Crown-containing styryl dyes

19.* Complexation and cation-induced aggregation of chromogenic aza-15-crown-5 ethers

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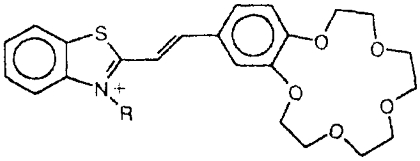
Complexation of styryl dyes containing the *N*-phenylaza-15-crown-5 fragment (*trans*-**2a,b**) with Ca^{2+} ions in MeCN was studied. Unlike cationic dye *trans*-**2a**, betaine *trans*-**2b** forms both complexes of 1 : 1 stoichiometry and aggregates consisting of four dye molecules and one Ca^{2+} ion. Cation-induced aggregation was observed also for the analog of dye *trans*-**2b**, which contains a dimethyiamino group instead of an azacrown ether fragment (*trans*-**3**). Apparently, the interaction between a metal cation and sulfo groups of molecules *trans*-**2b** or *trans*-**3** makes the main contribution to the stability of aggregates. The dependence of the stability of aggregates on the nature of the metal cation was studied.

Key words: crown-containing styryl dyes, betaines of styryl dyes, complexation with Ca^{2+} ions, cation-induced aggregation, absorption spectra of aggregates.

Macrocyclic compounds, which are capable of binding metal cations selectively and absorbing light in the visible region, can be used as reagents for colorimetric or luminescent determination of metal cations[2] and as elements of photoswitched molecular systems.[2,3]

Previously, we synthesized a number of styryl dyes *trans*-**1a—d** containing a 15-crown-5 fragment.[4,5]



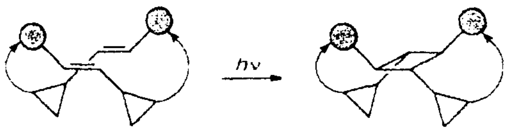
trans-**1a—d**

R = Et + X^-, X^- = ClO_4^- (**a**); R = $(CH_2)_nSO_3^-$ (**b—d**),
n = 2 (**b**), 3 (**c**), 4 (**d**)

Complexation of *trans*-**1a—d** with Mg^{2+}, Ca^{2+}, and Ba^{2+} ions in MeCN was studied by electronic spectroscopy (see Ref. 6). The relationship between complexation and photochemical conversions was studied for compounds **1c,d**.[1,4,5,7,8]

It was established that *trans*-**1a,b** form only 1 : 1 complexes. In going to *trans*-**1c,d**, the stability constants of the complexes increase by more than two orders of magnitude. In addition, compounds *trans*-**1c,d** form dimeric complexes (2 : 2) with Mg^{2+} and Ca^{2+} ions through the interaction between the sulfo group of one dye molecule and the metal cation located in the cavity of the crown ether fragment of other molecule. The constant of dimerization of complexes of *trans*-**1c** with Mg^{2+} is $3 \cdot 10^5$ L mol^{-1}. This constant increases by more than an order of magnitude in going to *trans*-**1d**.

Upon photolysis of solutions of complexes of *trans*-**1c,d** with Mg^{2+} or Ca^{2+} ions, two competing photochemical reactions, namely, *trans-cis*-isomerization and [2+2]-autocycloaddition, occur. A single stereoisomer of a cyclobutane derivative forms in the autocycloaddition reaction. The unique selectivity of the reaction is attributed to the fact that only dimeric complexes of the *trans* isomer in which the mutual arrangement of molecules is fixed by two intermolecular coordination bonds are involved in this reaction.



⊛ — benzo-15-crown-5 fragment with metal cation,

▷ — benzothiazole residue,

⌒ — $(CH_2)_nSO_3^-$, *n* = 3, 4

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[*] For Communication 18, see Ref. 1.

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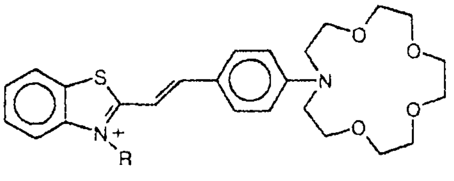
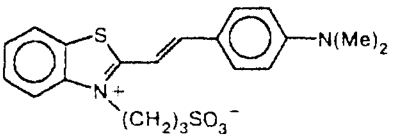
In this work, we report the results of studies of complexation of styryl dyes containing an *N*-phenylaza-15-crown-5 fragment (*trans*-**2a**,**b**) instead of a benzo-15-crown-5 fragment. This replacement causes a bathochromic shift of the long-wave absorption band of the dye (by almost 90 nm) because of the higher electron-donating ability of the azacrown group.

To establish the structures of complexes of *trans*-**2b**, we used also the analog of this dye (*trans*-**3**) containing a dimethylamino group instead of the crown ether fragment.



trans-**2a**,**b**

R = Et + X⁻, X⁻ = ClO_4^- (**a**); R = $(CH_2)_3SO_3^-$ (**b**)



trans-**3**

Experimental

The electronic absorption spectra were recorded on a Specord-M40 spectrophotometer. The stationary fluorescence spectra were obtained on a Elyumin spectrofluorometer.

Compounds *trans*-**2a**,**b** and *trans*-**3** were synthesized according to a procedure reported in Ref. 9. Acetonitrile and Mg, Ca, and Ba perchlorates were dehydrated according to procedures reported previously.[6] Na, Zn perchlorates , and Et_4NClO_4 were dried *in vacuo* at 230, 110, and 40 °C, respectively.

Complexation of *trans*-**2a**,**b** and *trans*-**3** with Ca^{2+} ions was studied in anhydrous MeCN by electronic spectroscopy. The dependences of the absorption and fluorescence spectra on the concentration of Ca^{2+} (C_M) were analyzed. The concentration of Ca^{2+} was varied by mixing two initial solutions (with equal concentrations of dye, $C_L = 1.0 \cdot 10^{-5}$ mol L^{-1}) in different proportions. One of these solutions contained a supporting electrolyte Et_4NClO_4 (0.01 mol L^{-1}), and the second solution contained $Ca(ClO_4)_2$ (0.005 mol L^{-1}). This made it possible to maintain constant concentrations of dye and ClO_4^- ions (C_A = 0.01 mol L^{-1}). The ionic strength of the solution varied within a very narrow range from 0.01 to 0.015 mol L^{-1}.

A supporting electrolyte was not added in the experiments carried out at high concentrations of *trans*-**2b**.

All experiments were carried out at 18±2 °C in quartz cells (d = 1 and 0.01 cm) whose inner surface was modified with hydrophobic groups.[6]

Results and Discussion

Complexation of dye *trans*-2a

Figure 1, *a* shows the dependence of the absorption spectrum of dye *trans*-**2a** on the concentration of Ca^{2+} ions at a constant concentration of perchlorate ions (C_A = 0.01 mol L^{-1}). The substantial ionochromic effect observed in this system may be attributed, as in the case of *trans*-**1a**—**d** (see Refs. 4, 5, and 10), to complexation of the metal cation with the crown ether fragment of the dye. The spectra have two isosbestic points, and the linear correlation between the optical densities at two different wavelengths is observed. The dependence of the optical density on C_M in the region of the maximum of the long-wave absorption band of the free dye and therefore, at other wavelengths is well approximated (Fig. 2) by the following equation:

$$\frac{(D_L - D)}{(D - D_{LM})\cdot K} + \frac{C_L \cdot (D_L - D)}{(D_L - D_{LM})} = C_M , \qquad (1)$$

where K is the stability constant of the complex, and D_L, D, and D_{LM} are the optical density at the fixed wavelength of the initial solution, the current optical density, and the optical density upon complete complexation, respectively. Equation (1) is true for the simplest scheme of complexation

$$\mathrm{L} + \mathrm{M} \xrightleftharpoons{K} \mathrm{LM}.$$

The absorption spectrum of the complex (Fig. 1, *a*, a dashed line) was calculated based on the values of the parameters K and D_{LM} obtained by approximation. Analysis of the shape of this spectrum demonstrated that the long-wave shoulder of the band with the maximum at 410 nm cannot be assigned to the residual absorption of the free ligand. This conclusion is confirmed by the fact that the calculated spectrum is virtually identical to the spectrum, which was recorded when a large amount of $Ca(ClO_4)_2$ (C_M = 0.5 mol L^{-1}) was added to a solution of *trans*-**2a**.

The measured stability constant of the complex of *trans*-**2a** with Ca^{2+} (log$K$ = 2.4) is the effective value because association of the triple-charged complex with the ClO_4^- ion was ignored in the calculations. Using *trans*-**1a** as an example, it was demonstrated[6] that the equilibrium constant of this process in MeCN can be higher than the constant of association of Ca^{2+} and ClO_4^- ions. Therefore, the scheme of complexation of *trans*-**2a** with Ca^{2+} should be represented as follows:

Scheme 1

$$\mathrm{L}^+ + \mathrm{M}^{2+} \xrightleftharpoons{K_{\mathrm{LM}}} (\mathrm{LM})^{3+},$$

$$(\mathrm{LM})^{3+} + \mathrm{A}^- \xrightleftharpoons{K_{\mathrm{LMA}}} (\mathrm{LMA})^{2+}.$$

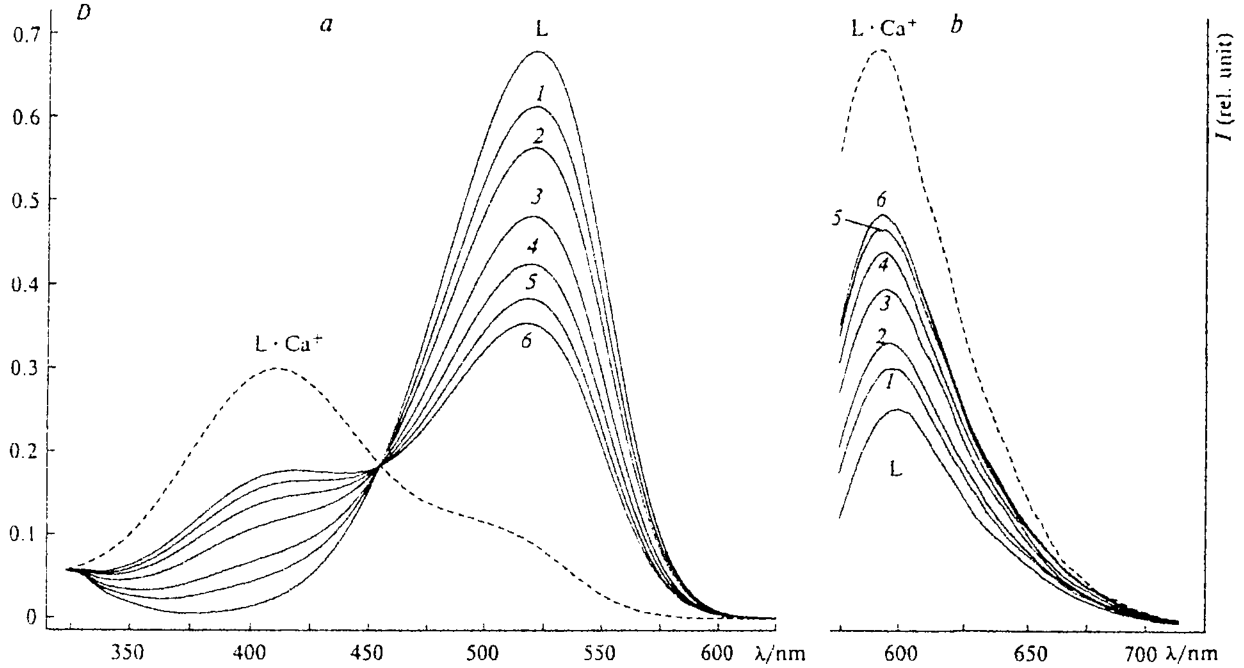


Fig. 1. Dependence of the absorption spectra (*a*) and fluorescence spectra (*b*) of *trans*-**2a** (C_L = 1.0 · 10^{-5} mol L^{-1}) in MeCN on the concentration of Ca^{2+} (C_M/C_L = 50 (*1*), 100 (*2*), 200 (*3*), 300 (*4*), 400 (*5*), and 500 (*6*)) at a constant concentration of perchlorate ions (0.01 mol L^{-1}). The calculated spectra of the complex are shown by dashed lines.

In this scheme, association of Ca^{2+} and Et_4N^+ ions with ClO_4^- is ignored. The constant of association of Ca^{2+} with ClO_4^- in MeCN is small ($\log K_{MA}$ = 1.4, see Ref. 11). This constant should be even smaller for Et_4N^+. Therefore, under conditions of the experiment, the concentration of free ClO_4^- ions changes only slightly, and it is close to the total constant concentration of ClO_4^- in a solution. It can easily be shown that in this case, the ratio of concentrations of the $(LM)^{3+}$ and $(LMA)^{2+}$ complexes remains virtually unchanged throughout the experimental range of C_M, and the relationship between D and C_M should adequately be described by Eq. (1) with the effective constant

$$K \approx K_{LM} \cdot (1 + K_{LMA} \cdot C_A)/(1 + K_{MA} \cdot C_A). \qquad (2)$$

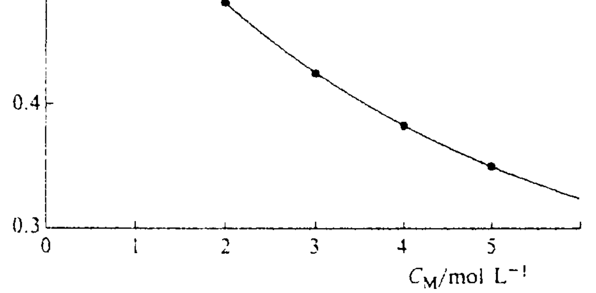


Fig. 2. Experimental and calculated (Eq. (1)) dependences of the optical density of a solution of *trans*-**2a** (C_L = 1.0 · 10^{-5} mol L^{-1}) in MeCN at 522 nm on the concentration of Ca^{2+} ions at a constant concentration of perchlorate ions (0.01 mol L^{-1}).

Association of the complex with anions (the second reaction in Scheme 1) was generally ignored in the measurements of the stability constants of complexes of crown ethers in MeCN. This may lead to questionable conclusions if the value of K_{LM} is small. Thus, in Ref. 12, both the main equilibrium and the reaction of the complex with the second cation were used for describing the results of spectrophotometric measurements of stability constants of the complexes of crown-containing styrylbenzodiazinone with doubly-charged metal cations.

In the above-mentioned work, the equilibrium constant of the second reaction ($\log K_{LM_2}$ = 2.5 for the Ca^{2+} ion) was reported, but the character of the interaction between LM^{2+} and M^{2+} was not considered. In our opinion, a more realistic process of association of the complex with the anion can be used instead of the above-mentioned reaction (note that in the cited work, experiments were carried out without a supporting electrolyte, and the concentration of ClO_4^- changed proportionally to the concentration of the metal cation).

To compare the capability of crown ether fragments of *trans*-**1a** and *trans*-**2a** to form complexes with Ca^{2+}, the constant K for *trans*-**1a** can be estimated from Eq. (2) using the following known values:[6] $\log K_{LM} = 4.0$ and $\log K_{LMA} = 2.8$. The estimation obtained ($\log K \approx 4.8$) demonstrated that the stability of the complexes decreases by more than two orders of magnitude in going from *trans*-**1a** to *trans*-**2a**. This effect is also observed in the case of simple crown ethers, namely, benzo-15-crown-5 ($\log K_{LM} = 6.6$, see Ref. 6) and *N*-phenylaza-15-crown-5 ($\log K_{LM} = 3.23$, see Ref. 13). The decrease in the stability of the complexes of *trans*-**2a** compared to *N*-phenylaza-15-crown-5 is attributable to the strong electron-withdrawing effect of the positively charged benzothiazole residue in the dye molecule.

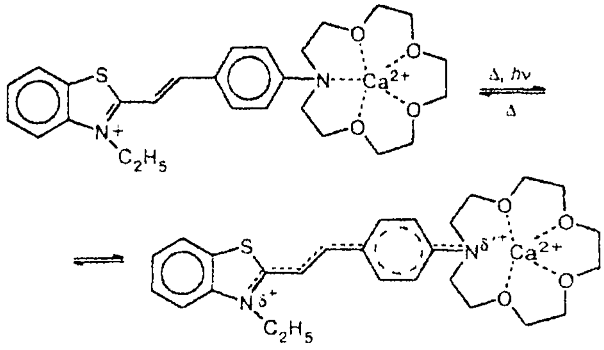
Figure 1, *b* shows the dependence of the fluorescence spectrum of *trans*-**2a** on the concentration of Ca^{2+} ions added. The wavelength of excitation (453 nm) coincides with the position of the isosbestic point in the absorption spectra. The dependence of the intensity of fluorescence at 610 nm, where secondary absorption is absent, was approximated by Eq. (1) with the fixed value of the constant K (see above) by substituting the corresponding intensities of fluorescence for the optical densities. The good agreement between the experimental data and the calculated curve ($r > 0.99$) made it possible to calculate the fluorescence spectrum of the complex (Fig. 1, *b*, a dashed line).

It can be seen from Fig. 1 that the quantum yield of fluorescence increases upon complexation of *trans*-**2a**, and in addition, the shift of the maximum of the fluorescence band from the long-wave maximum in the absorption spectrum increases sharply (Table 1). Analogous effects were observed previously[12] upon complexation of crown-containing styrylbenzodiazinone with Ca^{2+}. However, note that if the low intensity band, which appears as a long-wave shoulder of the band with the maximum at 410 nm, is taken into account in the absorption spectrum of complex of *trans*-**2a**, the increase in the Stokes shift upon complexation becomes insignificant.

Table 1. Spectral luminescence characteristics of crown-containing styryl dyes *trans*-**2a,b** and their complexes with metal cations in MeCN at 18±2 °C

Compound	λ_{max}^{abs} /nm	ε_{max} /L mol^{-1} cm^{-1}	λ_{max}^{fl} /nm
trans-**2a**	522	68000	600±2
(*trans*-**2a**) · Ca^{2+}	410		
	480—530 (sh)	30000	590±2
trans-**2b**	524	69000	601±2
$(trans\text{-}\mathbf{2b})_4 \cdot Ca^{2+}$	491		
	550—600 (sh)	58310	—
$(trans\text{-}\mathbf{2b})_4 \cdot Zn^{2+}$	501		
	550—600 (sh)	68230	—

We suggested that the complex of *trans*-**2a** with Ca^{2+} occurs in two forms, which are in thermodynamical equilibrium:



Then, the long-wave shoulder in the spectrum of the complex can be assigned to the form with a weakened coordination band between the metal cation and the nitrogen atom of the crown ether fragment.

The analogous equilibrium in the first excited state should be shifted rightward[14] due to the decrease in the electron density on the nitrogen atom of the crown ether fragment. As a result, the major fluorescent form is the form with a broken coordination bond, which accounts for the weak effect of the cation on the position of the fluorescence maximum.

Based on the available data, it is difficult to make definite conclusions about the reasons for the increase in the quantum yield of fluorescence of *trans*-**2a** upon complexation with Ca^{2+}. Generally, the opposite effect is observed for styryl compounds containing benzocrown[7,15] or *N*-phenylaza-crown[16] fragments, although there are exceptions to this rule.[12,15] In Ref. 12, the increase in the quantum yield of fluorescence upon complexation of crown-containing styrylbenzodiazinone was attributed to the fact that the metal cation prevents transition of the excited molecule to a twisted state with the charge transfer (the TICT state). In the case of *trans*-**2a**, the situation is complicated by the substantial contribution of *trans-cis*-photoisomerization to the radiationless deactivation.[9]

Complexation of *trans*-2b and *trans*-3 dyes

Figure 3, *a* shows the dependence of the absorption spectrum of *trans*-**2b** on the concentration of Ca^{2+} ions at constant $C_A = 0.01$ mol L^{-1}. It can be seen that, unlike the above-considered system, substantial spectral changes occur even when small amounts of the cation are added. The character of these changes is quite different. At $C_M/C_L = 0.5$, the maximum in the absorption spectrum is shifted hypsochromically, and the opti-

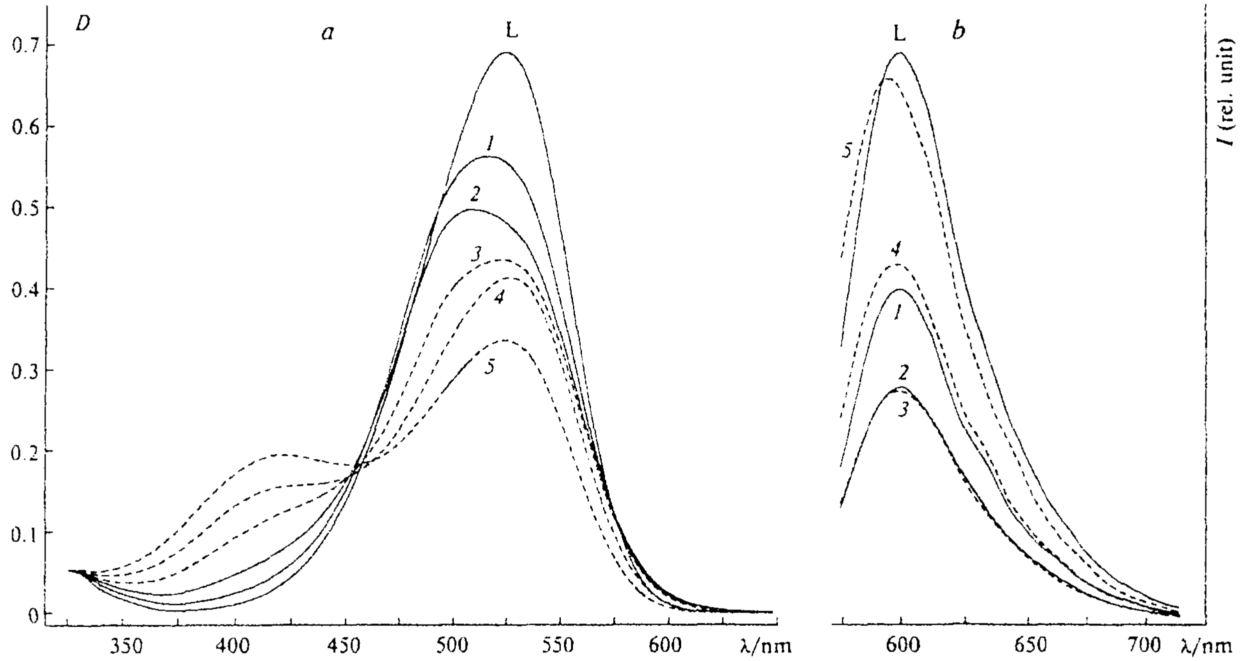


Fig. 3. Dependence of the absorption spectra (*a*) and fluorescence spectra (*b*) of *trans*-**2b** ($C_L = 1.0 \cdot 10^{-5}$ mol L^{-1}) in MeCN on the concentration of Ca^{2+} ions (C_M/C_L = 0.5 (*1*), 1.5 (*2*), 10 (*3*), 100 (*4*), and 500 (*5*)) at a constant concentration of perchlorate ions (0.01 mol L^{-1}).

cal density at the long-wave edge of the spectrum slightly increases. At high concentrations of Ca^{2+}, the shape of the absorption spectrum of *trans*-**2b** becomes close to that of the corresponding spectrum of *trans*-**2a**. However, there is a substantial peculiarity. At $C_M/C_L = 100$, the long-wave maximum in the spectrum of *trans*-**2b** is shifted bathochromically by 1 nm with respect to the maximum at $C_M = 0$.

Figure 3, *b* shows the dependence of the fluorescence spectrum of *trans*-**2b** (excitation at 453 nm) on the concentration of Ca^{2+} ions. The spectra are somewhat corrected taking into account the slight change (no more than 15%) in the optical density of the solution at the wavelength of excitation. It can be seen that first the intensity of the fluorescence band decreases (the position of the maximum remains unchanged) and then the intensity increases (the maximum of the band is slightly shifted to the short-wave region) as the concentration of the cation increases.

To account for the spectral regularities observed, it can be suggested that addition of a small amount of cations affords aggregation of molecules *trans*-**2b**. Apparently, formation of the complex of molecule *trans*-**2b** with a Ca^{2+} ion is an intermediate step of this process. Subsequent addition of one or several dye molecules to this complex yields an aggregate.

It is well known that many dyes, including polymethine dyes, are prone to aggregation.[17,18] The character of changes in the absorption spectra of dyes depends on the geometry of the aggregate, the number of associated molecules, and the energy of their interactions. One typical case is the splitting of the long-wave absorption band (exciton splitting). Apparently, this effect accounts for the hypsochromic shift of the maximum of the long-wave absorption band of *trans*-**2b** with a simultaneous increase in the optical density in the region of 600 nm at $C_M/C_L = 0.5$.

It is also known that dye aggregates are generally nonfluorescent in solution at room temperature, or quantum yields of fluorescence are low.[18] Therefore, the decrease in the intensity of the fluorescence band of *trans*-**2b**, which is observed when small amounts of the cation are added, agrees well with the suggestion that aggregates occur.

A more clear evidence for cation-induced aggregation of *trans*-**2b** is the dependences of the absorption and fluorescence spectra (excitation in the region of the constant optical density at 432 nm) obtained at high concentrations of the dye ($C_L = 5.9 \cdot 10^{-4}$ mol L^{-1}) on small amounts of $Ca(ClO_4)_2$ (Fig. 4). The splitting of the long-wave absorption band and the sharp decrease in the quantum yield of fluorescence (Fig. 4) are typical of aggregation of dye molecules in solution.

Analysis of the absorption spectra (Fig. 4) demonstrated that the relative change in the optical density $(D_L - D)/D_L$ in the region of 535—545 nm is more than twice the relative concentration of Ca^{2+} ions at $C_M/C_L \le 0.16$. Hence, it follows that there are more than two molecules *trans*-**2b** per Ca^{2+} ion in aggregates.

Figure 5 shows the dependence of the intensity of fluorescence of a solution of *trans*-**2b** ($C_L = 5.9 \cdot 10^{-4}$ mol L^{-1}) at 625 nm on the concentration of $Ca(ClO_4)_2$.

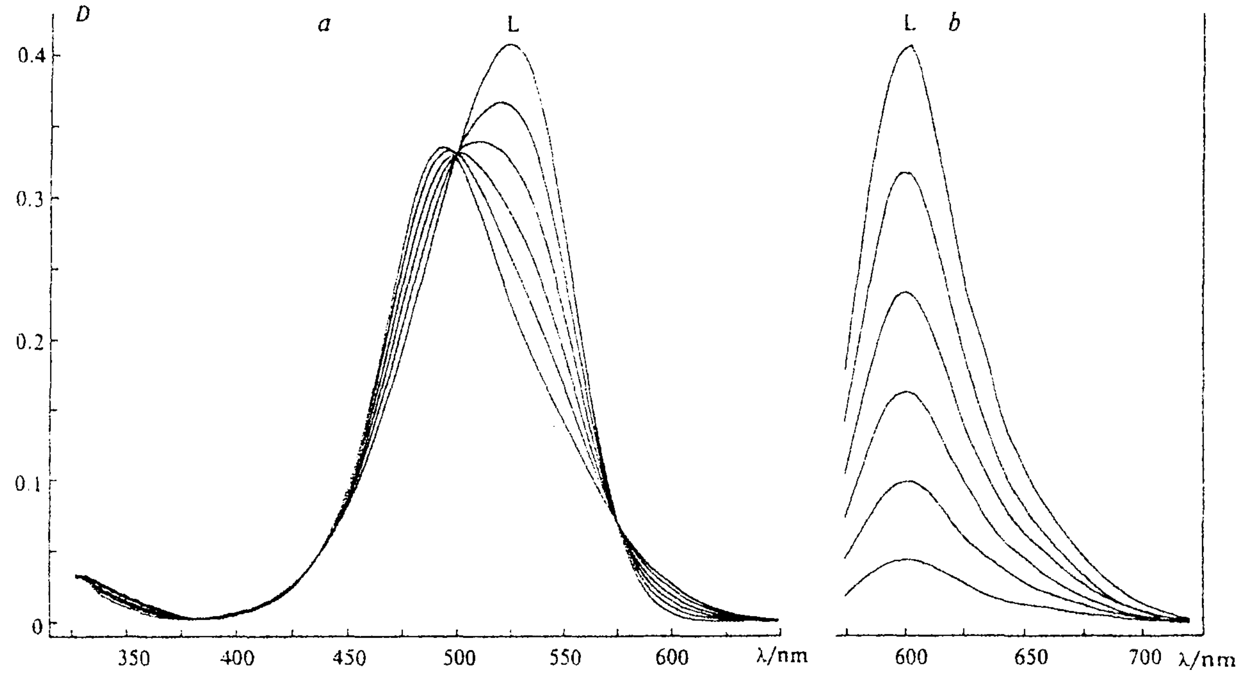


Fig. 4. Dependence of the absorption spectra (*a*) and fluorescence spectra (*b*) of *trans*-**2b** in MeCN at $C_L = 5.9 \cdot 10^{-4}$ mol L^{-1} on the concentration of $Ca(ClO_4)_2$, C_M/C_L = 0.05, 0.10, 0.16, 0.21, and 0.26.

Hypothetical dependences for nonfluorescent 4L : 1M and 3L : 1M complexes are shown by dashed lines. It can be seen that in the aggregate there can be an average of up to four molecules *trans*-**2b** per metal cation. When we made this conclusion, fluorescence quenching, which occurs owing to migration of the excitation energy from monomers to aggregates, was ignored. For this system, this mechanism of quenching at concentrations of order 10^{-4} mol L^{-1} is unlikely because the lifetime of the excited state of molecules of the *trans*-**2b** type is generally in the subnanosecond region[19] due to rapid deactivation in the *trans-cis*-isomerization reaction.

Addition of $Ca(ClO_4)_2$ to a solution of *trans*-**2b** caused no changes in the spectrum (except for the splitting of the long-wave absorption band), which could be indicative of an interaction of the Ca^{2+} ion with the azacrown fragment of the dye molecule (Fig. 4, *a*). Hence, we suggest that aggregation of molecules *trans*-**2b** is promoted by an interaction of the cation with the sulfo group of the *N*-substituent rather than by complexation with azacrown fragment.

To test this suggestion, we used dye *trans*-**3** containing, unlike *trans*-**2b**, the NMe_2 group, which reproduces the electron-donating properties of the azacrown fragment, which is evidenced by the virtually complete similarity of the absorption spectra of these dyes.

Because of the low solubility of *trans*-**3** in MeCN, the dependence of its absorption spectrum on the concentration of Ca^{2+} ions was studied only in a dilute solution at $C_L = 1 \cdot 10^{-5}$ mol L^{-1} (Fig. 6). The concentration of perchlorate ions (0.01 mol L^{-1}) was kept constant. The character of the spectral changes, which occur when small amounts of the cation are added, is similar to that observed for *trans*-**2b** (see Fig. 3, *a*). This

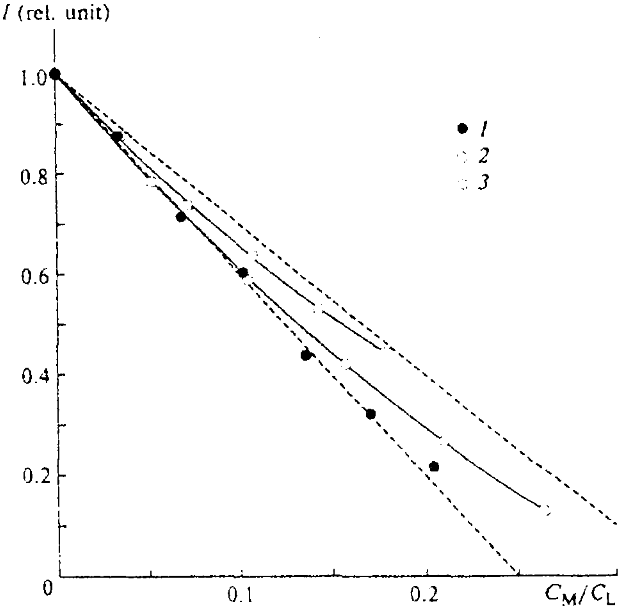


Fig. 5. Dependence of the intensity of fluorescence of a solution of *trans*-**2b** ($C_L = 6.5 \cdot 10^{-4}$ (*1*), $5.9 \cdot 10^{-4}$ (*2*), and $1.0 \cdot 10^{-3}$ (*3*) mol L^{-1}) in MeCN at 625 nm on the concentrations of $Zn(ClO_4)_2$ (*1*), $Ca(ClO_4)_2$ (*2*), and $Ba(ClO_4)_2$ (*3*). The hypothetical dependences for the 4L : 1M and 3L : 1M complexes are shown by dashed lines.

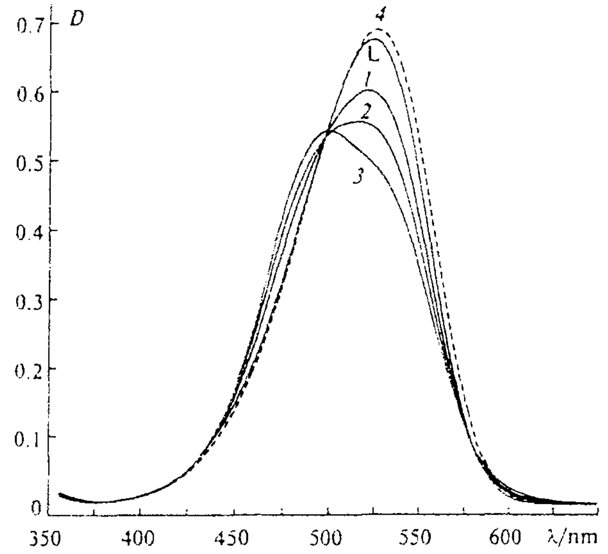


Fig. 6. Dependence of the absorption spectrum of *trans*-**3** (C_L = 1.0 · 10^{-5} mol L^{-1}) in MeCN on the concentration of Ca^{2+} ions (C_M/C_L = 0.25 (*1*), 0.50 (*2*), 1.5 (*3*), and 500 (*4*)) at a constant concentration of perchlorate ions (0.01 mol L^{-1}).

confirms the suggestion that the interaction of the cation with the sulfo group of the *N*-substituent is an intermediate step of aggregation of *trans*-**2b**.

The degree of aggregation of both dyes first increases, and then the equilibrium is shifted to complexes containing one dye molecule as the concentration of Ca^{2+} increases (Figs. 3 and 6). At C_M/C_L = 500, the absorption spectrum of *trans*-**3** differs from the initial one only by a small bathochromic shift and an insignificant increase in the optical density at the maximum of the long-wave absorption band. The spectrum remained virtually unchanged as C_M increased further. This spectrum can be attributed to molecules, whose sulfo group forms an ionic pair with Ca^{2+}. Therefore, the lower limit for the constant of association of the Ca^{2+} ion with the sulfo group of *trans*-**3** can be estimated ($\log K_{ass} \geq 4$).

At C_M/C_L = 500, the solution of *trans*-**2b** contains both ionic pairs of the above-described type (the long-wave absorption band) and complexes in which a Ca^{2+} ion is bonded to an azacrown fragment (the absorption band with the maximum at 410—420 nm). In this case, the absorption spectrum continues to change as the C_M increases further (this is not shown in the figures), apparently due to the interaction of Ca^{2+} with free crown fragments to form 1L : 2M complexes.

In addition to the above-mentioned data, note that the absorption spectrum of free *trans*-**2b** remains unchanged as the concentration of the dye in MeCN increases from 1 · 10^{-5} mol L^{-1} to ~1 · 10^{-3} mol L^{-1} (saturated solution). Therefore, the free dye is not capable of forming aggregates.

Based on the data obtained, complexation of *trans*-**2b** with Ca^{2+} ions may be represented by the following scheme of equilibria (interactions with perchlorate ions are ignored):

Scheme 2

$$\mathrm{A{-}L + M} \xrightleftharpoons{K_{011}} \mathrm{A{-}LM},$$

$$\mathrm{A{-}L + M} \xrightleftharpoons{K_{110}} \mathrm{MA{-}L},$$

$$\mathrm{M(A{-}L)}_{n-1} + \mathrm{A{-}L} \xrightleftharpoons{K_{1n0}} \mathrm{M(A{-}L)}_n,$$

$$\mathrm{MA{-}L + M} \xrightleftharpoons{K_{111}} \mathrm{MA{-}LM},$$

where A—L is molecule *trans*-**2b** (A is the sulfo group, and L is the azacrown fragment), and n = 2—4.

Because of the complexity of Scheme 2, it is very difficult to measure the equilibrium constants of all reactions. Apparently, the estimation of K_{110} made above for *trans*-**3** ($\log K_{110} \geq 4$) is also true for *trans*-**2b**. Based on the spectrum shown in Fig. 3, *a* (C_M/C_L = 100), it can be suggested that K_{011} is comparable to K_{110}, or, what is more probable, has a lower value. Apparently, changes in the spectra in going from C_M/C_L = 100 to C_M/C_L = 500 are determined mainly by the last reaction in Scheme 2, which makes it possible to estimate the constant K_{111} ($\log K_{111} < 2$).

We also established that aggregation of molecules *trans*-**2b** and *trans*-**3** can be promoted by Mg, Ba, or Zn perchlorates. Upon formation of aggregates, the solutions remain homogeneous. The only exception is $Mg(ClO_4)_2$ addition of which to a solution of *trans*-**2b** at C_L = 6 · 10^{-4} mol L^{-1} yields a precipitate at C_M/C_L = 0.25.

The tendency of betaines of styryl dyes to form aggregates of 4L : 1M composition is most pronounced in the case of Zn^{2+} ions.

Figure 5 shows the dependence of the intensity of fluorescence of *trans*-**2b** (C_L = 6.5 · 10^{-4} mol L^{-1}) at 625 nm (excitation in the region of the constant optical density at 457 nm) on the concentration of $Zn(ClO_4)_2$. It can be seen that the intensity of fluorescence decreases according to the rectilinear dependence for 4L : 1M aggregates.

Figure 7 shows the dependence of the absorption spectrum of *trans*-**2b** at C_L = 6.5 · 10^{-4} mol L^{-1} on the concentration of $Zn(ClO_4)_2$. The presence of a number of isosbestic points in the spectra demonstrated that predominantly one type of aggregates forms as salt is added (up to C_M/C_L = 0.2). Taking into account the fluorescence data, these complexes have the 4L : 1M composition.

It was established that the relationship between the optical density of a solution at different wavelengths and the concentration of $Zn(ClO_4)_2$, like the dependence of

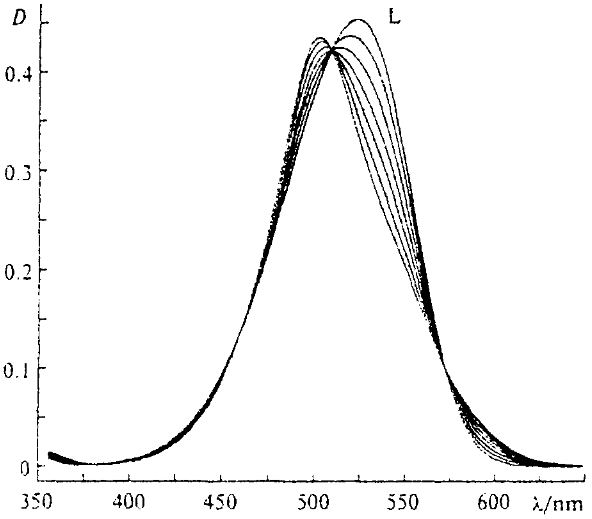


Fig. 7. Dependence of the absorption spectrum of *trans*-**2b** in MeCN at $C_L = 6.5 \cdot 10^{-4}$ mol L^{-1} on the concentration of $Zn(ClO_4)_2$, C_M/C_L = 0.035, 0.07, 0.105, 0.14, 0.175, and 0.21.

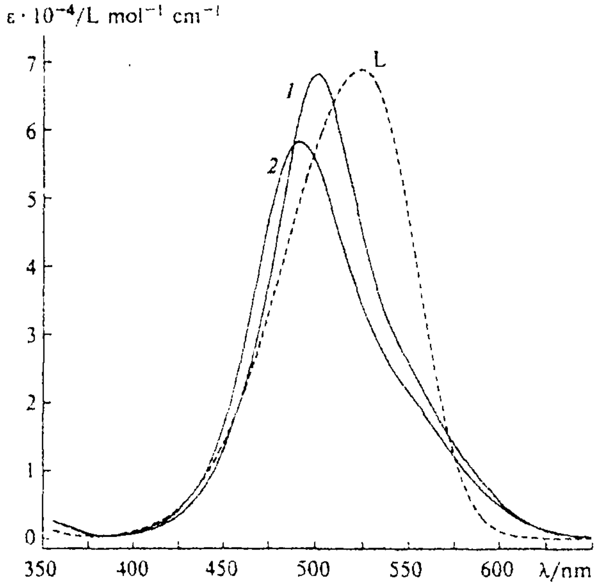


Fig. 8. Absorption spectra of aggregates of 4L : 1M composition, which form upon interaction of *trans*-**2b** with Zn^{2+} (*1*) and Ca^{2+} (*2*) ions in MeCN.

the intensity of fluorescence, is rectilinear up to C_M/C_L = 0.2. A similar situation is observed in the case of Ca^{2+} ions (but in a narrower C_M/C_L range from 0 to 0.1). For Ba^{2+} ions, it is difficult to locate a rectilinear region even at a higher concentration of *trans*-**2b** ($C_L = 1.0 \cdot 10^{-3}$ mol L^{-1}; the fluorescence data are shown in Fig. 5). These facts, apparently, indicate that the stability of 4L : 1M aggregates decreases as the diameter of the cation increases.

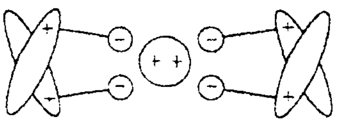
The absorption spectra of 4L : 1M aggregates were calculated by the linear extrapolation method for M = Zn^{2+} and Ca^{2+} (Fig. 8). Substantial differences in the spectra of aggregates are, apparently, determined by the fact that a change in the diameter of the cation causes a slight change in the mutual arrangement of dye molecules in the aggregate.

Apparently, single-charged cations, unlike double-charged cations, cannot cause aggregation of *trans*-**2b** and *trans*-**3**. For example, addition of $NaClO_4$ to a solution of *trans*-**2b** ($C_L = 6.5 \cdot 10^{-4}$ mol L^{-1}) up to C_M/C_L = 0.25 has no effect on the absorption and fluorescence spectra of the dye. At higher concentrations of $NaClO_4$, changes of the spectra typical of formation of 1L : 1M complexes are observed.

It is known that aggregation of some dyes, for example, cyanine dyes, can be promoted by electrolytes.[17] Generally, this effect is independent of the nature of ions and is determined mainly by the ionic strength of a solution. As was demonstrated above, in the case of solutions of *trans*-**3** and *trans*-**2b** in MeCN, aggregation substantially depends on the nature of ions added.

Previously,[20] the specific effect of cations of alkali metals on dimerization of Rose Bengal dye in an aqueous solution was observed. The authors suggested that formation of the neutral complex of a dye anion and a metal cation is an intermediate step of dimerization. Enhancement of aggregation is attributed to a decrease in the electrostatic repulsion between negatively charged chromophores owing to compensation of the charge on one chromophore by a metal cation. In the cases of *trans*-**3** and *trans*-**2b**, chromophore fragments carry positive charges, and therefore, the aggregation should proceed by an alternative mechanism.

The data obtained suggest that aggregates form through coordination of all sulfo groups of molecules *trans*-**3** or *trans*-**2b** to the double-charged metal cation. In our opinion, the structure, which is schematically shown below as two dimers bonded to each other through an interaction between sulfo groups and the cation, is the most probable for 4L : 1M aggregates.



The structure of aggregates in which four chromophores are packed in a stack is less probable. In this case, concurrent interaction of all sulfo groups with the metal cation is less efficient due to steric reasons and symmetry requirements.

Unfortunately, it is difficult to make unambiguous conclusions about the mutual orientation of dye molecules in the dimeric fragments of the aggregate based on only the spectral parameters. Apparently, the orientation shown in the scheme given above is consistent with the published data. For example, the character of spectral changes, which occur upon dimerization of some azo dyes in an aqueous solution,[21] is similar to that observed upon aggregation of *trans*-**2b**. It was established by NMR spectroscopy that molecules of azo dyes in dimers are arranged in a "head-to-tail" fashion in parallel planes.

In conclusion, note the substantial difference in complexation of *trans*-**2b** and *trans*-**1c**,**d** studied previously. Apparently, this difference is attributable, first, to the low ability of the *N*-phenylaza-15-crown-5 fragment to bind cations of alkaline-earth metals compared to the benzo-15-crown-5 fragment, and, second, to a higher tendency of chromophore fragments of *trans*-**2b** to form associates because of a higher degree of conjugation. Contrary to dimeric complexes, which are formed by *trans*-**1c**,**d**, aggregated molecules *trans*-**2b** cannot undergo photochemical conversions, namely, *trans-cis*-isomerization and cycloaddition. Deactivation of the excited state through internal conversion is the characteristic feature of aggregates of many dyes.[18] However, the causes of this effect remain unclear.

Thus, when interacted with Ca^{2+}, betaine *trans*-**2b**, unlike cation dye *trans*-**2a**, can form both 1 : 1 complexes and aggregates consisting of four dye molecules and one metal cation. Coordination of all sulfo groups of molecules *trans*-**2b** to the double-charged metal cation makes the major contribution to the stability of aggregates. In aggregates, the cation does not interact with crown ether fragments.

The stability of 4L : 1M aggregates depends on the charge and diameter of the metal cation and decreases in the Zn^{2+}, Ca^{2+}, Ba^{2+} series. In the case of single-charged cations, aggregates do not form.

Cation-induced aggregation of betaines of styryl dyes was previously unknown. This effect may be of significant interest from the standpoint of the supramolecular chemistry, for example, for an understanding of the major principles of molecular self-association.

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