

Photosensitive supramolecular systems based on amphiphilic crown ethers

S. Yu. Zaitsev* and V. P. Vereschetin

Institute of Bioorganic Chemistry, Russian Academy of Sciences, Miklucho-Maklaya Str. 16/10, Moscow 117871, Russia

and S. P. Gromov, O. A. Fedorova and M. V. Alfimov

Institute of Chemical Physics, Russian Academy of Sciences, Kosygin Str. 4, Moscow 117334, Russia

and H. Huesmann and D. Möbius

Max-Planck-Institut für Biophysikalische Chemie, Postfach 2841, 37018 Göttingen, Germany

(Received 6 September 1996; revised 15 December 1996)

An amphiphilic crown-ether styryl dye was synthesized and its properties at the interfaces were investigated. This dye, which in monolayers interacts with some cations and shows reversible changes of the light reflection after photoactivation near the absorption maximum, is an excellent component of functional organized systems. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: photochromic crown ether; monolayers; photoisomerization)

INTRODUCTION

The preparation and investigation of supramolecular systems based on various crown ethers is a relatively new, but quickly growing field of science, which has both fundamental and applied importance^{1–6}. These systems can serve as unique models for investigation of the interactions between biologically active molecules and various cations at interfaces, as well as for ion transport through biological or model membranes^{7–9}. They are also promising as sensitive elements in ionoselective electrodes^{7–11}. The main problem in preparing supramolecular systems based on simple crown-ether compounds is the unbalanced ratio between hydrophilic and hydrophobic parts of the molecule. Modification of the crown ethers with long hydrocarbon chains leads to surface-active derivatives which become very useful for various membrane model studies^{12–14}. Nevertheless, there are only a few investigations of monolayers^{12–18} and Langmuir–Blodgett films^{15–18} of various crown ethers, including photosensitive, azobenzene-containing benzo-15-crown-5¹⁹, 13-azo-phane-3²⁰ and benzothiazolium styryl dye containing the 1,10-dithia-18-crown-6 ether group^{21–24}. The results have been discussed in detail in the recent review of Lednev and Petty⁷.

The synthesis and investigation in solution of photoswitchable crown ethers with azobenzene moieties have attracted major attention^{25,26}. The advantages of the crown-ether dyes containing C=C bonds as photosensitive groups^{27–29}, especially in organized systems, have not yet been fully realized.

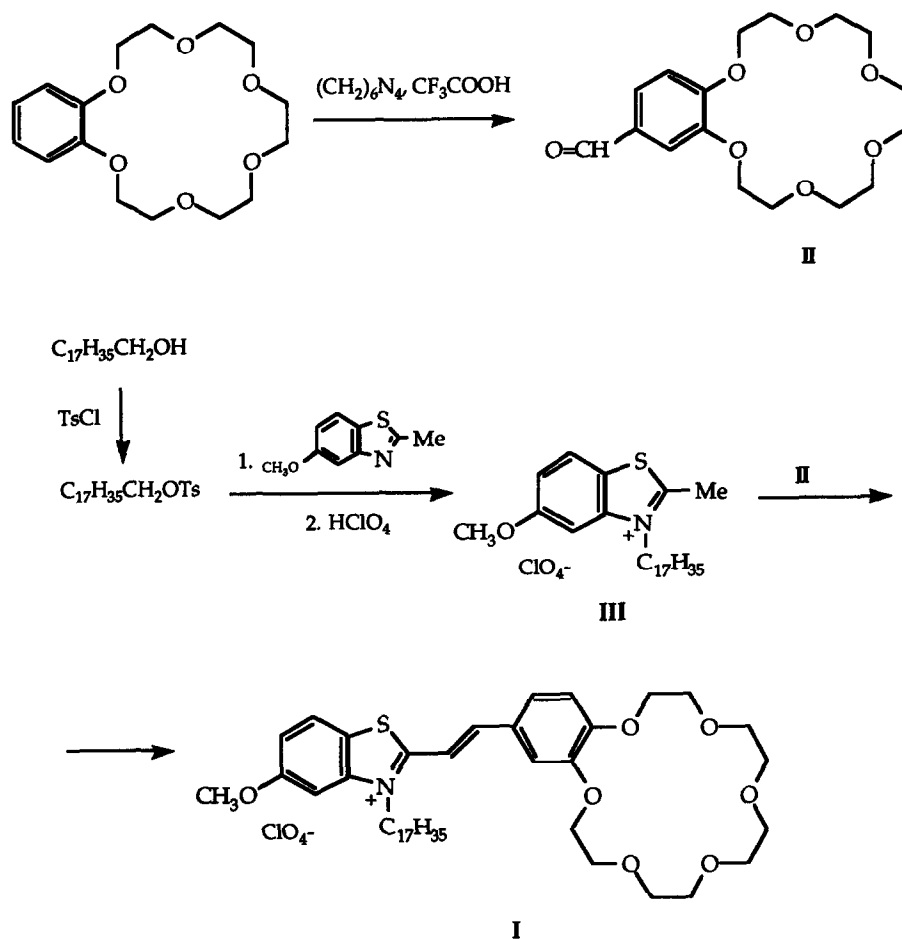
The aim of this work is the construction of supramolecular systems, e.g. organized monolayers, that are able to bind cations and photoisomerize.

RESULTS AND DISCUSSION

For this purpose the amphiphilic, benzo-18-crown-6 styryl dye (**I**) has been synthesized (see Experimental) and its properties in various organic solutions have been investigated. The dye **I** has been prepared by interaction of the active methylene group of benzothiazolium salt (**III**) with the formyl derivative of benzo-18-crown-6 (**II**) in the presence of pyridine as a catalyst (*Scheme 1*). The intermediate heterocyclic salt **III** has been obtained by reaction of 2-methyl-5-methoxy-benzothiazole with the octadecyl ester of *p*-tolylsulfuric acid (*Scheme 1*). According to nuclear magnetic resonance spectroscopy (NMR) data (see Experimental), the dye **I** has been prepared in the *trans* form.

The crown-ether dye **I** forms stable insoluble

*To whom correspondence should be addressed



Scheme 1

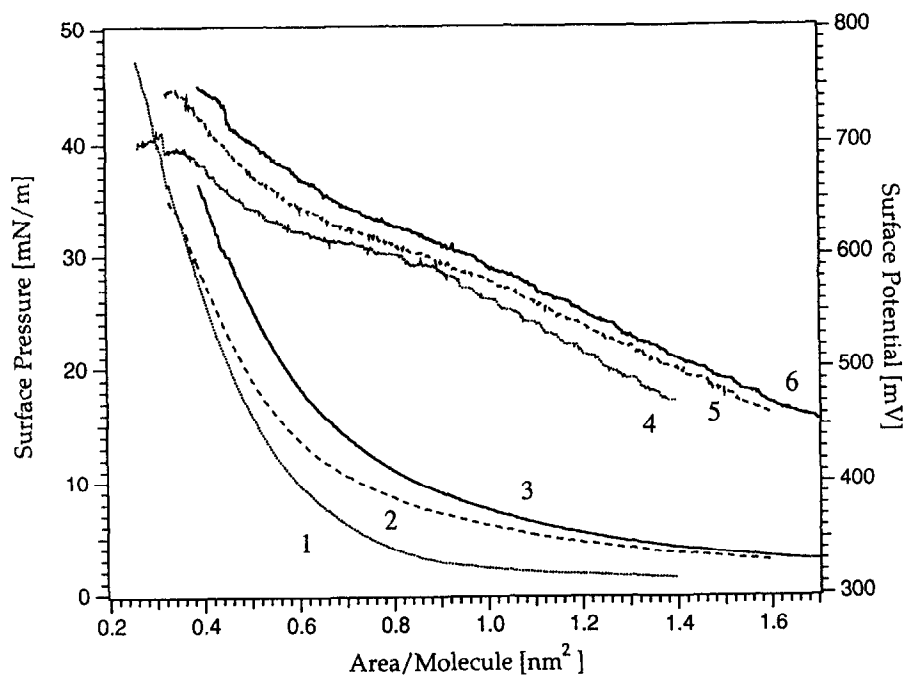


Figure 1 Surface pressure/molecular area (1–3) and surface potential/molecular area (4–6) isotherms of monolayers of the crown-ether dye I on distilled water (1, 4) and 1 mM solutions of KCl (2, 5) or NaCl (3, 6) at 18°C

monolayers on water (collapse pressure of about 52 mN m^{-1}) and various aqueous salt subphases (Figure 1). The area per molecule of the dye I is smallest on water and increases with increasing salt concentration in the aqueous subphase. For example, at 30 mN m^{-1} the values of the area are $0.39 \text{ nm}^2 \text{ molecule}^{-1}$ on distilled water and $0.46 \text{ nm}^2 \text{ molecule}^{-1}$ on 1 mM NaCl solution (Figure 1, curves 1–3). This is evidence for the existence of a dye–cation complex in the liquid-condensed monolayer because of the strong interaction of Na^+ with the polyether ring of the dye I molecule. In contrast, the area per molecule of dye I on 1 mM KCl at surface pressure of about 30 mN m^{-1} ($0.40 \text{ nm}^2 \text{ molecule}^{-1}$) is close to that on distilled water. There are two possibilities to explain this phenomenon: (1) at high pressures the cation is squeezed out of the polyether ring because of the formation of a weak complex and (2) the dye I– K^+ complex still exists, but it reorients in the liquid-condensed monolayer in the same manner as uncomplexed molecules. The second explanation is more reasonable, taking into consideration the differences in the surface potential/molecular area isotherms of dye I on water and KCl subphase (Figure 1, curves 4–6) and our previous knowledge of the complexation in 13-azaphane-3 crown-ether monolayers²⁰. A stronger interaction between monolayers of the dye I and Na^+ from the aqueous subphase, as compared with K^+ , correlates with the previously published data on monolayers of the surface-active derivatives of dibenzo-18-crown-6^{12–14}. These data are in contrast with those obtained for water-soluble crown ethers^{1–6}; however, such a comparison is not correct because the dye I and the surface-active derivatives of dibenzo-18-crown-6^{12–14} are not soluble in water.

The surface potential, ΔV , of monolayers of the dye I has the smallest value on water and increases in the presence of alkali metal cations in the aqueous subphase in the whole range of molecular areas and surface pressures. These differences are already pronounced at low surface pressures ($3\text{--}5 \text{ mN m}^{-1}$). For example, at a fixed molecular area of $1.4 \text{ nm}^2 \text{ molecule}^{-1}$, the ΔV values of dye I in monolayers on water, 1 mM KCl and NaCl are 471, 502 and 510 mV, respectively (Figure 1). Even higher differences in the ΔV values on various salts and water are observed at higher surface pressures and lower molecular areas. According to the increased ionic strength in the case of 1 mM KCl or NaCl salt solutions compared with water, a decrease of ΔV is expected. The enhanced values of ΔV clearly indicate complex formation not only for NaCl , but also for KCl at high surface pressures. In contrast, a lowering of the surface potential was found for monolayers of dye I in the presence of HClO_4 in the aqueous subphase compared with water, showing an example of non-specific interactions, as was described first for the analogue of the dye I in the publications of Lednev and Petty^{21–24}.

The reflection spectra (plotted as the difference, ΔR , between the reflectivity of the monolayer-covered subphase and that of the clean subphase³⁰) of dye I monolayers on distilled water show a strong band in the range $400\text{--}500 \text{ nm}$ with a shift of the maximum from 446 nm to 438 nm by increasing the surface pressure from 5 to 30 mN m^{-1} (Figure 2). There is also a less intense band at $330\text{--}340 \text{ nm}$ wavelength, which increases with increasing surface pressure (Figure 2). This increase in the reflection intensity is due to the increasing surface density of the chromophores by monolayer compression. The shift in the reflection

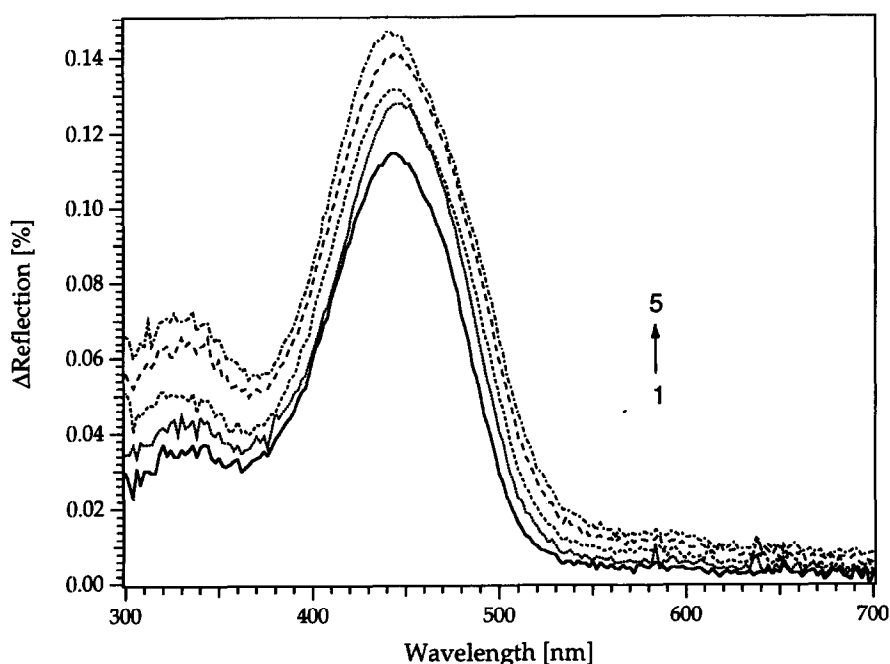


Figure 2 Reflection spectra of monolayers of the crown-ether dye I on distilled water at 5 (1), 10 (2), 15 (3), 20 (4) and 30 mN m^{-1} (5) at 18°C

band maximum is not observed in the presence of various salts or HClO_4 in the aqueous subphase (even at 1 mM concentration) and in the mixed monolayers of dye I with surface-active substances, such as the negatively charged dipalmitoylphosphatidic acid (DPPA) (Figure 3). We ascribe this effect to the inhibition of aggregate formation that takes place in the monolayers of pure dye I, especially at high surface pressures. This is in agreement with results obtained for the close analogue of dye I in monolayers on HClO_4 , described in detail in references 21–24.

The aggregates can be formed by interaction of the positively charged ammonium groups of one molecule of dye I with the crown-ether ring of the other, as was

suggested^{21–24} for analogues of such crown ethers in Langmuir–Blodgett films on hydrophobic glass slides. In this case, complexation with a cation or simply dilution of monolayers of dye I with DPPA disturbs the interactions between dye I molecules and restores the monomeric form. Additional evidence for this explanation is the increase in the reflection intensity for dye I monolayers on salt solutions, HClO_4 or even in the mixed monolayers, as compared with that on distilled water.

Monolayers of pure dye I on various aqueous salt subphases, as well as mixed monolayers with DPPA on water (Figure 4), showed a sharp decrease of reflection intensity at the maximum of the band at

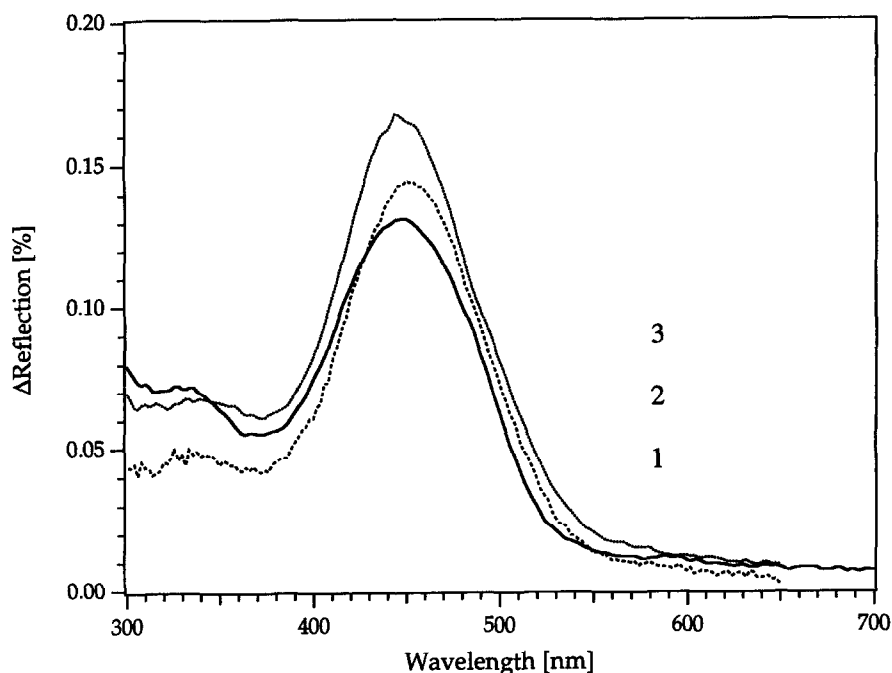


Figure 3 Reflection spectra of the crown-ether dye I (1) and the mixture of dye I:DPPA = 1:1 (M/M) (2, 3) in monolayers on distilled water (2) or 10 mM KCl subphase (1, 3) at 20 mN m^{-1} and 18°C

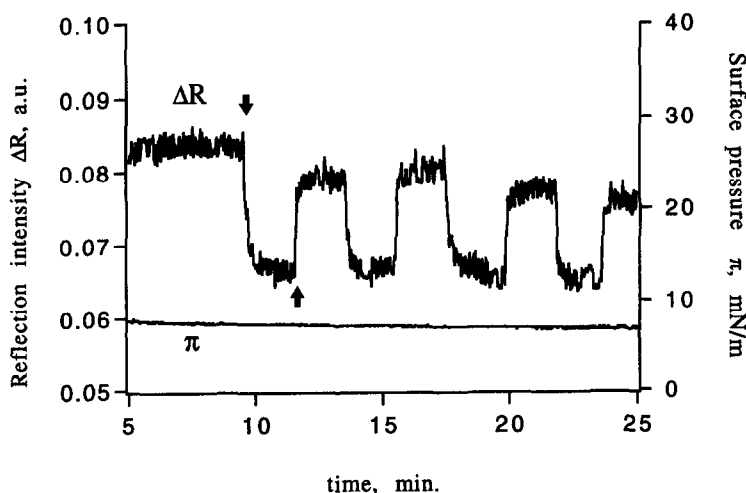


Figure 4 Reversible changes of the reflection intensity for the mixture of dye I:DPPA = 1:1 (M/M) in monolayers on distilled water at 8 mN m^{-1} by illumination with 438 nm and dark relaxation (↓, light on; ↑, light off)

446 nm within a few seconds by illumination with light of wavelength 438 nm, i.e. close to the maximum of the band. When the reflection intensity, ΔR , had become constant, the light was switched off, and an increase of the reflection intensity was observed to almost the initial values (Figure 4). These reversible changes in the reflection intensity arise from *trans*-*cis* and *cis*-*trans* isomerizations of the C=C bond in dye I molecules. In contrast, the pure dye I monolayers did not show any changes during illumination under the same conditions. This is another effect proving an aggregation of the dye I molecules on water subphases that prevents photoisomerization. Thus, the reversible changes in the reflection intensity (*trans*-*cis*-*trans* isomerization) can be observed only for non-aggregated dye I molecules in mixed monolayers with lipids and/or in the presence of various cations in the aqueous subphase.

The authors anticipate that the approach described here will be useful for the construction of supramolecular systems combining various functions, such as self-organization, ion recognition and photoisomerization.

EXPERIMENTAL

Syntheses

2-Methyl-5-methoxy-3-octadecylbenzothiazolium perchlorate (III). 1-Octadecanol (2 g, 5 mM) was dissolved in 50 ml of CH_2Cl_2 and 0.5 ml of Et_3N was added. The reagents were mixed and a solution of tosyl chloride (0.8 g, 5 mM) in CH_2Cl_2 was added. The reaction mixture was kept at 40°C for 40 h. After cooling, the mixture was reacted with water to leave the amine salt and CH_2Cl_2 was evaporated off under vacuum conditions. The resulting residue was purified by column chromatography using diethyl ether as eluent. Thus, 1.18 g (56%) of octadecyl ester of *p*-tolylsulfuric acid, m.p. 61–63°C, was prepared. The obtained ester (1 g, 2.3 mM) and 2-methyl-5-methoxybenzothiazole (0.22 ml, 2.3 mM) were heated at 150°C for 3 h. The resulting product was dissolved in hot benzene and, after cooling, the last of the precipitate of tosyl 2-methyl-5-methoxy-3-octadecylbenzothiazolium was formed. The salt was filtered and dissolved in hot methanol. Then 0.5 ml of concentrated HClO_4 was added to the hot methanol/salt solution. After cooling, the perchlorate of 2-methyl-5-methoxy-3-octadecylbenzo-thiazolium (III) (0.7 g, 61%) precipitated out and was separated, m.p. 125°C.

$^1\text{H-NMR}$ (CDCl_3 , δ ppm): 0.8 (m, 3H, CH_3), 1.2 (m, 30H, 15 CH_2), 1.6 (m, 2H, CH_2), 1.9 (2H, CH_2), 3.15 (s, 3H, CH_3), 4.00 (s, 3H, CH_3O), 4.65 (t, 2H, CH_2), 7.65 (t, H, heterocycle), 7.75 (t, H, heterocycle), 7.9 (d, H, heterocycle), 8.1 (d, H, heterocycle). Found (%): C, 61.92; H, 8.35; N, 2.65.

Calculated (%): C, 62.19; H, 8.83; N, 2.79. General formula: $\text{C}_{26}\text{H}_{44}\text{ClNO}_4\text{S}$.

2-(2,3,5,6,8,9,11,12,14,15-Octahydro-1,4,7,10,13,16-benzohexaoceta-cyclooctadecen-19-yl)ethenyl-5-methoxy-3-octadecylbenzothiazolium perchlorate (I). Pyridine (0.1 ml) was added to a solution of the heterocyclic salts III (0.27 g, 0.5 mM) in 10 ml anhydrous ethanol 4'-formylbenzo-18-crown-6. The mixture was boiled for 14 h, then the ethanol was evaporated off and the residue, after the washing with benzene and diethyl ether, was recrystallized from anhydrous methanol. 0.17 g (43%) of the dye I with m.p. 89°C was obtained.

$^1\text{H-NMR}$ (CDCl_3 , δ ppm): 0.86 (m, 3H, CH_3), 1.25 (m, 32H, 16 CH_2), 1.50 (m, 2H, CH_2), 3.60 (s, 4H, 2 CH_2O), 3.65 (m, 4H, 2 CH_2O), 3.69 (m, 4H, 2 CH_2O), 3.90 (m, 4H, 2 CH_2O), 4.02 (s, 3H, CH_3O), 4.25 (m, 4H, 2 CH_2O), 5.05 (t, 2H, CH_2), 7.10 (d, 1H, benzocrown ether), 7.40 (m, 1H, benzocrown ether), 7.55 (m, 1H, heterocyclic), 7.62 (s, 1H, benzocrown ether), 7.73 (s, 1H, heterocycle), 7.9 (d, 1H, $\text{H}\alpha$, $J_{\text{trans}} = 15.6$), 8.15 (d, 1H, $\text{H}\beta$, $J_{\text{trans}} = 15.6$), 8.2 (d, 1H, heterocycle). Found (%): C, 63.21; H, 7.88; N, 1.59. Calculated (%): C, 63.05; H, 8.17; N, 1.67. General formula: $\text{C}_{44}\text{H}_{68}\text{ClNO}_{10}\text{S}$.

Methods

$^1\text{H-NMR}$ spectra were obtained on a Bruker WM-400 SY spectrometer using SiMe_4 as an internal standard.

Monolayers of dye I, dipalmitoylphosphatidic acid (DPPA) and their mixtures were prepared and investigated on a self-made rectangular Teflon trough (area, 355 cm^2 ; depth, 1 cm) with using the Wilhelmy principle for surface pressure and a vibrating plate condenser for surface potential measurements, respectively. 10–20 μl of the dye I or DPPA 1 mM solutions in chloroform were spread with a microsyringe onto distilled water or aqueous salt subphases. As a standard procedure, monolayers were rested for 5 min before compression to allow sufficient evaporation of solvent and to reach equilibrium of the initial surface pressure and surface potential. Then, the surface pressure (π)/molecular area (A) and surface potential (ΔV)/molecular area (A) isotherms were recorded simultaneously during continuous compression of the monolayer by a movable barrier at a constant rate of 20 $\text{cm}^2 \text{min}^{-1}$. The temperature was 20.0 \pm 0.5°C. The accuracies of the parameter measurements were as follows: \pm 0.1 mN m^{-1} for π , 2 mV for ΔV and \pm 0.01 $\text{nm}^2 \text{molecule}^{-1}$ for A .

ACKNOWLEDGEMENT

This work was supported by the Deutsche Forschungsgemeinschaft (FRG) grant 436 RUS 113/56.

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