Aggregation and photoisomerization of amphiphilic crown-ether styryl dye in monolayers at the interface

E. Yu. Kryukov,[a] A. V. Feofanov,[a] V. A. Oleinikov,[a] V. P. Vereshchetin,[a] S. Yu. Zaitsev,[a] S. P. Gromov,[b] O. A. Fedorova,[b] S. A. Maskevich,[c] L. N. Kivach,[c] V. P. Zubov,[a] I. R. Nabiev,[a,d] and M. V. Alfimov[b]*

[a]*M. M. Shemyakin and Yu. A. Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences,*
16/10 ul. Miklukho-Maklaya, 117871 Moscow, Russian Federation.
Fax: 007 (095) 336 1766
[b]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
7A ul. Novatorov, 117421 Moscow, Russian Federation.
Fax: 007 (095) 938 2156
[c]*Ya. Kupala University of Grodno, 22 ul. Ozheshko, 230023 Grodno, Belarus'.*
Fax: 007 (015 2) 44 2769
[d]*Universite de Reims, F-51096 Reims Cedex, France.*
Fax: (332) 605 3350

The molecules of *trans*-isomer of styryl dye **1a**, containing the benzo-18-crown-6 moiety and the methoxybenzothiazole residue with the *N*-octadecyl substituent, were shown to form stable, highly ordered monolayers at the water/air interface. Increasing the surface pressure of the monolayer results in the formation of the H-aggregated molecules of compound **1a**. The H-aggregates tend to dissociate to the monomeric *trans*-form, when the monolayer forms in the Langmuir—Blodgett film (LB film). The light irradiation of the LB films leads to the partially reversible *trans—cis*-photoisomerization of compound **1a**, whose efficiency is much lower than that observed in an acetonitrile solution of **1a**. The aggregation of cis-**1a** isomers in the LB film is suggested to hamper the reverse *cis—trans*-isomerization. The aggregation of *trans*-**1a** molecules in the LB films does not occur in air, but, after dipping in an aqueous solution, molecules of the LB film slowly form J-aggregates. A model of the structural organization of *trans*-**1a** molecules in the LB films was proposed.

Key words: surface enhanced Raman scattering (SERS); crown-ether styryl dye, monolayers.

Ultrathin ion-selective films based on crown ethers are of interest for modeling processes of self-organization and molecular recognition at the interfaces typical of biological membranes.[1—6] These films can be used for developing membranes for ion-selective electrodes, chemical sensors,[7—10] new materials with nonlinear optical properties,[11] and new liquid-crystalline materials.[12,13]

In recent time, crown ethers, which contain photosensitive, hydrophobic, and polymerizing groups along with the ion-selective fragment,[14—17] have been eliciting special interest. Compounds based on crown ether styryl dyes, whose complex formation constants in solution can be controlled efficiently using light, were obtained.[18—20] These compounds are promising for the development of color indicators of the presence of metals in solutions and devices for the photocontrolled selective extraction of metal cations. Derivatives of these compounds, which are capable of forming monolayers and the Langmuir—Blodgett films (LB films), can possess unique properties.

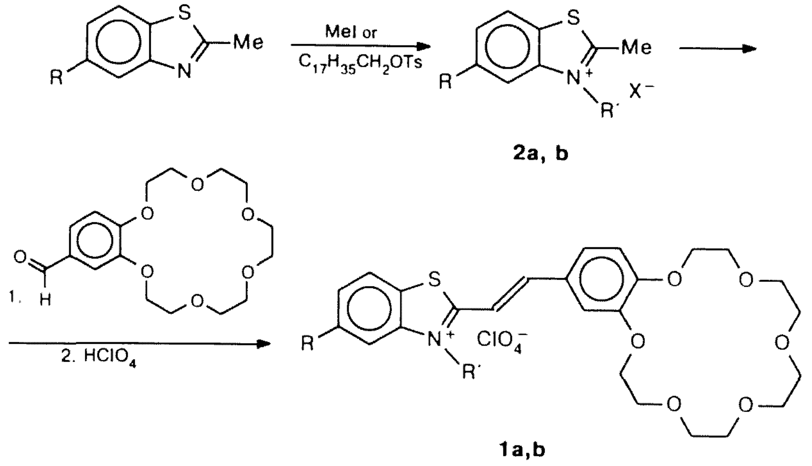
For the monolayers of dibenzo-18-crown-5 diacyl derivatives, a change in the selectivity of the formation of alkali metal complexes at the interface compared to the analogous selectivity series in solutions has been observed.[21] The molecular conformation, which provides the selective formation of complexes with certain cations, can be fixed by the polymerization of monolayers of acrylic and methacrylic crown ether derivatives.[21,22]

The methods of ellipsometry, polarization absorption spectroscopy,[23] and Bruster scattering microscopy[24] are widely used for studying the structure and properties of surfactant monolayers. In recent time, surface enhanced Raman scattering (SERS) spectroscopy[25—27] has been actively used to study monolayers of various compounds. This method makes it possible to study complex formation and aggregation of crown ether styryl dyes at very low concentrations down to 10^{-8} mol L^{-1}.[28,29]

In this work, 2-[2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-19-yl)ethenyl]-5-methoxy-3-octadecylbenzothiazolium perchlorate (**1a,** Scheme 1) was synthesized and its surfac-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2490—2496, October, 1996.

Scheme 1



1a,2a: R = OMe, R′ = $C_{18}H_{37}$, X = TsO
1b,2b: R = H, R′ = Me, X = I

tant and spectral properties in monolayers at the interface and in LB films were studied.

Experimental

Dyes **1a** and **1b** were obtained by the method for the synthesis of crown-containing styryl dyes developed previously.[30] The method is the condensation of the salt of a heterocyclic base with a crown ether formyl derivative in water-free ethanol in the presence of pyridine as the catalyst. 4′-Formylbenzo-18-crown-6 was obtained by the Duff reaction;[31] 2-methyl-3-octadecylbenzothiazolium perchlorate was synthesized for the first time by the known procedure.[32]

The initial quaternary salts **2a** and **2b** were obtained by the reactions of 2-methylbenzothiazole with methyl iodide and 2-methyl-5-methoxybenzothiazole and of 2-methyl-5-methoxybenzothiazole with octadecyl *p*-toluenesulfonate. When perchloric acid is added, perchlorates of dyes **1a** and **1b** form from the corresponding iodide and tosylate. According to the ^{1}H NMR spectra, compounds **1a** and **1b** have the *trans*-configuration, which follows from the values of the spin-spin coupling constants J_{trans} = 15.6—15.8 Hz. The elemental analysis data correspond to the compounds suggested.

2-[2-(2,3,5,6,8,9,11,12,14,15-Octahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-19-yl)ethenyl]-5-methoxy-3-octadecylbenzothiazolium perchlorate (1a). M.p. 89 °C. ^{1}H NMR (MeCN-d_3), δ: 0.86 (m, 3 H, Me); 1.25 (m, 32 H, 16 CH_2); 1.50 (m, 2 H, CH_2); 3.61 (s, 4 H, 2 CH_2O); 3.66 (m, 4 H, 2 CH_2O); 3.70 (m, 4 H, 2 CH_2O); 3.89 (m, 4 H, 2 CH_2O); 4.02 (s, 3 H, MeO); 4.25 (m, 4 H, 2 CH_2O); 5.04 (t, 2 H, CH_2); 7.09 (d, 1 H, benzocrown ether); 7.42 (d.d, 1 H, benzothiazole); 7.53 (m, 1 H, benzocrown ether); 7.62 (s, 1 H, benzocrown ether); 7.73 (s, 1 H, benzothiazole); 7.90 (d, 1 H, α-H, J_{trans} = 15.6 Hz); 8.16 (d, 1 H, β-H, J_{trans} = 15.6 Hz); 8.22 (d, 1 H, benzothiazole).

2-[2-(2,3,5,6,8,9,11,12,14,15-Octahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-19-yl)ethenyl]-3-methylbenzothiazolium perchlorate (1b). M.p. 195—197 °C. ^{1}H NMR (DMSO-d_6), δ: 3.60 (m, 12 H, 6 CH_2O); 3.85 (m, 4 H, 2 CH_2O); 4.23 (m, 4 H, 2 CH_2O); 4.36 (s, 3 H, Me); 7.15 (s, 1 H, benzocrown ether); 7.62 (dd, 1 H, benzocrown ether); 7.68 (s, 1 H, benzocrown ether); 7.79 (m, 1 H, benzothiazole); 7.88 (d, 1 H, α-H, J_{trans} = 15.8 Hz); 7.89 (m, 1 H, benzothiazole); 8.15 (d, 1 H, β-H, J_{trans} = 15.8 Hz); 8.22 (d, 1 H, benzothiazole); 8.40 (d, 1 H, benzothiazole).

Technique for the preparation of monolayers and the LB films. Monolayers of compound **1a** were obtained and studied on installations (NFT and Lauda Companies, Germany), which operate as a Langmuir balance. A solution of compound **1a** in chloroform (50 μL, concentration 6 μ*M*) was deposited with a microsyringe onto a water surface (bidistilled water was used) between the measuring and mobile barriers and was kept for 2 min for the relaxation of the pressure in the monolayer. The isotherms of the dependence of the surface pressure on the surface area per molecule were recorded upon the uniform compression of the monolayer with the mobile barrier with a velocity of 1 $cm^2\ s^{-1}$.

Mono- and bilayer LB films were prepared by the Langmuir—Blodgett method in which a solid substrate passed through the monolayer of molecules **1a** compressed at a surface pressure of 20 $mN\ m^{-1}$ and through the zone of pure water from top to bottom and then from bottom to top. Prior to the deposition of the second layer, the sample was thoroughly dried in air. When mono- and bilayer LB films were deposited, the transfer coefficient was close to unity.

Spectral measurements. SERS spectra in the 150—1700 cm^{-1} (scanning increment 1 cm^{-1}, integration time 1 s, 1 scan, spectral resolution 8 cm^{-1}) were recorded on a one-channel Ramanor HG-2S spectrometer (Jobin Yvon, France). The spectra were excited by an Ar^+ laser (Spectra-Physics, Model 164-03), the wavelength was 457.9 nm, and the power on the sample was 10 mW.

Annealed thin silver films (a-TSF) were used as the SERS-active substrates. They were prepared by the procedure described previously:[42] TSF of 5—10 nm thick were deposited with a rate of 0.04 nm s^{-1} on glass slides in the working chamber of a VUP5 vacuum post (p = 10^{-5} Torr) using a resistive evaporator containing silver (2—5 mg, 99.99% purity). The deposited TSF were annealed in a muffle furnace at 350 °C for 2—3 min. The result of the annealing was monitored by adsorption spectra. a-TSF with a maximum at 460 nm and a spectral width at a half-height of 70 nm in the adsorption spectrum were used for SERS measurements. The monolayer of molecules of compound **1a** were deposited on a-TSF by the Langmuir—Blodgett method as described above.

For measuring SERS spectra of solutions of compounds **1a** and **1b** in acetonitrile (concentration 10^{-5} mol L^{-1}), a quartz cell was used into which a glass plate with a-TSF was placed. The exciting beam irradiation, and the collection of scattered radiation was carried out through the front wall of the cell. The bulk signals of the Raman scattering and intrinsic fluorescence of dyes made a negligible contribution to the spectrum compared to the SERS signal from the molecules adsorbed on the a-TSF surface. Acetonitrile (special purity grade) was twice distilled to remove traces of water. All measurements were carried out at room temperature. The conformation state of dye molecules in solution and LB films was monitored by absorption spectra using a Varian Cary-209 spectrophotometer (USA).

Results and Discussion

The studies performed showed that compound **1a** can form stable monolayers at the interface. The isotherms of the surface potential and pressure of molecules of **1a** at the water—air interface recorded in the dark are presented in Fig. 1. It is seen (Fig. 1, curve *2*) that the uniform compression of molecules of compound **1a** even at low values of the surface pressure (5—7 mN m^{-1}) and relatively large surface areas (0.9—0.8 nm^2/molecule) results in a sharp jump of the surface potential (on the order of 0.4 V). An insignificant and gradual increase in the surface potential is observed during the further compression of the monolayer of compound **1a** up to the collapse surface pressure. The jumpwise change in the surface potential is evidence that the collective transition of molecules of **1a** from the liquid-extended state to the state with the ordered orientation of dipole moments and formation of the liquid-condensed monolayer of molecules of **1a** occurs when a certain surface pressure is achieved. The monolayer structure formed is characterized by a sufficiently high value of the collapse pressure (41 mN m^{-1}) at a collapse surface of 0.35 nm^2/molecule, which attests to its high stability.

When the monolayer of compound **1a** is irradiated with unfiltered white light, the surface potential increases gradually rather than jumpwise (see Fig. 1, curve *2'*). The irradiation results in the *trans—cis*-isomerization of molecules **1a** and the establishment of the equilibrium *trans—cis*-state, *i.e.*, it results in the distortion of the uniformity of packing of the molecular monolayer (the ordering of the molecular monolayer decreases). On the other hand, the isotherm of the surface pressure on the surface area per molecule undergoes only insignificant changes (see Fig. 1, curves *1* and *1'*). The *trans—cis*-isomerization of the double bond arranged parallel to the interface plane probably exerts no substantial effect on the value of the cross section surface area of a molecule of **1a** in the monolayer. With the extrapolation of the linear region of the isotherm to the zero surface pressure (A_0), the surface area per crown ether molecule is on the order of 0.80 nm^2, which agrees well with the value of A_0 for the analog of compound **1a**.[23]

The peculiarities of intermolecular interactions and orientation of molecules of **1a** in the monolayer at the water—air interface and in the LB films on the solid support and the photoisomerization in multilayers have been studied by spectrophotometry and SERS spectroscopy.

The absorption spectra of compound **1a** in the monolayer at the water—air interface recorded in the dark at a fixed surface pressure are presented in Fig. 2. It is seen that an increase in the surface pressure results in the "blue" shift of the absorption maximum from 440 nm at 5 mN m^{-1} to 426 nm at a pressure of 30 mN m^{-1} and an increase in the absorption intensity. This shift can be explained by the aggregation of molecules of **1a** in the monolayer as the surface pressure increases. A similar effect was observed for amphiphilic benzothiazolium azo dyes in the LB films, and was explained by the formation of H-aggregates,[33—35] which were also observed in the LB films of amphiphilic stilbazolium salts.[36] In our case, additional evidence for the formation of aggregates are found in the decrease in the value of the blue shift when the monolayer of molecules of **1a** are diluted with methyl stearate (MS) in a ratio of 1 : 1 (the spectra are not shown) and the complete disappearance of this shift at the ratio **1a** : MS = 1 : 3 (Fig. 3). The same changes

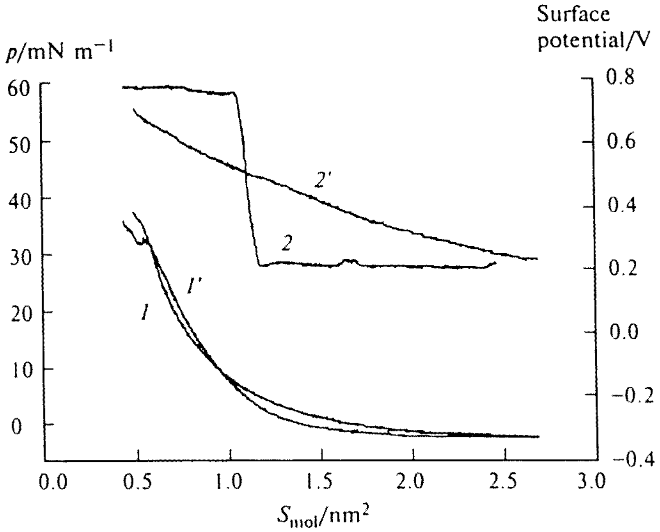


Fig. 1. Isotherms surface pressure—surface area per molecule (curves *1*, *1'*) and surface potential—surface area per molecule (*2*, *2'*) for the monolayer of molecules **1a** in dark (*1*, *2*) and upon the irradiation with the white light (*1'*, *2'*). Water is the subphase.

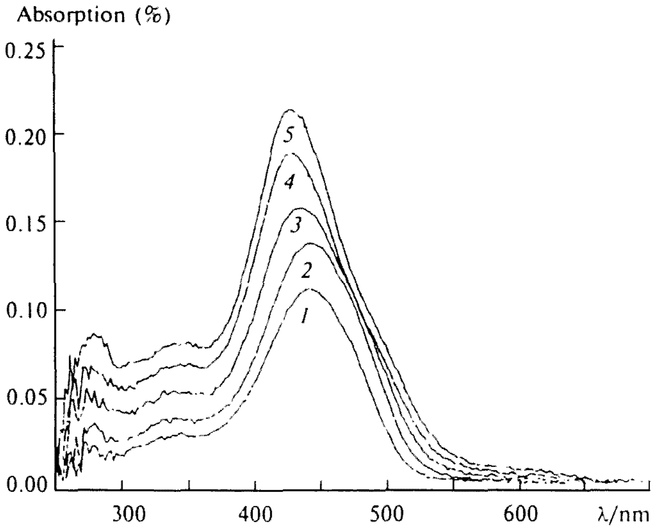


Fig. 2. Absorption spectra of the monolayer of molecules **1a** at the water—air interface at the surface pressure (mN m^{-1}): 5 (*1*), 10 (*2*), 15 (*3*), 20 (*4*), and 30 (*5*).

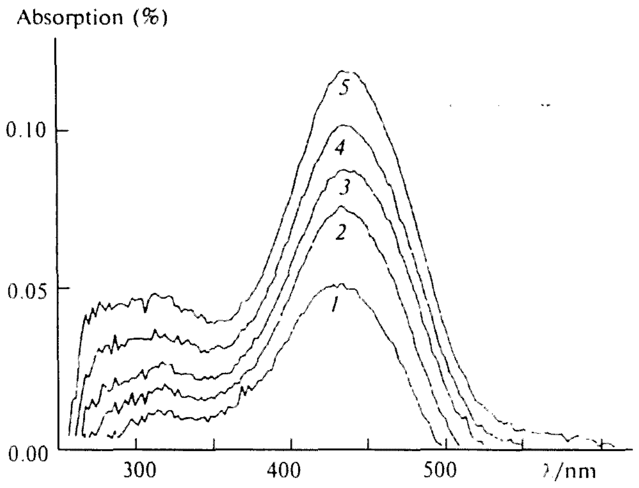


Fig. 3. Absorption spectra of the monolayer of a mixture of **1a** and MS molecules (a ratio 1 : 3) at the surface pressure (mN m^{-1}): 5 (*1*), 10 (*2*), 15 (*3*), 20 (*4*), and 30 (*5*).

were observed when the monolayer of **1a** molecules was diluted with other surfactants, which attests to the decomposition of the aggregates of compound **1a** in mixed monolayers.

The comparative analysis of the absorption spectra of the bilayer LB film of the **1a** molecules, which was deposited on a quartz plate in the dark, and of a solution of *trans*-**1a** in acetonitrile (Fig. 4) shows that the *trans*-conformation of the **1a** molecules is retained when the bilayer LB film is formed. In addition, the H-aggregates formed in the monolayer on the aqueous subphase are decomposed when they are deposited to a solid support. This confirms the fact that at a surface pressure of 20 mN m^{-1}, which is optimum for the transfer of the monolayer, the maximum of the absorption spectrum of the monolayer on the aqueous subphase shifts to the blue region up to 428 nm (see Fig. 2, curve *4*). At this transfer pressure, the LB film exhibits the absorption maximum at 440 nm typical of the monomeric *trans*-form (see Fig. 4, curve *2*).

The LB film is not static and changes slowly after being dipped into distilled water, which is seen from the absorption spectra (see Fig. 4). A maximum at 440 nm and a small shoulder at 485 nm are initially observed in the absorption spectrum of the bilayer LB film of the **1a** molecules dipped in water (see Fig. 4, curve *2*). The maximum shifts to 460 nm and the shoulder at 485 nm increases in time (see Fig. 4, curves *3* and *4*). The saturation occurs in 1.5—2 h. No changes in the absorption of the LB film in air were observed during the same time.

The shift of the band and the appearance of the shoulder in the absorption spectrum of the LB film can be explained by the formation of aggregates of the **1a** molecules in the presence of water. Unlike the monolayer of compound **1a** on the aqueous subphase, the aggregation in the LB film, which is accompanied by a red shift of the absorption maximum is typical of J-type aggregates.[37—40] When the aggregated film is dissolved in acetonitrile, the monomeric form of the dye is restored with the absorption maximum typical of the *trans*-form.

Thus, when the monolayer of molecules **1a** is deposited to a solid support, the H-type aggregates are decomposed, which is accompanied by recovery of the monomeric form of **1a**, and J-type aggregates form in the LB film in the presence of water. These results agree with the data obtained previously[41] for a compound with a similar structure for which the formation of J-aggregates was observed in the LB film dipped into acidified water (pH 3). Unlike Ref. 41, in our case, the formation of aggregates was observed at pH close to neutral.

When irradiating compound **1a** in a solution of acetonitrile, the *trans—cis*-isomerization and fast transition to the equilibrium *trans—cis*-state occur, which manifests itself in the absorption spectra as the shift of the maximum from 438 to 430 nm and a decrease in the optical density of the solution. Compound **1a** relaxes completely to the *trans*-form in the dark for 24 h, and the initial absorption spectrum is restored.

In the bilayer LB film, the quantum yield of the *trans—cis*-isomerization of compound **1a** decreases sharply. Nevertheless, a broad absorption band of compound **1a** with a maximum at 440 nm undergoes noticeable changes upon prolonged irradiation (up to 60 min) with white light (Fig. 5). It is likely that a considerable number of **1a** molecules are transformed into the *cis*-form upon irradiation. The dark relaxation of compound

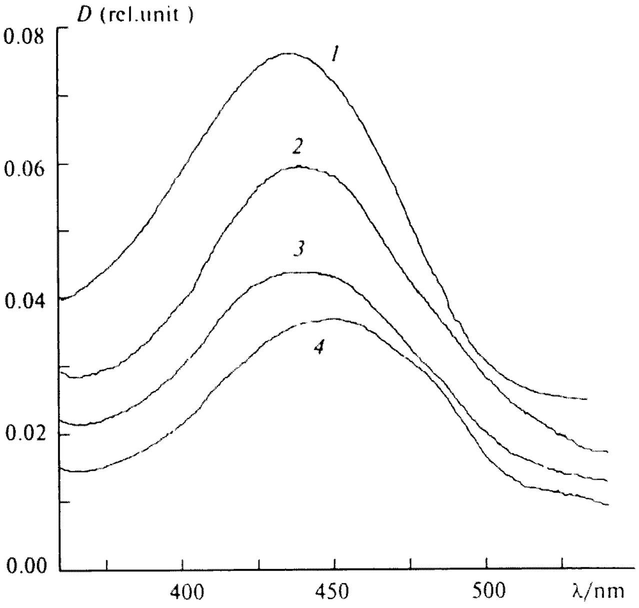


Fig. 4. Absorption spectra of *trans*-**1a** in acetonitrile (**1a** = 10^{-5} mol L^{-1}) (*1*) and the LB film of molecules **1a** (2 monolayers on each side of the quartz plate) dipped into a cell with distilled water for 2 (*2*), 20 (*3*), and 120 min (*4*).

1a to the *trans*-form occurs, but the initial level of *trans*-isomers are not completely restored: some molecules remain in the *cis*-form (see Fig. 5).

When the bilayer LB film is deposited on quartz in the light, the *cis*-form of compound **1a** predominates, which is detected by the absorption spectrum with a maximum at 430 nm. The prolonged (up to 48 h) dark adaptation does not result in the noticeable recovery of the *trans*-form of **1a** molecules. The multiple irradiation of the LB film formed of *trans*-**1a** molecules also results in the gradual loss of the ability of **1a** molecules to relax to the *trans*-form. The possible explanation of this effect can be the formation of dimers or aggregates of the **1a** molecules in the *cis*-form. If the dissociation of these aggregates of *cis*-**1a** requires energy much greater than κT, the dark relaxation to *trans*-**1a** becomes almost impossible. A more detailed study is planned to elucidate the role and type of the aggregation of *cis*-**1a** in the LB films.

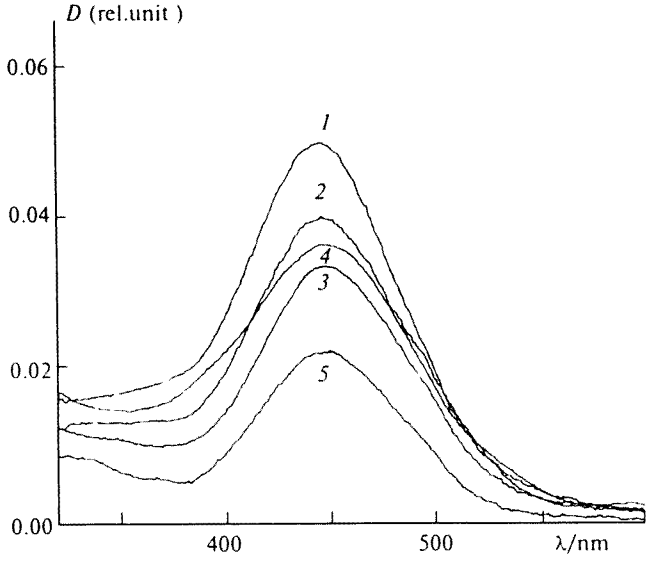


Fig. 5. Absorption spectra of the LB film of molecules **1a** (2 monolayers on each side of the quartz plate) formed in dark (*1*), after irradiation with the white light for 15 (*2*), 45 (*3*), 90 min (*4*), and stored for 24 h after irradiation (*5*).

To investigate the structural organization of the monolayer of molecules **1a** in the LB film, the SERS spectra of the monolayer of **1a** deposited on the surface of the annealed thin silver film (a-TSF) by the Langmuir—Blodgett method were studied (Fig. 6). The intense SERS spectrum obtained from the molecular monolayer makes it possible to confirm the conclusion based on the absorption spectra that compound **1a** exists in the *trans*-form in the LB film. We have previously shown for similar crown ether styryl dyes that it is the resonance with the longwave electronic transition of the *trans*-isomer that determines the possibility of recording the SERS spectrum of small amounts of a substance. The SERS spectrum of compound **1a** in the LB film resembles greatly (in number, positions, and relative intensities of the lines) the spectra of the previously studied *trans*-isomers of styryl dyes containing the benzo-15-crown-5 moiety and the benzothiazole residue with the alkyl or sulfoalkyl *N*-substituent.[28,29]

The comparative analysis of the absorption spectra of compound **1a** (see Fig. 6), related styryl dyes, and several model compounds[28,29] makes it possible to con-

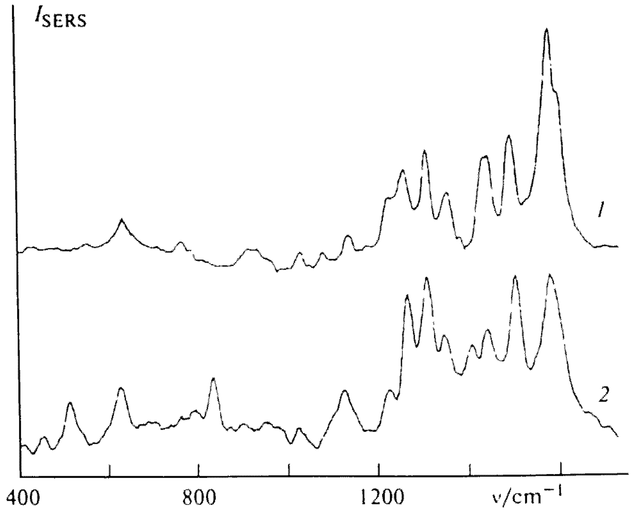


Fig. 6. SERS spectra of the monolayer LB film of molecules **1a** (*1*) and compound **1b** (*2*) in a solution of acetonitrile.

Table 1. Interpretation of SERS spectra of compounds **1a** and 2-[2-(benzo-1,4,7,10,13-pentaoxacyclopentadec-15-yl)vinyl]-3-ethylbenzothiazolium perchlorate (**3**)

ν/cm^{-1}		Assignment[a]
1a	**3**[a]	
1608 sh[b]	1608 sh	ν_{8b}[c]
1586 v.s	1589 v.s	ν_{8a}
1505 s	1508 s	ν_{19b}
1447 s	1439 s	ν_{19a}
1360 s	1361 s	ν_{14}
1315 s	1319 s	δ(C—C—H), w(CH$_2$)
1266 s	1264 s	ν_3
1232 sh	1225 m	ν_{7a}
1170 w	1176 m	ν_{9a}
1140 m	1140 m	ν_{as}(C—O—C)
1085 m	1075 w	ν(C—C)
1030 m	1036 w	ν_s(C—C—O)
932 m		ν(ClO$_4^-$)
770 m	796 w	ν_{11}
636 m	633 m	ν_4
556 w	611 w	ν_{6a}
427 w	454 w	δ_s(C-O-C)

[a] From the data of Refs. 28 and 29. [b] Designations of the relative intensity of the lines: w is weak, m is medium intensity, s is strong, v.s is very strong, and sh is a shoulder. [c] The Wilson notation was used for the vibrational modes of benzene derivatives.

clude that the vibrations of the benzene ring of the benzo-18-crown-6 fragment of the molecule comprise the main contribution to the SERS spectrum of compound **1a**. The spectrum exhibits no vibrations of the methoxybenzothiazole chromophore, C=C bond, and alkyl substituent. Since the resonance with the electronic transition of the molecule exerts almost no effect on the vibrations of the bonds of the crown ether moiety of the molecule, the size of the crown cycle does not affect the pattern of the SERS spectrum. The assignment of the lines in the SERS spectrum of *trans*-**1a** based on the comparative analysis and the assignment of the lines in the SERS spectra of related compounds are presented in Table 1.

Based on the analysis of the SERS spectrum of **1a** and the approach to the interpretation of the spectra of related compounds developed previously,[28,29] we can determine the orientation of *trans*-**1a** molecules in the LB film relative to the a-TSF surface. Only the benzo-18-crown-6 moiety of the molecule is in contact with a-TSF, which determines its predominant contribution to the SERS spectrum. The plane of the benzene ring of the benzo-18-crown-6 moiety is almost perpendicular to the plane of a-TSF. This follows, in particular, from the fact that the out-of-plane vibrations of the benzene ring are almost not manifested in the SERS spectrum of compound **1a**. The methoxybenzothiazole chromophore, C=C bond, and alkyl substituent are removed from the a-TSF surface, and hence, they do not contribute to the spectrum (Fig. 7, *a*).

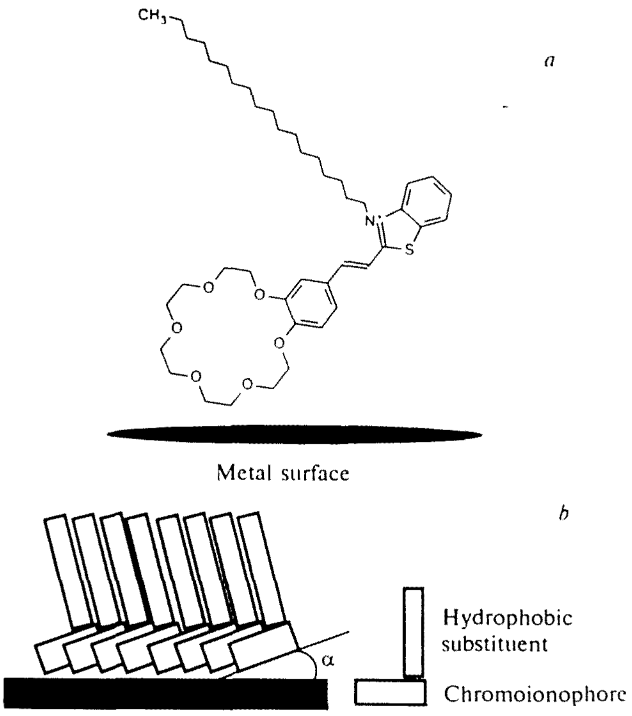


Fig. 7. Geometry of the adsorption of a molecule of **1a** on the a-TSF surface (*a*) and the model of the orientation of molecules **1a** in the monolayer LB film (*b*).

The possibility of determining whether particular molecular groups of the crown ether styryl dyes are far from or close to the surface of SERS-active substrate by the shape of the spectrum is confirmed by the SERS spectrum of compound **1b** dissolved in acetonitrile (see Fig. 6, curve *2*). Along with the lines of the vibrations of the benzene ring of the benzo-18-crown-6 moiety, the spectrum of compound **1b** contains the vibrations of the benzothiazole chromophore, which result in an increase in the relative intensity of the lines at 1514, 1314, 1270, and 1131 cm^{-1} and the appearance of new lines at 1414, 837, 628, and 514 cm^{-1}. The majority of the lines, which have changed, are characteristic and they are present in the SERS spectrum of the benzothiazole chromophore.[28,29] The appearance of intense lines at 837 and 514 cm^{-1} corresponding to the ν_{sym}(C—S—C) and ν_{bend}(C—S—C) vibrations indicates the direct contact of the sulfur atom of the benzothiazole chromophore with the a-TSF surface.

The data on the high ordering of the dipole moments of **1a** molecules in the monolayer and the orientation of these molecules on the a-TSF surface (see Fig. 7, *a*) make it possible to suggest the model of the organization of **1a** molecules in the monolayer on the solid support presented in Fig. 7, *b*.

It is noteworthy that the SERS spectra of *trans*-**1a** molecules in the LB film and *trans*-**1a** molecules adsorbed on a-TSF from a solution in acetonitrile are almost identical, which indicates the capability of **1a** molecules for self-organization of the monolayer upon the spontaneous adsorption on the a-TSF surface from a solution. The existence of the long alkyl substituent is likely a necessary condition for the stabilization of this self-organized monolayer.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 94-03-08760a).

References

1. F. Voegtle, *Supramolekulare Chemie*, Ed. B. G. Teubner, Stuttgart, 1989.
2. E. Weber, *Crown-ether and Analogs*, Eds. S. Patai and Z. Rappoport, John Wiley & Sons, New York, 1989, 305.
3. G. W. Gokel and S. H. Korzeniowski, *Macrocyclic Polyether Syntheses*, Springer-Verlag, Berlin, 1982.
4. Yu. A. Ovchinnikov, V. T. Ivanov, and A. M. Shkrob, *Membrane-active Complexones*, Elsevier, Amsterdam, 1974.
5. K. Kimura and T. Shono, *Cation Binding by Macrocycles: Complexation of Cationic Species by Crown-ethers*, Eds. Y. Inoue and G. W. Gokel, Marcel Dekker, Inc., New York, 1990, 429.
6. E. Blasius and K.-P. Janzen, *Host Guest Complex Chemistry. Macrocycles: Synthesis, Structures, Applications*, Eds. F. Voegtle and E. Weber, Springer-Verlag, Berlin, 1985, 189.
7. M. Sugawara, M. Kataoka, K. Odashima, and Y. Umezawa, *Thin Solid Films*, 1989, **180**, 129.
8. V. V. Lapachev, S. A. Stekhova, E. G. Lubenets, and V. S. Kobrin, *Sib. Khim. Zh.* [*Siberian Chem. J.*], 1992, **2**, 94 (in Russian).
9. S. M. Balashov, V. V. Kislov, V. V. Lapachev, I. E. Nevernov, A. Yu. Potapov, and G. B. Khomutov, *Biol. Membrany* [*Biol. Membranes*], 1990, **7**, 1205 (in Russian).
10. U. Z. Mirkhodzhaev, Kh. F. Abdullaev, and A. K. Tashmukhamedova, *Uzb. Biol. Zh.* [*Uzbekistan Biol. J.*], 1990, **5**, 61 (in Russian).
11. Z. Q. Yao, P. Liu, R. Z. Yan, L. Y. Liu, X. H. Liu, and W. C. Wang, *Thin Solid Films*, 1992, **210/211**, 208.
12. X. Zhang, Z. Lin, J. Shen, and X. Y. Fang, *Thin Solid Films*, 1992, **210/211**, 628.
13. Y.-M. Zhu and Yu Wei, *J. Chem. Phys.*, 1994, **101**, 10023.
14. M. Takagi, *Cation Binding by Macrocycles: Complexation of Cationic Species by Crown-ethers*, Eds. Y. Inoue and G. W. Gokel, Marcel Dekker, Inc., New York, 1990, 465.
15. S. Shinkai and O. Manabe, *Host Guest Complex Chemistry. Macrocycles: Synthesis, Structures, Applications*, Eds. F. Voegtle and E. Weber, Springer-Verlag, Berlin, 1985, 245.
16. S. Shinkai, *Cation Binding by Macrocycles: Complexation of Cationic Species by Crown-ethers*, Eds. Y. Inoue and G. W. Gokel, Marcel Dekker, Inc., New York, 1990, 397.
17. J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1304.
18. M. V. Alfimov, I. K. Lednev, and S. P. Gromov, *Chem. Phys. Lett.*, 1991, **185**, 455.
19. S. P. Gromov, M. V. Fomina, G. K. Chudinova, V. A. Barachevskii, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **321**, 739 [*Dokl. Chem. SSSR*, 1991, **321** (Engl. Transl.)].
20. O. Fedorova, S. Gromov, M. Fomina, G. Chudinova, V. Savransky, V. Barachevsky, and M. Alfimov, *The Seventh International Conference on Organized Molecular Films*, September 10—15, 1995, P-8.3, 108.
21. S. Yu. Zaitsev, V. V. Lytsenko, and V. P. Zubov, *Bioorg. Khim.*, 1983, **9**, 567 [*Bioorg. Chem.*, 1983, **9** (Engl. Transl.)].
22. H.-J. Winter and G. Manecke, *Macromol. Chem.*, 1985, **186**, 1979.
23. I. K. Lednev and M. C. Petty, *Advanced Materials for Optics and Eletronics*, 1992, **4**, 225.
24. S. Yu. Zaitsev, M. Belohradsky, J. Zavada, and D. Moebius, *Thin Solid Films*, 1994, **248**, 78.
25. C. Jennings, G. J. Kovacs, and R. Aroca, in *Proc. 13 Intern. Conf. on Raman Spectrosc.*, Eds. W. Kiefer and M. Cardona, Wiley, 1992, 640.
26. S. Yu. Zaitsev, N. A. Kalabina, V. P. Zubov, G. Chumanov, D. Gaul, and T. M. Cotton, *Colloids and Surf. A: Physicochem. and Engineering Aspects*, 1993, **78**, 211.
27. T. Terashita, Y. Wang, Y. Ozaki, and K. Iriyama, in *Proc. 14 Intern. Conf. on Raman Spectrosc.*, Eds. N.-T. Yu and X.-Y. Li, Wiley, Hong Cong, 1994, 672.
28. A. Feofanov, A. Ianoul, V. Oleinikov, S. Gromov, O. Fedorova, M. Alfimov, and I. Nabiev, *J. Phys. Chem.*, 1996, **100**, 2154.
29. A. V. Feofanov, A. I. Yanul', V. A. Oleinikov, I. R. Nabiev, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2429 [*Russ. Chem. Bull.*, 1995, **44**, 2323 (Engl. Transl.)].
30. M. V. Alfimov and S. P. Gromov, *NATO ASI Ser., Ser. C*, 1992, **371**, 343.
31. F. Wada, H. Hiroayama, H. Namiki, H. Kikukawa, and T. Matsuda, *Bull. Chem. Soc. Jap.*, 1980, **53**, 1473.
32. J. Sondermann, *Liebigs Ann. Chem.*, 1971, 183.
33. S. Enomoto, Y. Ozaki, and N. Kuramoto, *Langmuir*, 1993, **9**, 3219.
34. N. Katayama, M. Fukui, Y. Ozaki, N. Kuramoto, T. Araki, and K. Iriyama, *Langmuir*, 1991, **7**, 2827
35. N. Katayama, Y. Ozaki, and N. Kuramoto, *Chem. Phys. Lett.*, 1991, **179**, 227
36. D. A. Styrkas, I. K. Lednev, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1990, **312**, 407 [*Dokl. Chem. SSSR*, 1990, **312**, (Engl. Transl.)].
37. D. Mobius, *D. Acc. Chem. Res.*, 1981, **14**, 63
38. H. Kuhn, B. Mann, H. Bucher, D. Mobius, L. V. Szentpaly, and P. Tillmann, *Photogr. Sci. Eng.*, 1967, **11**, 233.
39. H. Kuhn, *Pure Appl. Chem.*, 1979, **51**, 341.
40. H. Nakahara, K. Fukuda, D. Mobius, and H. Kuhn, *J. Phys. Chem.*, 1986, **90**, 6144
41. I. K. Lednev and M.C. Petty, *Langmuir*, 1994, **10**, 4185.

Received April 17, 1996