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Pseudodimeric Complexes of an (18-Crown-6)stilbene with Styryl Dyes Containing an Ammonioalkyl Group: Synthesis, Structure, and Stereospecific [2 + 2] Cross-Photocycloaddition

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and spectral characteristics of the complexes were measured by spectrophotometric and fluorescence titration. Photoirradiation of the pseudodimeric complex of (18-crown-6)stilbene with the ammoniopropyl dye resulted in the stereospecific [2 + 2] cross-photocycloaddition reaction. The replacement of the stilbene moiety in the crown compound by a styrylpyridine moiety led to a 5-fold increase in the quantum yield of the photoprocess. The most probable cause for this effect is the presence of photoinduced electron transfer in (18-crown-6)stilbene complexes. This assumption is confirmed by fluorescence lifetime spectroscopy and density functional theory calculations.

■ INTRODUCTION

The [2 + 2] photocycloaddition (PCA) reaction of unsaturated compounds is an important photoreaction used in synthetic organic chemistry.¹ The problems of low stereoselectivity and low quantum yields observed for intermolecular PCA of diarylethylenes are solved by supramolecular self-assembly of molecules into dimer pairs with a definite orientation of double bonds.² Cross-PCA, which takes place between different olefins, markedly expands the synthetic potential of the reaction.³ In the case where an unsaturated electron donor and electron acceptor are used as the starting reactants, it is very difficult to predict the possibility and efficiency of cross-PCA. There is only one published example considering the competition between the intermolecular cross-PCA reaction and photoinduced electron transfer (PET).⁴ That study addressed the complex formed by bis(18-crown-6)stilbene St with diammonium styryl dye Am, in which the unsaturated moieties of the two molecules were located close to each other because of ditopic coordination. By photolysis of this complex, the 1-hetaryl-2,3,4-triarylcyclobutane derivative was obtained for the first time.

derivative was synthesized for the first time. The stability constants

Previously,^{5,6} we have demonstrated that two-site binding of olefins is not a necessary condition for stereospecific synthesis of cyclobutane derivatives. This study is concerned with (18-crown-6)stilbene (E)-1, N-ammonioalkyl (E)-4-(4-methyl-



thiostyryl)pyridine derivatives (*E*)-2, and their pseudodimeric complexes (Scheme 1). The electron-donating capacity of monocrown stilbene (*E*)-1 is somewhat lower than that of biscrown stilbene St, because of the absence of a second crown ether moiety, but somewhat higher than that of styrylpyridine analogue (*E*)-3.

In relation to the pseudodimeric complexes of crowncontaining styrylpyridine (E)-3 with *N*-ammoniopropyl styryl dye derivatives (including dye (E)-2b), it was shown that visible light irradiation of the complexes in solution also gives

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Scheme 1. Formation of Pseudodimeric Complexes (E)-1• (E)-2



rise to a single *rctt* isomer of cyclobutane derivative.⁶ The occurrence of PET in these complexes is unlikely.



Thus, it is impossible to predict with certainty whether deactivation of the excited state via PET or cross-PCA reaction would be possible in complexes (E)-1·(E)-2. In this study, we synthesized for the first time styryl dye (E)-2a with an *N*-ammonioethyl substituent and developed the synthesis of (18-crown-6)stilbene (E)-1. Experiments confirmed the formation of pseudodimeric complexes (E)-1·(E)-2 (Scheme 1) and partial occurrence of PET in them. Long-term light irradiation of a solution of the complex involving the *N*-ammoniopropyl derivative afforded a single isomer of the cyclobutane derivative.

RESULTS AND DISCUSSION

Synthesis. 18-Crown-6-containing stilbene (E)-1 was previously synthesized from the corresponding halogenated benzocrown ether and styrene in the presence of a palladium catalyst.⁷ Considering reported data for distyrylbenzenes,⁸ we proposed using the Horner–Wadsworth–Emmons reaction for the synthesis of (E)-1. In the first step, condensation of benzyl bromide with triethyl phosphite was carried out by a known procedure, which gave diethyl benzylphosphonate **4** in 98% yield (Scheme 2).⁹

The condensation of 18-crown-6-containing benzaldehyde with compound **4** was carried out at room temperature under

Scheme 2. Synthesis of Compound 4

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the action of *t*-BuONa; the yield of the product was 60% (Scheme 3).



According to ¹H NMR spectroscopy data, stilbene **1** was isolated as the *E* isomer, which was evidenced by the spin–spin coupling constants for olefinic protons ($J_{CH=CH} = 16.9$ Hz). Comparison of the melting points of compound **1** (104–105 °C) with published data⁷ (96–98 °C) implies that the authors probably dealt with insufficiently pure product.

Thus, the use of available diethyl benzylphosphonate 4 and 18-crown-6-containing benzaldehyde as the starting reactants, simplicity of the synthesis, and relatively high yields of final products make this method more convenient than the method previously proposed in the literature, and the purity and structure of product 1 can be regarded as more trustworthy in our case.

Styryl dye **2a** was prepared similarly to the previously described dye **2b** (Scheme 4).⁵ Quaternization of styrylpyridine (*E*)-**5** with 2-bromoethylammonium bromide was conducted under mild conditions (boiling MeCN) to prevent quaternization of sulfur. In the second step, bromide anions

Scheme 4. Synthesis of Dye 2a



Article

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Figure 1. Fluorescence spectra and spectrophotometric data on the steady-state photolysis of synthesized compounds in MeCN (1 cm cell): (a) crown compound (*E*)-1 exposed to 313 nm light, total ligand concentration of 2.1×10^{-5} M, light intensity of 1.4×10^{-9} mol cm⁻² s⁻¹; (b) styryl dye (*E*)-2a exposed to 365 nm light, total dye concentration of 2.1×10^{-5} M, light intensity of 2.7×10^{-9} mol cm⁻² s⁻¹; (b) styryl dye (*E*)-2a exposed to 365 nm light, total dye concentration of 2.1×10^{-5} M, light intensity of 2.7×10^{-9} mol cm⁻² s⁻¹. The blue curves are the corrected fluorescence spectra (excitation at (a) 329 nm and (b) 347 nm); the solid black curves are the absorption spectra of *E* isomers; the red curves are the absorption spectra of *Z* isomers; the green curves are the absorption spectra of the *E*–*Z* photostationary states (PSS).

were exchanged with perchlorate anions by treatment with concentrated $HClO_4$ in EtOH.

Optical Spectroscopy. Crown-containing stilbene (E)-1 and dye (E)-2a exhibit an intense S_0-S_1 absorption band (Figure 1) related to the $\pi-\pi^*$ electronic transition (similarly for (E)-2b). Irradiation of acetonitrile solutions of these compounds, similarly to irradiation of dye (E)-2b,⁶ with absorbable light induces reversible E-Z photoisomerization. The intensity of the long-wavelength band substantially decreases, and the absorption maximum is somewhat blueshifted.

The key spectral and photochemical parameters for compounds (E)-1 and (E)-2a,b are summarized in Table 1.

Table 1. Spectral and Photochemical Parameters of Compounds (E)-1 and (E)-2a, b^a

| Compound | λ_{\max}^{abs} , nm | $\epsilon_{\rm max} \times 10^{-4}, M^{-1} {\rm cm}^{-1}$ | λ_{\max}^{fl} , nm | $arphi_{ m fl}$ | φ_{E-Z} | φ_{Z-E} |
|-----------------------------|-----------------------------|---|----------------------------|-----------------|-----------------|-----------------|
| (E)-1 | 325 | 2.94 | 383 | 0.064 | 0.39 | 0.40 |
| (E)- 2a | 407 | 3.71 | 576 | 0.33 | 0.22 | 0.48 |
| (E)- 2b ^b | 401 | 3.72 | 571 | 0.26 | 0.27 | 0.42 |

^{*a*}In MeCN; λ_{\max}^{abs} is the peak position of the S_0 - S_1 absorption band; ε_{\max} is the molar absorption coefficient at λ_{\max}^{abs} ; λ_{\max}^{ab} is the peak position in the corrected fluorescence spectrum; φ_{fl} is the fluorescence quantum yield; φ_{E-Z} and φ_{Z-E} are the quantum yields of the forward and reverse E-Z photoisomerization reactions, respectively. ^{*b*}Data for dye **2b** are taken from ref 6.

The main pathway for deactivation of the singlet excited state of stilbene (E)-**1** is E-Z photoisomerization. In the case of styryl dyes (E)-**2a**,**b** containing a methylthio group, radiative transition and E-Z photoisomerization make comparable contributions to the excited state deactivation.

The complex formation of dyes (E)-**2a**,**b** with (18-crown-6)stilbene (E)-**1** was studied by spectrophotometric titration (SPT) (Figure 2). More data on the fluorescence of complexes were derived from the results of fluorescence titration. The formation of pseudodimeric complexes induces small bathoand hypochromic shifts in the absorption band of styryl dye. Similar spectral changes were observed previously for the complex of crown-containing styrylpyridine (E)-**3** with dye (E)-**2b** and were attributed to stacking interactions.⁶ In the case of *N*-ammonioethyl derivative (E)-**2a**, the spectral changes are considerably more pronounced than in the case of *N*-ammoniopropyl analogue (E)-**2b**. Apparently, the differences are due to the greater proximity of the pyridinium residue to the benzocrown ether group in the case of (E)-**1**·(E)-**2a**, due to the shorter ammonioalkyl chain of dye **2a**.

Upon complex formation of dyes (E)-2a and (E)-2b with ligand (E)-1, the dye luminescence is quenched 7.8- and 5.1fold, respectively (Figure 2, Tables 1 and 2). A probable cause for the decrease in $\varphi_{\rm fl}$ is PET taking place in these complexes. A more detailed discussion of this effect is given below. The stability constants and the spectra of the complexes were calculated from spectrophotometric and fluorescence titration data by global analysis of spectral data¹⁰ using the complex formation model that includes one equilibrium

$$S + D \stackrel{\kappa}{\rightleftharpoons} SD$$
 (1)

where S is stilbene (E)-1, D is dye (E)-2a or (E)-2b, SD is complex (E)-1·(E)-2a or (E)-1·(E)-2b, and K/M^{-1} is the stability constant of complex SD.

Table 2 presents the stability constants for the complexes of crown compounds (E)-1 and (E)-3 with dyes (E)-2a,b in MeCN, as measured by absorption and fluorescence spectroscopy. The main spectral and photochemical characteristics of these complexes are shown in the same table.

The stability constants of the pseudodimeric complexes are very similar and fall in the range log K = 4.4-4.5, which is somewhat higher than the stability constant of the complex of stilbene (*E*)-1 with the ethylammonium cation (log K = 4.24, Figure S1), because of the additional stacking interactions in the former case. The differences between the measured constants and the stability constant of complex (*E*)-3•(*E*)-2**b** are within the accuracy of measurements (Table 2).

The irradiation of an acetonitrile solution of an equimolar mixture of dye (*E*)-**2b** with crown compound (*E*)-1 with 405 nm light for short time periods (300 s) induced E-Z photoisomerization of the dye (Figure S2). Long-term irradiation of the mixture (40 h) gave rise to a new product exhibiting characteristic cyclobutane signals at 4.5–5 ppm in the ¹H NMR spectrum (Figure S4), which indicated that cross-PCA reaction took place (Scheme 5). This assumption was confirmed by preparative photolysis (see Experimental Section,



Figure 2. Spectrophotometric and fluorescence titration data for the systems (a) (E)-1-(E)-2a and (b) (E)-1-(E)-2b in MeCN (1 cm cell, excitation wavelengths (a) 431 and (b) 424 nm): (a) 2.1×10^{-5} M (E)-2a, (b) 1.8×10^{-5} M (E)-2b; the concentration of the crown compound varies from 0 to 7×10^{-4} M.

Table 2. Stability Constants, Spectroscopic and Photochemical Parameters for the Complexes of Crown Compounds (E)-1 and (E)-3 with Dyes (E)-2a,b^a

| Complex | $\log K$ (fl) | log K (abs) | λ_{\max}^{abs} , nm | $\Delta\lambda^{\rm abs}$, nm | $\varepsilon_{\rm max} \times 10^{-4}$, ${\rm M}^{-1} {\rm ~cm}^{-1}$ | $\lambda_{\max}^{\ \ \text{fl}}$, nm | $arphi_{ m fl}$ | $\Phi_{PCA} 	imes 10^4$ |
|--|---------------|-------------|-----------------------------|--------------------------------|--|---------------------------------------|-----------------|-------------------------|
| (E)-1· (E) -2a ^b | 4.44 | 4.45 | 413 | +6 | 3.18 | 580 | 0.043 | < 0.05 |
| (E)-1· (E) -2b ^b | 4.43 | 4.44 | 403 | +2 | 3.39 | 572 | 0.051 | 3.1 |
| $(E)-\mathbf{3\cdot}(E)-\mathbf{2b}^c$ | - | 4.48 | 402 | +1 | 3.67 | 566 | 0.10 | 14 |

^{*a*}In MeCN; log *K* (fl) is the logarithm of the stability constant that was measured by fluorimetry; log *K* (abs) is the logarithm of the stability constant that was measured by spectrophotometry; $\Delta \lambda_{abs}$ is the complexation-induced shift of λ_{max}^{abs} ; Φ_{PCA} is the effective value of cross-PCA quantum yield. ^{*b*}The *K* values (M⁻¹) are measured to within about ±20%; the Φ_{PCA} values were measured upon selective excitation of styryl dyes with 405 nm light. ^{*c*}Data for the complex (*E*)-**3**·(*E*)-**2b** were taken from ref 6; the *K* values (M⁻¹) are measured to within about ±30%; the Φ_{PCA} value was measured upon irradiation with 436 nm light (selective excitation of the dye).

Scheme 5. Formation of Cyclobutane rctt-6



Figure 6, and Figures S20–S26). The quantum yield of cross-PCA reaction Φ_{PCA} was determined by a specific procedure described previously¹¹ and used to determine Φ_{PCA} for complex (*E*)-**3**•(*E*)-**2b** (Figures S5–S8).⁶ The results of measurements indicated that long-term irradiation of complex (*E*)-**1**•(*E*)-**2b** at $\lambda = 405$ nm was accompanied by consumption of both dye **2b** and stilbene **1** (Figure S6). Photoirradiation of the purified cyclobutane *rctt*-**6** with 254 nm light led to the formation of a mixture of isomers of the starting components in acetonitrile (Figure S9). In the case of complex (*E*)-**1**•(*E*)-**2a**, NMR study failed to unambiguously confirm the formation of the cyclobutane derivative upon photolysis (Figure S3).

However, its formation cannot be ruled out either. We estimated the upper limit of the Φ_{PCA} value for complex (*E*)-1· (*E*)-2a (Table 2, Figure S10).

As follows from the results (Table 2), the quantum efficiency of the cross-PCA reaction decreases 4.5-fold upon the replacement of the pyridine ring in the crown component of (E)-**3**·(E)-**2b** by a benzene ring (complex (E)-**1**·(E)-**2b**). In order to verify the presence of a competing excited state deactivation channel such as PET in pseudodimeric complexes (E)-**1**·(E)-**2**, we carried out a time-resolved fluorescence spectroscopy study. The kinetic curves for the decay of fluorescence of free dyes (E)-**2a**,**b** correspond to a monoexponential decay (Figures S11, S12). For unambiguous determination of the fluorescence lifetime τ of complex (E)-**1**·(E)-**2b**, we carried out titration (Figure 3). The concentration of crown compound (E)-**1** in solution was varied, the concentration of dye (E)-**2b** was invariable, and fluorescence of the dye was monitored.

The obtained set of spectral data (Figure 3) was satisfactorily described by the kinetic equation for biexponential decay. The titration showed that the increasing concentration of crown stilbene (*E*)-1 in a solution of dye (*E*)-2b is accompanied by the decreasing contribution of the long-lived component (1.33 ns), which corresponds to the dye, and by the increasing contribution of the short-lived component (0.48 ns), which is apparently due to fluorescence of the complex (Figure 4). The τ value for complex (*E*)-1·(*E*)-2a is similar to the τ of complex (*E*)-1·(*E*)-2b.

The ratio of the complex and free dye concentrations is related to photophysical parameters by the following equation:



Figure 3. Fluorescence decay kinetics for dye (*E*)-**2b** in the presence of various amounts of (*E*)-**1** in MeCN: excitation with 372 nm laser pulse; observation at 572 nm; the blue curve is the laser pulse profile; the colored crosses are experimental data; the solid colored curves are from global fitting to the biexponential model $I_{\rm fl}(\lambda,t) = A_1(\lambda) \times \exp(-t/\tau_1) + A_2(\lambda) \times \exp(-t/\tau_2)$, with τ_1 (free dye) = 1.33 ns and τ_2 (complexed dye) = 0.48 ns.



Figure 4. Effect of the concentration of crown compound (*E*)-1 ($C_{\rm S}$) in solution referred to the constant concentration of dye 2b ($C_{\rm D}$ = 1.86×10^{-5} M) on the partial concentration of complex (*E*)-1·(*E*)-2b calculated from the data on the biexponential fluorescence decay (Figure 3, eq 3); circles are experimental data, and the curve fits with the use of one equilibrium reaction (1) of the formation of 1:1 complexes.

$$\frac{[\text{SD}]}{[\text{D}]} = \frac{A_{1}\tau_{1}}{A_{2}\tau_{2}} \frac{\varepsilon_{2}}{\varepsilon_{1}} \frac{\varphi_{\text{fl}}^{2}}{\varphi_{\text{fl}}^{1}}$$
(2)

where A_1 and A_2 are pre-exponential factors; ε_1 and ε_2 are absorption coefficients of complex SD and dye D at the excitation wavelength (372 nm); and $\varphi_{\rm fl}^1$ and $\varphi_{\rm fl}^2$ are the fluorescence quantum yields for the complex and the dye at the observation wavelength (572 nm). For the convenience of calculations, we replaced the [SD]/[D] ratio in the left-hand part by the partial concentration of the complex, while $\varepsilon_2/\varepsilon_1$ was replaced by $\varepsilon_{\rm r}$ and $\varphi_{\rm fl}^2/\varphi_{\rm fl}^1$ was replaced by $\varphi_{\rm r}$:

$$\frac{[\text{SD}]}{C_{\text{D}}} = \frac{1}{1 + A_2 \tau_2 / (A_1 \tau_1 \varepsilon_r \varphi_r)}$$
(3)

Using the obtained relation (eq 3), equilibrium (eq 1), and the mass balance, we calculated the stability constant K for complex (E)-1·(E)-2b (Figure 4). In order to check the data of steady state fluorescence spectroscopy, the parameter $\varphi_{\rm r}$ (as well as *K*) was made variable.

The stability constant measured in this way (log K = 4.56) proved to be similar to the value derived from the data on steady-state spectroscopy (log K = 4.43); the differences are within the accuracy of the measurements (Table 2). It is noteworthy that the calculated ratio of the quantum yields φ_r (5.4) is somewhat higher than the experimental value (5.1). If the φ_r value is set to be equal to the experimental one, the standard deviation is little affected and the stability constant somewhat decreases (log K = 4.53).

Presumably, in the case of free dye, the rate constants for the internal conversion and intersystem crossing for the excited state are low in comparison with the radiative rate constant $(k_{\rm rad})$; therefore, E-Z photoisomerization with the rate constant $k_{\rm iso}$ is the only process for the nonradiative deactivation. With the known quantum yield and fluorescence lifetime ($\varphi_{\rm fl}$ and τ), it is possible to estimate $k_{\rm iso}$ and $k_{\rm rad}$ using the following relations:

$$\tau = 1/(k_{\rm iso} + k_{\rm rad})$$
$$\varphi_{\rm fl} = k_{\rm rad}/(k_{\rm iso} + k_{\rm rad})$$

By substituting $\varphi_{\rm fl}$ and τ values of free dye (*E*)-2b, one gets

$$k_{\rm rad} = \varphi_{\rm fl} / \tau = 1.95 \times 10^8 \,{\rm s}^{-1}$$

 $k_{\rm iso} = 1 / \tau - k_{\rm rad} = 5.56 \times 10^8 \,{\rm s}^{-1}$

The radiative lifetime $1/k_{rad} = 5.1$ ns. For complex (*E*)-1·(*E*)-**2b**, this gives

$$k_{\rm rad} = \varphi_{\rm fl} / \tau = 1.06 \times 10^8 \, {\rm s}^{-1}$$

The radiative lifetime $1/k_{rad} = 9.4$ ns.

An almost 2-fold increase in the radiative lifetime upon complex formation is highly unlikely, because the longwavelength absorption band of the dye changes insignificantly (p S10 in Supporting Information). If we assume that the radiative time actually does not change, $\varphi_{\rm fl}$ should amount to 0.094; i.e., it is almost twice as high as the experimental value. A possible explanation for this contradiction is coexistence of different conformations of the pseudodimeric complex, in some of which the dye almost does not fluoresce, because of the superfast deactivation of the excited state, for example, as a result of PET (the relative content of these conformations is slightly below 50%). A similar change in the radiative lifetime upon complex formation was also observed for dye (*E*)-2a.

The question arises of how to explain the considerable (~3-fold) decrease in the τ value of the dye upon complex formation. One assumption is a pronounced increase in $k_{\rm iso}$; however, the causes behind this increase are difficult to understand, because the form of the fluorescence spectrum of the dye barely changes upon complex formation. One more assumption is the formation of nonradiative exciplex with a rate constant exceeding $k_{\rm iso}$.

rate constant exceeding k_{iso} . **NMR Spectroscopic Study.** The formation of pseudodimers (*E*)-**1**•(*E*)-**2** is confirmed by comparison of the ¹H NMR spectra of individual compounds (*E*)-**1** and (*E*)-**2** with those of their equimolar mixtures in MeCN- d_3 . For example, equimolar mixing of (*E*)-**1** and (*E*)-**2b** causes upfield shifts ($\Delta \delta_{\rm H}$ up to -0.25 ppm) of the signals of ethylene protons and most aromatic protons of these compounds (see Figure 5; the proton numbering is given in Scheme 1). On the contrary, the



Figure 5. ¹H NMR (500 MHz) spectra (aromatic proton region) of (a) dye (*E*)-2b, (b) a 1:1 mixture of (*E*)-1 and (*E*)-2b, and (c) compound (*E*)-1; 2×10^{-3} M, MeCN- d_3 .



Figure 6. ¹H NMR (500 MHz) spectra (aliphatic proton region) of (a) dye (*E*)-2b, (b) a 1:1 mixture of (*E*)-1 and (*E*)-2b, and (*c*) compound (*E*)-1; 2×10^{-3} M, MeCN- d_3 .

signals from the CH₂O groups of the crown ether fragment of (E)-1 exhibit downfield shifts ($\Delta\delta_{\rm H}$ up to 0.1 ppm; see Figure 6), which indicates hydrogen bonding of the NH₃⁺ group to the macroheterocycle.¹² The signals of the (CH₂)₃NH₃⁺ group of dye (E)-**2b** move upfield upon complexation ($\Delta\delta_{\rm H}$ up to -0.29 ppm, Figure 6). The upfield shifts observed upon the formation of pseudodimeric complex (E)-**1**·(E)-**2b** testify that the styrylpyridinium and stilbene moieties in this complex are arranged one above the other, which results in various anisotropic effects. Equimolar mixing of (E)-**1** and (E)-**2a** in MeCN- d_3 led to similar changes in proton chemical shifts (Figures S14, S15).

The NOESY spectra were measured for mixtures of dyes (E)-2a,b and crown compound (E)-1 (Figures S16–S19). All of the observed NOE interactions were intramolecular.

As a result of preparative photolysis of an acetonitrile solution of stilbene (E)-1 and styryl dye (E)-2b, cyclobutane derivative 6 was isolated in a pure state. The signals of

cyclobutane ring protons in the ¹H NMR spectrum of *rctt-6* in DMSO-*d*₆ (Figure 7) are manifested as four doublets of doublets. The vicinal coupling constants calculated for this ABCD spin system, ${}^{3}J_{cis-ab} = 10.2$ Hz, ${}^{3}J_{trans-bc} = 7.0$ Hz, ${}^{3}J_{cis-cd} = 9.8$ Hz, and ${}^{3}J_{trans-da} = 7.6$ Hz, are typical of the *rctt* isomers of 1,2,3,4-tetra(het)aryl-substituted cyclobutanes.⁴⁻⁶

X-ray Diffraction Analysis. We succeeded in growing very small and thin single crystals of (18-crown-6)stilbene 1. The view of the molecule in two projections is shown in Figure 8.

The stilbene moiety of the molecule is slightly nonplanar. The dihedral angle between two benzene rings is equal to 23.8° . The dihedral angles between planes of the C1···C6 ring/C6-C7=C8-C9 moiety and C9···C14 ring/C6-C7=C8-C9 moiety amount to 10.2° and 13.7° respectively. With these deviations from planarity, the conjugation over the stilbene moiety is still present. The bond lengths in the C6-C7=C8-C9 moiety are 1.463(3), 1.323(4), and 1.453(3) Å. The macrocycle adopts the typical crown-like conformation

 $\begin{array}{c} \mathbf{d} \\ \mathbf{4.73} \\ \mathbf{4.83} \\ \mathbf{4.83} \\ \mathbf{4.9} \\ \mathbf{4.8} \\ \mathbf{4.8} \\ \mathbf{4.8} \\ \mathbf{4.8} \\ \mathbf{4.7} \\ \mathbf{4.7} \\ \mathbf{4.7} \\ \mathbf{4.7} \\ \mathbf{5/ppm} \\ \mathbf{4.6} \\ \mathbf{4.6} \\ \mathbf{4.6} \\ \mathbf{4.6} \\ \mathbf{4.5} \\ \mathbf{4.5} \\ \mathbf{5/ppm} \\ \mathbf{5/ppm}$

Figure 7. ¹H NMR (500 MHz) spectrum (cyclobutane proton region) of cyclobutane derivative *rctt-6*.

preorganized toward binding to a metal cation and primary ammonium ions. The mean plane through the macrocycle oxygen atoms significantly deviates from the stilbene moiety (see Figure 8, bottom).

The crystal packing is built of alternating doubled crown ether and conjugated stilbene layers (Figure 9).

In the stilbene layer, any pair of adjacent molecules has a T-shaped arrangement of the conjugated moieties (Figure S27), which is unfavorable for the [2 + 2] photocycloaddition of an ethylene compound.

Molecular Structure Calculations. The structures of stilbene (E)-1, styryl dyes (E)-2a,b, and pseudodimeric complexes (E)-1·(E)-2 in MeCN were calculated by density functional theory (DFT). The solvation model known as solution model density (SMD) was used to simulate solvent effects. Computational details are presented in the Experimental Section. Tables S2–S4 (Supporting Information)



Figure 9. Fragment of crystal packing of (E)-1.

show the Gibbs free energies in solution (G_{soln}) calculated for various conformers of (E)-1, (E)-2a,b, and (E)-1·(E)-2. Figure 10 presents the lowest-energy conformations of (E)-1 and (E)-2a,b, as derived from the DFT/SMD calculations.

Generally, stilbene (*E*)-1 can adopt two principal conformations (*s-trans* and *s-cis*) due to rotation around the single bond connecting the benzocrown ether moiety to the ethylenic bond. According to calculations, the *s-cis* conformer of (*E*)-1 is 0.98 kcal mol⁻¹ more stable than the *s-trans* conformer. The bond lengths in the C_{Ph}-C=C-C_{Ar} bridge of (*s-cis*)-[(*E*)-1] were calculated to be 1.471, 1.343, and 1.468 Å. These values are very close to those observed for the crystalline (*s-trans*)-[(*E*)-1] (Figure 8); the deviations between the calculated and observed bond lengths are 0.7–1.3%.

The most stable conformers of styryl dyes (*E*)-**2a**,**b** are characterized by *s*-*trans* orientation of the SMe group relative to the ethylenic bond (Table S3). The *s*-*cis* conformers of (*E*)-**2a** and (*E*)-**2b** are 1.24 and 0.18 kcal mol⁻¹ less stable than the corresponding *s*-*trans* conformers. The ammonioalkyl sub-



Figure 8. Structure of s-trans conformer of (E)-1 in two projections; thermal displacement ellipsoids are drawn at the 50% probability level.



Figure 10. Most stable conformers of crown compound (E)-1 and dyes (E)-2a,b in MeCN, according to DFT/SMD calculations.

stituent of the dye can adopt *trans* and *gauche* conformations: in the case of (E)-2a, the lowest energy is inherent in the *gauche* conformation, while in the case of (E)-2b, *trans,trans* conformation has the lowest energy. Pictorial views of various conformers of stilbene (E)-1, dyes (E)-2a,b, and their complexes are depicted in Figure S29.

Figure 11 shows the lowest-energy conformations of complexes (E)-1·(E)-2a,b with the *syn* and *anti* orientations of the two ethylenic bonds with respect to each other.

Both the syn and anti conformers of complex (E)-1•(E)-2a are characterized by gauche conformation of the ammonioethyl group. The ammoniopropyl group in both conformers of complex (E)-1•(E)-2b adopts a trans,gauche conformation. The styryl dyes in complexes (E)-1•(E)-2a,b have the s-trans orientation of the SMe group. Crown stilbene (E)-1 in the syn and anti conformers of the pseudodimeric complexes adopts different conformations: s-cis and s-trans, respectively. In the case of complex (E)-1•(E)-2a, the anti conformer is more stable than the syn conformer (the difference in G_{soln} was calculated to be 0.64 kcal mol⁻¹), whereas, in the case of (E)-1• (E)-2b, the syn-conformer is more stable than the anti conformer (the difference in G_{soln} is 0.91 kcal mol⁻¹). The small differences in G_{soln} between the syn and anti conformers of complexes imply the coexistence of these conformers in solution.

The distances between the centers of the double bonds for two complexes $syn{[(E)-1\cdot(E)-2a]}$ and $syn{[(E)-1\cdot(E)-2b]}$ differ little (3.454 and 3.489 Å, Figure 11) and meet the topochemical criteria required for PCA reactions to occur.¹³ The angles between the ethylenic bonds in the complexes are 27.9° and 23.6°, respectively. The fact that DFT calculations predict the predominance of the anti-conformations for complex (E)-1·(E)-2a in solutions (Table S4) and the greater deviation from the parallel arrangement of the bonds appears not to be the major cause of the lower Φ_{PCA} value compared to that of (E)-1·(E)-2b. Presumably, in the excited state of syn- $[(E)-1\cdot(E)-2a]$, the rigidity of the ammonioethyl moiety of the dye prevents the double bonds from approaching each other. For the lowest-energy conformers of $syn-[(E)-1\cdot(E)-2a]$ and syn-[(E)-1·(E)-2b], we optimized the geometries of the S_1 states (Figure S30); the distances between the centers of the double bonds are 3.612 and 3.053 Å, respectively. The angles between the ethylenic bonds are 15.2° and 8.4° , respectively. Apparently, less favorable relative arrangement of the double bonds in the excited state of (E)-1·(E)-2a compared with (E)- $1 \cdot (E) - 2b$ is responsible for the dramatically low efficiency of the cross-PCA reaction (Table 2). On the whole, the quantum yield of cross-PCA for pseudodimeric (E)-1·(E)-2b and (E)-3· (E)-2b is relatively low. The most probable explanation is the unfavorable orientation of ethylenic bonds, i.e., a great angle between them ($\sim 24^{\circ}$).

Using time-dependent DFT (TDDFT), we calculated the vertical electronic transition energies for the dyes and their complexes (Table S5) and the molecular orbitals between which these transitions take place (Table S6). The results indicate that the long-wavelength absorption band of the pseudodimeric complexes is associated with two transitions of similar energy $(S_0 - \overline{S}_1 \text{ and } S_0 - S_2)$. In the case of (E)-1·(E)-2a, the $S_0 - S_1$ transitions of the two lowest-energy conformers with the syn- and anti-orientations of the double bonds are completely or predominantly related to the intermolecular electron transfer (ET) from the donor moiety (stilbene) to the acceptor one (dye). In this case, the photoexcitation to the long-wavelength absorption band of the complex may be followed by internal conversion from the S_2 state to the S_1 state, which has a lower energy and is actually an ET-based radical ion pair. While considering the electronic transitions of complex (E)-**1**·(E)-**2b**, one can notice that the S₀-S₁ transition of the lowest-energy conformer $(syn-(up-sc)\cdot(tg-st))$ is not



Figure 11. Most stable syn and anti conformers of complexes (E)-1·(E)-2a and (E)-1·(E)-2b in MeCN, as derived from DFT/SMD calculations; hydrogen atoms are hidden except those of the NH₃⁺ group.

related to ET, but is due to electron density redistribution in the dye. In the case of the second low-energy conformer of (E)-1·(E)-2b, the S₀-S₁ transition is approximately half related to the intermolecular ET. Apparently, the experimentally established fluorescence lifetime of 0.48 ns corresponds to the conformers without PET (Table 3). For other conformers for

Table 3. Fluorescence Lifetimes of Styryl Dyes (E)-2a,b and Their Complexes with Stilbene (E)-1 in MeCN

| Compound | au, ns |
|-------------------------------|--------|
| (E)- 2a | 1.44 |
| (E)-1· (E) -2a ^a | 0.46 |
| (E)- 2b | 1.33 |
| (E)-1· (E) -2b ^b | 0.48 |

^aFluorescence lifetime was obtained for mixture of 1 (7×10^{-4} M) and 2a (2×10^{-5} M) (Figure S13). ^bFluorescence lifetime was calculated from titration data (Figure 3).

which the state with the intermolecular ET has the lowest energy, the excited state lifetime is substantially shorter, being less than the laser pulse width (<75 ps). It is important that, for the *syn-* and *anti*-conformers of the pseudodimeric complex (*E*)-**3**•(*E*)-**2b** formed by crown-containing styrylpyridine, the S₁ state is not related to the intermolecular ET, which is also confirmed by a slight decrease in the fluorescence quantum yield of (*E*)-**2b** upon the complex formation with (*E*)-**3**.⁶

CONCLUSIONS

(18-Crown-6)stilbene with a high degree of purity was prepared using the Horner-Wadsworth-Emmons reaction. As expected, spectral features and quantum yields of E-Zphotoisomerization and fluorescence for N-(2-ammonioethyl)-4-styrylpyridinium and N-(3-ammoniopropyl)-4-styrylpyridinium dyes are quite similar. The complex formation of these dyes with (18-crown-6)stilbene gives pseudodimeric complexes with stacked molecules. Light irradiation of the complex with the ammoniopropyl dye gave rise to a single *rctt* isomer of cyclobutane. The quantum yield of this reaction proved to be 5 times lower than the quantum yield of cross-PCA for a similar complex based on crown-containing 4-styrylpyridine. This is apparently caused by the competing excited state deactivation in approximately half of the conformers of the complex with the crown-containing stilbene, namely, photoinduced electron transfer. The other conformers show an almost 3-fold decrease in the lifetime of the singlet excited state relative to the free dye, which can be attributed to the formation of nonradiative exciplexes. The low quantum yield or complete exclusion of cross-PCA in the crown stilbene complex with the ammonioethyl styryl dye is probably due to higher rigidity and the small length of the ammonioalkyl chain of the Nsubstituent, which prevents the ethylenic bonds of the components from approaching each other in the excited state.

The results of the present study markedly expand the boundary conditions for conducting the cross-PCA reactions of diarylethylenes using the supramolecular assembly. They will also be useful for the development of methods for the synthesis of cyclobutane derivatives. It was shown that the possibility of photoinduced electron transfer should be taken into account in the consideration of the photochemistry of heterodimeric structures of aromatic olefins.

EXPERIMENTAL SECTION

Melting points (uncorrected) were measured in capillaries on a Mel-Temp II apparatus. Elemental analyses were carried out in the Microanalytical Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow, Russian Federation). The samples for elemental analyses were dried at 80 °C in vacuo. NMR spectra were recorded on a Bruker DRX500 spectrometer (¹H NMR, 500 MHz; ¹³C NMR, 125 MHz); chemical shifts were measured to within ± 0.01 ppm using the residual solvent peak (MeCN- d_3 or DMSO- d_6) as the internal standard ($\delta_{\rm H}$ 1.94, 2.50 ppm and $\delta_{\rm C}$ 1.32, 39.52 ppm, respectively); spin-spin coupling constants were determined with an accuracy of ± 0.1 Hz. ESI mass spectra were obtained on a MicrOTOF II instrument (Bruker Daltonics) in the range m/z = 50-3000 for positive ions (a solution was injected in a nitrogen gas flow, voltage of 4500 V). Al₂O₃ (Aluminumoxid 90 active neutral, 0.063-0.200 mm, Merck) was used for column chromatography. Reactions were monitored by thin-layer chromatography (TLC) on DC-Alufolien Aluminumoxid 60 F254 neutral (Typ E) (Merck). All initial compounds were purchased and used without purification. Acetonitrile (Cryochrom, special purity grade, H₂O content <0.03%, v/v) was used as received. UV-vis absorption spectra were measured on a Specord M40 spectrophotometer using 1 and 0.2 cm quartz cells with ground-in stoppers. Solutions of stilbene 1 and dyes 2a,b were prepared in a darkroom under red light to avoid the E-Z photoisomerization that occurs upon exposure to daylight. Steady-state fluorescence spectra were obtained on a PerkinElmer LS 55 spectrometer; the spectra were corrected according to the spectral sensitivity curve for the photodetector. Photolyses were carried out using glass-filtered light (λ = 313, 365, or 405 nm) of a DRSh-250 high-pressure mercury lamp (250 W). The 313 nm spectral line was isolated with an efficiency of 99.0% using a combination of optical filters UFS-2 (3 mm thick) and ZhS-3 (2.5 mm thick); the 365 nm line was isolated with an efficiency of >99.8% using a combination of optical filters UFS-6 (5 mm) and BS-7 (3 mm); the 405 nm line was isolated with an efficiency of 99.4% using a combination of optical filters ZhS-10 (5 mm) and PS-13 (3 mm). The intensity of actinic light was measured by chemical actinometry. Fluorescence decay curves were recorded on a FluoTime 200 system (PicoQuant GmbH) using a pulsed diode laser as the excitation source operating at a wavelength of 372 nm with a pulse duration of ~75 ps.

Diethyl Benzylphosphonate (4). A mixture of (bromomethyl)benzene (6.6 g, 0.039 mol) and triethyl phosphite (11.6 mL, 0.070 mol) was heated under reflux with stirring for 6 h with simultaneous distilling of bromoethane formed. Excess triethyl phosphite was removed *in vacuo* for 1 h. The residue was distilled at 156 °C/10 mbar (lit. data: bp 120 °C/1.5 mbar (1.1 mmHg)⁹) to give compound 4 (8.4 g, 98% yield) as a colorless liquid. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 7.34–7.20 (m, 5H), 3.98–3.89 (m, 4H), 3.21 (d, 2H, *J* = 21.5 Hz), 1.16 (t, 6H, *J* = 7.0 Hz).

18-[(E)-2-Phenylvinyl]-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine ((E)-1). A solution of compound 4 (0.20 mL, 0.97 mmol) in dry DMF (5 mL) was added to a solution of t-BuONa (0.38 g, 3.98 mmol) in dry DMF (8 mL), and the resulting mixture was stirred under nitrogen gas flow for 40 min. A solution of 4'-formylbenzo-18-crown-6 ether (0.33 g, 0.97 mmol) in dry DMF (4 mL) was added (in portions) to the mixture and then stirred for 75 h in the dark. The reaction mixture was diluted with water (100 mL), and the precipitate thus formed was filtered and then purified by column chromatography on Al₂O₃ using a benzene-MeCN gradient mixture (up to 25% of the latter) as an eluent. Compound (E)-1 was obtained in 60% yield (0.24 g) as a white powder, mp 104-105 °C (cf. lit.:⁷ mp 96-98 °C). ¹H NMR (MeCN d_{3} , 500 MHz): δ 7.54 (d, 2H, J = 7.4 Hz), 7.37 (t, 2H, J = 7.8 Hz), 7.25 (t, 1H, J = 7.4 Hz), 7.20 (d, 1H, J = 1.8 Hz), 7.14 (d, 1H, J = 16.9 Hz), 7.09 (d, 1H, J = 16.9 Hz), 7.06 (dd, 1H, J = 8.4, 1.8 Hz), 6.91 (d, 1H, J = 8.4 Hz), 4.23–4.19 (m, 2H), 4.17–4.13 (m, 2H), 3.80-3.73 (m, 4H), 3.64-3.59 (m, 4H), 3.59-3.53 (m, 8H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (MeCN- $d_{3},$ 125 MHz): δ 149.3, 149.1, 138.8, 131.3,

129.7, 129.4, 128.3, 127.5, 127.2, 120.8, 113.1, 110.5, 71.2, 71.1, 71.05, 71.03, 69.9, 69.8, 68.7, 68.6. HRMS (ESI-TOF) m/z: [M + NH₄⁺] Calcd for C₂₄H₃₄NO₆⁺ 432.2381; Found 432.2390. Anal. Calcd for C₂₄H₃₀O₆: C, 69.54; H, 7.30. Found: C, 69.70; H, 7.34.

1-(2-Ammonioethyl)-4-{(*E***)-2-[4-(methylthio)phenyl]vinyl}pyridinium Diperchlorate ((***E***)-2a). A mixture of 4-{(***E***)-2-[4-(methylthio)phenyl]vinyl}pyridine (5)¹⁴ (150 mg, 0.66 mmol), 2bromoethylammonium bromide (162 mg, 0.79 mmol), and MeCN (10 mL) was heated under reflux for 30 h in the dark using an oil bath placed on a hot plate magnetic stirrer. The reaction mixture was cooled to room temperature, and the precipitate was filtered, washed with MeCN (3 mL), and dried in air to give the dibromide salt of the dye (182 mg, 64% yield) as a yellow powder, mp 250–252 °C. ¹H NMR (DMSO-***d***₆, 500 MHz): \delta 8.90 (d, 2H,** *J* **= 6.8 Hz), 8.28 (d, 2H,** *J* **= 6.8 Hz), 8.09 (br.s, 3H), 8.06 (d, 1H,** *J* **= 16.3 Hz), 7.71 (d, 2H,** *J* **= 8.4 Hz), 7.52 (d, 1H,** *J* **= 16.3 Hz), 7.37 (d, 2H,** *J* **= 8.4 Hz), 4.76 (t, 2H,** *J* **= 5.7 Hz), 3.55–3.48 (m, 2H), 2.54 (s, 3H).**

The dibromide salt (100 mg, 0.23 mmol) was dissolved in EtOH (3 mL) at heating, conc. HClO₄ (70%, aq.) (100 μ L, 1.16 mmol) was added, and the reaction mixture was cooled to room temperature. The precipitate thus formed was filtered, washed with EtOH (2 mL) and then with Et₂O (3 mL), and dried in air to give dye (*E*)-**2a** (75 mg, 71% yield) as dark-yellow crystals, mp 222–224 °C. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 8.86 (d, 2H, *J* = 6.9 Hz), 8.26 (d, 2H, *J* = 6.9 Hz), 8.04 (d, 1H, *J* = 16.3 Hz), 8.03 (br.s, 3H), 7.71 (d, 2H, *J* = 8.5 Hz), 7.51 (d, 1H, *J* = 16.3 Hz), 7.36 (d, 2H, *J* = 8.5 Hz), 4.74 (t, 2H, *J* = 5.8 Hz), 3.50 (br.s, 2H), 2.53 (s, 3H). ¹³C{¹H} NMR (DMSO-*d*₆, 125 MHz): δ 153.8, 144.8, 142.2, 141.0, 131.5, 128.8, 125.8, 123.8, 122.1, 56.9, 14.2. Anal. Calcd for C₁₆H₂₀Cl₂N₂O₈S: C, 40.78; H, 4.28; N, 5.94. Found: C, 40.61; H, 4.37; N, 5.81.

1-(2-Ammoniopropyl)-4-r-{2-c-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-4t-[4-(methylthio)phenyl]-3-t-phenylcyclobutyl}pyridinium Diperchlorate (rctt-6). A mixture of compound (E)-1 (12.3 mg, 29.7 μ mol) and dye (E)-2b (13.4 mg, 27.6 μ mol) was dissolved in MeCN (20 mL) in a glass flask and irradiated with a glass-filtered light of a high pressure Hg lamp (λ = 405 nm, distance from the light source is ~ 20 cm) for 50 h. The reaction mixture was evaporated in air to dryness without heating. The solid residue was dissolved in MeCN (3.5 mL) and slowly saturated with benzene vapor for 3 weeks at room temperature. The resulting crystalline precipitate was decanted and dried in vacuo to afford compound rctt-6 in 17% yield (4.2 mg) as a slightly yellowish powder, mp 188-190 °C dec. ¹H NMR (DMSO d_{6i} 500 MHz): δ 8.76 (d, 2H, J = 6.4 Hz), 7.93 (d, 2H, J = 6.4 Hz), 7.25-7.11 (m, 9H), 7.11-7.03 (m, 4H), 6.92 (d, 1H, J = 8.4 Hz), 6.49 (d, 1H, J = 2.0 Hz), 4.83 (dd, 1H, J = 10.2, 7.6 Hz), 4.73 (dd, 1H, J = 9.8, 7.6 Hz), 4.65 (dd, 1H, J = 9.8, 7.0 Hz), 4.61 (dd, 1H, J = 10.2, 7.0 Hz), 4.56-4.49 (m, 2H), 4.13-4.02 (m, 2H), 3.96-3.86 (m, 2H), 3.84-3.74 (m, 4H), 3.74-3.68 (m, 4H), 3.68-3.59 (m, 8H), 2.41–2.19 (m, 2H), 2.37 (s, 3H), 2.17–2.02 (m, 2H). ¹³C{¹H} NMR (DMSO-d₆, 125 MHz): δ 161.6, 146.3, 145.4, 143.1, 139.9, 136.1, 135.7, 131.7, 128.6, 128.0, 127.3, 126.1, 125.5, 120.5, 111.7, 111.6, 69.8, 69.7, 69.3, 69.2, 68.6, 68.5, 68.3, 67.2, 67.1, 57.2, 48.1, 47.4, 44.3, 42.4, 35.8, 28.2, 14.6. UV-vis (MeCN, Figure S9) λ_{max} ~290 sh. (ε 4500), 260 (ε 20 900), 228 nm (ε 24 400 M⁻¹ cm⁻¹). HRMS (ESI-TOF) m/z: [M²⁺] Calcd for C₄₁H₅₂N₂O₆S²⁺ 350.1773; Found 350.1768.

Fluorescence Quantum Yields and Lifetimes. Fluorescence quantum yields (φ_{fl}) were calculated according to the equation

$$\varphi_{\rm fl} = (\varphi_{\rm fl_r} D_{\rm ex_r} n^2 S) / (D_{\rm ex} n_r^2 S_r)$$

where the subscript *r* refers to the reference standard (anthracene in ethanol), $D_{\rm ex}$ is the optical density at the excitation wavelength, *S* is the integrated intensity of the corrected emission spectrum, *n* is the refractive index of the solvent, and $\varphi_{\rm fl}$ _r = 0.28.¹⁵

Fluorescence lifetimes for free dyes and complex (E)-**1**·(E)-**2a** were derived from global analysis of fluorescence decays observed at three different wavelengths. The fluorescence lifetime of complex (E)-**1**·(E)-**2b** was obtained from titration data. The general procedure of

global analysis of time-dependent spectroscopic data has been described previously. $^{16}\,$

Spectrophotometric Titration. Titration experiments were conducted in quartz cells (1 cm path length) using MeCN as the solvent. The total concentration of dye (E)-2 was maintained at a constant value, and the total concentration of stilbene (E)-1 gradually increased from zero. The absorption spectra of pure complexes (E)-1·(E)-2 as well as the complex stability constants were derived from fitting of the spectrophotometric titration data to a 1:1 complexation model using the global analysis methods reported previously.¹⁰

Quantum Yields of E-Z Photoisomerization. Measurements were conducted in MeCN solutions using quartz cells with a path length of 1 cm. The quantum yields for the forward and reverse E-Zphotoisomerization reactions (φ_{E-Z} and φ_{Z-E} , respectively) were obtained from the kinetics of UV-vis absorption spectra measured upon steady-state irradiation of *E* isomer with 313 nm light (for 1) or with 365 nm light (for 2a). In the case of dye 2a, the spectrum of the initial E isomer and the spectra of the E-Z photostationary states attained upon irradiation at different wavelengths were used to calculate the absorption spectrum of the pure Z isomer under the assumption that the $\varphi_{E-Z}/\varphi_{Z-E}$ ratio does not depend on the irradiation wavelength. In the case of crown stilbene 1, the spectrum of the Z isomer was derived by subtracting the normalized spectrum of the E isomer from the spectrum of the photostationary state (313 nm). The amount of the *E* isomer in the photostationary mixture was estimated from the fluorescence spectrum taking into account the fact that the Z isomer almost does not fluoresce. The treatment of photoirradiation-dependent spectra was carried out using global analysis methods, as described previously.¹¹ The φ_{E-Z} and φ_{Z-E} values were determined to within $\pm 20\%$.

Quantum Yields of Cross-PCA. The quantum yield of cross-PCA for complex (E)-1·(E)-2b in MeCN was estimated from the spectrophotometric data on the photolysis of an equimolar solution of (E)-1 and (E)-2b $(1 \times 10^{-4} \text{ M}, 0.2 \text{ cm cell})$ with 405 nm light (selective excitation of dye 2b). The dye consumption in the cross-PCA reaction was determined on the basis of spectrophotochemical data using the specific procedure reported previously.¹¹ The cross-PCA quantum yield obtained in this way is an effective value, since the complexed dye 2b is able to undergo the reversible E-Z photoisomerization.

The upper limit of the quantum yield of cross-PCA for complex (E)-1·(E)-2a was derived from the kinetics of the absorption spectra observed during steady-state irradiation of the complex in solution (30-fold excess of stilbene 1 over dye 2a) at $\lambda = 405$ nm using the kinetic equation for irreversible unimolecular photoreactions:

$$\frac{dC_{\rm D}(t)}{dt} = \Phi_{\rm PCA} I N_{\rm A}^{-1} 10^3 \frac{(1 - 10^{-\varepsilon C_{\rm D}(t)l})}{l}$$

where I is the light intensity, cm⁻² s⁻¹; N_A is the Avogadro number, M^{-1} ; ε is the molar absorptivity of the complex at the irradiation wavelength (405 nm), M^{-1} cm⁻¹; C_D is the concentration of the dye as a part of the complex; and l is the cell length, cm. The quasiphotostationary state that was established after fast E-Z photo-isomerization of the dye was taken as the starting point (Figure S10). It was assumed that the observed long-wavelength absorbance is entirely due to (E)-1·(E)-2a.

X-ray Diffraction Experiments. Single crystals of compound (*E*)-1 were grown by slow evaporation of a CH_2Cl_2 -hexane (~1:1, v/ v) solution at ambient temperature in the dark. A crystal suitable for X-ray structure determination was mounted on a CCD area Smart APEX-II diffractometer under a stream of cooled nitrogen where crystallographic parameters and intensities of X-ray reflection were measured. The redaction of experimental data was performed using the SAINT program.¹⁷ The structure was solved using direct methods. The structure refinement was carried out in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were put into the calculated position and refined using the riding model. The crystallographic parameters and parameters of structure refinement are listed in Table S1.

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All the calculations were performed using the OLEX-2 software program.¹⁸ The full set of the X-ray crystal data for (E)-1 has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2038923) deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/ data request/cif.

DFT Calculations. All calculations were carried out using the Gaussian 09 program package.¹⁹ Molecular geometries were optimized using the M06-2X functional²⁰ and the 6-31G(d) basis set. The universal solvation model known as solution model density $(SMD)^{21}$ was used to account for solvent effects (solvent MeCN). The SMD calculations were performed using a value of 10 Å⁻² for the average density of integration points on the surface (the default value is 5 Å⁻²). The internal option IOp(1/7 = 100) was used to tighten the default optimization criteria 3-fold. In order to verify the nature of stationary points as well as to compute thermochemical quantities, all geometry optimizations were followed by harmonic frequency calculations. A value of 0.96 was used as the scale factor for harmonic frequencies in the thermochemical analysis. The Gibbs free energy in solution (G_{soln}) was calculated as follows:

$$G_{\rm soln} = E_{\rm soln} + \Delta G_{\rm corr}$$

where $E_{\rm soln}$ is the electronic energy in solution and $\Delta G_{\rm corr}$ is the thermal correction to $G_{\rm soln}$, including the zero-point energy. To minimize basis set superposition errors for complexes, the $E_{\rm soln}$ values were derived from single-point M06-2X/SMD calculations with the larger 6-311G(2df,2p) basis set.

TDDFT calculations (Tables S5, S6) were carried out at the CAM-B3LYP/6-311G(2d,p)/SMD(MeCN) level of theory for geometries determined by the M06-2X/6-31G(d)/SMD(MeCN) method. A similar calculation with the M06-2X functional (Tables S7, S8) resulted in similar parameters of electronic transitions.

ASSOCIATED CONTENT

9 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02514.

Additional figures and tables including spectrophotometric, NMR, and X-ray data (PDF)

Accession Codes

CCDC 2038923 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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