.4 Hz); 7.77 (s, 1 H, HC(2′)); 7.82 (d, 2 H, Ph); 8.01 (d, 1 H, HC(6),

$J_{C(6)C(7)}$ = 8.7 Hz); 8.09 (d, 1 H, HC(7), $J_{C(7)C(6)}$ = 8.7 Hz); 8.34 (d, 1 H, β-CH, ^3J_t = 15.7 Hz); 8.37 (s, 1 H, HC(4)). Found (%): C, 59.98; H, 5.51; N, 2.18. $C_{31}H_{34}ClNO_{10}$. Calculated (%): C, 60.44; H, 5.56; N, 2.27.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-ethylbenzothiazolium perchlorate (1e). 2-Methyl-3-ethylbenzothiazolium iodide **2e** (0.15 g, 0.5 mmol), 4-formylbenzo-15-crown-5 **3c** (0.16 g, 0.55 mmol), abs. EtOH (4 mL), and pyridine (0.02 mL, 0.24 mmol) were mixed in a flask equipped with reflux condenser. The reaction mixture was refluxed for 9 h, then 57 % $HClO_4$ (0.2 mL, 1.5 mmol) was added and the mixture was cooled. The precipitate formed was filtered and two times recrystallized from MeOH to give 0.18 g (66 %) of **1e**, m.p. 192—194 °C (*cf.* Ref. 4: m.p. 192—195 °C). Found (%): C, 52.18; H, 5.13; N, 2.31. $C_{25}H_{30}ClNO_9S \cdot H_2O$. Calculated (%): C, 52.31; H, 5.62; N, 2.44.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-ethylnaphtho[1,2-*d*]-thiazolinium perchlorate (1f) was obtained similarly to **1e** from 2-methyl-3-ethylnaphtho[1,2-*d*]thiazolium tosylate **2f** and compound **3c** in 40 % yield. M.p. 199—202 °C. ^{1}H NMR, δ: 1.75 (t, 3 H, Me, J_{MeCH_2} = 7.2 Hz); 3.64 (br. s, 8 H, 4 CH_2O); 3.83 (m, 4 H, 2 CH_2O); 4.21 (m, 4 H, 2 CH_2O); 5.34 (q, 2 H, CH_2N, J_{CH_2Me} = 7.2 Hz); 7.13 (d, 1 H, HC(5′), $J_{C(5')C(6')}$ = 8.5 Hz); 7.63 (dd, 1 H, HC(6′), $J_{C(6')C(5')}$ = 8.5 Hz, $J_{C(6')C(2')}$ = 2.0 Hz); 7.71 (d, 1 H, HC(2′), $J_{C(2')C(6')}$ = 2.0 Hz); 7.86 (m, 1 H, HC(6), $J_{C(6)C(5)}$ = 7.1 Hz, $J_{C(6)C(7)}$ = 8.1 Hz); 7.89 (d, 1 H, α-CH, ^3J_t = 15.6 Hz); 7.94 (m, 1 H, HC(5), $J_{C(5)C(4)}$ = 8.9 Hz, $J_{C(5)C(6)}$ = 7.1 Hz); 8.11 (d, 1 H, β-CH, ^3J_t = 15.6 Hz); 8.30 (d, 1 H, HC(8), $J_{C(8)C(9)}$ = 8.9 Hz); 8.32 (d, 1 H, HC(7), $J_{C(7)C(6)}$ = 8.1 Hz); 8.39 (d, 1 H, HC(9), $J_{C(9)C(8)}$ = 8.9 Hz); 8.74 (d, 1 H, HC(4), $J_{C(4)C(5)}$ = 8.9 Hz). Found (%): C, 54.21; H, 5.58; N, 2.30. $C_{29}H_{32}ClNO_9S \cdot 2H_2O$. Calculated (%): C, 54.25; H, 5.65; N, 2.18.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-1-ethylquinolinium perchlorate (1g) was obtained similarly to **1e** from 1-ethyl-2-methylquinolinium iodide **2g** and compound **3c** in 47 % yield. M.p. 205—208 °C. ^{1}H NMR, δ: 1.59 (t, 3 H, Me, J_{MeCH_2} = 7.3 Hz); 3.64 (br.s, 8 H, 4 CH_2O); 3.83 (m, 4 H, 2 CH_2O); 4.20 (m, 4 H, 2 CH_2O); 5.16 (q, 2 H, CH_2N, J_{CH_2Me} = 7.3 Hz); 7.12 (d, 1 H, HC(5′), $J_{C(5')C(6')}$ = 8.4 Hz); 7.55 (dd, 1 H, HC(6′), $J_{C(6')C(5')}$ = 8.4 Hz, $J_{C(6')C(2')}$ = 2.1 Hz); 7.61 (d, 1 H, HC(2′), $J_{C(2')C(6')}$ = 2.1 Hz); 7.67 (d, 1 H, α-CH, ^3J_t = 16.0 Hz); 7.93 (m, 1 H, HC(6), $J_{C(6)C(5)}$ = 8.2 Hz, $J_{C(6)C(7)}$ = 7.0 Hz); 8.17 (m, 1 H, HC(7), $J_{C(7)C(8)}$ = 9.0 Hz, $J_{C(7)C(6)}$ = 7.0 Hz); 8.20 (d, 1 H, β-CH, ^3J_t = 16.0 Hz); 8.34 (d, 1 H, HC(5), $J_{C(5)C(6)}$ = 8.2 Hz); 8.54 (2d, 2 H, HC(3) and HC(8), $J_{C(3)C(4)}$ = $J_{C(8)C(7)}$ = 9.0 Hz); 9.00 (d, 1 H, HC(4), $J_{C(4)C(3)}$ = 9.0 Hz). Found (%): C, 57.25; H, 6.04; N, 2.46. $C_{27}H_{32}ClNO_9 \cdot H_2O$. Calculated (%): C, 57.09; H, 6.03; N, 2.47.

5-Methoxy-2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-ethylbenzothiazolium perchlorate (1h) was obtained similarly to **1e** from 2-methyl-5-methoxy-3-ethylbenzothiasolinium iodide **2h** and compound **3c** in 45 % yield. M.p. 215—217 °C. ^{1}H NMR, δ: 1.48 (t, 3 H, Me, J_{MeCH_2} = 7.2 Hz); 3.63 (br. s, 8 H, 4 CH_2O); 3.82 (m, 4 H, 2 CH_2O); 3.98 (s, 3 H, OMe); 4.20 (m, 4 H, 2 CH_2O); 4.96 (q, 2 H, CH_2N, J_{CH_2Me} = 7.2 Hz); 7.11 (d, 1 H, HC(5′), $J_{C(5')C(6')}$ = 8.4 Hz); 7.39 (d, 1 H, HC(6), $J_{C(6)C(7)}$ = 8.9 Hz); 7.61 (d, 1 H, HC(6′), $J_{C(6')C(5')}$ = 8.4 Hz); 7.66 (s, 1 H, HC(2′)); 7.72 (s, 1 H, HC(4)); 7.79 (d, 1 H, α-CH, ^3J_t = 15.6 Hz); 8.07 (d, 1 H, β-CH, ^3J_t = 15.6 Hz); 8.27 (d, 1 H, HC(7), $J_{C(7)C(6)}$ = 8.9 Hz). Found (%): C, 51.52; H, 5.58; N, 2.30. $C_{26}H_{32}ClNO_{10}S \cdot H_2O$. Calculated (%): C, 51.70; H, 5.67; N, 2.32.

2-{2-[4-(4,7,10,13-Tetraoxa-1-azacyclopentadecyl)phenyl]ethenyl}-1-ethylquinolinium iodide (1i) was obtained similarly to **1e** from 1-ethyl-2-methylquinolinium iodide **2g** and 4-formylphenylaza-15-crown-5 **3i** in 43 % yield. M.p. 215—218 °C. ^{1}H NMR, δ: 1.56 (t, 3 H, Me, J_{MeCH_2} = 7.2 Hz); 3.52 (br. s, 4 H, 2 CH_2O); 3.58 (m, 8 H, 4 CH_2O); 3.68 (m, 4 H, 2 CH_2O); 3.71 (m, 4 H, 2 CH_2O); 5.03 (q, 2 H, CH_2N, J_{CH_2Me} = 7.2 Hz); 6.84 (2d, 2 H, HC(3′) and HC(5′), $J_{C(3')C(2')}$ = $J_{C(5')C(6')}$ = 9.0 Hz); 7.44 (d, 1 H, α-CH, ^3J_t = 15.4 Hz); 7.83 (2d, 2 H, HC(2′) and HC(6′), $J_{C(2')C(3')}$ = $J_{C(6')C(5')}$ = 9.0 Hz); 7.84 (m, 1 H, HC(6), $J_{C(6)C(5)}$ = 7.9 Hz, $J_{C(6)C(7)}$ = 7.0 Hz); 8.09 (m, 1 H, HC(7), $J_{C(7)C(8)}$ = 9.0 Hz, $J_{C(7)C(6)}$ = 7.0 Hz); 8.24 (d, 1 H, HC(5), $J_{C(5)C(6)}$ = 7.9 Hz); 8.26 (d, 1 H, β-CH, ^3J_t = 15.4 Hz); 8.41 (d, 1 H, HC(8), $J_{C(8)C(7)}$ = 9.0 Hz); 8.50 (d, 1 H, HC(3), $J_{C(3)C(4)}$ = 9.2 Hz); 8.78 (d, 1 H, HC(4), $J_{C(4)C(3)}$ = 9.2 Hz). Found (%): C, 54.48; H, 6.22; N, 4.19. $C_{29}H_{37}IN_2O_4 \cdot 2H_2O$. Calculated (%): C, 54.38; H, 6.45; N, 4.37.

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References

1. S. P. Gromov, A. A. Golosov, O. A. Fedorova, D. E. Levin, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 129 [*Russ. Chem. Bull.*, 1995, **44**, 124 (Engl. Transl.)].
2. *Organicheskie fotokhromy* [*Organic Photochromes*], Ed. A. V. El'tsova, Khimiya, Moscow, 1982, 285 (in Russian).
3. S. P. Gromov, M. V. Fomina, E. N. Ushakov, I. K. Lednev, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1990, **314**, 1135 [*Dokl. Chem.*, 1990, **314** (Engl. Transl.)].
4. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavskii, I. K. Lednev, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **317**, 1134 [*Dokl. Chem.*, 1991, **317** (Engl. Transl.)].
5. *The Theory of the Photographic Process*, Ed. T. H. James, Macmillan Publ., N. Y., 1977, Ch. 8.
6. S. P. Gromov, M. V. Fomina, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1625 [*Russ. Chem. Bull.*, 1993, **42**, 1561 (Engl. Transl.)].
7. S. P. Gromov, O. A. Fedorova, M. V. Alfimov, V. V. Tkachev, and L. O. Atovmyan, *Dokl. Akad. Nauk SSSR*, 1991, **319**, 1141 [*Dokl. Chem.*, 1991, **319** (Engl. Transl.)].
8. A. I. Kiprianov and A. I. Tolmachev, *Zh. Obshch. Khim.*, 1957, **27**, 142 [*J. Gen. Chem. USSR*, 1957, **27** (Engl. Transl.)].
9. V. Rodionov, *Bull. Soc. Chim.*, 1929, **45**, 121.
10. A. T. Peggy and J. D. Simon, *J. Chem. Phys.*, 1992, **97**, 4792.
11. A. V. Barzykin, M. A. Fox, E. N. Ushakov, O. B. Stanislavsky, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *J. Am. Chem. Soc.*, 1992, **114**, 6381.

12. B. M. Bolotin and B. M. Krasovitskii, *Organicheskie lyuminofory* [*Organic Luminophores*], Khimiya, Moscow, 1984, 334 (in Russian).
13. M. M. Martin, P. Plaza, N. Dai Hung, Y. H. Meyer, J. Bourson, and B. Valeur, *Chem. Phys. Letters.*, 1993, **202**, 425.
14. G. A. Krestov, V. N. Afanas'ev, and L. S. Efremova, *Fiziko-khimicheskie svoistva binarnykh rastvoritelei* [*Physicochemical Properties of Binary Solvents*], Khimiya, Leningrad, 1988, 688 (in Russian).
15. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.

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