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Complexation of crown-containing butadienyl dyes with alkali and alkaline earth metal cations in the ground and excited electron states*

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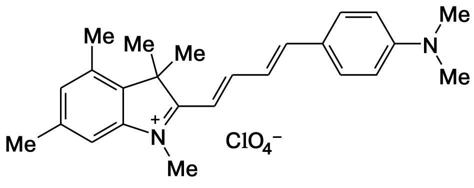
Spectrophotometry and steady-state fluorimetry were used for the study of complexation of crown-containing butadienyl dyes with alkali and alkaline earth metal cations in acetonitrile, as well as protonation of these dyes with trifluoroacetic acid. Complexation of the compounds studied with the metal cations leads to the 1 : 1 product, whereas protonation with trifluoroacetic acid affords the 1 : 2 product containing 2 moles of the acid per 1 mole of the dye. Stability constants of the complexes are varied from 10 to 10^6 L mol^{-1}, basicity of the crown-containing dyes in the reaction with trifluoroacetic acid increases with the increase in the macrocycle size. On complexation, the fluorescence spectra are shifted considerably less than the absorption spectra. This indicates that photorecoordination of the cation in the complex excited molecules occurred. Based on the correlation of the spectral shifts with the metal cation charge density, three types of complexes differing in the extent of influence of the cation charge on the spectral shifts can be singled out: "tight", "loose", and "solvent-separated".

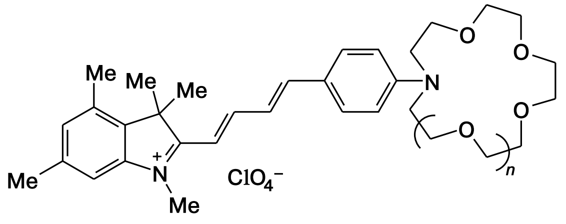
Key words: crown ethers, butadienyl dyes, fluorescence, complexation, photorecoordination, intramolecular electrochromy.

The presence of crown ether fragments in dyes can sharply change their spectral luminescent properties on complexation and serve as optical molecular sensors for determination of a wide number of inorganic and organic cations.[1—6] Crown-containing dyes can serve as a basis for the development of systems with a light-controlled function of the cation bindings, capable upon irradiation to rapidly liberate necessary amount of free ions into solution.[2,5—7] Complexation with cations can serve as an instrument for the control of chromophore or acid-base functions of a dye,[2,5—9] including influence on the excited state intramolecular proton transfer.[10,11] Since all the varieties in behavior of crown-containing dyes are defined by their complexing ability, it is necessary to quantitatively characterize this ability by determination of stability constants of the crown complexes with metal cations.

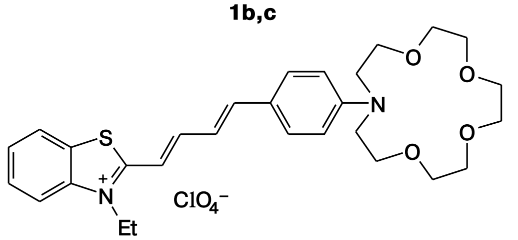
In the present work, influence of the nature of a metal cation, a heterocyclic residue of the dye, and the size of a macrocycle cavity on the complexation of crown-containing butadienyl dyes **1b,c** and **2** with alkali and alkaline earth metal perchlorates in acetonitrile have been studied. To find the limits of the complexation effects and a possi-



1a



1b,c



2

n = 1 (**b**), 2 (**c**)

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* Dedicated to Academician I. L. Eremenko on his 60th birthday.

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bility of the proton phototransfer, protonation of these compounds with trifluoroacetic acid at the nitrogen atom of a macrocycle has been studied, as well as protonation of compound **1a** with trifluoroacetic and sulfuric acids in acetonitrile and ethanol.

Experimental

Acetonitrile (Kriokhrom, especially pure grade) suitable for UV spectroscopy was used as purchased. Before experiments, acetonitrile was dried by distillation over CaH_2. Also were used commercial lithium, sodium, magnesium (all pure grade), calcium (pure for analysis grade), strontium, and barium (both chemically pure grade) perchlorates. Before experiments, the perchlorates were dried *in vacuo* of an oil pump for 12 h at 140 °C. Sulfuric acid (especially pure grade) was used as purchased. Trifluoroacetic acid (pure grade) was distilled over sulfuric acid. Butadienyl dyes **1a—c** and **2** were synthesized according to the known procedure.[12] Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer, fluorescence spectra on a Elyumin 2M spectrofluorimeter. Quantum yields of fluorescence (φ_f) were determined by comparison of the areas under corrected spectra of the substances studied and Cresyl Violet ($\varphi_f = 0.38$ in ethanol[13]) at the wavelength of the exciting light of 580 nm.

Solutions of dyes **1a—c** and **2** were prepared in the absence of direct sources of light to prevent photoinduced *E—Z*-isomerization,[14] which can lead to the change in the optical density of solutions. Fluorescence spectra were recorded at excitation in the isosbestic point. Irradiation of solutions with the excitation light of the fluorimeter virtually produced no changes in their absorption spectra.

Results and Discussion

Due to the strong conjugation of the multiple bonds and increased rigidity of the molecule, the quantum yield of fluorescence for butadienyl dyes is higher by the order of magnitude than for styryl dyes.[15,16] Introduction of a macrocycle into dye **1a** virtually does not affect position of its absorption and fluorescence spectra, however, this leads to a considerable increase in the quantum yield of fluorescence (Table 1).

As it is seen from the data shown in Fig. 1, the short-wave shift of the absorption maximum for dye **1b** on complexation (5100 cm^{-1}) considerably exceeds the shift of the fluorescence maximum (210 cm^{-1}), that indicates that there proceeds the photorecoordination reaction in the excited state of the molecule of complex **1b** with calcium cation. In this case, the Stokes shift for the spectra of the complex (7800 cm^{-1}) is abnormally high as compared to the Stokes shift for the spectra of compound **1b** (2900 cm^{-1}). The quantum yield of fluorescence of the complex exceeds that of the free dye **1b** by a factor of ~1.5, indicating that in the recoordinated state the metal cation is still maintained in the cavity of the macrocycle and thus influences the photophysical properties of the excited molecule. The growth in the quantum yield of fluorescence on complexation for the most of the systems studied distinguishes them from the systems, in which complexation leads to the quenching of fluorescence and the cation was supposed to completely come out of the cavity of the macrocycle of the excited molecule.[17—23]

Table 1. The absorption (λ_a) and fluorescence (λ_f) maxima, molar coefficients of absorption (ε) and quantum yields of fluorescence (φ) for compounds **1a—c** and **2** in acetonitrile

Compound	λ_a /nm	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	λ_f /nm	$\varphi \cdot 10^2$
1a	586	6.44	705	1.4
1b	586	6.73	705	5.0
1c	588	7.28	707	4.6
2	561	6.32	705	5.4

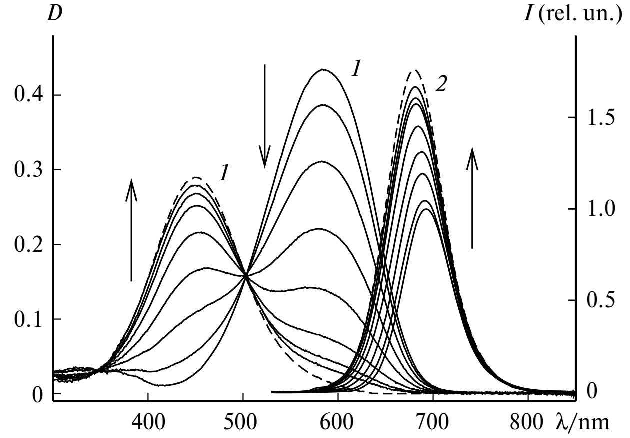


Fig. 1. Absorption spectra (*1*) and uncorrected fluorescence spectra (*2*) of dye **1b** in MeCN in the absence and in the presence of $Ca(ClO_4)_2$ in the concentration of 0.000467, 0.00123, 0.00241, 0.00450, 0.00943, 0.0187, and 0.0453 mol L^{-1}. The calculated absorption and fluorescence spectra of the 1 : 1 complex are shown in the dashed line.

For all the systems studied, the absorption spectra having clear isosbestic point (all the systems except **1c** + $Ca(ClO_4)_2$), the dependence of the indicatory ratio (*I*) from the analytic concentration of the salts (C_M) satisfactorily fits the linear function

$$I = KC_M, \tag{1}$$

where *K* is the stability constant. The indicatory ratio *I* is determined by the expression

$$I = [ML]/[L] = (D_L - D)/(D - D_{ML}), \tag{2}$$

where [ML] is the equilibrium concentration of a complex; [L] is the equilibrium concentration of the dye initial form; D_L is the optical density of a solution containing the initial form of a ligand; D_{ML} is the optical density of a solution containing completely complexed form of a ligand; D is the optical density of a solution at the current concentration of the salt on the wavelength of the absorbed light.

In contrast to the ligand—metal systems studied, protonation of compounds **1a—c** and **2** not always is described by the direct linear dependence of the indicatory ratio versus analytic concentration of acid C_H. For the dependence

$$I = KC_H{}^n \tag{3}$$

it was found that for the systems **1a—c** and **2** with trifluoroacetic acid in acetonitrile, the power n is equal to 2, whereas for the system **1a** with sulfuric acid in acetonitrile and ethanol, n is equal to 1 and 1.5, respectively.

Verification of the dependence (3) and determination of the reaction product composition were made choosing the unoverlaped parts of the spectrum, in which only the initial form of the dye absorbs.

Verification of the dependence (1) was made after its reduction to the form allowing to determine a stability constant and absorption of the completely complexed form by finding parameters of the linear regression

$$1/(D_L - D) = [1/(K\Delta D)]\cdot(1/C_M) + 1/\Delta D, \tag{4}$$

where $\Delta D = D_L - D_{ML}$.

As it is seen from the graphs shown in Figs 2 and 3 (all are built in the coordinates of dependencies (3) and (4)), the complexation of the dyes studied with metal cations up to the concentrations of the salts about 10^{-1} mol L^{-1} can be satisfactorily described by the scheme

$$L + M^{n+} \rightleftharpoons LM^{n+}, \tag{5}$$

which supposes a complete dissociation of the perchlorates in acetonitrile and formation of the 1 : 1 complex with the stability constant

$$K = [LM^{n+}]/([L][M^{n+}]). \tag{6}$$

The equilibrium of the dyes studied with acids is described by the equation

$$B + n\,HA \rightleftharpoons B(HA)_n \tag{7}$$

with the equilibrium constant

$$K = [B(HA)_n]/([B][HA]^n), \tag{8}$$

where n is the integer or half-integer.

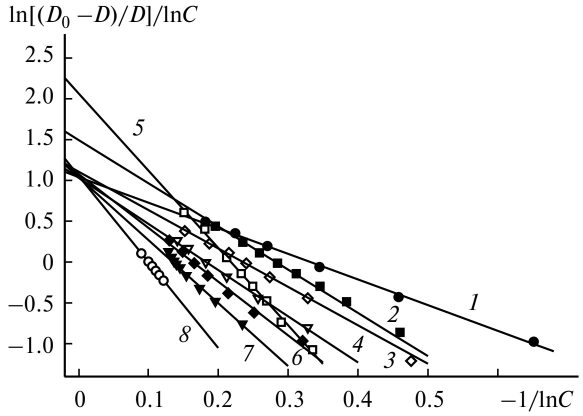


Fig. 2. Indicatory ratio versus analytic concentration of reagent (C) in the coordinates allowing one to determine the product composition through the cutoff for different systems: **1b** + $NaClO_4$ in MeCN, λ_D = 680 nm (*1*); **1a** + H_2SO_4 in ethanol, λ_D = = 600 nm (*2*); **2** + $Mg(ClO_4)_2$ in MeCN, λ_D = 610 nm (*3*); **2** + $Ba(ClO_4)_2$ in MeCN, λ_D = 610 nm (*4*); **1c** + CF_3COOH in MeCN, λ_D = 580 nm (*5*); **1b** + $Ca(ClO_4)_2$ in MeCN, λ_D = = 630 nm (*6*); **1a** + H_2SO_4 in MeCN (logarithm with the base 4 was used for clearness), λ_D = 580 nm (*7*); **1c** + $Ba(ClO_4)_2$ in MeCN, λ_D = 580 nm (*8*).

At first glance, it is surprising that the molecule of the dye having only one basic center, *viz.*, the nitrogen atom of the macrocycle, upon protonation forms an acidic form with the stoichiometry more complex than 1 : 1. In this case, trifluoroacetic acid in the moderately concentrated acetonitrile solutions virtually completely exists as monomers associated with the solvent.[24] It can be assumed that the second molecule of trifluoroacetic acid is tightly held by the anion of the same acid due to the hydrogen bond.[25]

Ion pairs of the composition 1 : 2 are observed, for example, on protonation of 2,4,6-triarylpyridine with trifluoroacetic acid in dioxane,[26] as well as on protonation of 7-aminocoumarins in acetonitrile with the same acid.[27]

The reaction of dye **1a** with sulfuric acid in ethanol can be described by the alternative scheme including forma-

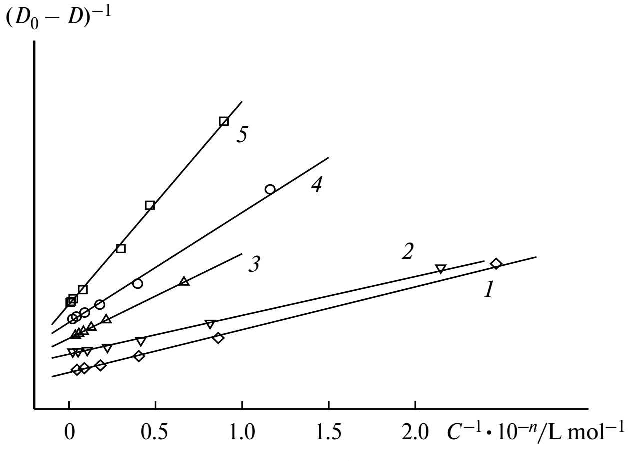


Fig. 3. Dependence of $(D_0 - D)^{-1}$ (the scale is not preserved) from the inverse value of the salt analytic concentration (C) on the wavelengths where both forms of the dye absorb for different systems: **1b** + $NaClO_4$, λ_D = 600 nm, n = 2 (*1*); **1b** + $Ca(ClO_4)_2$, λ_D = 550 nm, n = 3 (*2*); **1c** + $Ba(ClO_4)_2$, λ_D = 520 nm, n = 5 (*3*); **1b** + $Ba(ClO_4)_2$, λ_D = 540 nm, n = 3 (*4*); **1b** + $Mg(ClO_4)_2$, λ_D = 550 nm, n = 3 (*5*).

tion of the inactive ethyloxonium ion and protonation products of the compositions 1 : 1 and 1 : 2.

$$\mathrm{HA} \xrightleftharpoons{K_1} \mathrm{H^+ + A^-}$$

$$\mathrm{B + HA} \xrightleftharpoons{K_2} \mathrm{BHA} \tag{9}$$

$$\mathrm{B + 2\,HA} \xrightleftharpoons{K_3} \mathrm{B(HA)_2}$$

The values $K_1 = 88$ L mol^{-1}, $K_2 = 44$ L mol^{-1}, $K_3 = 370$ L^2 mol^{-2} give the best agreement with the experiment, though, the residual sum of squares and the correlation coefficient, considered as a criterion whether the model agrees with the experiment, are on the same level that in the case of simpler scheme (7) at $n = 1.5$, allowing to make no preference in favor of this or that model. Note that the ionization constant value for sulfuric acid in alcohol (88 L mol^{-1}) obtained by such an indirect way agrees with its evaluation for the methanol-butanol mixture with the given relative permittivity (140 L mol^{-1}).[28]

The complex compositions, their stability constants, and limiting spectra of pure products were obtained by the method of global numerical analysis.[29]

Upon complexation of dyes **1b,c** and **2** with alkali and alkaline earth metal cations, the hypso- and hypochromic effects are observed in the absorption spectra, consisting in the short-wave displacement of the absorption maxima by ~500—6000 cm^{-1} and weakening the absorption coefficients by 20—30% (Table 2, Fig. 4).

In the case when diameter of the cation is considerably less than diameter of the macrocycle cavity (1.7—2.2 and 2.6—3.2 Å for 15-crown-5 and 18-crown-6, respectively),[2] an abnormally small shift of the absorption maxima is observed for the cations with a high charge density. For instance, the shifts in the absorption spectra for complexes **1b** and **2** with Li^+ is less than the shifts for the complexes of the same dyes with Na^+ cation by a factor of 1.6, despite that the charge density for Li^+ is higher. The shifts for the complexes of dye **1c** with small and medium cations, *viz.*, Li^+, Na^+, Mg^{2+}, Ca^{2+} (the diameters are 1.36, 1.90, 1.32, and 1.98 Å, respectively),[2] are less than the

Table 2. Stability constants of complexes and protonation products of compounds **1a—c** and **2** in acetonitrile (log$K$), their composition, hypsochromic shifts of the absorption maxima ($\Delta\nu$), isosbestic points (λ_i), absorption coefficients with respect to absorption of the starting dyes (ε_r), and the complex types

Compound	Cation	Composition	log$K$	$\Delta\nu$/cm^{-1}	λ_i/nm	ε_r	Complex type
1a	H^+	1 : 2	2.37	7440	470	0.637	—
	H_2SO_4 in EtOH	1 : 1.5	2.19	7620	479	0.651	—
	H_2SO_4 in MeCN	1 : 1	4.40	7400	469	0.652	—
1b	Li^+	1 : 1	1.96	1300	547	0.808	"Loose"
	Na^+	1 : 1	1.40	2130	534	0.681	"Tight"
	Mg^{2+}	1 : 1	1.94	5910	492	0.733	"Tight"
	Ca^{2+}	1 : 1	2.63	5120	503	0.675	"Tight"
	Sr^{2+}	1 : 1	1.99	4770	510	0.725	"Tight"
	Ba^{2+}	1 : 1	2.39	4220	516	0.764	"Tight"
	H^+	1 : 2	3.49	7400	472	0.625	—
1c	Li^+	1 : 1	1.89	500	578	1.023	"Solvent-separated"
	Na^+	1 : 1	3.02	470	571	0.982	"Solvent-separated"
	Mg^{2+}	1 : 1	2.17	1290	548	0.834	"Solvent-separated"
	Ca^{2+}	1 : 1	6.38	680	542	0.819	"Solvent-separated"
		1 : 2	11.00*	1790	528	0.641	"Solvent-separated"
	Sr^{2+}	1 : 1	5.29	5400	497	0.700	"Tight"
	Ba^{2+}	1 : 1	4.99	5500	494	0.654	"Tight"
	H^+	1 : 2	5.20	7370	471	0.612	—
2	Li^+	1 : 1	2.13	1460	526	0.823	"Loose"
	Na^+	1 : 1	1.54	2400	512	0.701	"Tight"
	Mg^{2+}	1 : 1	1.81	6000	471	0.868	"Tight"
	Ca^{2+}	1 : 1	2.93	5400	480	0.717	"Tight"
	Sr^{2+}	1 : 1	2.11	4950	488	0.806	"Tight"
	Ba^{2+}	1 : 1	2.29	4400	493	0.770	"Tight"
	H^+	1 : 2	4.26	7570	446	0.727	—

* For the reaction of 1 mole of the ligand with 2 moles of Ca^{2+}.

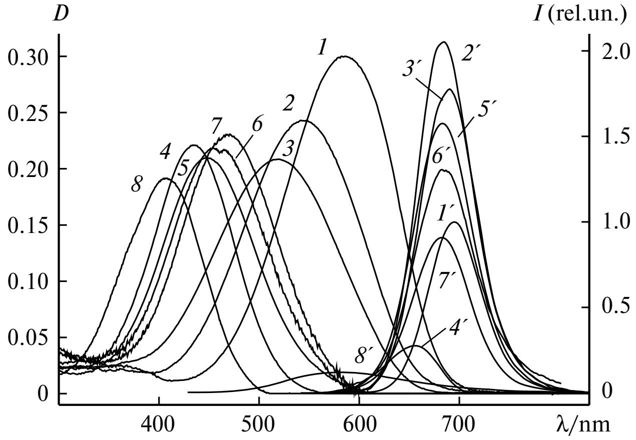


Fig. 4. Calculated absorption spectra (*1—8*) and uncorrected fluorescence spectra (*1′—8′*) of dye **1b** (*1, 1′*), complexes of dye **1b** with Li^+ (*2, 2′*), Na^+ (*3, 3′*), Mg^{2+} (*4, 4′*), Ca^{2+} (*5, 5′*), Sr^{2+} (*6, 6′*), Ba^{2+} (*7, 7′*), and protonated form of dye **1b** (*8, 8′*). The intensity of spectrum *8′* is increased by a factor of 10.

shifts for the complexes with large cations, Sr^{2+} and Ba^{2+} (the diameters are 2.24 and 2.68 Å, respectively) by a factor of 5—10.[2] This is due to the fact that if a diameter of the macrocycle cavity is considerably larger than a diameter of the metal cation, the cation prefers to coordinate only with the oxygen atoms of the crown ether fragment and only slightly touches the nitrogen atom conjugated with the chromophore part of the dye.

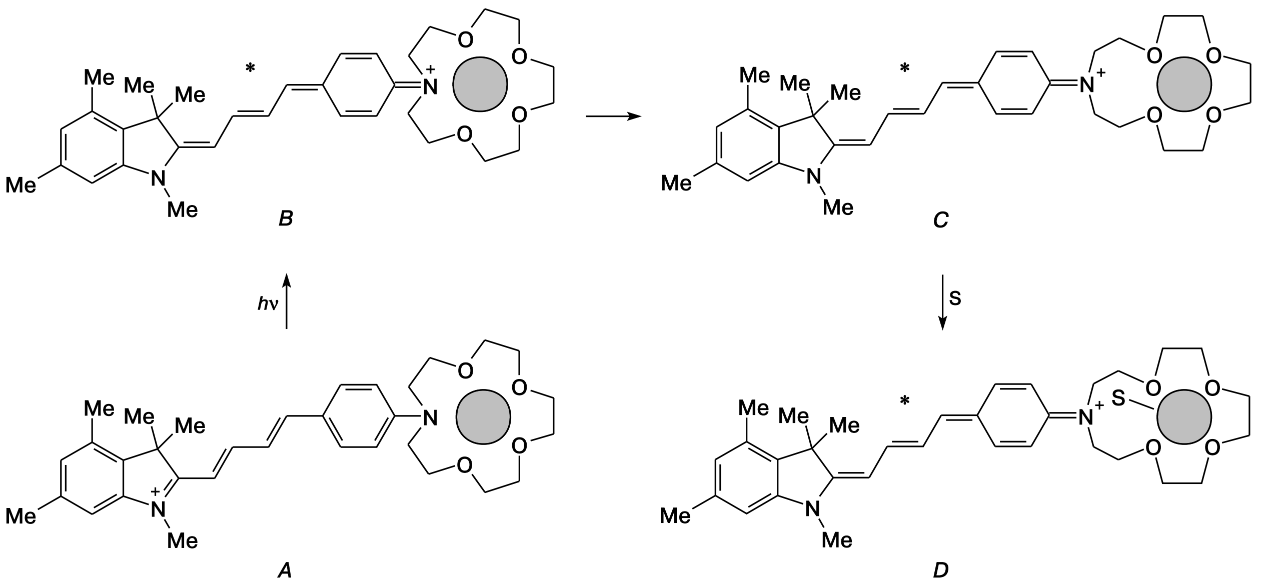
The fluorescence spectra of dyes **1b,c** and **2**, as their absorption spectra, undergo a short-wave shift upon complexation (Table 3). However, this shift is considerably less than the shift in the absorption spectra and in most cases it is equal to ~100—200 cm^{-1}. In these cases the Stokes shift can reach abnormally high values in the order of 8000—9000 cm^{-1} as compared to 3000—4000 cm^{-1} for the free dyes. This phenomenon can be explained by the photorecoordination reaction in the excited state of the metallocomplex molecules. The explanation consists in the weakening or cleavage of the metal—ligand coordination bond due to the charge transfer on excitation and positive polarization of the heteroatom (Scheme 1). The quantum yield of fluorescence of metallocomplexes in most cases is higher than that for the free dyes by a factor of 1.5—2. This finding can be explained either by the hindrance in accomplishing the *trans—cis*-photoisomerization, whose quantum yield is equal to ~0.5 for the stytryl

Table 3. Stability constants of complexes and protonation products of compounds **1a—c** and **2** in acetonitrile (log*K*), their composition, hypsofloric shifts of the fluorescence maxima (Δν), quantum yields of fluorescence with respect to fluorescence of the starting dyes (φ_r), and the complex types

Compound	Cation	Composition	log*K*	$\Delta\nu/cm^{-1}$	φ_r	Complex type
1a	H^+	1 : 2	2.39	1920	0.080	—
	H_2SO_4 in EtOH	1 : 1.5	2.08	2430	0.034	—
	H_2SO_4 in MeCN	1 : 1	4.41	2120	0.079	—
1b	Li^+	1 : 1	1.87	210	1.900	"Solvent-separated"
	Na^+	1 : 1	1.38	60	1.927	"Solvent-separated"
	Mg^{2+}	1 : 1	1.66	1000	0.129	"Loose"
	Ca^{2+}	1 : 1	2.66	220	1.355	"Solvent-separated"
	Sr^{2+}	1 : 1	1.95	220	1.206	"Solvent-separated"
	Ba^{2+}	1 : 1	2.42	230	0.864	"Loose"
	H^+	1 : 2	3.43	2130	0.012	—
1c	Li^+	1 : 1	1.94	120	1.926	"Solvent-separated"
	Na^+	1 : 1	3.16	60	1.624	"Solvent-separated"
	Mg^{2+}	1 : 1	2.11	240	2.000	"Solvent-separated"
	Ca^{2+}	1 : 1	6.83	180	1.624	"Solvent-separated"
		1 : 2	11.50*	260	1.983	"Solvent-separated"
	Sr^{2+}	1 : 1	5.10	410	0.377	"Loose"
	Ba^{2+}	1 : 1	4.98	290	0.456	"Loose"
	H^+	1 : 2	5.10	2070	0.036	—
2	Li^+	1 : 1	2.14	190	2.191	"Solvent-separated"
	Na^+	1 : 1	1.52	90	2.152	"Solvent-separated"
	Mg^{2+}	1 : 1	1.65	1150	0.075	"Loose"
	Ca^{2+}	1 : 1	3.07	210	2.468	"Solvent-separated"
	Sr^{2+}	1 : 1	2.00	200	1.949	"Solvent-separated"
	Ba^{2+}	1 : 1	2.35	100	1.340	"Solvent-separated"
	H^+	1 : 2	4.38	5010	0.013	—

* For the reaction of 1 mole of the ligand with 2 moles of Ca^{2+}.

Scheme 1



Note. Photorecoordination of the cation in the excited molecule of the complex: the "tight" complex in the ground (*A*) and excited (*B*) electron states, the "loose" (*C*) and the "solvent-separated" (*D*) complexes in the excited electron states.

dyes,[14,30] or by the difficulty in the formation of the twisted TICT-state[31—35] due to the binding the metal cation with the crown ether fragment and retardation of rotation.

The accuracy in reproduction of stability constants from the results of two—three series of experiments is about 10%.

Calculations of changes in the complex stability constants on excitation according to the Förster thermodynamic cycle for the hypsochromic shifts of complexes **1b** with Ca^{2+} and Li^{+} cations give the ΔpK values, equal to 10.7 and 2.7, respectively.

Despite these evaluations, the constants obtained from the absorption and fluorescence spectra are in good agreement with each other. Statistical analysis shows that the differences between them are insignificant, and these two selections of the data belong to the same general collection. The correlation coefficient r is equal to 0.996, the slope, to 1.006±0.009, the Student and Wilcoxon criteria are 0.0015 and 4 for the allowable values of 2.0 and 89 with error probability of 0.05, respectively. All of this is an evidence that the quenching of fluorescence of the initial form follows the static mechanism, and the degree of the complex transformations in the excited state is determined by the extent of the reaction in the ground state. Thus, a conclusion can be drawn that the photorecoordination reaction occurs during period of time much shorter than the lifetime of the excited molecule, and during the lifetime of the complex excited molecule no complete liberation of a cation from the cavity of the macrocycle takes place.

Analysis of the spectra matrix rank by the Wallace—Katz method[36] showed that in all the cases, except complex **1c** with Ca^{2+}, two absorbing or emitting component (the initial form and the complex) are present in the absorption and fluorescence spectra, and the equilibrium is described by the scheme leading to the formation of 1 : 1 complex (the correlation coefficient between calculated and experimental spectra is no lower than 0.998). For the complex of **1c** with Ca^{2+}, three components are found in the absorption and fluorescence spectra, which are assigned to dye **1c** and its 1 : 1 and 1 : 2 complexes with Ca^{2+} (2 moles of Ca per 1 mole of compound **1c**), and in this case no isosbestic point is present in the absorption spectra (Fig. 5).

Protonation of compounds **1a—c** and **2** with trifluoroacetic acid is of interest from the point of view of finding limits in possible effects of complexation caused by the complete binding of the lone pair of electrons on the auxochromic nitrogen atom of the macrocycle. Like complexation, protonation leads to a short-wave shift of the absorption spectra. This displacement has the value of ~7000 cm^{-1}, that is by 1000 cm^{-1} higher than the maximum spectral effects observed on complexation with metal cations. The fluorescence spectra are short-wave shifted by ~2000 cm^{-1} in the case of compounds **1a—c** and by ~5000 cm^{-1} in the case of compound **2**. The differences in the shifts on protonation of compounds **1a—c** and **2** can

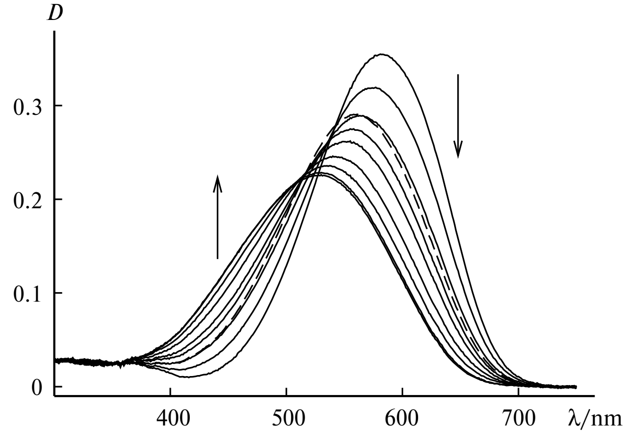


Fig. 5. Absorption spectra of dye **1c** in MeCN in the absence and in the presence of $Ca(ClO_4)_2$ in the concentration of $3.47 \cdot 10^{-6}$, $6.89 \cdot 10^{-6}$, $1.36 \cdot 10^{-5}$, $2.66 \cdot 10^{-5}$, $3.94 \cdot 10^{-5}$, $1.15 \cdot 10^{-4}$, $3.88 \cdot 10^{-4}$, and $1.02 \cdot 10^{-3}$ mol L^{-1}. The calculated spectrum of the intermediately formed 1 : 1 complex is shown in the dashed line.

be apparently caused by a considerably higher electronegativity of the indoleninium residue as compared to the benzothiazolium residue and the formation of the ICT-state upon the charge transfer from the aniline fragment even in the case when the latter is protonated. The protonated forms of all the compounds studied fluoresce poorly, the quantum yields are ~0.001. Their composition is 1 : 2 (2 moles of trifluoroacetic acid per 1 mole of a dye), and no intermediate 1 : 1 forms are observed. Despite that dyes **1a,b,c** are full analogs and differ only in the presence or in the size of a macrocycle, their basicities in the reaction with trifluoroacetic acid are not the same: the stability constants of the protonated forms of compounds **1a,b,c** are $2.34 \cdot 10^2$, $3.09 \cdot 10^3$, and $1.58 \cdot 10^5$ L^2 mol^{-2}, respectively. This can be caused by the stabilization of the protonated forms due to the coordination of the ammonia proton with a macrocycle. Basicity constants found from the absorption spectra agree with the constants found from the fluorescence spectra.

The influence of a charged substituent on the spectral properties of molecules can be considered in the framework of intramolecular Stark effect, which relates the static electric field of the substituent with the displacement of electron energy levels of the molecule.[10,37] In the case if a charged substituent is isolated from the chromophore part of the molecule with a methylene bridge, the values of spectral effects can reach 1000—2000 cm^{-1}.[10,37,38] The spectral effects of complexation of crown-containing dyes may well correlate with the charge density of a metal cation,[39—41] with Li^+ cation having the largest effect among the alkali metal cations and with Mg^{2+} having the same effect among the alkaline earth metal cations.

It can be supposed that for the complexes of compounds **1b,c** and **2** with metal cations, a significant part will be played by effects of conjugation and change of geometry of the macrocycle nitrogen atom on complexation. Nevertheless, a model of intramolecular electrochromy is reasonable to apply for finding anomalies in the complexes spectral shifts as a function of the cation charge density. It was found that the value of the absorption maximum shift on complexation is directly proportional to the cation charge and inversely proportional to the internuclear distance between the cation and the macrocycle nitrogen atom

$$hc\Delta\nu = (\Delta q Z)/[\varepsilon(r_M + r_N)], \qquad (10)$$

where $\Delta\nu$ is the spectral shift of the absorption maximum (in wave numbers), Δq is the charge change on the nitrogen atom on excitation, Z is the metal cation charge, ε is the medium microscopic relative permittivity, r_M is the metal cation radius, r_N is the difference between the metal—nitrogen internuclear distance and the cation radius, h is the Planck constant, c is the velocity of light in free space.

To describe shifts in the absorption spectra of the complexes studied in the framework of the dependence (10), it is reasonable to divide all the complexes into three types. In the "tight" complexes (see Table 2), the ion-dipole interaction operates between a metal cation and the macrocycle nitrogen atom, the metal—nitrogen internuclear distance is approximately equal to the sum of a crystallographic radius of the cation and Van der Waals radius of the nitrogen atom. In the "loose" complexes (see Table 2), there is no coordination bond between metal cation and the nitrogen atom, whereas the metal— nitrogen internuclear distance is increased by ~1.5 Å. In the "solvent-separated" complexes, in addition to the differences for the "tight" and "loose" complexes, shielding of the cation with the solvent molecule or counterion is present. The best agreement between the experimental data and expression (10) (Fig. 6, $r = 0.994$) was obtained for the following parameter values: $\Delta q/(hc\varepsilon) = (6.5 \pm 1.1) \cdot 10^3$ Å cm^{-1} (which corresponds to 0.056 of the electron charge), $r_N = 1.4 \pm 0.2$ and 3.1 ± 0.6 Å for the "tight" and "loose" complexes, respectively, $\varepsilon_c = 2.7 \pm 0.2$ (additional shielding parameter for the "solvent-separated" complexes).

According to the model of connecting spherical species placed in a highly polar continual solvent, the microscopic relative permittivity of acetonitrile is close to four.[42]

Existence of complexes with elongated metal—nitrogen bond is confirmed by calculation methods[43—45] (the bond distance is 3.8—4.2 Å) and the X-ray data[46,47] (3.2 Å). An increase in the metal—heteroatom internuclear distance is also possible in the case of complexation of 18-crown-6 with cations of small radii[48] (3.3—4.2 Å). Existence of complexes of crown ethers with a solvent in the first coordination sphere is also confirmed by the calculation and X-ray data.[44,45] To sum up, the model of intramolecular electrochromy allows one to single out three types of complexes differing in the extent of influence of

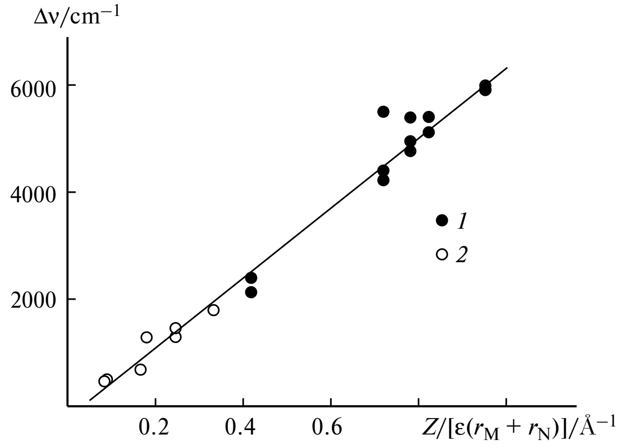


Fig. 6. Correlation of the absorption maxima shifts on complexation with the charge density according to Eq. (10): *1* are the "tight" complexes, *2* are the rest of the complexes.

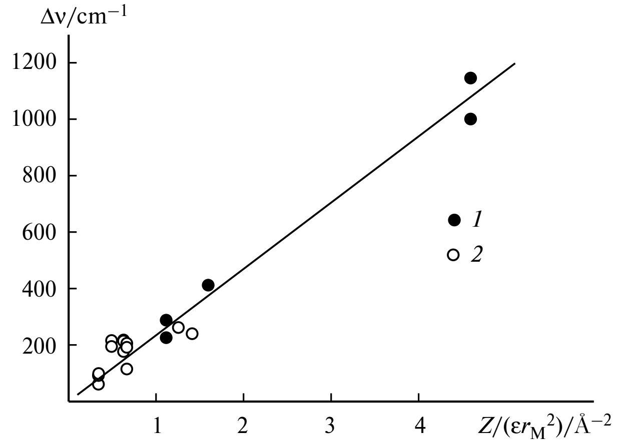


Fig. 7. Correlation of the fluorescence maxima shifts on complexation with the charge density according to Eq. (11): *1* are the "loose" complexes, *2* are the "solvent-separated" complexes.

a cation charge on the hypsochromic shifts: the "tight", "loose", and "solvent-separated". Apparently, such a division corresponds to the notions obtained in the course of theoretical calculations, according to which starting from the complex geometries and macrocycle conformation, axial and equatorial complexes can be singled out, as well as complexes with the solvent in the first coordination sphere.[43—45]

In contrast to the shifts of the absorption maxima, the dependence of the fluorescence maximum shift exhibits satisfactory correlation not with the radial, but with the surface charge density of the cation

$$hc\Delta\nu = (\Delta\mu Z)/(\varepsilon r_M{}^2), \qquad (11)$$

where $\Delta\nu$ is the fluorescence maximum spectral shift on complexation; $\Delta\mu$ is the proportional coefficient having unit of a dipole moment. The best agreement between the experimental data and expression (11) (Fig. 7, $r = 0.985$) was obtained for the following parameter values: $\Delta\mu/(hc\varepsilon) = (2.35\pm0.09)\cdot10^2$ Å^2 cm^{-1}, $\varepsilon_c = 3.3\pm0.4$ (additional shielding parameter for the "solvent-separated" complexes).

To calculate charge density for two Ca^{2+} cations in the cavity of macrocycle **1c**, an effective radius was assigned to bication $Ca_2{}^{4+}$. The best correlation with the dependencies (10) and (11) was obtained in the case, when the effective radius of the bication has been supposed to be equal to the radius of one cation. This can correspond to the case when one cation is placed over another and the mutual shielding of the cations in the bication is absent.

To explain certain anomalies in the values of spectral shifts depending on the cation charge density and describe spectral effects of complexation in the excited state, like in the case of the ground electron state, it is necessary to divide complexes to several types.

Even the strongest shift observed in the fluorescence spectra for complex **2** with Mg^{2+} (1150 cm^{-1}), is a considerable inferior in its value to the shift of absorption spectrum (6000 cm^{-1}), as well as to the fluorescence spectrum shift for dye **2** on protonation (5000 cm^{-1}). That is why the complex of **2** with Mg^{2+}, as some other complexes, was assigned to the "loose" type, whereas complexes with an additional shielding were assigned to the "solvent-separated" type. Spectral shifts for the related compound, where the *N*-phenylazacrown ether fragment is replaced with the analogous benzocrown ether,[49] also indirectly indicate to the proceeding the recoordination reaction in the complex of **2** with Mg^{2+}. No photorecoordination reaction occurs in the complex of this compound with magnesium, and the absorption and fluorescence spectra shifts are of the same value and equal to ~2000 cm^{-1}.

To sum up, the photorecoordination reactions can be considered as a change in the complex type upon its transition to the excited state. A degree to which the photorecoordination proceeds can be different for different systems. Thus, photorecoordination of the "tight" complex of **1b** with Mg^{2+} leads to the "loose" complex with hypsofloric shift of 1000 cm^{-1}, whereas photorecoordination of the "tight" complex of **1b** with Ca^{2+}, to the "solvent-separated" complex with hypsofloric shift of 220 cm^{-1}. For all the complexes studied, the recoordination reaction proceeds to some extent, except for the complexes of **1c** with cations Li^+, Na^+, Mg^{2+}, Ca^{2+}, whose diameters are considerably less than the 18-crown-6 cavity size and which in the ground state already have a cation isolated from the chromophore part of the molecule and the nitrogen atom of the macrocycle by a solvent molecule or a counterion. Assignment of the excited complexes to one of the two types according to expression (11) is confirmed by the quantum yield values of their fluorescence: for the "solvent-separated" complexes the value of relative quantum yield of fluorescence is higher than unity, whereas for the "loose" complexes it is lower. Closer placement of a cation with an excited molecule in the "loose" complexes as compared to the "solvent-separated" causes quenching of fluorescence.

Due to the fact that the diameter of cation Ba^{2+} considerably exceeds the diameter of the 15-crown-5 fragment cavity (2.68 and 1.7—2.2 Å, respectively[2]), upon the formation of the complex this cation should adopt position outside the mean-square plane of the macrocycle, as if "sitting down" over it, and along with the formation of the 1 : 1 complexes, formation of the 2 : 1 sandwich-type complexes (2 moles of the ligand per 1 mole of barium) is very characteristic.[30,49,50] At the same time, since stability of the complexes of alkali and alkaline earth metal cations with derivatives of nitrogen-containing aza-15-crown-5 is lower by the two—three orders of magnitude[51] than with 15-crown-5 derivatives, formation of sandwiches is not characteristic of the dyes bearing the nitrogen-containing macrocycles.[17,41,51—57] In the order of cations Ca^{2+}, Sr^{2+}, and Ba^{2+}, stability constants of their complexes with aza-15-crown-5 derivatives usually monotonously decrease with the reduction of the cation charge density.[41,56,57] However, there are known cases of abnormally low stability of Sr^{2+} complexes as compared to Ba^{2+} complexes. For instance, logarithms of the stability constants of the crown-containing merocyanine dye complexes with cations Ca^{2+}, Sr^{2+}, and Ba^{2+} in acetonitrile are equal to 3.79, 2.64, and 2.87, respectively.[17,21] Therefore, the stability constants obtained for complexes of **1b** and **2** with cations Sr^{2+} and Ba^{2+}, as well as equimolar composition of these complexes and the absence of the sandwich-type complexes, do not contradict to the literature data.

Considering influence of the heterocyclic residue on the complexation of compounds **1b** and **2**, it can be noted that compound **2** exhibits higher basicity in the reaction with trifluoroacetic acid. This agrees with the notions on higher electron-withdrawing power of the indoleninium residue as compared to the benzothiazolium residue.[12] At the same time, no considerable differences in the stability constants of the complexes of **1b** and **2** with alkali and alkaline earth metal cations were found.

With the growth in the size of a macrocycle in the order of compounds **1b,c**, stability constants of their complexes formed with the smallest cations (Li^{+} and Mg^{2+}) virtually do not change, whereas in the case of larger cations, stability of the complexes increases by the two—three orders of magnitude. This is due to the increase in the amount of oxygen atoms in the macrocycle and weakening of the destabilizing effect of the nitrogen atom, owing to which stability constants of oxygen crown ether complexes exceed stability constants of complexes formed by azacrown ethers.[51]

* * *

In conclusion, crown-containing butadienyl dyes **1b,c** and **2** form 1 : 1 complexes with alkali and alkaline earth metal cations in acetonitrile. If the cavity size of the macrocycle exceeds diameter of the cation, coordination of two cations with one molecule of the ligand is also possible.

Protonation of compounds **1a,b,c** and **2** with trifluoroacetic acid leads to the formation of the product with two molecules of acid per one molecule of the dye. The macrocycle size considerably affects basicity of the compounds studied.

The changes in the fluorescence spectra of dyes **1b,c** and **2** caused by complexation are insignificant, that is explained by the photorecoordination reaction in the excited molecules of these complexes. The extent of photorecoordination can vary from system to system.

The stability constants of complexes found from the fluorescence spectra are close to the constants found from the absorption spectra, that indicates that no photoliberation of the cation from the macrocycle cavity occurs during the lifetime of the excited state.

Hypsochromic shifts of the absorption spectra are satisfactorily described in the framework of the Coulomb electrostatic model of intramolecular electrochromy, according to which the spectral shift on complexation is directly proportional to the cation charge and inversely proportional to the internuclear distance between a cation and the macrocycle nitrogen atom. The model of intramolecular electrochromy allows one to divide the complexes into three types differing in the extent of influence of the cation charge on the hypsochromic shifts: "tight", "loose", and "solvent-separated".

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