Styryl dyes. Synthesis and study of the solid-state [2+2] autophotocycloaddition by NMR spectroscopy and X-ray diffraction*

A. I. Vedernikov,[a] L. G. Kuz´mina,[b] S. K. Sazonov,[a] N. A. Lobova,[a] P. S. Loginov,[a] A. V. Churakov,[b] Yu. A. Strelenko,[c] J. A. K. Howard,[d] M. V. Alfimov,[a] and S. P. Gromov[a]★

[a]*Photochemistry Center, Russian Academy of Sciences, 7A ul. Novatorov, 119421 Moscow, Russian Federation. Fax: +7 (495) 936 1255. E-mail: gromov@photonics.ru*

[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 954 1279*

[c]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328*

[d]*Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK*

New styryl dyes of the pyridine and benzothiazole series were synthesized with the aim of investigating the solid-state [2+2] autophotocycloaddition (PCA) reaction. The ^{1}H NMR spectroscopy showed that for most of the compounds under study, the visible light irradiation of thin polycrystalline films of the dyes affords cyclobutane derivatives. The rate of the photoreaction depends on the structure of the dye and is higher for compounds, which contain a short *N*-substituent in the heterocyclic moiety and have strong absorption in the visible region. Dyes bearing electron-releasing substituents in the benzene ring undergo the stereospecific PCA in the *syn*-head-to-tail dimeric pair to give the only *rctt* isomer of cyclobutane derivatives. Electron-withdrawing and bulky substituents in the benzene fragment of styryl dyes extend the range of the mutual orientations of the molecules in the dimeric pairs, resulting in the formation of two or even four isomeric cyclobutanes in the PCA reactions. The structures of some dyes were established by X-ray diffraction. In the overwhelming majority of the structures, one of two packing modes, either *syn*-head-to-tail or *syn*-head-to-head, with extensive stacking interactions is observed. A rare example of the *anti*-head-to-head stacking mode was found for the dicationic dye containing the bulky $N^+(Et)Me_2$ substituent in the benzene ring. The *syn*-head-to-tail and *anti*-head-to-head stacking modes can facilitate the PCA reaction due to the close spatial proximity of the ethylenic bonds and their parallel orientation in the dimeric pairs of the dye molecules.

Key words: styryl dyes, crown ethers, structure, [2+2] photocycloaddition, topochemical reaction, cyclobutanes, X-ray diffraction, ^{1}H NMR spectroscopy.

The photochemical [2+2] cycloaddition (PCA) reaction of organic compounds was discovered in 1960s,[1,2] and interest in this reaction has been quickened in recent years.[3—11] The advantages of this method for the carbon—carbon bond formation are the relative simplicity of the synthesis (irradiation of samples with light of a specified wavelength), the reversibility of the reaction, which allows the regeneration of the starting compounds by changing the wavelength, and, in some cases, high stereoselectivity of PCA reactions resulting from the preorganization of pairs of the starting structural units. It should also be noted that the preparation of many PCA reaction products with the use of other synthetic approaches presents difficulties. The PCA reactions with compounds containing the C=C bond can proceed in concentrated solutions, gels, and polymers, as well as in the solid state (in polycrystalline films and single crystals). In some cases, the PCA reactions can proceed as single crystal—single crystal transformations, *i.e.*, with-

* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1797—1819, September, 2007.

1066-5285/07/5609-1860

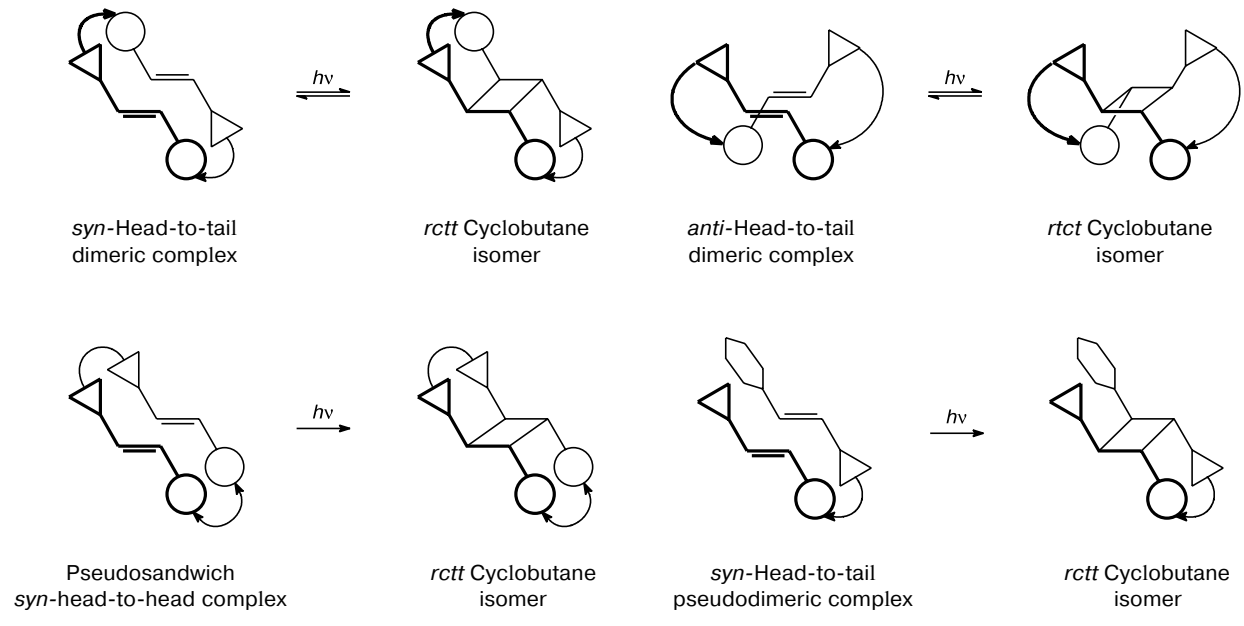
out degradation of single crystals.[12–15] However, this method has not gained wide acceptance because it is difficult to predict the possibility of the PCA reaction proceeding with a particular type of unsaturated compounds and due to the fact that these reactions produce, as a rule, mixtures of unseparable stereoisomers.

The PCA reactions in single crystals of extended π-conjugated unsaturated compounds can proceed not only very efficient but also stereoselectively, *i.e.*, produce only some of the possible isomers of cyclobutane derivatives. This is associated with particular geometric requirements[11,14] for the formation of the preceding dimeric pair of the starting molecules, in which the ethylene fragments should be arranged approximately parallel to one another at a distance of up to 4.2 Å. The stacking interactions between the π systems of adjacent molecules meet these requirements. Styryl dyes, which have an extensive chain of conjugation and contain an ethylenic bond in the middle of this chain, hold promise for the stereoselective solid-state PCA reactions.

Earlier, we have found[16–19] that supramolecular complexes of crown-containing styryl dyes can be involved in the stereospecific PCA reaction in solution in the presence of metal or ammonium cations to form cyclobutane derivatives (Scheme 1; examples of the preorganization of crown-containing styryl dyes for the PCA reaction in solution and the stereochemistry of the products, cyclobutane derivatives, are presented). Recently, we have found[20–23] that some of these compounds, as well as model dyes containing no crown-ether moieties, can be involved in topochemical PCA reactions in thin polycrystalline films and single crystals, including those proceeding without degradation of the latter. We were the first to study this area of photochemistry of styryl dyes, although these compounds are rather easily accessible by organic synthetic methods, and a wide range of these compounds can be prepared by varying the nature of substituents at the ethylenic bond. Due to the destruction of the conjugation chain of the styryl chromogen as a result of the PCA reaction and, consequently, due to a strong color contrast between the starting and final compounds, styryl dyes can be promising reagents for the design of reversible data recording and storage systems at the molecular level.

In the present study, we performed the ^{1}H NMR spectroscopic investigation of the ability of styryl dyes of the pyridine (**1**—**4**) and benzothiazole (**5**) series to be involved in the [2+2] autophotocycloaddition reaction in thin polycrystalline films depending on the structure of the dye and determined the compositions and three-dimensional structures of the final products (cyclobutane derivatives). Most of the dyes were characterized by X-ray diffraction, and the packing modes formed by the dyes were analyzed in terms of the preorganization of the dye molecules for the solid-state photochemical cycloaddition.

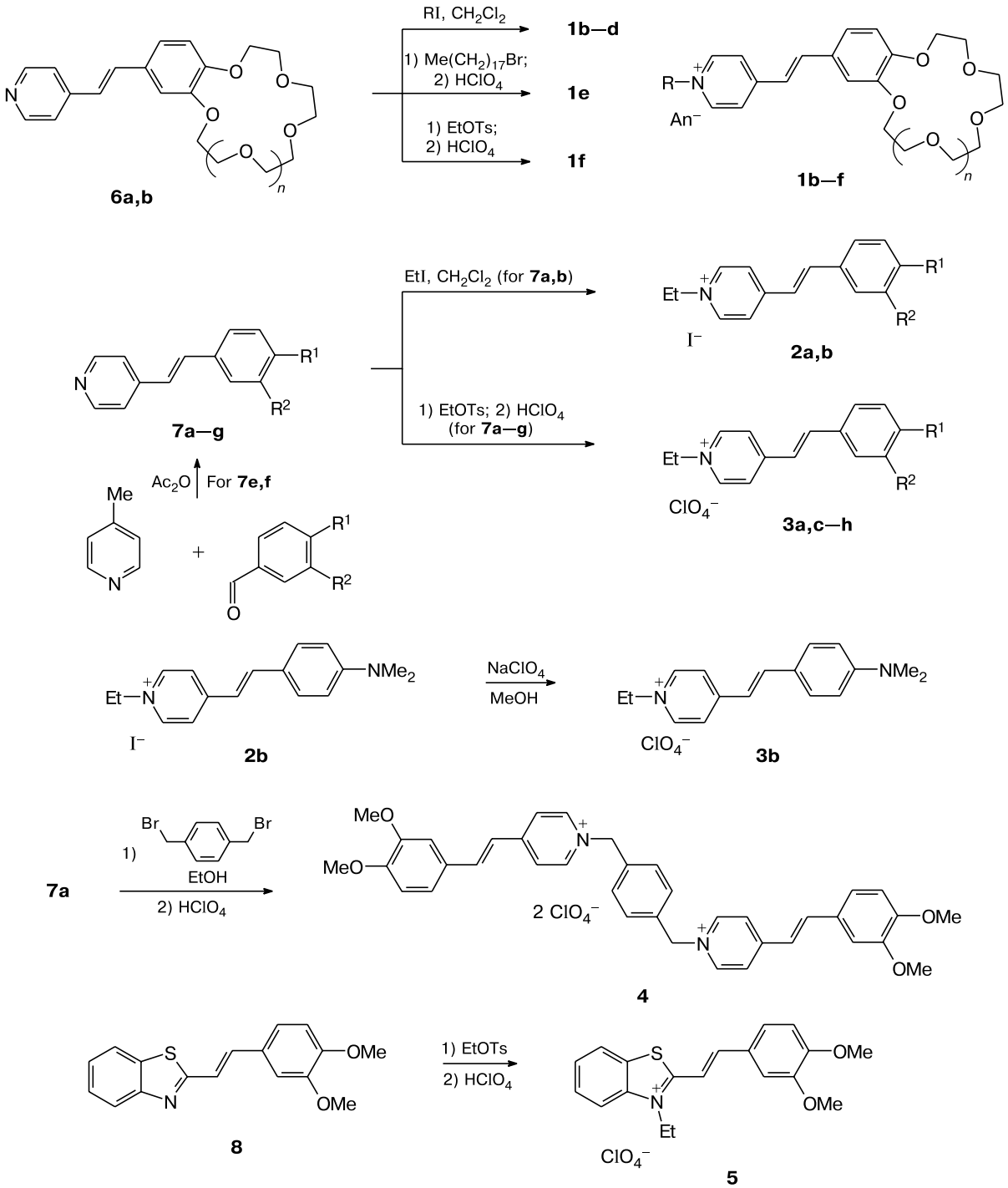
Scheme 1



Results and Discussion

Synthesis and spectroscopic studies. The synthesis of styryl dye **1a** with the perchlorate anion, which is an analog of iodide **1b**, has been described in our earlier study.[20] In the present study, styryl dyes were synthesized according to Scheme 2. Crown-containing dyes **1b—f** were prepared by the *N*-alkylation of 4-styrylpyridines **6a,b** fol-

Scheme 2

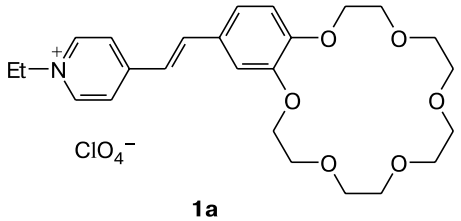


n = 1 (**1f**, **6b**), 2 (**1b—e**, **6a**)
1: R = Et (**b,f**), Bu^n (**c**), Pr^i (**d**), Me(CH$_2$)$_{17}$ (**e**); An$^-$ = I$^-$ (**b—d**), ClO$_4^-$ (**e,f**)
2, 3, 7: R^1 = R^2 = OMe (**a**); R^1 = NMe$_2$, R^2 = H (**b**); R^1 = R^2 = H (**c**); R^1 = OMe, R^2 = H (**d**); R^1 = SMe, R^2 = H (**e**); R^1 = R^2 = Cl (**f**); R^1 = NO$_2$, R^2 = H (**g**); R^1 = N$^+$(Et)Me$_2$ClO$_4^-$, R^2 = H (**h**)

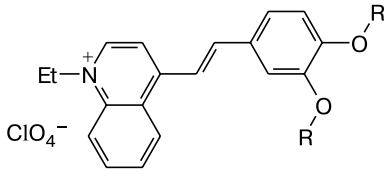
lowed by the treatment with concentrated perchloric acid in the case of the synthesis of perchlorate salts. Compound **7e** and new dichloro-substituted 4-styrylpyridine **7f** were synthesized by the condensation of 4-picoline and the corresponding substituted benzaldehyde in acidic conditions by analogy with the synthesis of related compounds **7c,d,g**.[24] Analogs of dyes **1** containing different substituents in the benzene fragment instead of the crown-ether moiety, *viz.*, iodides **2a,b** and perchlorates **3a,c—g** and **5**, were synthesized by the treatment of 4-styrylpyridines **7a—g** and 2-styrylbenzothiazole **8** with ethyl iodide or ethyl tosylate followed by the ionic exchange with $HClO_4$ in the case of the preparation of perchlorate salts. Compound **7b** containing the NMe_2 substituent in the benzene fragment was subjected to the double *N*-alkylation by fusion with an excess of EtOTs followed by the transformation into the perchlorate salt, which resulted in the formation of dicationic dye **3h** instead of the expected monocationic dye **3b**. Dye **3b** was synthesized by the ionic exchange of iodide **2b** with $NaClO_4$. Bis(styryl) dye **4** was prepared by the quaternization of 4-styrylpyridine **7a** with 1,4-bis(bromomethyl)benzene followed by the treatment with $HClO_4$.

The structures of new compounds **1b—f**, **2a**, **3a—h**, **4**, **5**, and **7f** were determined by ^1H NMR spectroscopy, spectrophotometry, and mass spectrometry and were confirmed by elemental analysis. According to the NMR data, all 4-styrylpyridines and styryl dyes were prepared in the *E* configuration ($^3J_{trans\text{-}CH=CH}$ = 15.6—16.5 Hz).

Earlier,[20] we have demonstrated that the phototransformation pathway of 18-crown-6-containing styryl dye (*E*)-**1a** principally depends on its aggregation state.



1a

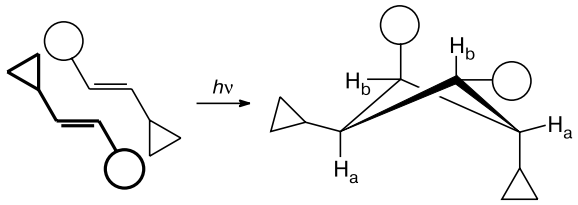


9a,b

R = Me (**9a**), R + R = $CH_2(CH_2OCH_2)_4CH_2$ (**9b**)

In MeCN, the *Z* isomer of dye **1a** existing in photostationary equilibrium with the *E* isomer was obtained as the only product. The visible light irradiation of a thin polycrystalline film of this dye affords another product, *viz.*, the only *rctt* stereoisomer of the cyclobutane derivative, in quantitative yield (Scheme 3, type **A**). This product corresponds to the PCA reaction of two dye molecules in the *syn*-head-to-tail dimeric pair. Isomers of type **A** of cyclobutane derivatives were prepared also by irradiation of thin polycrystalline films of styryl dyes of the quinoline series **9a,b**.[22] It was hypothesized that the ability of dyes **1a** and **9a,b** to be involved in the solid-state PCA reaction is determined by two factors. First, the tendency of these dyes to form pairs of molecular cations (stacking dimeric pairs) in a *syn*-head-to-tail fashion due to the pronounced intramolecular charge transfer and the strongest intermolecular interaction between the p_z orbitals of the conjugated fragments results in that the ethylenic bonds are brought into proximity and are arranged in an antiparallel fashion. Second, the presence of flexible crown-ether moieties, perchlorate anions, and solvent molecules gives rise to a loose labile shell about the dimeric pair, which can reduce strains as a result of substantial shifts of the atoms in the course of PCA. An investigation of the characteristic features of PCA for a large series of dyes **1—5** provides a deeper insight into the factors responsible for high efficiency and stereoselectivity of this reaction.

Scheme 3



1a—f, 2a, 3a,c—e → **A_{1a-f}, A_{2a}, $A_{3a,c-e}$**

syn-Head-to-tail dimeric pair → *rctt* Cyclobutane isomer (type **A**)

▷ is the pyridine fragment; ◯ is the benzene fragment

We compared the ability of homologous crown-containing styryl dyes **1a—f** to be involved in the PCA reaction under similar conditions. The influence of the length and branching of the substituent at the N atom, the size of the macrocycle, and the nature of the counterion on the efficiency of the photoreaction was investigated. For this purpose, samples of the dyes as thin polycrystalline films on glass were irradiated with visible light for 10 h followed by the analysis of the photolysis products by the NMR method. These experiments showed (Table 1) that in all cases, cyclobutane derivatives of type **A** were obtained as the only photoproducts, which corresponds[20] to the cycloaddition in *syn*-head-to-tail dimeric pairs of these dyes. The nature of the anion (perchlorate in **1a** or iodide in **1b**) has an insignificant effect on the rate of the PCA reaction.

Table 1. Spectroscopic characteristics of dyes **1a—f**, **2a,b**, **3a—h**, **4**, **5**, and **9a,b**, the ratios of the isomers of the cyclobutane derivatives, and the degrees of conversion (x) in thin polycrystalline films of the dyes under visible light irradiation for 10 h

Dye	λ_{max}/nm (ε/L mol^{-1} cm^{-1})[a]	Ratio of isomers[b] **A** : **B** : **C** : **D**	x[b] (%)
1a	399 (30800)	1 : 0 : 0 : 0	87
1b	400 (28900)	1 : 0 : 0 : 0	91
1c	401 (37300)	1 : 0 : 0 : 0	64
1d	400 (42900)	1 : 0 : 0 : 0	44
1e	398 (23500)[c]	1 : 0 : 0 : 0	85
1f	397 (29400)	1 : 0 : 0 : 0	88
2a	398 (41100)	1 : 0 : 0 : 0	27
2b	472 (37800)	0 : 0 : 0 : 0	0
3a	397 (39900)	1 : 0 : 0 : 0	92
3b	472 (43700)	0 : 0 : 0 : 0	0
3c	345 (35500)	1 : 0 : 0 : 0	48
3d	381 (36200)	1 : 0 : 0 : 0	88
3e	393 (37100)	1 : 0 : 0 : 0	85
3f	342 (37800)	1.7 : 1 : <0.1 : <0.1	77
3g	343 (47800)	2.3 : 1 : <0.1 : <0.1	35
3h	328 (39800)[d]	1.9 : 1 : 4.7 : 2.2	35
4	408 (48200)[e]	0 : 0 : 0 : 0	0
5	427 (34600)	1 : 0 : 0 : 0	84
9a[f]	440 (23200)	1 : 0 : 0 : 0	70
9b[f]	434 (33900)	1 : 0 : 0 : 0	83

[a] MeCN, $C = 5 \cdot 10^{-5}$ mol L^{-1}, ~20 °C.
[b] From the ^{1}H NMR spectrum.
[c] $CHCl_3$, $C = 5 \cdot 10^{-5}$ mol L^{-1}, ~20 °C (sh ~420 nm).
[d] A broad charge transfer band at 470 nm (ε = 850 L mol^{-1} cm^{-1}).
[e] MeCN, $C = 2.5 \cdot 10^{-5}$ mol L^{-1}, ~20 °C.
[f] The published data.[22]

Apparently, the size of the anion and its ability to be aligned to the environment, which changes in the course of PCA, is of little importance in the case of crown-containing dyes, because the flexible crown-ether moieties serves this function by providing a sufficient looseness of the molecular packing. The replacement of the pyridine fragment (compound **1a**) with the more extended quinoline fragment (compound **9b**) also has only a slight effect on the rate of PCA. Other parameters important for the photoreaction, such as the closely spaced arrangement of two molecules of a styryl dye in the parallel planes and the close proximity of their ethylenic bonds, substantially depend on the length and branching of the substituent at the N atom. For example, the presence of the *n*-butyl substituent in dye **1c** leads to a substantial decrease in the rate of PCA compared to dye **1b** containing the *N*-ethyl group. The branching at the first carbon atom of the *N*-substituent in crown ether **1d** makes the conversion into the cyclobutane derivative even more difficult. Evidently, a long or bulky substituent is unfavorable for the closely spaced arrangement of C=C bonds in the dimeric pair of the dye. However, the steric factor is weakly pronounced in the case of amphiphilic dye **1e** containing the *N*-octadecyl substituent. The presence of this long hydrocarbon fragment most likely ensures the preorganization of the dye molecules for the PCA reaction by assisting in bringing into proximity the polar chromophoric fragments in a nonpolar environment. These effects of the concentration of the reaction centers are typical of micelles and monolayers of amphiphilic compounds.[25] Changes in the length of substituents (with retention of their electron-donating nature) at another end of the styryl chromophore (in the benzene ring) have no substantial effect on the rate of the PCA reaction. Compared to crown ether **1a**, the decrease in the size of the macrocycle in crown ether **1f** or even the replacement of the macrocycle by two methoxy groups (compound **3a**) has virtually no influence on the high degree of conversion of the above-mentioned dyes into cyclobutane derivatives (87—92% during 10 h). These results provide indirect evidence that the perchlorate ions play a considerable role in the solid-state photoreaction. In the absence of flexible polyether fragments, these anions can also create a rather loose environment about the dimer pairs of cations and/or efficiently reduce the steric strain that appears in the course of PCA.[20,22]

The ability of related styryl dyes **2a,b** and **3a—h**, which contain various substituents in the benzene ring instead of the crown-ether moiety and differ in the nature of the counterion, to undergo PCA was investigated under comparable conditions (see Table 1).

Unlike dyes **1a,b**, in which the influence of the counterion is not manifested, the related pair of dyes **2a** and **3a**, in which two methoxy groups reproduce, on the whole, the electron-releasing effect of the crown-ether moiety, shows a difference in the rate of the photoreaction (a noticeable decrease in the case of iodide **2a**). The absence of flexible macrocyclic fragments and, consequently, the absence of loose regions in the packing created by these fragments can enhance the role of the anion in the rearrangement of the environment in the course of PCA. The spherical shape of the I^- ion and its tendency to form numerous secondary contacts with the nearest atoms[26,27] can hinder the rearrangement of weak interatomic interactions with this ion and do not allow the latter to efficiently compensate the strain created in the molecular packing of dye **2a** by the PCA reaction. It should be noted that the PCA reaction does not proceed at all in single crystals of **2a** (see below). In this case, a rather large distance between the C=C bonds in the adjacent dye molecules within the dimeric pair (4.18 Å), which is close to the limiting value for the cycloaddition reaction, has a considerable effect. Assuming that this dye has the same molecular packing in films, an alternative explanation can be given for a substantial decrease in the rate of the photocycloaddition compared to the rate of this reaction in perchlorate **3a**, in which the above-mentioned distance is 3.72 Å. However, the molecular arrangement in

polycrystalline films is less rigid than that in single crystals, and substantial thermal vibrations of atoms and fragments and even the movement of molecules as a whole with respect to each other can occur. Because of this, the PCA reaction was observed for dye **2a**. It should be noted that the elemental analysis data for the cyclobutane derivatives prepared from iodides **1b,c** appeared to be satisfactory for photoadducts, in which either a part or all iodine atoms exist in the oxidized state (see the Experimental section). Apparently, the irradiation of dye films is accompanied by the photooxidation of I^- to IO_3^- (or oxides of another composition) with atmospheric oxygen.[28,29] Presumably, an analogous reaction slowly proceeds in films of dye **2a**, resulting in the rearrangement of the molecular packing, and, apparently, promotes the PCA reaction.

A comparison of the influence of the substituents in the benzene rings of styryl dyes **3** on the PCA reaction shows that the latter substantially depends on the nature of these substituents and their size. Dyes **3a,d,e** containing electron-releasing substituents conjugated with the chromophore undergo the most rapid phototransformation. Undoubtedly, this is associated with a substantial absorption of these dyes in the visible spectral region due to an efficient electron density transfer from the electron-releasing benzene ring to the electron-withdrawing heterocyclic fragment.[30] This increases the efficiency of the photoreaction under visible light irradiation. In the case of unsubstituted dye **3c**, the degree of conversion into the cyclobutane derivative is substantially lower in accordance with the shift of the long-wavelength absorption maximum to the near-UV region compared to that for dyes **3a,d,e**. An analogous dependence is observed for dyes **3f,g,h** containing electron-withdrawing substituents. The absorption maximum for the latter compounds is shifted to even shorter wavelengths because the electron density transfer from the benzene ring to the pyridine fragment is less favorable than that in dye **3c** (see Table 1). It should be emphasized that the rate of the PCA reaction of dichloro derivative **3f** decreases to a lesser extent than that in the case of dyes **3a,d,e**. Apparently, the presence of a substituent at position 3 of the benzene ring directed away from the line of the chromophore results in the formation of a looser molecular packing of styryl dye **3f**, which promotes the PCA reaction. An analogous, but less pronounced, effect is observed for 3,4-disubstituted dye **3a** compared to 4-monosubstituted dyes **3d,e**. In a film of dye **3f**, the PCA reaction is accompanied by the *E*—*Z* isomerization (according to the ^{1}H NMR data, the *E* to *Z* isomer ratio is 65 : 35 after irradiation for 10 h), which indirectly confirms the looseness of the molecular packing of this dye.

Interestingly, bis(styryl) dye **4** containing perchlorate anions and two styryl chromogens identical to the chromogen of dye **3a** is not involved in the solid-state PCA reaction (see Table 1). Such a sharp change in the reactivity compared to related dye **3a** is, apparently, attributed to the mode of binding of two styryl moieties and the rigidity of the *para*-xylyl spacer. The close proximity of the cationic centers should hinder the formation of intramolecular *syn*-head-to-head dimeric pairs due to Coulomb interactions between like-charged fragments. In addition, the intramolecular formation of the cyclobutane derivative in the case of compound **4** would be hindered by the presence of the strongly strained ring containing the conformationally rigid *para*-xylyl moiety in the photoadduct. It should be noted that the related bis(styryl) dye of the pyridine series containing two 18-crown-6 moieties and the *meta*-xylyl spacer can undergo the intramolecular PCA reaction in solution (see Scheme 1). In this case, the preorganization of styryl chromogens into a pseudosandwich *syn*-head-to-head complex is favored by the complexation of crown-ether moieties of the dye with the diammonium compound.[18] Apparently, the intermolecular oligomerization accompanied by the formation of dimeric pairs by the styryl fragments of the adjacent molecules of dye **4** through *syn*-head-to-tail stacking interactions (which is more favorable in view of electrostatic interactions) does not proceed in the solid state as well. If this were not so, the PCA reaction in such oligomeric structures would lead to the partial or complete polymerization of the dye.

Dyes **2b** and **3b** bearing the dimethylamino group in the benzene ring appeared to be nonreactive under these conditions in spite of the most considerable and efficient absorption in the visible region among all the compounds under study (see Table 1). As mentioned in the discussion of the X-ray diffraction data, these dyes are packed exclusively in a head-to-head fashion, and the PCA reaction cannot proceed because of a large distance between the ethylenic bonds of the adjacent molecules (>6.4 Å). However, it should be emphasized that the photostability of styryl dyes containing the nitrogen atom conjugated with the chromophore is, most likely, determined by the nature of the chromophore rather than by the packing mode. This is evidenced by the fact that PCA does not proceed in the related azacrown-containing dyes bearing the nitrogen atom conjugated with the styryl chromophore, which we have studied earlier.[21,31] It was also noted that the internal conversion with the retention of the *trans* configuration of the chromogen is the major relaxation pathway for the excited state of dyes of type **3b**,[32] whereas the efficient *E*→*Z* isomerization is typical of dyes of types **1a** and **3a**.[20] Hence, the unusual stability of such dyes is probably attributed to the strong (compared to other heteroatoms) electron-donating properties of the nitrogen atom, resulting in an increase in the energy of conjugation in the chromophore and, consequently, hindering the chain cleavage in the course of PCA. It should be noted that the photooxidation of the iodide ions in dye **2b**,

as opposed to those in dyes **1b,c**, is not observed taking into accout that the elemental analysis data for the compound before and after the irradiation of a thin film for 150 h are virtually identical.

Styryl dyes of the benzothiazole (**5**) and quinoline (**9a**) series bearing two methoxy groups in the benzene ring show a considerable decrease in the rate of the PCA reaction in polycrystalline films compared to the rate of the phototransformation of analogous dye **3a** of the pyridine series (see Table 1). Apparently, this tendency can be attributed to an increase in the steric hindrance that appears in the course of PCA as a result of a change in the position of the bulkier heterocycle, although the more extended conjugated system of the benzothiazole or quinoline moiety can partially compensate a decrease in the flexibility of these fragments due to stronger stacking interactions in the dimeric pair and, consequently, the closer proximity of the ethylenic bonds; the fact that the *N*-substituent points away from the line of the chromophore in compound **5** can also be responsible for the looser packing allowing a decrease in the steric strain upon the formation of the cyclobutane derivative.

It is important that the visible light irradiation of polycrystalline films of most of the dyes over a long period of time (up to 100 h) leads to the complete transformation of the starting compounds into cyclobutane derivatives (NMR monitoring).

An analysis of the ^{1}H NMR spectra of the cyclobutane derivatives showed that the photoreactions of dyes **2a** and **3a,d,e** bearing electron-releasing substituents in the benzene ring and of unsubstituted dye **3c** proceed stereospecifically (Fig. 1, *a*). Cyclobutane derivatives of type **A** were obtained as the only irradiation products of these dyes in films, as in the case of crown-containing dyes **1a—f** (see Scheme 3). The photoreactions of dyes

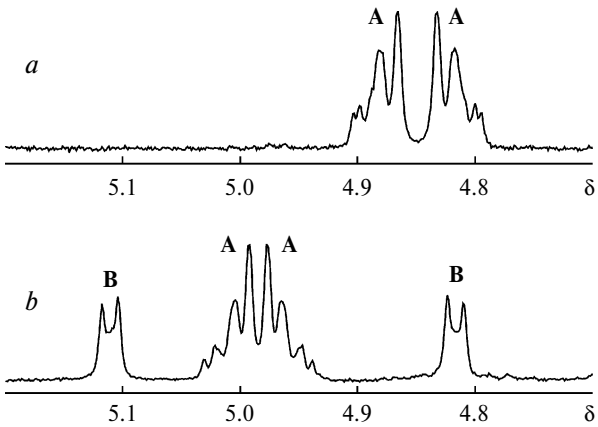
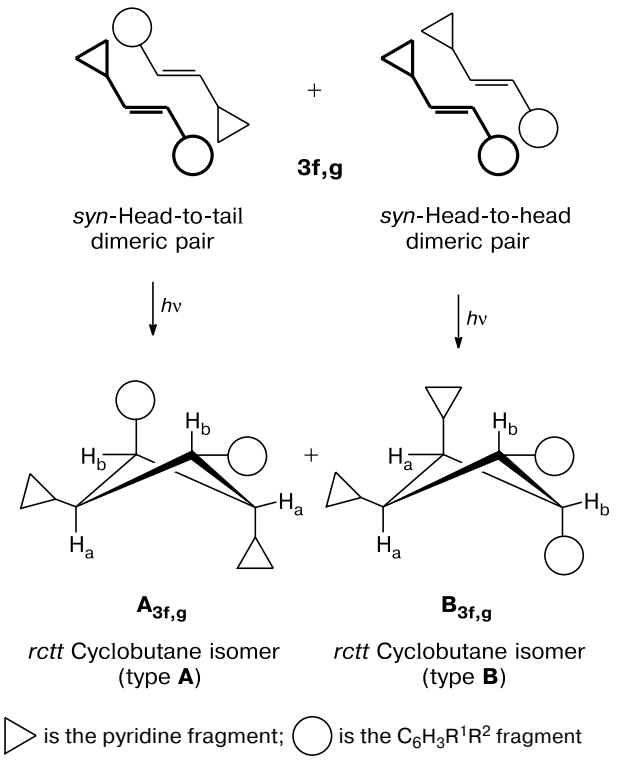


Fig. 1. ^{1}H NMR spectra (DMSO-d_6, 25 °C, the region of cyclobutane protons) of the photoproducts prepared by irradiation of thin films of dyes **3d** (*a*) and **3f** (*b*) for 10 h (cyclobutane isomer $\mathbf{A_{3d}}$ for compound **3d** and a mixture of isomers $\mathbf{A_{3f}}$ and $\mathbf{B_{3f}}$ in a ratio of 1.7 : 1 for compound **3f**).

containing electron-withdrawing substituents are less stereoselective. The NMR spectra of the photolysis products of dyes **3f,g** show two main sets of signals corresponding to the protons of two *rctt* isomers of cyclobutane derivatives (Fig. 1, *b*). In both cases, isomer of type **A** corresponding to the cycloaddition in the *syn*-head-to-tail dimeric pairs (*E*)-**3f,g** was obtained as the major isomer (an AA´BB´ spin system for the cyclobutane protons, two doublets of doublets with $^3J_{cis\text{-}H_a,H_b}$ = 8.8—9.2 Hz, $^3J_{trans\text{-}H_a,H_b}$ = 5.3—6.1 Hz). The second isomer (type **B**) corresponds to the PCA reaction in the *syn*-head-to-head dimeric pairs (*E*)-**3f,g** (an AA´BB´ spin system, two multiplets with $^3J_{trans\text{-}H_a,H_b}$ = 6.7 Hz) (Scheme 4). The positions, multiplicities, and the spin-spin coupling constants for the signals of the cyclobutane protons in the spectra of the photoadducts of type **B** are similar to the corresponding characteristics of the analogous *syn*-head-to-head isomers of cyclobutane derivatives, which we prepared by the PCA reaction in solution for the complexes of crown-containing 2-styrylbenzothiazole and a bis(styryl) dye of the pyridine series.[18,33]

Scheme 4



The irradiation of a film of dye **3h** containing the bulky $N^+(Et)Me_2$ group afforded a more complex mixture of the major photoproducts (Scheme 5). An analysis of the signals for the pyridine protons in the ^{1}H NMR spectrum of the photolysis product showed the presence

of six compounds. Two of these compounds appeared to be the *E* and *Z* isomers of compound **3h** in a ratio of 9 : 1, the signals of the ethylene protons of the latter being observed as two doublets at δ 6.96 and 7.26 with the typical coupling constants $^3J_{cis\text{-}HC=CH}$ = 12.2 Hz. As in the spectra of other dyes containing electron-withdrawing substituents, characteristic signals for the protons of two *rctt* cyclobutane isomers are observed at δ 4.9—5.2 (Fig. 2), which corresponds to the cycloaddition in the *syn*-head-to-tail dimeric pairs (*E*)-**3h** (type **A**, $^3J_{cis\text{-}H_a,H_b}$ = 7.1 Hz, $^3J_{trans\text{-}H_a,H_b}$ = 4.5 Hz) and the *syn*-head-to-head dimeric pairs (type **B**, $^3J_{trans\text{-}H_a,H_b}$ = 6.5 Hz). However, these isomers were the minor products, whereas two new *rtct* cyclobutane isomers generated in the photoreaction in the *anti*-head-to-tail dimeric pairs (*E*)-**3h** (type **C**, an A_2B_2 spin system, two triplets with $^3J_{trans\text{-}H_a,H_b}$ = 9.7 Hz) and the *anti*-head-to-head dimeric pairs (type **D**, an AA´BB´ spin system, two multiplets with $^3J_{trans\text{-}H_a,H_b}$ = 10.0 Hz) were the major products. Cyclobutane derivatives **C** have been synthesized in our earlier study by the photolysis of metal complexes of betaines of crown-containing styryl dyes of the benzothiazole series in solution; the characteristics of the signals for the cyclobutane protons of the *rtct* isomers of types **C** and **D**, which were synthesized from dye **3h**, are similar to both those described in the literature[34—36] and the calculated[37] parameters. It should be noted that the packing mode of this dye in the single crystals is favorable for the formation of isomers of type **D** in the PCA reaction (see the discussion of the X-ray diffraction data). The signals for the cyclobutane protons of the isomers of types **C** and **D** are observed at higher field (at δ 4.2—4.4; see Fig. 2) compared to the signals of the isomers of types **A** and **B**, which is associated with the *trans* arrangement of the adjacent substituents in the cyclobutane rings of the first two isomers. It should be emphasized that the low-intensity signals at δ 4.1—4.4 are observed also in the spectra of irradiated samples of dyes **3f,g**, which is indicative of the formation of cyclobutane isomers **C** and **D**.

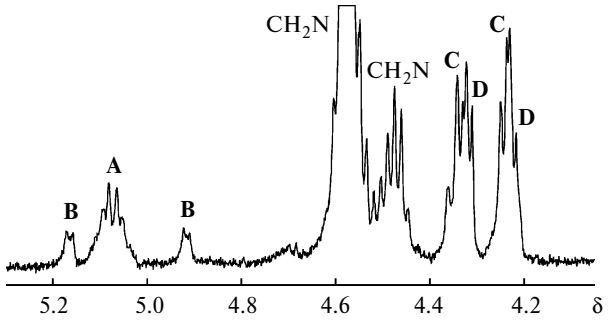
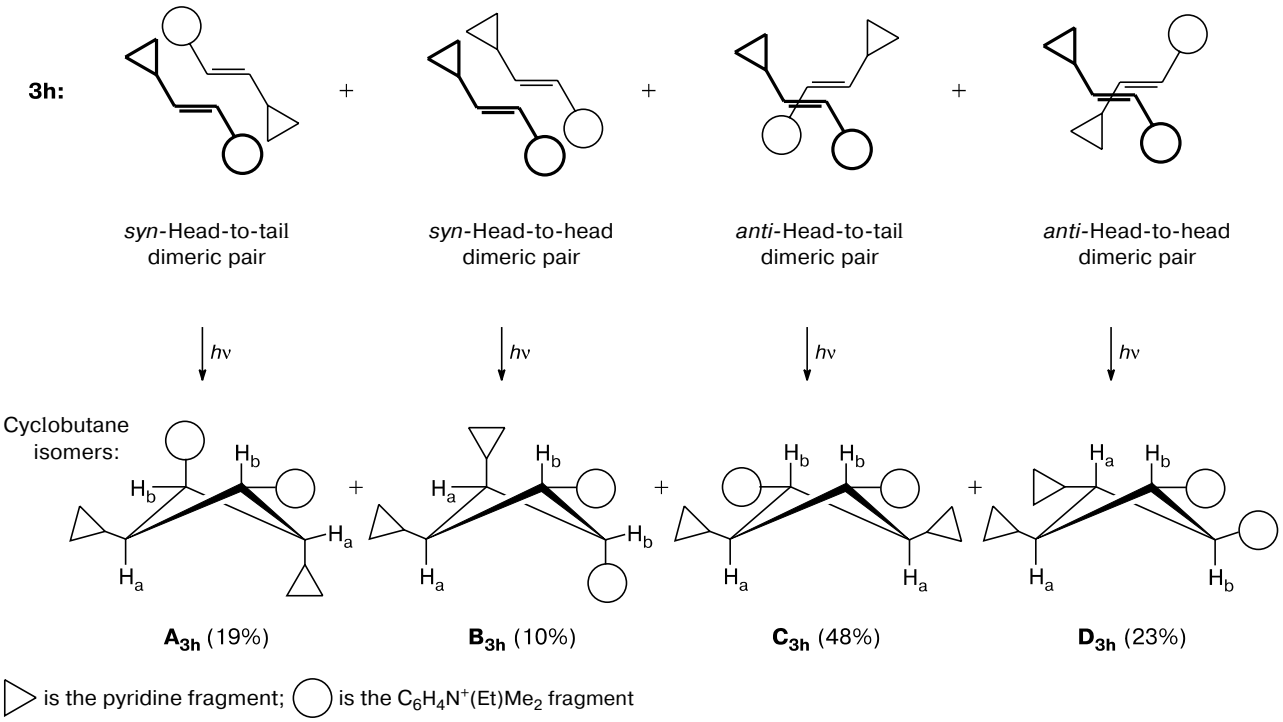


Fig. 2. ^{1}H NMR spectrum (DMSO-d_6, 25 °C, the region of cyclobutane protons) of the photoproducts prepared by irradiation of a thin film of dye (*E*)-**3h** for 110 h (a mixture of *rctt* and *rtct* cyclobutane isomers $\mathbf{A_{3h}}$—$\mathbf{D_{3h}}$ in a ratio of 1.9 : 1 : 4.7 : 2.2).

The tendency of styryl dyes **3f—h** containing electron-withdrawing substituents to form dimeric pairs with different mutual orientations of the *E* isomers is, apparently,

Scheme 5



associated with the less pronounced intramolecular charge transfer compared to that in dyes, which contain electron-releasing substituents and, consequently, make the smaller donor-acceptor contribution to the stacking interactions between the conjugated fragments. In the case of dye **3h** bearing the bulky electron-withdrawing substituent, the parallel *syn* orientation of the molecules is also hindered, resulting apparently in the predominant formation of the cross-like *anti* orientation with an overlapping only in the central part of the styryl chromogens.

The photoreaction of dye **5** affords cyclobutane derivative **A** as the only product, which corresponds to the PCA reaction proceeding in the *syn*-head-to-tail dimeric pair. However, as opposed to cyclobutane derivatives based on dyes of the pyridine and quinoline series, the *rctt* cyclobutane isomer derived from **5** undergoes the fast isomerization (completed in several hours) in CD_3CN or DMSO-d_6, resulting in the complete disappearance of the isomer of type **A**. The analysis of the compositions of the isomerization products presented difficulties because of a strong overlapping of the sets of signals corresponding to protons of three or more new cyclobutane derivatives. Evidently, a rather high acidity of the protons of the cyclobutane ring adjacent to the benzothiazolium moieties promotes the deprotonation of these carbon atoms of the cyclobutane fragment followed by their inversion. Earlier,[20] we have observed this behavior of the cyclobutane derivative of type **A** prepared from dye **1a**. The presence of a base is required for the isomerization in cyclobutane derivatives containing pyridinium fragments; in the case of benzothiazolium derivatives, the close proximity of the cationic center, apparently, facilitates the deprotonation of the cyclobutane moiety.

Therefore, as follows from our investigations on polycrystalline films of styryl dyes, to increase the efficiency and stereoselectivity of the visible light-induced [2+2] photocycloaddition, the dye molecule should have the following structural characteristics: (1) the presence of a not too bulky heterocyclic moiety, which increases its mobility in the course of considerable structural rearrangements of the compound; (2) the presence of an electron-releasing O- or S-substituent conjugated with the chromophore in the benzene ring, which leads to a shift of absorption of the dye to the visible spectral region and is favorable for the arrangement of the dye molecules in the *syn*-head-to-tail dimeric pairs due to the more pronounced intramolecular charge transfer; (3) the presence of structural units, which can allow the reaction centers to come into close proximity in the course of the PCA reaction.

X-ray diffraction analysis. As mentioned above, the solid-state PCA reactions of unsaturated compounds can proceed only if the necessary conditions are met, such as the approximately parallel (or antiparallel) mutual arrangement of the ethylene fragments of two adjacent structural units at distances shorter than 4.2 Å.[11,14,38] Earlier,[20,21,39—42] we have found that the stacking mode is the only crystal packing for crown-containing unsaturated dyes. In the framework of this stacking mode, stacks with both the centrosymmetric *syn*-head-to-tail arrangement and the translationally related *syn*- and *anti*-head-to-head arrangement of the dye molecules can exist, the first type of stacks (with the arrangement of the molecules suitable for the PCA reaction) being observed much more frequently. Single crystals were grown for most of the compounds considered in the present study. A brief analysis of the main packing modes and their relationship with the reactivity of dyes in thin polycrystalline films is given below. These packing modes were discussed in detail in the study[23] in connection with the possibility of the topochemical [2+2] photocycloaddition reaction proceeding without degradation of single crystals, as has been earlier exemplified[20,22] for the single crystals of styryl dyes **1a** and **9a**.

The structures of the formula units in the crystals of dyes **1b**, **2a,b**, **3a—h**, and **5** are shown in Figs 3 and 4. Some of these dyes form both solvated and unsolvated forms; benzene, MeCN, and water serve as the solvent molecules. In all cases, the ethylenic bond in the dyes is in the *trans* configuration, and the conjugated fragment is almost planar as a whole, which is indicative of a high degree of conjugation over the chromophore. In some structures, the central fragment of the cation is disordered over two positions corresponding to two *s* conformers occupying the same sites in the crystal lattice. In all structures, the ethylene fragment is essentially localized; the C=C bond length varies from 1.24 to 1.37 Å, whereas the lengths of the adjacent formally single bonds are in a range of 1.42—1.66 Å.

Of all the crown-containing dyes synthesized in the present study, we succeeded in growing two forms of single crystals only of iodide **1b** (yellow long blocks and plates) in a single sample. The former type of crystals (**1b** · C_6H_6 · H_2O) was obtained as the major form (~80—90%); the latter (unsolvated form **1b**), as the minor form. These forms differ in the packing mode of the dye molecules and are examples of the two most widespread stacking modes typical also of all other dyes under study (except for **3c** · C_6H_6 and **3h**). The detailed consideration of these crystal forms is given below.

The fragment of the stacking mode in the crystals of **1b** · C_6H_6 · H_2O is shown in Fig. 5, *a*. In the crystals of this compound, the cations of the dye are arranged in a *syn*-head-to-tail fashion, which is most favorable from the standpoint of minimization of the Coulomb repulsion between the like-charged fragments and the maximum secondary interactions between the p_z orbitals of the conjugated fragments. This is characteristic of unsaturated dyes belonging to intramolecular charge-transfer systems. The stacks run along the crystallographic *b* axis, and each

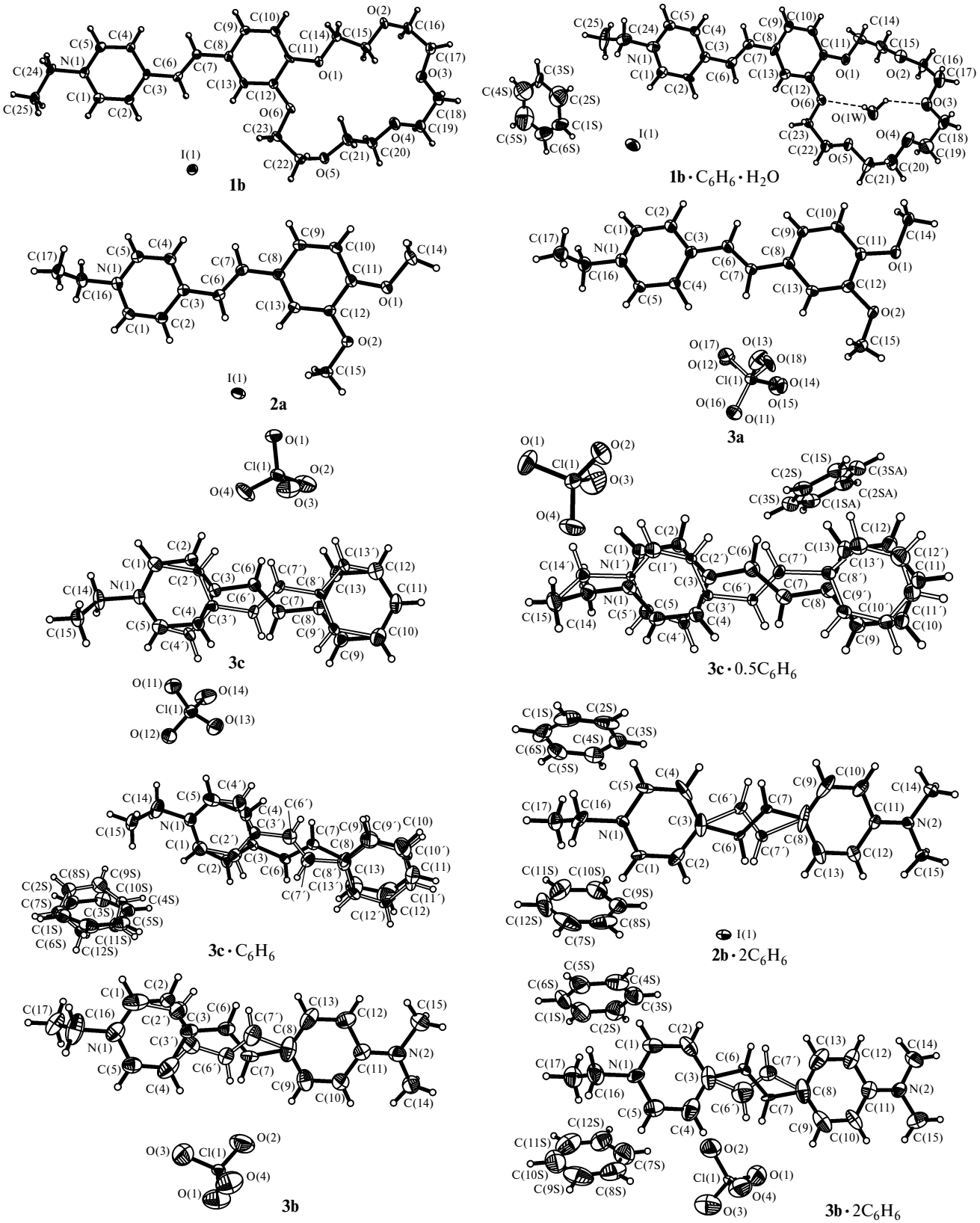


Fig. 3. Structures of dyes **1b**, **1b** · C_6H_6 · H_2O, **2a**, **3a**, **3c**, **3c** · 0.5C_6H_6, **3c** · C_6H_6, **2b** · 2C_6H_6, **3b**, and **3b** · 2C_6H_6. For the structures of **1b** · C_6H_6 · H_2O, **2b** · 2C_6H_6, **3b**, **3b** · 2C_6H_6, and **3c** · C_6H_6, the thermal ellipsoids are drawn at the 40% probability level; for the other structures, at the 50% probability level.

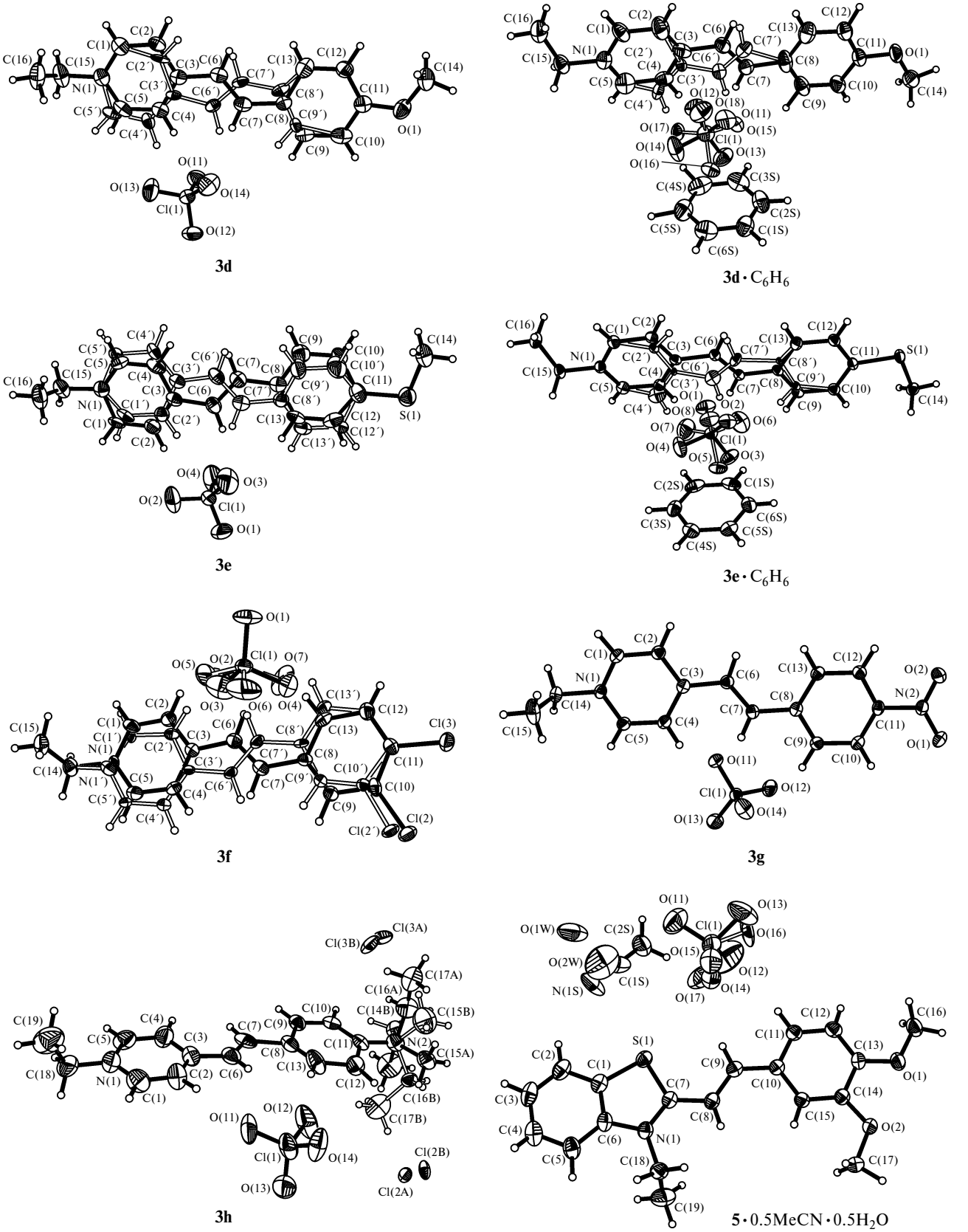


Fig. 4. Structures of dyes **3d**, **3d** · C_6H_6, **3e**, **3e** · C_6H_6, **3f—h**, and **5** · 0.5MeCN · 0.5H_2O. For the structure of **3h**, the thermal ellipsoids are drawn at the 15% probability level; for the other structures, at the 50% probability level.

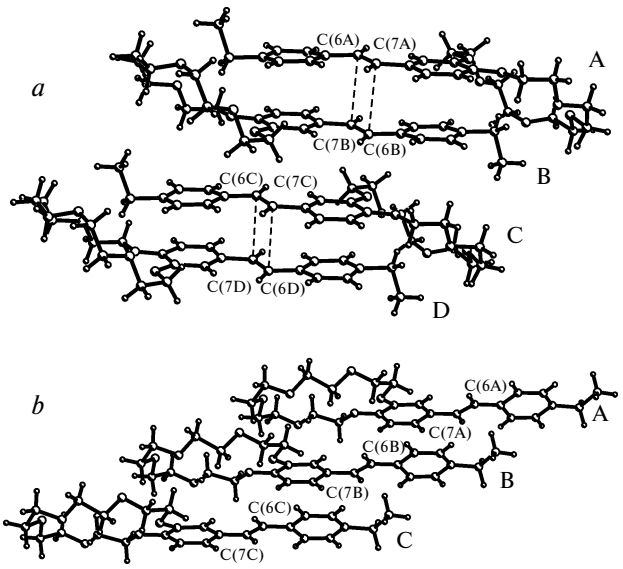


Fig. 5. Fragment of the stacking arrangement in the crystal structures of **1b** · C_6H_6 · H_2O (*a*) and **1b** (*b*).

pair of the adjacent cations in the stacks (A and B, B and C, C and D) (see Fig. 5, *a*) is related by a center of symmetry. The centers of symmetry in the stacks alternately belong to two different crystallographic systems. This, in fact, means that the stacks are divided into dimeric pairs of cations (stacking dimeric pairs), in which the distance between the ethylenic bonds d_1 is shorter than the distance between the ethylenic bonds of the adjacent dimeric pairs d_2 (Scheme 6, *a*). In the crystals of **1b** · C_6H_6 · H_2O, the distances d_1 and d_2 are 3.65 and 5.52 Å, respectively. Therefore, the stacking dimeric pairs of dye **1b** are preorganized for the PCA reaction, because the centrosymmetric arrangement of the adjacent molecular cations implies that the ethylenic bonds in the cations are in the antiparallel arrangement and the distance between the atoms of the ethylenic bonds in the stacking dimeric pair is substantially smaller than the upper limiting value suitable for the PCA reaction. The efficient photoreaction in a thin polycrystalline film of dye **1b** giving rise to centrosymmetric *rctt* cyclobutane isomers of type **A** (see Table 1) is indicative of a similar crystal packing in this film.

Earlier, the same structural packing mode has been found[20,22] in the crystals of **1a** · H_2O and **9a** · $0.5C_6H_6$, for which the cyclobutane derivatives of type **A** produced in the single crystal—single crystal PCA reaction were detected. The stacking modes of the molecular cations in a *syn*-head-to-tail fashion were found also in the crystals of **2a**, **3a**, **3c**, **3c** · $0.5C_6H_6$, **3d—g**, and **5** · 0.5MeCN · $0.5H_2O$. For most of these crystals, the stacks of the cations are clearly divided into stacking dimeric pairs with the distances d_1 varying in a range of 3.49—3.83 Å (Table 2), which correlates with the efficient and stereospecific PCA reaction proceeding in polycrystalline films of almost all

Table 2. Stacking modes in the crystal structures and the distances between the adjacent ethylene fragments (d_1 and d_2) in the unsolvated and solvated forms of dyes **1a,b**, **2a,b**, **3a—h**, **5**, and **9a**

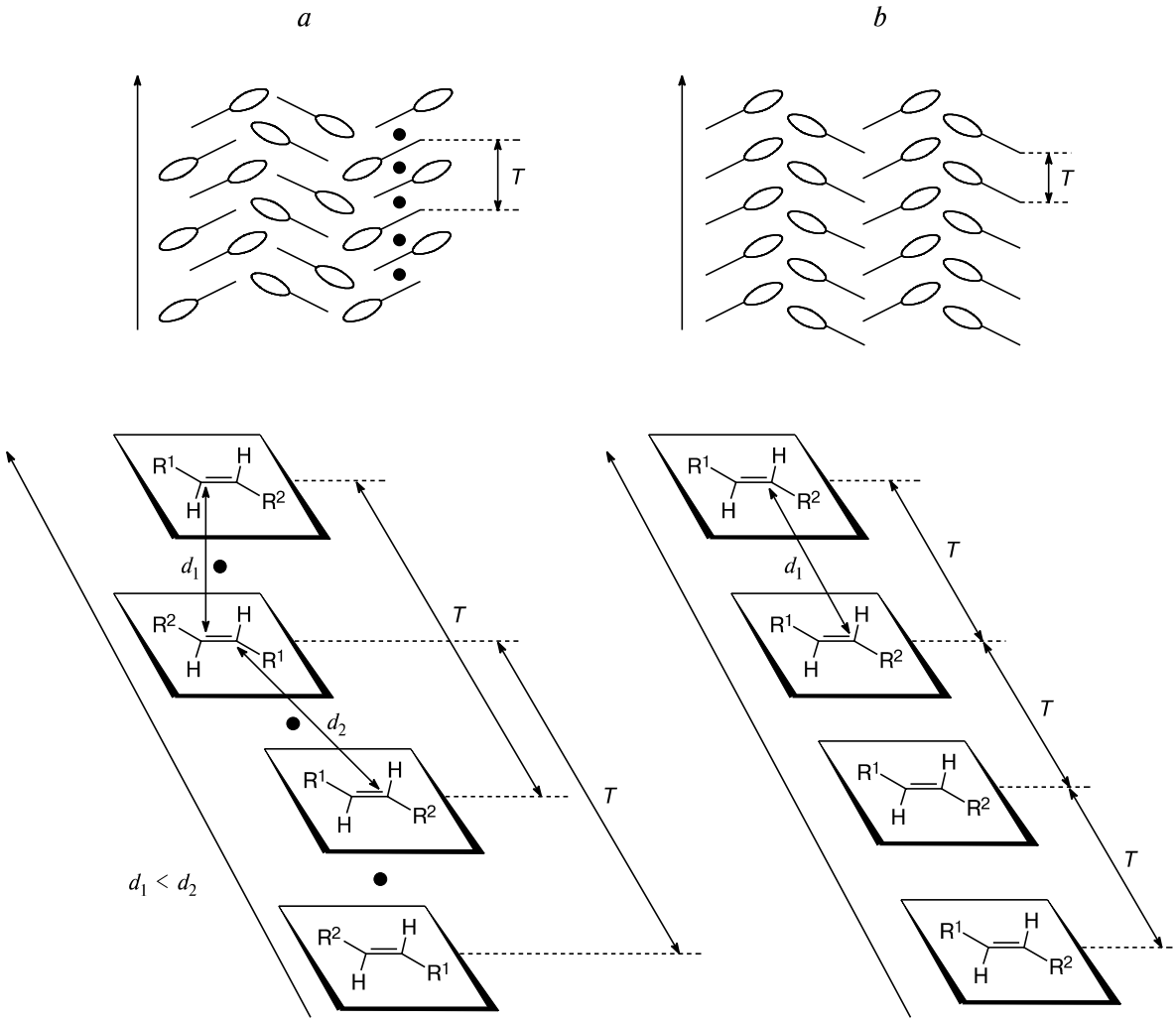
Structure	Stacking mode	d_1, d_2*/Å
1a · H_2O	*syn*-head-to-tail	3.55, 6.61
1b	*syn*-head-to-head	6.70
1b · C_6H_6 · H_2O	*syn*-head-to-tail	3.65, 5.52
2a	*syn*-head-to-tail	4.18, 6.86
2b · $2C_6H_6$	*syn*-head-to-head	6.47
3a	*syn*-head-to-tail	3.72, 3.73
3b	*syn*-head-to-head	6.87
3b · $2C_6H_6$	*syn*-head-to-head	6.48
3c	*syn*-head-to-tail	3.66, 3.91
3c · $0.5C_6H_6$	*syn*-head-to-tail	3.65, 5.39
3c · C_6H_6	*syn*-head-to-tail**	3.76
3d	*syn*-head-to-tail	3.83, 4.20
3d · C_6H_6	*syn*-head-to-head	6.57
3e	*syn*-head-to-tail	3.52, 4.76
3e · C_6H_6	*syn*-head-to-head	6.66
3f	*syn*-head-to-tail	3.62, 4.44
3g	*syn*-head-to-tail	3.71, 4.59
3h	*anti*-head-to-head	3.30—3.48, 5.95
5 · 0.5MeCN · · $0.5H_2O$	*syn*-head-to-tail	3.57, 3.87
9a · $0.5C_6H_6$	*syn*-head-to-tail	3.49, 3.76

* For the major *s* conformer.
** The herringbone-sandwich packing.

the above-mentioned dyes. The crystal of dye **2a** is an exception. In the crystal structure of **2a**, the distance d_1 is 4.18 Å, which is virtually equal to the upper limiting value for the PCA reaction (4.2 Å) and is consistent with a considerable decrease in the rate of the photoreaction in a film of this dye (see Table 1). This difference is apparently attributed to the structure-forming influence of the I^- ion, which is prone to form C—H...I^- secondary bonds,[26,27] resulting in the orientation of the molecular cations in the centrosymmetric dimeric pair untypical of styryl dyes.[23] It should also be noted that the molecular arrangement in the crystals of dyes **3f,g** containing electron-withdrawing substituents in the benzene ring is, apparently, different from that in their polycrystalline films. The simultaneous formation of isomers **A** and **B** of cyclobutane derivatives is indicative of an either less ordered arrangement of the molecules in the films of these compounds compared to their single crystals or the fact that, when performing the X-ray diffraction study, we did not select crystals with other types of the molecular arrangement from a mixture of crystals because of their poor quality.

The fragment of the stacking mode in the minor crystal form of unsolvated **1b** is shown in Fig. 5, *b*. The stacks of the molecular cations in these crystals are translationally related and belong to the second most abundant packing

Scheme 6



Note. The stacking arrangement of the dye cations in the crystals of **1b** · C_6H_6 · H_2O (*a*) and **1b** (*b*) represented in two ways: the crown-ether moieties are indicated by ovals, the conjugated fragments are shown by lines, *T* are translations along the crystallographic axis, ● are the centers of symmetry, and d_1 and d_2 are the distances between the ethylene fragments.

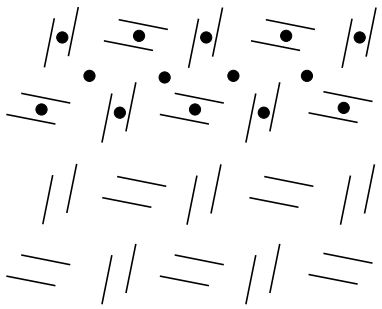
mode of styryl dyes, *syn*-head-to-head. In these stacks, the distances between the like atoms of adjacent cations, for example, between cations A and B, B and C, are equal (see Fig. 5, *b*), *i.e.*, the stacks are not divided into dimeric pairs (see Scheme 6, *b*). The translational relation between the adjacent cations in the stack implies the parallel mutual arrangement of their C=C bonds. However, the cations are strongly shifted in the parallel planes with respect to each other due to minimization of the Coulomb repulsions between the like-charged fragments with the partial retention of stacking interactions between the conjugated systems of the cations. This shift of the adjacent molecular cations in the stack results in an increase in the distance between the ethylene fragments, which is far outside the above-mentioned region suitable for the PCA reaction (d_1 = 6.70 Å). Actually, the prolonged irradiation of the crystals of dye **1b** does not lead to changes in their structure and quality, which is indicative of the absence of the photoreaction, as opposed to the crystals of **1b** · C_6H_6 · H_2O, which undergo degradation under visible light as a result of the PCA reaction.[23]

An analogous *syn*-head-to-head packing mode was found in the crystals of **2b** · $2C_6H_6$, **3b**, **3b** · $2C_6H_6$, **3d** · C_6H_6, and **3e** · C_6H_6. In all cases, the distances between the adjacent ethylenic bonds are in a range of 6.47—6.87 Å (see Table 2), which is unfavorable for the PCA reaction. For dyes **2b** and **3b** bearing the dimethylamino group in the benzene ring, this type of the crystal packing is, apparently, the most typical because it is independent of the nature of the counterion or the presence of solvent molecule in the unit cell. The fact that the photoreaction does not proceed in polycrystalline films of these

compounds may be associated with the absence of the geometric conditions favorable for the PCA reaction, although other factors may be responsible for high stability of dyes with this structure to light (see the discussion of the results of NMR spectroscopy). As can be exemplified by dyes **3d,e**, the highest-quality crystals grown from a benzene-containing mixture of solvents consist of stacks of translationally related molecules, which is unfavorable for the PCA transformation.

The following two types of crystals of dye **3c** were grown from a benzene-containing solvent mixture: crystals of hemisolvate **3c** · $0.5C_6H_6$ stable on storage under solvent-free conditions and crystals of monosolvate **3c** · C_6H_6, which undergo rapid degradation as a result of erosion. The sandwich-herringbone packing mode observed in the latter crystals is rare for styryl dyes. Earlier, we have found this packing mode only in one neutral precursor of styryl dyes, *viz.*, dimethoxy-substituted 4-styrylquinoline.[22] In the crystals of **3c** · C_6H_6, the cations of the dye form centrosymmetric *syn*-head-to-tail dimeric pairs with the possible efficient stacking interactions in the pairs but without these stacking interactions between the dimeric pairs (Scheme 7). The distance between the C=C bonds of two molecular cations in the dimeric pair (d_1 = 3.76 Å) and their antiparallel orientation implies that in this case, like in the crystals of **3c** and **3c** · $0.5C_6H_6$,[23] the dye molecules are preorganized for the PCA reaction giving rise to a cyclobutane derivative of type **A**.

Scheme 7



Note. The sandwich-herringbone arrangement of the dye cations in the crystals of **1c** · C_6H_6: the lines show the side projection of the conjugated fragment of the dye, ● are the centers of symmetry.

The unusual molecular packing was found in the crystals of styryl dye **3h**. Apparently, the presence of the double positive charge on the organic cation and the bulky $N(Et)Me_2$ substituent in the benzene ring hinder the formation of both the centrosymmetric packing mode and the packing mode consisting of translationally related molecules. The crystal packing of **3h** can be arbitrarily

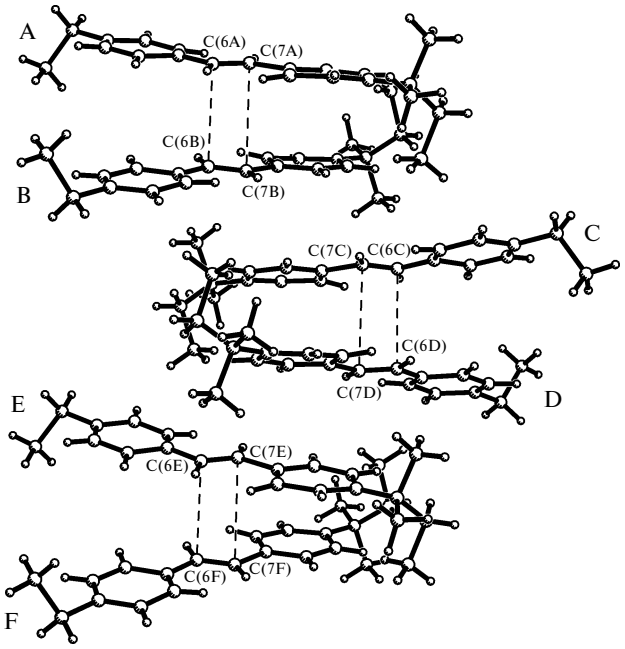


Fig. 6. Fragment of the crystal packing of dye **3h**. The disorder of the $N(Et)Me_2$ substituent is omitted.

described as stacks running along the *a* axis, and the stacks are divided into *anti*-head-to-head dimeric pairs of cations A and B, C and D, E and F (Fig. 6). The mean planes of the conjugated fragments of two molecular cations in the dimeric pair are almost parallel (the dihedral angle is 2°), and the carbon atoms of the ethylene fragments are spaced by 3.30—3.48 Å. As can be seen from Fig. 7, the ethylene fragments of the adjacent cations of **3h** in the dimeric pair are in a slightly staggered conformation. The angle of their mutual twisting is ~24°, which differs from the ideal value for the PCA reaction (0°; the parallel orientation). Cations B and C, D and E from the adjacent dimeric pairs are projected onto one another only by the benzene rings, but the spatial arrangement of these ben-

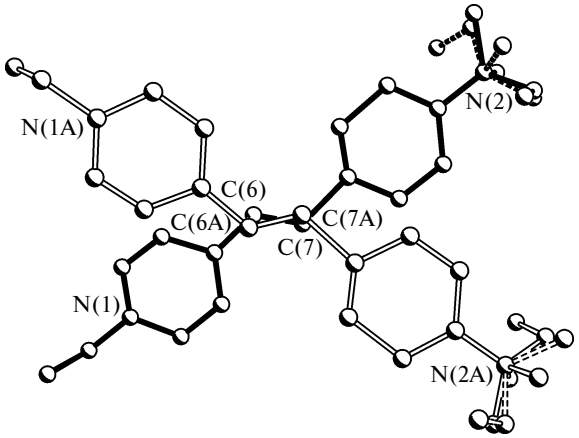


Fig. 7. Mutual projection of two cations of dye **3h** in the dimeric pair. Hydrogen atoms are omitted.

zene rings substantially deviates from the parallel arrangement (the dihedral angle between the benzene rings is 22°).

This is a principally new packing mode, which has not been observed earlier in the crystals of styryl and butadienyl dyes. The adjacent cations in the stack are related by alternating twofold axes along the crystallographic *b* and *c* axes. In this stack, the preorganization of the structural units differs from those shown in Schemes 6 and 7, and this arrangement should lead to the formation of the new *rtct* isomer of the cyclobutane derivative (type **D**, see above) in the PCA reaction.

It should be emphasized that our X-ray diffraction studies of the possibility of the PCA reaction proceeding without degradation of single crystals for all new dyes considered in the present study were successful only for the crystals of **3c**·$0.5C_6H_6$ and **3h**.[23] The [2+2] autophotocycloaddition of these compounds affords cyclobutane derivatives, *viz.*, the *rctt* isomer of type **A** and the *rtct* isomer of type **D** in the case of **3c**·$0.5C_6H_6$ and **3h**, respectively.

To summarize, the investigation of the solid-state [2+2] autophotocycloaddition for a series of styryl dyes showed that, in most cases, the visible light irradiation leads to the efficient and stereospecific formation of *rctt* isomers of 1,2,3,4-tetrasubstituted cyclobutanes. A high rate of the photoreaction is favored by the presence of a short *N*-alkyl substituent in the heterocyclic moiety of the dye, the electron-releasing alkoxy or alkylsulfanyl substituent in the benzene ring, and perchlorate ions. The X-ray diffraction study revealed the presence of almost exclusively the stacking modes for the styryl dyes under consideration, among which *syn*-head-to-tail packing modes favorable for the PCA reactions are observed much more often than head-to-head packing modes. Due to this fact, this class of compounds holds promise for the design of reversible data recording and storage systems at the molecular level.

Experimental

The melting points (uncorrected) were measured in capillaries on a Mel-Temp II instrument. The mass spectra were obtained on a Finnigan MAT 8430 instrument using a direct inlet system; the ionization energy was 70 eV. The elemental analysis was carried out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). The absorption spectra of solutions in acetonitrile or chloroform were measured on a UV-3101PC spectrophotometer (Shimadzu) in the 200—600 nm region (with a step of 0.5 nm) in 1 cm quartz cells. The ^{1}H NMR spectra were recorded on a Bruker DRX500 spectrometer (500.13 MHz) in DMSO-d_6 at 21—30 °C using the residual signals of the undeuterated solvent as the internal standard (δ_H 2.50). The chemical shifts and spin-spin coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. The assignment of the signals for the protons was made based on two-dimensional homonuclear ^{1}H—^{1}H COSY spectra.

4-Picoline, 3,4-dichlorobenzaldehyde, 4-(methylsulfanyl)-benzaldehyde, iodoethane, 1-iodobutane, 2-iodopropane, 1-bromooctadecane, ethyl *p*-toluenesulfonate, 1,4-di(bromomethyl)benzene, and 70% perchloric acid (Aldrich) were used without additional purification. 4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-1-ethenyl]-1-ethylpyridinium perchlorate (**1a**),[20] 4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-1-ethenyl]pyridine (**6a**),[20] 4-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydrobenzo-1,4,7,10,13-pentaoxacyclopentadecin-15-yl)-1-ethenyl]pyridine (**6b**),[43] 4-[(*E*)-2-(3,4-dimethoxyphenyl)-1-ethenyl]pyridine (**7a**),[43] *N*,*N*-dimethyl-*N*-{4-[(*E*)-2-(4-pyridyl)-1-ethenyl]phenyl}amine (**7b**),[44] 4-[(*E*)-2-phenyl-1-ethenyl]pyridine (**7c**),[24] 4-[(*E*)-2-(4-methoxyphenyl)-1-ethenyl]pyridine (**7d**),[24] 4-[(*E*)-2-(4-nitrophenyl)-1-ethenyl]pyridine (**7g**),[24] and 2-[(*E*)-2-(3,4-dimethoxyphenyl)-1-ethenyl]-1,3-benzothiazole (**8**)[45] were synthesized according to known procedures.

Synthesis of styryl dyes 1b—d and 2a,b (general procedure). A solution of 4-styrylpyridine **6a** or **7a,b** (0.5 mmol) and iodoethane, 1-iodobutane, or 2-iodopropane (3.0 mmol) in dichloromethane (5—10 mL) was kept in the dark at ~20 °C for 2—4 weeks. The solvent was removed *in vacuo*, and the residue was extracted with hot benzene (10 mL). The undissolved compound was filtered off, washed with benzene (2×3 mL), and dried. The UV spectroscopic data for the dyes are given in Table 1.

4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-1-ethenyl]-1-ethylpyridinium iodide (1b) was obtained in 92% yield as a yellow powder, m.p. 210—213 °C. Found (%): C, 52.36; H, 5.77; N, 2.50. $C_{25}H_{34}INO_6$. Calculated (%): C, 52.55; H, 6.00; N, 2.45. ^{1}H NMR, δ: 1.53 (t, 3 H, Me, J = 7.3 Hz); 3.54 (s, 4 H, 2 CH_2O); 3.57 and 3.63 (both m, 4 H each, 4 CH_2O); 3.78 and 3.81 (both m, 2 H each, 2 $C\underline{H}_2CH_2OAr$); 4.17 and 4.19 (both m, 2 H each, 2 $C\underline{H}_2OAr$); 4.52 (q, 2 H, CH_2N, J = 7.3 Hz); 7.08 (d, 1 H, H(5′), J = 8.4 Hz); 7.29 (br.d, 1 H, H(6′), J = 8.4 Hz); 7.40 (br.s, 1 H, H(2′)); 7.42 (d, 1 H, H_a, J = 16.2 Hz); 7.96 (d, 1 H, H_b, J = 16.2 Hz); 8.16 (d, 2 H, H(3), H(5), J = 6.7 Hz); 8.92 (d, 2 H, H(2), H(6), J = 6.7 Hz).

1-Butyl-4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-1-ethenyl]pyridinium iodide (1c) was obtained in 88% yield as a yellow powder, m.p. 182—184 °C. Found (%): C, 53.97; H, 6.07; N, 2.21. $C_{27}H_{38}INO_6$. Calculated (%): C, 54.09; H, 6.39; N, 2.34. ^{1}H NMR, δ: 0.93 (t, 3 H, Me, J = 7.4 Hz); 1.32 (m, 2 H, $C\underline{H}_2Me$); 1.90 (m, 2 H, $C\underline{H}_2CH_2N$); 3.54 (s, 4 H, 2 CH_2O); 3.57 and 3.63 (both m, 4 H each, 4 CH_2O); 3.78 and 3.81 (both m, 2 H each, 2 $C\underline{H}_2CH_2OAr$); 4.17 and 4.20 (both m, 2 H each, 2 $C\underline{H}_2OAr$); 4.48 (t, 2 H, CH_2N, J = 7.4 Hz); 7.08 (d, 1 H, H(5′), J = 8.4 Hz); 7.29 (dd, 1 H, H(6′), J = 8.4 Hz, J = 1.8 Hz); 7.40 (br.s, 1 H, H(2′)); 7.42 (d, 1 H, H_a, J = 16.2 Hz); 7.96 (d, 1 H, H_b, J = 16.2 Hz); 8.16 (d, 2 H, H(3), H(5), J = 6.9 Hz); 8.91 (d, 2 H, H(2), H(6), J = 6.9 Hz).

4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-1-ethenyl]-1-isopropylpyridinium iodide (1d) was obtained in 31% yield as a yellow powder, m.p. 178—180 °C. Found (%): C, 53.04; H, 6.02; N, 2.49. $C_{26}H_{36}INO_6$. Calculated (%): C, 53.34; H, 6.20;

N, 2.39. ^{1}H NMR, δ: 1.60 (d, 6 H, $\underline{Me}_2CH$, J = 6.7 Hz); 3.54 (s, 4 H, 2 CH_2O); 3.57 and 3.63 (both m, 4 H each, 4 CH_2O); 3.78 and 3.81 (both m, 2 H each, 2 $C\underline{H}_2CH_2OAr$); 4.17 and 4.19 (both m, 2 H each, 2 $C\underline{H}_2OAr$); 4.90 (sept, 1 H, $C\underline{H}Me_2$, J = 6.7 Hz); 7.08 (d, 1 H, H(5′), J = 8.4 Hz); 7.29 (dd, 1 H, H(6′), J = 8.4 Hz, J = 1.6 Hz); 7.41 (d, 1 H, H(2′), J = 1.6 Hz); 7.43 (d, 1 H, H_a, J = 16.2 Hz); 7.98 (d, 1 H, H_b, J = 16.2 Hz); 8.16 (d, 2 H, H(3), H(5), J = 6.8 Hz); 9.00 (d, 2 H, H(2), H(6), J = 6.8 Hz).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-ethylpyridinium iodide (2a) was obtained in 98% yield as a yellow powder, m.p. 233—235 °C (with decomp.). Found (%): C, 51.18; H, 5.07; N, 3.34. $C_{17}H_{20}INO_2$. Calculated (%): C, 51.40; H, 5.08; N, 3.53. ^{1}H NMR, δ: 1.53 (t, 3 H, Me, J = 7.3 Hz); 3.84 and 3.86 (both s, 3 H each, 2 MeO); 4.51 (q, 2 H, CH_2, J = 7.3 Hz); 7.09 (d, 1 H, H(5′), J = 8.3 Hz); 7.30 (br.d, 1 H, H(6′), J = 8.3 Hz); 7.40 (br.s, 1 H, H(2′)); 7.42 (d, 1 H, H_a, J = 16.4 Hz); 7.98 (d, 1 H, H_b, J = 16.4 Hz); 8.17 (d, 2 H, H(3), H(5), J = 6.6 Hz); 8.92 (d, 2 H, H(2), H(6), J = 6.6 Hz).

4-{(*E*)-2-[4-(Dimethylamino)phenyl]-1-ethenyl}-1-ethylpyridinium iodide (2b) was obtained in 94% yield as a dark-red powder, m.p. 250—253 °C (from a MeCN—benzene mixture) (*cf.* lit. data[32]: m.p. 244—246 °C). Found (%): C, 53.57; H, 5.54; N, 7.19. $C_{17}H_{21}IN_2$. Calculated (%): C, 53.69; H, 5.57; N, 7.37. ^{1}H NMR, δ: 1.51 (t, 3 H, Me, J = 7.3 Hz); 3.03 (s, 6 H, Me_2N); 4.45 (q, 2 H, CH_2, J = 7.3 Hz); 6.80 (d, 2 H, H(3′), H(5′), J = 8.9 Hz); 7.19 (d, 1 H, H_a, J = 16.1 Hz); 7.60 (d, 2 H, H(2′), H(6′), J = 8.9 Hz); 7.93 (d, 1 H, H_b, J = 16.1 Hz); 8.07 (d, 2 H, H(3), H(5), J = 6.9 Hz); 8.80 (d, 2 H, H(2), H(6), J = 6.9 Hz).

4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-1-ethenyl]-1-octadecylpyridinium perchlorate (1e). A mixture of 4-styrylpyridine **6a** (100 mg, 0.24 mmol) and 1-bromooctadecane (80 mg, 0.24 mmol) was heated in the dark at 140 °C (oil bath) for 3 h. The reaction mixture was heated with ethyl acetate (20 mL) and then cooled to ~20 °C. The undissolved compound was filtered off and dried. Bromide of the dye was obtained in a yield of 118 mg (0.16 mmol, 66%) as a yellow-orange powder, m.p. 165—167 °C. The bromide was dissolved in a minimum amount of hot anhydrous EtOH, 70% perchloric acid (28 μL, 0.32 mmol) was added, the mixture was cooled to −10 °C, and the precipitate was filtered off, washed with cold anhydrous EtOH (5 mL), and dried. Compound **1e** was obtained in a yield of 114 mg (62%) as a yellow powder, m.p. 162—164 °C. Found (%): C, 64.10; H, 8.81; N, 1.81. $C_{41}H_{66}ClNO_{10}$. Calculated (%): C, 64.08; H, 8.66; N, 1.82. ^{1}H NMR, δ: 0.85 (t, 3 H, Me, J = 6.6 Hz); 1.23 (s, 26 H, $(CH_2)_{13}$); 1.23—1.30 (m, 4 H, 2 CH_2); 1.90 (m, 2 H, $C\underline{H}_2CH_2N$); 3.54 (s, 4 H, 2 CH_2O); 3.57 and 3.63 (both m, 4 H each, 4 CH_2O); 3.78 and 3.81 (both m, 2 H each, 2 $C\underline{H}_2CH_2OAr$); 4.17 (m, 4 H, 2 $C\underline{H}_2OAr$); 4.46 (t, 2 H, CH_2N, J = 7.5 Hz); 7.07 (d, 1 H, H(5′), J = 8.6 Hz); 7.28 (br.d, 1 H, H(6′), J = 8.6 Hz); 7.39 (br.s, 1 H, H(2′)); 7.39 (d, 1 H, H_a, J = 15.9 Hz); 7.94 (d, 1 H, H_b, J = 15.9 Hz); 8.14 (d, 2 H, H(3), H(5), J = 6.6 Hz); 8.88 (d, 2 H, H(2), H(6), J = 6.6 Hz).

Synthesis of 4-styrylpyridines 7e,f (general procedure). A solution of 4-picoline (1.81 mL, 0.02 mol) and 4-(methylsulfanyl)benzaldehyde or 3,4-dichlorobenzaldehyde (0.02 mol) in acetic anhydride (3.6 mL) was heated at 140 °C (oil bath) for 16 h. Then the reaction mixture was cooled, poured into water (150 mL), and extracted with benzene (3×30 mL). A 10% NaOH solution was added to the aqueous phase (to pH > 9). The precipitate that formed was filtered off and recrystallized from EtOH. Compounds **7e,f** were obtained as yellowish powders.

4-{(*E*)-2-[4-(Methylsulfanyl)phenyl]-1-ethenyl}pyridine (7e) was obtained in 51% yield, m.p. 155—157 °C (*cf.* lit. data[46]: m.p. 118—120 °C). Found (%): C, 72.77; H, 5.43. $C_{14}H_{13}NS \cdot 0.25H_2O$. Calculated (%): C, 72.53; H, 5.87. ^{1}H NMR, δ: 2.50 (s, 3 H, Me); 7.21 (d, 1 H, H_a, J = 16.4 Hz); 7.29 (d, 2 H, H(3′), H(5′), J = 8.3 Hz); 7.51 (d, 1 H, H_b, J = 16.4 Hz); 7.54 (d, 2 H, H(3), H(5), J = 5.4 Hz); 7.60 (d, 2 H, H(2′), H(6′), J = 8.3 Hz); 8.53 (d, 2 H, H(2), H(6), J = 5.4 Hz). MS, m/z (I_{rel} (%)): 227 $[M]^+$ (100), 226 (32), 182 (31), 181 (37), 180 (82), 179 (32), 168 (19), 167 (22), 152 (22), 69 (18). UV (MeCN), λ_{max}/nm (ε): 331 (33900).

4-[(*E*)-2-(3,4-Dichlorophenyl)-1-ethenyl]pyridine (7f) was obtained in 49% yield, m.p. 100—101 °C. Found (%): C, 60.55; H, 3.75; N, 5.37. $C_{13}H_9Cl_2N \cdot 0.5H_2O$. Calculated (%): C, 60.26; H, 3.89; N, 5.41. ^{1}H NMR, δ: 7.40 (d, 1 H, H_a, J = 16.2 Hz); 7.54 (d, 1 H, H_b, J = 16.2 Hz); 7.55 (d, 2 H, H(3), H(5), J = 6.4 Hz); 7.65 (dd, 1 H, H(6′), J = 8.1 Hz, J = 1.9 Hz); 7.69 (d, 1 H, H(5′), J = 8.1 Hz); 7.97 (d, 1 H, H(2′), J = 1.9 Hz); 8.58 (d, 2 H, H(2), H(6), J = 6.4 Hz). MS, m/z (I_{rel} (%)): 253 $[M]^+$ (2 ^{37}Cl) (37), 251 $[M]^+$ (^{35}Cl, ^{37}Cl) (80), 250 (31), 249 $[M]^+$ (2 ^{35}Cl) (100), 248 (25), 216 (21), 214 (44), 148 (23), 69 (31), 57 (22), 55 (22). UV (MeCN), λ_{max}/nm (ε): 299 (22300).

Synthesis of styryl dyes 1f, 3a,c—h, and 5 (general procedure). A mixture of 4-styrylpyridine **6b** or **7a—g** or 2-styrylbenzothiazole **8** (0.5 mmol) and ethyl *p*-toluenesulfonate (1.5 mmol in the case of **6b**, **7a,c—g**, and **8** or 2.0 mmol in the case of **7b**) was heated in the dark at 120 °C (oil bath) for 2 h (**6b**, **7a,c—g**, **8**) or 20 h (**7b**). The reaction mixture was extracted with hot benzene (10—15 mL). The undissolved compound was separated by decantation and dissolved in MeOH (5 mL). Then 70% perchloric acid (1.0 mmol in the case of **6b**, **7a,c—g**, and **8** or 1.5 mmol in the case of **7b**) was added. The mixture was cooled to −10 °C, and the precipitate that formed was filtered off, washed with cold MeOH (2×2 mL), and dried. The UV spectroscopic data for these dyes are given in Table 1.

1-Ethyl-4-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydrobenzo-1,4,7,10,13-pentaoxacyclopentadecin-15-yl)-1-ethenyl]pyridinium perchlorate (1f) was obtained in 84% yield as a yellow powder, m.p. 209—211 °C. Found (%): C, 55.46; H, 6.01; N, 2.74. $C_{23}H_{30}ClNO_9$. Calculated (%): C, 55.26; H, 6.05; N, 2.80. ^{1}H NMR, δ: 1.53 (t, 3 H, Me, J = 7.3 Hz); 3.63 (m, 8 H, 4 CH_2O); 3.79 and 3.81 (both m, 2 H each, 2 $C\underline{H}_2CH_2OAr$); 4.13 (m, 4 H, 2 $C\underline{H}_2OAr$); 4.50 (q, 2 H, CH_2N, J = 7.3 Hz); 7.06 (d, 1 H, H(5′), J = 8.1 Hz); 7.28 (dd, 1 H, H(6′), J = 8.1 Hz, J = 1.9 Hz); 7.38 (d, 1 H, H_a, J = 16.4 Hz); 7.39 (d, 1 H, H(2′), J = 1.9 Hz); 7.94 (d, 1 H, H_b, J = 16.4 Hz); 8.14 (d, 2 H, H(3), H(5), J = 7.1 Hz); 8.90 (d, 2 H, H(2), H(6), J = 7.1 Hz).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-ethylpyridinium perchlorate (3a) was obtained in 74% yield as a yellow powder, m.p. 224—226 °C (with decomp.). Found (%): C, 55.37; H, 5.33; N, 3.85. $C_{17}H_{20}ClNO_6$. Calculated (%): C, 55.21; H, 5.45; N, 3.79. ^{1}H NMR, δ: 1.53 (t, 3 H, Me, J = 7.3 Hz); 3.83 and 3.85 (both s, 3 H each, 2 MeO); 4.51 (q, 2 H, CH_2, J = 7.3 Hz); 7.08 (d, 1 H, H(5′), J = 8.3 Hz); 7.30 (dd, 1 H, H(6′), J = 8.3 Hz, J = 1.8 Hz); 7.38 (br.s, 1 H, H(2′)); 7.40 (d, 1 H, H_a, J = 16.5 Hz); 7.96 (d, 1 H, H_b, J = 16.5 Hz); 8.16 (d, 2 H, H(3), H(5), J = 6.7 Hz); 8.90 (d, 2 H, H(2), H(6), J = 6.7 Hz).

1-Ethyl-4-[(*E*)-2-phenyl-1-ethenyl]pyridinium perchlorate (3c) was obtained in 76% yield as yellowish crystals, m.p. 142—144 °C. Found (%): C, 58.18; H, 5.14; N, 4.23. $C_{15}H_{16}ClNO_4$. Calculated (%): C, 58.16; H, 5.21; N, 4.52. ^{1}H NMR, δ: 1.54 (t, 3 H, Me, J = 7.3 Hz); 4.54 (q, 2 H, CH_2, J = 7.3 Hz); 7.47 (t, 1 H, H(4′), J = 7.2 Hz); 7.50 (t, 2 H, H(3′), H(5′), J = 7.2 Hz); 7.54 (d, 1 H, H_a, J = 16.3 Hz); 7.77 (d, 2 H, H(2′), H(6′), J = 7.4 Hz); 8.03 (d, 1 H, H_b, J = 16.3 Hz); 8.26 (d, 2 H, H(3), H(5), J = 6.5 Hz); 8.98 (d, 2 H, H(2), H(6), J = 6.5 Hz).

1-Ethyl-4-[(*E*)-2-(4-methoxyphenyl)-1-ethenyl]pyridinium perchlorate (3d) was obtained in 87% yield as a yellow powder, m.p. 158—160 °C. Found (%): C, 56.88; H, 5.48; N, 3.99. $C_{16}H_{18}ClNO_5$. Calculated (%): C, 56.56; H, 5.34; N, 4.12. ^{1}H NMR, δ: 1.53 (t, 3 H, Me, J = 7.3 Hz); 3.84 (s, 3 H, MeO); 4.51 (q, 2 H, CH_2, J = 7.3 Hz); 7.08 (d, 2 H, H(3′), H(5′), J = 8.8 Hz); 7.38 (d, 1 H, H_a, J = 16.3 Hz); 7.73 (d, 2 H, H(2′), H(6′), J = 8.8 Hz); 7.99 (d, 1 H, H_b, J = 16.3 Hz); 8.18 (d, 2 H, H(3), H(5), J = 6.7 Hz); 8.92 (d, 2 H, H(2), H(6), J = 6.7 Hz).

1-Ethyl-4-{(*E*)-2-[4-(methylsulfanyl)phenyl]-1-ethenyl}pyridinium perchlorate (3e) was obtained in 76% yield as a yellow powder, m.p. 193—195 °C. Found (%): C, 54.06; H, 5.12; N, 3.74. $C_{16}H_{18}ClNO_4S$. Calculated (%): C, 54.01; H, 5.10; N, 3.94. ^{1}H NMR, δ: 1.54 (t, 3 H, Me, J = 7.3 Hz); 2.55 (s, 3 H, MeS); 4.52 (q, 2 H, CH_2, J = 7.3 Hz); 7.38 (d, 2 H, H(3′), H(5′), J = 8.3 Hz); 7.48 (d, 1 H, H_a, J = 16.4); 7.70 (d, 2 H, H(2′), H(6′), J = 8.3 Hz); 7.99 (d, 1 H, H_b, J = 16.4 Hz); 8.21 (d, 2 H, H(3), H(5), J = 6.5 Hz); 8.94 (d, 2 H, H(2), H(6), J = 6.5 Hz).

4-[(*E*)-2-(3,4-Dichlorophenyl)-1-ethenyl]-1-ethylpyridinium perchlorate (3f) was obtained in 44% yield as a yellowish powder, m.p. 133—135 °C. Found (%): C, 47.47; H, 3.46; N, 3.67. $C_{15}H_{14}Cl_3NO_4$. Calculated (%): C, 47.58; H, 3.73; N, 3.70. ^{1}H NMR, δ: 1.54 (t, 3 H, Me, J = 7.3 Hz); 4.55 (q, 2 H, CH_2, J = 7.3 Hz); 7.66 (d, 1 H, H_a, J = 16.4 Hz); 7.72 (dd, 1 H, H(6′), J = 8.4 Hz, J = 1.9 Hz); 7.80 (d, 1 H, H(5′), J = 8.4 Hz); 7.99 (d, 1 H, H_b, J = 16.4 Hz); 8.06 (d, 1 H, H(2′), J = 1.9 Hz); 8.22 (d, 2 H, H(3), H(5), J = 6.8 Hz); 9.02 (d, 2 H, H(2), H(6), J = 6.8 Hz).

1-Ethyl-4-[(*E*)-2-(4-nitrophenyl)-1-ethenyl]pyridinium perchlorate (3g) was obtained in 59% yield as a cream-colored powder, m.p. 173—175 °C. Found (%): C, 51.09; H, 4.15; N, 7.94. $C_{15}H_{15}ClN_2O_6$. Calculated (%): C, 50.79; H, 4.26; N, 7.90. ^{1}H NMR, δ: 1.56 (t, 3 H, Me, J = 7.3 Hz); 4.57 (q, 2 H, CH_2, J = 7.3 Hz); 7.77 (d, 1 H, H_a, J = 16.5 Hz); 8.01 (d, 2 H, H(2′), H(6′), J = 8.7 Hz); 8.13 (d, 1 H, H_b, J = 16.5 Hz); 8.32 (d, 2 H, H(3), H(5), J = 6.6 Hz); 8.36 (d, 2 H, H(3′), H(5′), J = 8.7 Hz); 9.05 (d, 2 H, H(2), H(6), J = 6.6 Hz).

1-Ethyl-4-{(*E*)-2-(4-[ethyl(dimethyl)ammonio]phenyl)-1-ethenyl}pyridinium diperchlorate (3h) was obtained in 78% yield as a pinkish powder, m.p. >270 °C (with decomp.). Found (%): C, 47.15; H, 5.70; N, 5.60. $C_{19}H_{26}Cl_2N_2O_8$. Calculated (%): C, 47.41; H, 5.45; N, 5.82. ^{1}H NMR, δ: 1.01 (t, 3 H, $\underline{Me}CH_2NMe_2$, J = 7.2 Hz); 1.55 (t, 3 H, $\underline{Me}CH_2N$, J = 7.3 Hz); 3.59 (s, 6 H, Me_2N); 3.95 (q, 2 H, $MeC\underline{H_2}NMe_2$, J = 7.2 Hz); 4.56 (q, 2 H, $MeC\underline{H_2}N$, J = 7.3 Hz); 7.69 (d, 1 H, H_a, J = 16.2 Hz); 7.97 and 8.00 (both d, 2 H each, H(2′), H(6′) and H(3′), H(5′), J = 9.3 Hz, J = 9.3 Hz); 8.07 (d, 1 H, H_b, J = 16.2 Hz); 8.26 (d, 2 H, H(3), H(5), J = 6.7 Hz); 9.03 (d, 2 H, H(2), H(6), J = 6.7 Hz).

2-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-3-ethyl-1,3-benzothiazol-3-ium perchlorate (5) was obtained in 61% yield as an orange powder, m.p. 236—239 °C (with decomp.). Found (%): C, 53.48; H, 4.60; N, 3.02. $C_{19}H_{20}ClNO_6S$. Calculated (%): C, 53.58; H, 4.73; N, 3.29. ^{1}H NMR, δ: 1.48 (t, 3 H, Me, J = 7.3 Hz); 3.89 and 3.90 (both s, 3 H each, 2 MeO); 4.97 (q, 2 H, CH_2, J = 7.3 Hz); 7.16 (d, 1 H, H(5′), J = 8.7 Hz); 7.68 (br.s, 1 H, H(2′)); 7.69 (br.d, 1 H, H(6′), J = 8.7 Hz); 7.78 (m, 1 H, H(6)); 7.87 (m, 1 H, H(5)); 7.87 (d, 1 H, H_a, J = 15.6 Hz); 8.20 (d, 1 H, H_b, J = 15.6 Hz); 8.27 (d, 1 H, H(4), J = 8.7 Hz); 8.42 (d, 1 H, H(7), J = 8.1 Hz).

4-{(*E*)-2-[4-(Dimethylamino)phenyl]-1-ethenyl}-1-ethylpyridinium perchlorate (3b). A solution of $NaClO_4$ (43 mg, 0.35 mmol) in MeOH (1 mL) was added to a solution of iodide **2b** (110 mg, 0.29 mmol) in MeOH (4 mL). The reaction mixture was cooled to −10 °C, and the precipitate was filtered off, washed with cold MeOH (2×1 mL), and dried. Compound **3b** was obtained in a yield of 91 mg (89%) as brown crystals, m.p. 214—217 °C (with decomp.). Found (%): C, 57.99; H, 6.20; N, 7.79. $C_{17}H_{21}ClN_2O_4$. Calculated (%): C, 57.87; H, 6.00; N, 7.94. ^{1}H NMR, δ: 1.50 (t, 3 H, Me, J = 7.3 Hz); 3.02 (s, 6 H, Me_2N); 4.44 (q, 2 H, CH_2, J = 7.3 Hz); 6.79 (d, 2 H, H(3′), H(5′), J = 9.3 Hz); 7.18 (d, 1 H, H_a, J = 16.2 Hz); 7.60 (d, 2 H, H(2′), H(6′), J = 9.3 Hz); 7.92 (d, 1 H, H_b, J = 16.2 Hz); 8.06 (d, 2 H, H(3), H(5), J = 7.0 Hz); 8.78 (d, 2 H, H(2), H(6), J = 7.0 Hz).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-{4-[4-(*E*-2-(3,4-dimethoxyphenyl)-1-ethenyl)pyridiniomethyl]benzyl}pyridinium diperchlorate (4). A solution of 4-styrylpyridine **7a** (100 mg, 0.42 mmol) and 1,4-di(bromomethyl)benzene (50 mg, 0.19 mmol) in anhydrous EtOH (10 mL) was heated (oil bath) in the dark at 80 °C for 22 h. After cooling to ~20 °C, the precipitate was filtered off, and dibromide of the dye was obtained in a yield of 58 mg. The dibromide was dissolved with heating in a mixture of EtOH (~15 mL) and a minimum amount of water. Then 70% perchloric acid (28 μL, 0.32 mmol) was added, the mixture was cooled to −10 °C, and the precipitate that formed was filtered off, washed with cold EtOH (2 mL), and dried. Compound **4** was obtained in a yield of 50 mg (37%) as orange crystals, m.p. 310—312 °C (with decomp.). Found (%): C, 56.10; H, 4.91; N, 3.38. $C_{38}H_{38}Cl_2N_2O_{12}\cdot 1.5H_2O$. Calculated (%): C, 56.16; H, 5.09; N, 3.45. ^{1}H NMR, δ: 3.82 and 3.84 (both s, 6 H each, 4 MeO); 5.71 (s, 4 H, 2 CH_2); 7.07 (d, 2 H, 2 H(5′), J = 8.6 Hz); 7.28 (dd, 2 H, 2 H(6′), J = 8.6 Hz, J = 1.8 Hz); 7.37 (d, 2 H, 2 H(2′), J = 1.8 Hz); 7.40 (d, 2 H, 2 H_a, J = 16.4 Hz); 7.59 (s, 4 H, C_6H_4); 7.96 (d, 2 H, 2 H_b, J = 16.4 Hz); 8.17 (d, 4 H, 2 H(3), 2 H(5), J = 6.8 Hz); 8.98 (d, 4 H, 2 H(2), 2 H(6), J = 6.8 Hz).

Synthesis of cyclobutane derivatives from dyes 1a—f, 2a, 3a,c—h, and 5 (general procedure). A solution of dye **1a—f**, **2a**, **3a,c—h**, or **5** (15 μmol) in MeCN (0.5 mL; in the case of **1e** in chloroform (0.5 mL)) was concentrated in a 10 cm Petri dish until a thin polycrystalline film of the dye formed. The sample thus prepared was irradiated with unfiltered light from a 60 W incandescent bulb from a distance of 15 cm for 10—100 h, dissolved in MeCN (except for the sample of dye **5**, which was collected mechanically), and concentrated *in vacuo*. The compositions of the products and the degrees of conversion into cyclobutane derivatives were analyzed based on the ^{1}H NMR spectroscopic data by comparing the integrated intensities of the signals for the protons. In the case of formation of a single

isomer, the elemental analysis data are given. The results of experiments, in which the exposure time was 10 h, are presented in Table 1.

***r*-4-[*c*-2,*t*-4-Di(2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-*t*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diperchlorate** (A_{1a}, *rctt* isomer of the cyclobutane derivative from compound **1a**, type **A**) has been described earlier.[20]

***r*-4-[*c*-2,*t*-4-Di(2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-*t*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diiodate** (A_{1b}, *rctt* isomer of the cyclobutane derivative from compound **1b**, type **A**) was prepared as a pale-yellow powder, m.p. 105—107 °C. Found (%): C, 48.65; H, 5.27; N, 2.28. $C_{50}H_{68}N_2O_{12}\cdot(IO_3)_2$. Calculated (%): C, 48.47; H, 5.53; N, 2.26. ^{1}H NMR, δ: 1.43 (t, 6 H, 2 Me, J = 7.3 Hz); 3.51 (s, 8 H, 4 CH_2O); 3.52—3.61 (m, 16 H, 8 CH_2O); 3.69 and 3.72 (both m, 4 H each, 4 C<u>H</u>$_2$CH$_2$OAr); 3.95 and 3.98 (both m, 4 H each, 4 C<u>H</u>$_2$OAr); 4.50 (q, 4 H, 2 CH_2N, J = 7.3 Hz); 4.79 (dd, 2 H, 2 C<u>H</u>Ar, J = 9.0 Hz, J = 7.5 Hz); 4.89 (dd, 2 H, 2 C<u>H</u>Py, J = 9.0 Hz, J = 7.5 Hz); 6.77 (s, 4 H, 2 H(5′), 2 H(6′)); 6.83 (s, 2 H, 2 H(2′)); 7.94 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.89 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz).

1-Butyl-*r*-4-[*t*-3-(1-butylpyridinium-4-yl)-*c*-2,*t*-4-di(2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)cyclobutyl]pyridinium iodide/iodate (A_{1c}, *rctt* isomer of the cyclobutane derivative from compound **1c**, type **A**) was prepared as a pale-yellow powder. Found (%): C, 51.40; H, 6.20; N, 2.09. $C_{54}H_{76}N_2O_{12}\cdot I_{0.7}(IO_3)_{1.3}$. Calculated (%): C, 51.42; H, 6.07; N, 2.22. ^{1}H NMR, δ: 0.85 (t, 6 H, 2 Me, J = 7.3 Hz); 1.12 (m, 4 H, 2 C<u>H</u>$_2$Me); 1.77 (m, 4 H, 2 C<u>H</u>$_2$CH$_2$N); 3.52 (s, 8 H, 4 CH_2O); 3.53—3.62 (m, 16 H, 8 CH_2O); 3.70 and 3.73 (both m, 4 H each, 4 C<u>H</u>$_2$CH$_2$OAr); 3.94 and 4.00 (both m, 4 H each, 4 C<u>H</u>$_2$OAr); 4.47 (t, 4 H, 2 CH_2N, J = 7.0 Hz); 4.81 (dd, 2 H, 2 C<u>H</u>Ar, J = 8.8 Hz, J = 8.3 Hz); 4.90 (dd, 2 H, 2 C<u>H</u>Py, J = 8.8 Hz, J = 8.3 Hz); 6.73 (br.d, 2 H, 2 H(6′), J = 8.5 Hz); 6.75 (d, 2 H, 2 H(5′), J = 8.5 Hz); 6.85 (br.s, 2 H, 2 H(2′)); 7.94 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.87 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz).

***r*-4-[*c*-2,*t*-4-Di(2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-*t*-3-(1-isopropylpyridinium-4-yl)cyclobutyl]-1-isopropylpyridinium diiodide (diiodate)** (A_{1d}, *rctt* isomer of the cyclobutane derivative from compound **1d**, type **A**). ^{1}H NMR, δ: 1.505 and 1.512 (both d, 12 H, 2 <u>Me</u>$_2$CH, J = 6.4 Hz); 3.51 (s, 8 H, 4 CH_2O); 3.52—3.61 (m, 16 H, 8 CH_2O); 3.69 and 3.72 (both m, 4 H each, 4 C<u>H</u>$_2$CH$_2$OAr); 3.95 (m, 8 H, 4 C<u>H</u>$_2$OAr); 4.83 (dd, 2 H, 2 C<u>H</u>Ar, J = 9.0 Hz, J = 8.2 Hz); 4.90 (sept, 2 H, 2 C<u>H</u>Me$_2$, J = 6.4 Hz); 4.93 (dd, 2 H, 2 C<u>H</u>Py, J = 9.0 Hz, J = 8.2 Hz); 6.75 (br.d, 2 H, 2 H(6′), J = 8.4 Hz); 6.77 (d, 2 H, 2 H(5′), J = 8.4 Hz); 6.80 (br.s, 2 H, 2 H(2′)); 7.92 (d, 4 H, 2 H(3), 2 H(5), J = 6.3 Hz); 8.98 (d, 4 H, 2 H(2), 2 H(6), J = 6.3 Hz).

***r*-4-[*c*-2,*t*-4-Di(2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin-18-yl)-*t*-3-(1-octadecylpyridinium-4-yl)cyclobutyl]-1-octadecylpyridinium diperchlorate** (A_{1e}, *rctt* isomer of the cyclobutane derivative from compound **1e**, type **A**) was prepared as a yellowish powder, m.p. 127—128 °C. Found (%): C, 63.16; H, 8.98; N, 1.98. $C_{82}H_{132}Cl_2N_2O_{20}\cdot H_2O$. Calculated (%): C, 63.34; H, 8.69; N, 1.80. ^{1}H NMR (DMSO-d_6—$CDCl_3$ (4 : 1)), δ: 0.85 (t, 6 H, 2 Me, J = 6.8 Hz); 1.23 (s, 60 H, 2 $(CH_2)_{15}$); 1.78 (m, 4 H, 2 C<u>H</u>$_2$CH$_2$N); 3.52 (s, 8 H, 4 CH_2O); 3.53—3.63 (m, 16 H, 8 CH_2O); 3.71 and 3.74 (both m, 4 H each, 4 C<u>H</u>$_2$CH$_2$OAr); 3.94 and 4.00 (both m, 4 H each, 4 C<u>H</u>$_2$OAr); 4.46 (t, 4 H, 2 CH_2N, J = 7.0 Hz); 4.78 (dd, 2 H, 2 C<u>H</u>Ar, J = 8.9 Hz, J = 7.7 Hz); 4.87 (dd, 2 H, 2 C<u>H</u>Py, J = 8.9 Hz, J = 7.7 Hz); 6.71 (s, 4 H, 2 H(5′), 2 H(6′)); 6.85 (s, 2 H, 2 H(2′)); 7.91 (d, 4 H, 2 H(3), 2 H(5), J = 6.1 Hz); 8.87 (d, 4 H, 2 H(2), 2 H(6), J = 6.1 Hz).

1-Ethyl-*r*-4-[*t*-3-(1-ethylpyridinium-4-yl)-*c*-2,*t*-4-di(2,3,5,6,8,9,11,12-octahydrobenzo-1,4,7,10,13-pentaoxacyclopentadecin-15-yl)cyclobutyl]pyridinium diperchlorate (A_{1f}, *rctt* isomer of the cyclobutane derivative from compound **1f**, type **A**) was prepared as a yellowish powder, m.p. >150 °C (with decomp.). Found (%): C, 53.83; H, 6.01; N, 2.83. $C_{46}H_{60}Cl_2N_2O_{18}\cdot 1.5H_2O$. Calculated (%): C, 53.80; H, 6.18; N, 2.73. ^{1}H NMR, δ: 1.42 (t, 6 H, 2 Me, J = 7.3 Hz); 3.55—3.62 (m, 16 H, 8 CH_2O); 3.70 and 3.73 (both m, 4 H each, 4 C<u>H</u>$_2$CH$_2$OAr); 3.92 and 3.94 (both m, 4 H each, 4 C<u>H</u>$_2$OAr); 4.49 (q, 4 H, 2 CH_2N, J = 7.3 Hz); 4.78 (dd, 2 H, 2 C<u>H</u>Ar, J = 8.2, J = 7.7 Hz); 4.88 (dd, 2 H, 2 C<u>H</u>Py, J = 8.2 Hz, J = 7.7 Hz); 6.76 (s, 4 H, 2 H(5′), 2 H(6′)); 6.83 (s, 2 H, 2 H(2′)); 7.94 (d, 4 H, 2 H(3), 2 H(5), J = 6.8 Hz); 8.89 (d, 4 H, 2 H(2), 2 H(6), J = 6.8 Hz).

***r*-4-[*c*-2,*t*-4-Bis(3,4-dimethoxyphenyl)-*t*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diiodide (diiodate)** (A_{2a}, *rctt* isomer of the cyclobutane derivative from compound **2a**, type **A**). ^{1}H NMR, δ: 1.42 (t, 6 H, 2 Me, J = 7.2 Hz); 3.66 and 3.68 (both s, 6 H each, 4 MeO); 4.50 (q, 4 H, 2 CH_2, J = 7.2 Hz); 4.82 (dd, 2 H, 2 C<u>H</u>Ar, J = 10.5 Hz, J = 7.4 Hz); 4.91 (dd, 2 H, 2 C<u>H</u>Py, J = 10.5 Hz, J = 7.4 Hz); 6.78 (s, 4 H, 2 H(5′), 2 H(6′)); 6.82 (s, 2 H, 2 H(2′)); 7.97 (d, 4 H, 2 H(3), 2 H(5), J = 6.5 Hz); 8.89 (d, 4 H, 2 H(2), 2 H(6), J = 6.5 Hz).

***r*-4-[*c*-2,*t*-4-Bis(3,4-dimethoxyphenyl)-*t*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diperchlorate** (A_{3a}, *rctt* isomer of the cyclobutane derivative from compound **3a**, type **A**) was prepared as a pale-yellow powder, m.p. 155—158 °C. Found (%): C, 55.32; H, 5.37; N, 4.05. $C_{34}H_{40}Cl_2N_2O_{12}$. Calculated (%): C, 55.22; H, 5.45; N, 3.79. ^{1}H NMR, δ: 1.42 (t, 6 H, 2 Me, J = 7.3 Hz); 3.66 and 3.68 (both s, 6 H each, 4 MeO); 4.50 (q, 4 H, 2 CH_2, J = 7.3 Hz); 4.81 (dd, 2 H, 2 C<u>H</u>Ar, J = 9.8 Hz, J = 7.5 Hz); 4.90 (dd, 2 H, 2 C<u>H</u>Py, J = 9.8 Hz, J = 7.5 Hz); 6.78 (s, 4 H, 2 H(5′), 2 H(6′)); 6.80 (s, 2 H, 2 H(2′)); 7.95 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.87 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz).

1-Ethyl-*r*-4-[*t*-3-(1-ethylpyridinium-4-yl)-*c*-2,*t*-4-diphenylcyclobutyl]pyridinium diperchlorate (A_{3c}, *rctt* isomer of the cyclobutane derivative from compound **3c**, type **A**) was prepared as a colorless powder, m.p. 129—135 °C. Found (%): C, 57.99; H, 5.15; N, 4.51. $C_{30}H_{32}Cl_2N_2O_8$. Calculated (%): C, 58.16; H, 5.21; N, 4.52. ^{1}H NMR, δ: 1.40 (t, 6 H, 2 Me, J = 7.2 Hz); 4.47 (q, 4 H, 2 CH_2, J = 7.2 Hz); 4.90 (dd, 2 H, 2 C<u>H</u>Ph, J = 10.0 Hz, J = 7.2 Hz); 5.01 (dd, 2 H, 2 C<u>H</u>Py, J = 10.0 Hz, J = 7.2 Hz); 7.14 (t, 2 H, 2 H(4′), J = 7.3 Hz); 7.23 (t, 4 H, 2 H(3′), 2 H(5′), J = 7.8 Hz); 7.26 (d, 4 H, 2 H(2′), 2 H(6′), J = 7.5 Hz); 7.96 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.86 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz).

1-Ethyl-*r*-4-[*t*-3-(1-ethylpyridinium-4-yl)-*c*-2,*t*-4-bis(4-methoxyphenyl)cyclobutyl]pyridinium diperchlorate (A_{3d}, *rctt* isomer of the cyclobutane derivative from compound **3d**, type **A**) was prepared as a pale-yellow powder, m.p. 110—113 °C. Found (%): C, 56.39; H, 5.24; N, 4.31. $C_{32}H_{36}Cl_2N_2O_{10}$. Calculated (%): C, 56.56; H, 5.34; N, 4.12. ^{1}H NMR, δ: 1.41 (t,

6 H, 2 Me, J = 7.3 Hz); 3.66 (s, 6 H, 2 MeO); 4.48 (q, 4 H, 2 CH_2, J = 7.3 Hz); 4.81 (dd, 2 H, 2 C<u>H</u>Ar, J = 10.9 Hz, J = 7.5 Hz); 4.88 (dd, 2 H, 2 C<u>H</u>Py, J = 10.9 Hz, J = 7.5 Hz); 6.77 (d, 4 H, 2 H(3′), 2 H(5′), J = 9.0 Hz); 7.18 (d, 4 H, 2 H(2′), 2 H(6′), J = 9.0 Hz); 7.92 (d, 4 H, 2 H(3), 2 H(5), J = 6.9 Hz); 8.87 (d, 4 H, 2 H(2), 2 H(6), J = 6.9 Hz).

1-Ethyl-*r*-4-{*t*-3-(1-ethylpyridinium-4-yl)-*c*-2,*t*-4-bis[4-(methylsulfanyl)phenyl]cyclobutyl}pyridinium diperchlorate (**A_{3e}**, *rctt* isomer of the cyclobutane derivative from compound **3e**, type **A**) was prepared as a pale-yellow powder, m.p. >169 °C (with decomp.). Found (%): C, 51.35; H, 4.89; N, 4.06. $C_{32}H_{36}Cl_2N_2O_8S_2 \cdot 2H_2O$. Calculated (%): C, 51.40; H, 5.39; N, 3.75. ^{1}H NMR, δ: 1.42 (t, 6 H, 2 Me, J = 7.2 Hz); 2.39 (s, 6 H, 2 MeS); 4.49 (q, 4 H, 2 CH_2, J = 7.2 Hz); 4.85 (dd, 2 H, 2 C<u>H</u>Ar, J = 9.8 Hz, J = 6.9 Hz); 4.93 (dd, 2 H, 2 C<u>H</u>Py, J = 9.8 Hz, J = 6.9 Hz); 7.11 (d, 4 H, 2 H(3′), 2 H(5′), J = 8.1 Hz); 7.20 (d, 4 H, 2 H(2′), 2 H(6′), J = 8.1 Hz); 7.94 (d, 4 H, 2 H(3), 2 H(5), J = 6.4 Hz); 8.88 (d, 4 H, 2 H(2), 2 H(6), J = 6.4 Hz).

***r*-4-[*c*-2,*t*-4-Bis(3,4-dichlorophenyl)-*t*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diperchlorate** (**A_{3f}**, *rctt* isomer of the cyclobutane derivative from compound **3f**, type **A**). ^{1}H NMR, δ: 1.42 (t, 6 H, 2 Me, J = 7.3 Hz); 4.51 (q, 4 H, 2 CH_2, J = 7.3 Hz); 4.96 (dd, 2 H, 2 C<u>H</u>Ar, J = 9.2 Hz, J = 6.1 Hz); 5.01 (dd, 2 H, 2 C<u>H</u>Py, J = 9.2 Hz, J = 6.1 Hz); 7.24 (dd, 2 H, 2 H(6′), J = 8.5 Hz, J = 1.9 Hz); 7.49 (d, 2 H, 2 H(5′), J = 8.5 Hz); 7.60 (d, 2 H, 2 H(2′), J = 1.9 Hz); 7.96 (d, 4 H, 2 H(3), 2 H(5), J = 7.1 Hz); 8.92 (d, 4 H, 2 H(2), 2 H(6), J = 7.1 Hz).

***r*-4-[*t*-2,*t*-3-Bis(3,4-dichlorophenyl)-*c*-4-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diperchlorate** (**B_{3f}**, *rctt* isomer of the cyclobutane derivative from compound **3f**, type **B**). ^{1}H NMR, δ: 1.43 (t, 6 H, 2 Me, J = 7.3 Hz); 4.48 (q, 4 H, 2 CH_2, J = 7.3 Hz); 4.82 (m, 2 H, 2 C<u>H</u>Ar, $^3J_{trans\text{-}H_b,H_a}$ = 6.7 Hz); 5.11 (m, 2 H, 2 C<u>H</u>Py, $^3J_{trans\text{-}H_a,H_b}$ = 6.7 Hz); 7.20 (dd, 2 H, 2 H(6′), J = 8.5 Hz, J = 1.9 Hz); 7.52 (d, 2 H, 2 H(5′), J = 8.5 Hz); 7.57 (d, 2 H, 2 H(2′), J = 1.9 Hz); 7.98 (d, 4 H, 2 H(3), 2 H(5), J = 6.8 Hz); 8.90 (d, 4 H, 2 H(2), 2 H(6), J = 6.8 Hz).

1-Ethyl-*r*-4-[*t*-3-(1-ethylpyridinium-4-yl)-*c*-2,*t*-4-bis(4-nitrophenyl)cyclobutyl]pyridinium diperchlorate (**A_{3g}**, *rctt* isomer

Table 3. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of **1b**, **1b**·C_6H_6·H_2O, **2a**, and **2b**·$2C_6H_6$

Compound	**1b**	**1b**·C_6H_6·H_2O	**2a**	**2b**·$2C_6H_6$
Molecular formula	$C_{25}H_{34}INO_6$	$C_{31}H_{42}INO_7$	$C_{17}H_{20}INO_2$	$C_{29}H_{33}IN_2$
M/g mol^{-1}	571.43	667.56	397.24	536.47
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a/Å	8.5838(12)	10.0116(19)	8.1982(7)	6.4685(3)
b/Å	6.6948(9)	8.0191(16)	9.5753(9)	16.3121(9)
c/Å	21.707(3)	38.651(8)	12.1059(10)	25.4514(14)
α/deg	90	90	69.928(3)	90
β/deg	92.289(4)	90.657(9)	73.081(3)	90
γ/deg	90	90	71.771(3)	90
V/Å^3	1246.4(3)	3102.9(11)	829.64(13)	2685.5(2)
Z	2	4	2	4
d_{calc}/g cm^{-3}	1.523	1.429	1.590	1.327
F(000)	584	1376	396	1096
μ(Mo-$K\alpha$)/mm^{-1}	1.324	1.078	1.934	1.210
Crystal dimensions/mm	0.28×0.18×0.04	0.30×0.14×0.10	0.24×0.20×0.04	0.48×0.22×0.10
θ Scan mode/range, deg	ω/2.59—29.00	ω/2.10—30.11	ω/1.83—29.00	ω/1.60—30.03
Ranges of indices of measured reflections	$-11 \le h \le 11$, $-9 \le k \le 7$, $-26 \le l \le 29$	$-13 \le h \le 12$, $-11 \le k \le 11$, $-54 \le l \le 52$	$-11 \le h \le 10$, $-13 \le k \le 12$, $-16 \le l \le 16$	$-7 \le h \le 9$, $-22 \le k \le 16$, $-33 \le l \le 34$
Number of measured reflections	8603	19384	4677	15887
Number of independent reflections (R_{int})	5811 (0.0354)	8711 (0.1442)	3923 (0.0157)	6941 (0.0418)
Number of reflections with $I > 2\sigma(I)$	4953	3869	3604	6227
Number of variables	298	368	270	305
R factors based on reflections with $I > 2\sigma(I)$	$R_1 = 0.0508$, $wR_2 = 0.1008$	$R_1 = 0.2277$, $wR_2 = 0.4949$	$R_1 = 0.0226$, $wR_2 = 0.0586$	$R_1 = 0.0688$, $wR_2 = 0.1596$
R factors based on all reflections	$R_1 = 0.0645$, $wR_2 = 0.1052$	$R_1 = 0.3052$, $wR_2 = 0.5214$	$R_1 = 0.0253$, $wR_2 = 0.0597$	$R_1 = 0.0779$, $wR_2 = 0.1640$
Goodness-of-fit on F^2	1.030	1.070	1.073	1.166
Residual electron density (min/max)/e Å^{-3}	−0.841/1.938	−3.245/2.339	−0.611/0.554	−3.017/1.802

of the cyclobutane derivative from compound **3g**, type **A**). ^{1}H NMR, δ: 1.41 (t, 6 H, 2 Me, J = 7.3 Hz); 4.47 (q, 4 H, 2 CH_2, J = 7.3 Hz); 5.13 (dd, 2 H, 2 C<u>H</u>Ar, J = 8.8 Hz, J = 5.3 Hz); 5.18 (dd, 2 H, 2 C<u>H</u>Py, J = 8.8 Hz, J = 5.3 Hz); 7.57 (d, 4 H, 2 H(2′), 2 H(6′), J = 8.7 Hz); 7.99 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.12 (d, 4 H, 2 H(3′), 2 H(5′), J = 8.7 Hz); 8.90 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz).

1-Ethyl-*r*-4-[*c*-2-(1-ethylpyridinium-4-yl)-*t*-3,*t*-4-bis(4-nitrophenyl)cyclobutyl]pyridinium diperchlorate (**B_{3g}**, *rctt* isomer of the cyclobutane derivative from compound **3g**, type **B**). ^{1}H NMR, δ: 1.44 (t, 6 H, 2 Me, J = 7.4 Hz); 4.50 (q, 4 H, 2 CH_2, J = 7.4 Hz); 5.07 (m, 2 H, 2 C<u>H</u>Ar, $^3J_{trans\text{-}H_b,H_a}$ = 6.7 Hz); 5.21 (m, 2 H, 2 C<u>H</u>Py, $^3J_{trans\text{-}H_a,H_b}$ = 6.7 Hz); 7.53 (d, 4 H, 2 H(2′), 2 H(6′), J = 8.9 Hz); 8.04 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.10 (d, 4 H, 2 H(3′), 2 H(5′), J = 8.9 Hz); 8.93 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz).

***r*-4-[*c*-2,*t*-4-Bis{4-[ethyl(dimethyl)ammonio]phenyl}-*t*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium tetraperchlorate** (**A_{3h}**, *rctt* isomer of the cyclobutane derivative from compound **3h**, type **A**). ^{1}H NMR, δ: 0.95 (t, 6 H, 2 <u>Me</u>$CH_2$$NMe_2$, J = 6.9 Hz); 1.52 (t, 6 H, 2 <u>Me</u>CH_2N, J = 7.2 Hz); 3.52 (s, 12 H, 2 Me_2N); 3.90 (q, 4 H, 2 MeC<u>H</u>$_2$$NMe_2$, J = 6.9 Hz); 4.58 (q, 4 H, 2 MeC<u>H</u>$_2$N, J = 7.2 Hz); 5.05 (dd, 2 H, 2 C<u>H</u>Ar, J = 7.1 Hz, J = 4.5 Hz); 5.10 (dd, 2 H, 2 C<u>H</u>Py, J = 7.1 Hz, J = 4.5 Hz); 7.50 (d, 4 H, 2 H(2′), 2 H(6′), J = 8.6 Hz); 7.70 (d, 4 H, 2 H(3′), 2 H(5′), J = 8.6 Hz); 7.95 (d, 4 H, 2 H(3), 2 H(5), J = 6.6 Hz); 8.89 (d, 4 H, 2 H(2), 2 H(6), J = 6.6 Hz).

***r*-4-[*t*-2,*t*-3-Bis{4-[ethyl(dimethyl)ammonio]phenyl}-*c*-4-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium tetraperchlorate** (**B_{3h}**, *rctt* isomer of the cyclobutane derivative from compound **3h**, type **B**). ^{1}H NMR, δ: 1.00 (t, 6 H, 2 <u>Me</u>$CH_2$$NMe_2$, J = 7.3 Hz); 1.51 (t, 6 H, 2 <u>Me</u>CH_2N, J = 7.2 Hz); 3.55 (s, 12 H, 2 Me_2N); 3.93 (q, 4 H, 2 MeC<u>H</u>$_2$$NMe_2$, J = 7.3 Hz); 4.59 (q, 4 H, 2 MeC<u>H</u>$_2$N, J = 7.2 Hz); 4.92 (m, 2 H, 2 C<u>H</u>Ar, $^3J_{trans\text{-}H_b,H_a}$ = 6.5 Hz); 5.17 (m, 2 H, 2 C<u>H</u>Py, $^3J_{trans\text{-}H_a,H_b}$ = 6.5 Hz); 7.55 (d, 4 H, 2 H(2′), 2 H(6′), J = 8.6 Hz); 7.83 (d, 4 H, 2 H(3′), 2 H(5′), J = 8.6 Hz); 7.99 (d, 4 H, 2 H(3), 2 H(5), J = 6.5 Hz); 8.92 (d, 4 H, 2 H(2), 2 H(6), J = 6.5 Hz).

Table 4. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of **3a**, **3b**, **3b**·2C_6H_6, and **3c**·C_6H_6

Compound	**3a**	**3b**	**3b**·2C_6H_6	**3c**·C_6H_6
Molecular formula	$C_{17}H_{20}ClNO_6$	$C_{17}H_{21}ClN_2O_4$	$C_{29}H_{33}ClN_2O_4$	$C_{21}H_{22}ClNO_4$
M/g mol^{-1}	369.79	352.81	509.02	387.85
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$Pbca$
a/Å	6.9564(10)	6.8668(2)	6.4752(4)	12.7358(15)
b/Å	21.202(3)	8.0649(3)	16.5448(11)	16.560(2)
c/Å	11.4501(16)	30.7437(9)	25.7090(16)	18.182(2)
α/deg	90	90	90	90
β/deg	91.514(6)	90	90	90
γ/deg	90	90	90	90
V/Å^3	1688.2(4)	1702.59(9)	2754.2(3)	3834.6(8)
Z	4	4	4	8
d_{calc}/g cm^{-3}	1.455	1.376	1.228	1.344
F(000)	396	744	1080	1632
μ(Mo-$K\alpha$)/mm^{-1}	0.261	0.248	0.174	0.226
Crystal dimensions/mm	0.36×0.26×0.14	0.42×0.36×0.08	0.40×0.14×0.10	0.38×0.26×0.26
θ Scan mode/range, deg	ω/1.78—27.00	ω/2.61—28.99	ω/2.01—30.01	ω/2.24—30.53
Ranges of indices of measured reflections	$-8 \le h \le 8$, $-27 \le k \le 26$, $-14 \le l \le 14$	$-8 \le h \le 9$, $-7 \le k \le 10$, $-41 \le l \le 37$	$-8 \le h \le 9$, $-19 \le k \le 23$, $-35 \le l \le 33$	$-15 \le h \le 18$, $-21 \le k \le 23$, $-15 \le l \le 25$
Number of measured reflections	11767	10955	18951	26879
Number of independent reflections (R_{int})	3649 (0.0725)	4386 (0.0350)	7444 (0.1679)	5855 (0.0723)
Number of reflections with $I > 2\sigma(I)$	2953	3739	3333	3026
Number of variables	344	255	342	401
R factors based on reflections with $I > 2\sigma(I)$	$R_1 = 0.1367$, $wR_2 = 0.3761$	$R_1 = 0.0791$, $wR_2 = 0.2262$	$R_1 = 0.1364$, $wR_2 = 0.2889$	$R_1 = 0.1018$, $wR_2 = 0.2840$
R factors based on all reflections	$R_1 = 0.1506$, $wR_2 = 0.3872$	$R_1 = 0.0912$, $wR_2 = 0.2368$	$R_1 = 0.2560$, $wR_2 = 0.3553$	$R_1 = 0.1735$, $wR_2 = 0.3004$
Goodness-of-fit on F^2	1.574	1.064	1.012	1.075
Residual electron density (min/max)/e Å^{-3}	−0.976/1.927	−0.462/0.948	−0.501/1.533	−0.695/0.408

***r*-4-[*t*-2,*t*-4-Bis{4-[ethyl(dimethyl)ammonio]phenyl}-*c*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium tetraperchlorate** ($\mathbf{C_{3h}}$, *rctct* isomer of the cyclobutane derivative from compound **3h**, type **C**). ^{1}H NMR, δ: 0.95 (t, 6 H, 2 MeCH$_2$NMe$_2$, J = 6.9 Hz); 1.52 (t, 6 H, 2 MeCH$_2$N, J = 7.2 Hz); 3.52 (s, 12 H, 2 Me$_2$N); 3.89 (q, 4 H, 2 MeCH$_2$NMe$_2$, J = 6.9 Hz); 4.23 (t, 2 H, 2 CHAr, J = 9.7 Hz); 4.34 (t, 2 H, 2 CHPy, J = 9.7 Hz); 4.58 (q, 4 H, 2 MeCH$_2$N, J = 7.2 Hz); 7.71 (d, 4 H, 2 H(2′), 2 H(6′), J = 8.6 Hz); 7.84 (d, 4 H, 2 H(3′), 2 H(5′), J = 8.6 Hz); 8.24 (d, 4 H, 2 H(3), 2 H(5), J = 6.6 Hz); 9.06 (d, 4 H, 2 H(2), 2 H(6), J = 6.6 Hz).

***r*-4-[*t*-2,*c*-3-Bis{4-[ethyl(dimethyl)ammonio]phenyl}-*t*-4-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium tetraperchlorate** ($\mathbf{D_{3h}}$, *rtct* isomer of the cyclobutane derivative from compound **3h**, type **D**). ^{1}H NMR, δ: 0.76 (t, 6 H, 2 MeCH$_2$NMe$_2$, J = 7.0 Hz); 1.39 (t, 6 H, 2 MeCH$_2$N, J = 7.2 Hz); 3.46 (s, 12 H, 2 Me$_2$N); 3.82 (q, 4 H, 2 MeCH$_2$NMe$_2$, J = 7.0 Hz); 4.23 (m, 2 H, 2 CHAr, $^3J_{trans\text{-}H_a,H_b}$ = 10.0 Hz); 4.32 (m, 2 H, 2 CHPy, $^3J_{trans\text{-}H_a,H_b}$ = 10.0 Hz); 4.47 (q, 4 H, 2 MeCH$_2$N, J = 7.2 Hz); 7.68 (d, 4 H, 2 H(2′), 2 H(6′), J = 8.7 Hz); 7.83 (d, 4 H, 2 H(3′), 2 H(5′), J = 8.7 Hz); 8.20 (d, 4 H, 2 H(3), 2 H(5), J = 6.5 Hz); 9.06 (d, 4 H, 2 H(2), 2 H(6), J = 6.5 Hz).

***r*-2-[*c*-2,*t*-4-Bis(3,4-dimethoxyphenyl)-*t*-3-(3-ethyl-1,3-benzothiazol-3-ium-2-yl)cyclobutyl]-3-ethyl-1,3-benzothiazol-3-ium diperchlorate** ($\mathbf{A_5}$, *rctt* isomer of the cyclobutane derivative from compound **5**, type **A**) was prepared as a yellow powder, m.p. >192 °C (with decomp.). Found (%): C, 53.56; H, 4.68; N, 3.44. $C_{38}H_{40}Cl_2N_2O_{12}S_2$. Calculated (%): C, 53.58; H, 4.73; N, 3.29. ^{1}H NMR, δ: 1.34 (t, 6 H, 2 MeCH$_2$N, J = 7.1 Hz); 3.59 (s, 6 H, 2 3-MeO); 3.66 (s, 6 H, 2 4-MeO); 4.55 (m, 2 H, 2 MeCHH′N); 4.69 (m, 2 H, 2 MeCHH′N); 5.30 (dd, 2 H, 2 CHAr, J = 8.6 Hz, J = 7.9 Hz); 5.47 (dd, 2 H, 2 CHHet, J = 8.6 Hz, J = 7.9 Hz); 6.91 (d, 2 H, 2 H(5′), J = 8.4 Hz); 7.03 (d, 2 H, 2 H(2′), J = 1.9 Hz); 7.19 (dd, 2 H, 2 H(6′), J = 8.4 Hz, J = 1.9 Hz); 7.82 (m, 2 H, 2 H(6)); 7.90 (m, 2 H, 2 H(5)); 8.25 (d, 2 H, 2 H(4), J = 8.5 Hz); 8.48 (d, 2 H, 2 H(7), J = 8.2 Hz).

X-ray diffraction study. Crystals of dyes **1b**, **2a,b**, **3a—e,g,** and **5** were grown by slow diffusion of benzene vapor into their

Table 5. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of **3d**, **3d**·C_6H_6, **3e**, and **3e**·C_6H_6

Compound	**3d**	**3d**·C_6H_6	**3e**	**3e**·C_6H_6
Molecular formula	$C_{16}H_{18}ClNO_5$	$C_{22}H_{24}ClNO_5$	$C_{16}H_{18}ClNO_4S$	$C_{22}H_{24}ClNO_4S$
M/g mol^{-1}	339.76	417.87	355.82	433.93
Crystal system		Monoclinic		
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	7.5224(5)	17.738(3)	7.9144(3)	17.9283(7)
b/Å	11.3017(8)	6.5673(12)	11.1005(4)	6.6644(3)
c/Å	18.8763(13)	18.083(3)	19.0056(7)	18.0521(6)
α/deg	90	90	90	90
β/deg	91.2130(10)	99.680(7)	96.345(2)	101.031(2)
γ/deg	90	90	90	90
V/Å^3	1604.43(19)	2076.6(6)	1659.49(11)	2117.04(14)
Z	4	4	4	4
d_{calc}/g cm^{-3}	1.407	1.337	1.424	1.361
F(000)	712	880	744	912
μ(Mo-$K\alpha$)/mm^{-1}	0.263	0.217	0.375	0.308
Crystal dimensions/mm	0.44×0.24×0.16	0.18×0.10×0.02	0.36×0.18×0.14	0.48×0.30×0.12
θ Scan mode/range, deg	ω/2.10—30.01	ω/2.29—29.00	ω/2.69—30.03	ω/3.27—30.51
Ranges of indices of measured reflections	$-10 \le h \le 10$, $-7 \le k \le 15$, $-26 \le l \le 21$	$-24 \le h \le 24$, $-8 \le k \le 8$, $-24 \le l \le 24$	$-10 \le h \le 11$, $-15 \le k \le 13$, $-26 \le l \le 26$	$-20 \le h \le 25$, $-9 \le k \le 7$, $-21 \le l \le 25$
Number of measured reflections	10899	13926	15415	12632
Number of independent reflections (R_{int})	4409 (0.0434)	5458 (0.2621)	4826 (0.0524)	6244 (0.0255)
Number of reflections with $I > 2\sigma(I)$	2700	1536	2718	4838
Number of variables	329	393	349	439
R factors based on reflections with $I > 2\sigma(I)$	$R_1 = 0.0538$, $wR_2 = 0.0987$	$R_1 = 0.0919$, $wR_2 = 0.1891$	$R_1 = 0.0533$, $wR_2 = 0.1245$	$R_1 = 0.0478$, $wR_2 = 0.1153$
R factors based on all reflections	$R_1 = 0.1053$, $wR_2 = 0.1138$	$R_1 = 0.2930$, $wR_2 = 0.2370$	$R_1 = 0.1122$, $wR_2 = 0.1504$	$R_1 = 0.0657$, $wR_2 = 0.1257$
Goodness-of-fit on F^2	1.029	0.730	1.003	1.026
Residual electron density (min/max)/e Å^{-3}	−0.318/0.226	−0.519/0.496	−0.387/0.506	−0.329/0.586

acetonitrile solutions in the dark. Solvent-free crystals of dyes **3b—e** were grown by saturating acetonitrile solutions with ethyl acetate vapor. Crystals of dye **3f** were grown by saturating a solution in an acetonitrile—ethyl acetate mixture with hexane vapor.

Single crystals of the dyes, which were stored in the dark, were mounted on a Bruker SMART-CCD diffractometer in a cold nitrogen stream ($T = 120.0(2)$ K). The experimental X-ray reflections were measured using Mo-Kα radiation (0.71073 Å, graphite monochromator, ω-scanning technique). The X-ray diffraction data were processed using the SAINT program.[47] All structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms. For the crystals of **1b**, **1b**·C_6H_6·H_2O, **2a**, and **2b**·$2C_6H_6$, absorption corrections were applied using the SADABS method. The hydrogen atoms were positioned geometrically and refined either isotropically (**2a** and **3a,g**) or using a riding model (**1b**, **1b**·C_6H_6·H_2O, **2b**·$2C_6H_6$, **3b**, **3b**·$2C_6H_6$, and **3c**·C_6H_6). In the structures of **3d**, **3d**·C_6H_6, **3e**, **3e**·C_6H_6, **3f**, and **5**·0.5MeCN·0.5H_2O, the hydrogen atoms were refined either isotropically or using a riding model.

In most of the crystal structures, the dye cation is disordered over two positions. The occupancy ratios for two *s* conformers were 0.63 : 0.37 (**2b**·$2C_6H_6$), 0.50 : 0.50 (**3b**), 0.55 : 0.45 (**3b**·$2C_6H_6$), 0.53 : 0.47 (**3c**·C_6H_6), 0.74 : 0.26 (**3d**), 0.77 : 0.23 (**3d**·C_6H_6), 0.52 : 0.48 (**3e**), 0.91 : 0.09 (**3e**·C_6H_6), and 0.64 : 0.36 (**3f**). In some crystals, the perchlorate ion is rotationally disordered over two positions (the rotation about the center of gravity) with an occupancy ratio of 0.65 : 0.35 (**3a**), 0.93 : 0.07 (**3d**·C_6H_6), and 0.95 : 0.05 (**3e**·C_6H_6). In the other crystals, the disorder of this anion is described as a spinning top with an occupancy ratio of 0.71 : 0.29 (**3f**) and 0.68 : 0.32 (**5**·0.5MeCN·0.5H_2O). In the crystals of **3c**·C_6H_6, the benzene molecule is disordered over two close positions with an occupancy ratio of 0.77 : 0.23. In the crystal of **5**·0.5MeCN·0.5H_2O, the MeCN solvent molecules and two water solvent molecules alternately occupy close positions with an occupancy ratio of 0.50 : 0.25 : 0.25 (the H atoms of the water molecules were not located).

Table 6. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of **3f,g** and **5**·0.5MeCN·0.5H_2O

Compound	**3f**	**3g**	**5**·0.5MeCN·0.5H_2O
Molecular formula	$C_{15}H_{14}Cl_3NO_4$	$C_{15}H_{15}ClN_2O_6$	$C_{20}H_{22.5}ClN_{1.5}O_{6.5}S$
M/g mol^{-1}	378.62	354.74	455.41
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	7.2511(6)	7.8098(5)	7.4197(15)
b/Å	20.8503(16)	18.2263(13)	11.398(2)
c/Å	11.1782(8)	10.9959(8)	14.333(3)
α/deg	90	90	108.40(3)
β/deg	108.769(2)	95.505(2)	100.66(3)
γ/deg	90	90	92.56(3)
V/Å^3	1600.1(2)	1557.98(19)	1123.3(4)
Z	4	4	2
d_{calc}/g cm^{-3}	1.572	1.512	1.346
F(000)	776	736	476
μ(Mo-$K\alpha$)/mm^{-1}	0.591	0.281	0.302
Crystal dimensions/mm	0.16×0.08×0.08	0.62×0.32×0.26	0.56×0.22×0.08
θ Scan mode/range, deg	ω/1.95—30.03	ω/2.17—29.00	ω/1.89—28.99
Ranges of indices of measured reflections	$-7 \le h \le 9$, $-28 \le k \le 17$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-24 \le k \le 14$, $-11 \le l \le 15$	$-10 \le h \le 10$, $-8 \le k \le 15$, $-17 \le l \le 16$
Number of measured reflections	10982	7380	5886
Number of independent reflections (R_{int})	4364 (0.0549)	3887 (0.0199)	5226 (0.0189)
Number of reflections with $I > 2\sigma(I)$	2793	3070	3548
Number of variables	378	277	386
R factors based on reflections with $I > 2\sigma(I)$	$R_1 = 0.0552$, $wR_2 = 0.0951$	$R_1 = 0.0357$, $wR_2 = 0.0964$	$R_1 = 0.0753$, $wR_2 = 0.2323$
R factors based on all reflections	$R_1 = 0.1038$, $wR_2 = 0.1075$	$R_1 = 0.0507$, $wR_2 = 0.1018$	$R_1 = 0.1062$, $wR_2 = 0.2516$
Goodness-of-fit on F^2	1.030	1.053	1.128
Residual electron density (min/max)/e Å^{-3}	−0.334/0.260	−0.356/0.361	−0.727/0.913

The crystals of **1b** · C_6H_6 · H_2O were of low quality, and the quality became worse in the course of the X-ray data collection. This is, apparently, associated with the fact that the autophotocycloaddition rather rapidly proceeded in these crystals under the action of light, resulting in the gradual degradation of single crystals. Nevertheless, we succeeded in performing the X-ray diffraction experiment. Benzene and water solvent molecules were located in difference electron density maps. The water molecule occupies the cavity of the crown ether and forms hydrogen bonds with the oxygen atoms of the macrocycle. In spite of a low accuracy of the X-ray diffraction data, it is sufficient for the discussion of the crystal packing of this compound.

All calculations were carried out with the use of the SHELXTL-Plus program package.[48] The crystallographic characteristics and the X-ray diffraction data collection and refinement statistics are given in Tables 3—6. The atomic coordinates and other experimental data were deposited with the Cambridge Structural Database;* the CSD refcodes 648503 (**1b**), 648504 (**1b** · C_6H_6 · H_2O), 648505 (**2a**), 648506 (**2b** · $2C_6H_6$), 648507 (**3a**), 648508 (**3b**), 648509 (**3b** · $2C_6H_6$), 648510 (**3c** · C_6H_6), 648511 (**3d**), 648512 (**3d** · C_6H_6), 648513 (**3e**), 648514 (**3e** · C_6H_6), 648515 (**3f**), 648516 (**3g**), and 648517 (**5** · 0.5MeCN · 0.5H_2O).

The X-ray diffraction data for the crystals of **3c**, **3c** · 0.5C_6H_6, and **3h** have been reported earlier[23] and were deposited with the Cambridge Structural Database (CSD refcodes 647441, 647442, and 647445, respectively).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 06-03-32434, 06-03-33162, and 06-03-08202-ofi), the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program No. 7), and the Royal Society of Chemistry (Great Britain, Personal Grants for L. G. Kuz´mina, A. V. Churakov, and J. A. K. Howard).

References

1. M. D. Cohen and G. M. Schmidt, *J. Chem. Soc.*, 1964, 1996.
2. G. M. Schmidt, *J. Pure Appl. Chem.*, 1971, **27**, 647.
3. V. Ramamurthy and K. Venkatesan, *Chem. Rev.*, 1987, **87**, 433.
4. K. S. S. P. Rao, S. M. Hubig, J. N. Moorthy, and J. K. Kochi, *J. Org. Chem.*, 1999, **64**, 8098.
5. T. D. Hamilton, G. S. Papaefstathiou, and L. R. MacGillivray, *J. Am. Chem. Soc.*, 2002, **124**, 11606.
6. L. R. MacGillivray, *Cryst. Eng. Commun.*, 2002, **4**, 37.
7. V. Darcos, K. Griffith, X. Sallenave, J.-P. Desvergne, C. Guyard-Duhayon, B. Hasenknopf, and D. M. Bassani, *Photochem. Photobiol. Sci.*, 2003, **2**, 1152.
8. J. Hockemeyer, J. C. Burbiel, and C. E. Müller, *J. Org. Chem.*, 2004, **69**, 3308.
9. T. Caronna, R. Liantonio, T. A. Logothetis, P. Metrangolo, T. Pilati, and G. Resnati, *J. Am. Chem. Soc.*, 2004, **126**, 4500.
10. H. Maeda, K. Nishimura, K. Mizuno, M. Yamaji, J. Oshima, and S. Tobita, *J. Org. Chem.*, 2005, **70**, 9693.
11. F. H. Allen, M. F. Mahon, P. R. Raithby, G. P. Shields, and H. A. Sparkes, *New J. Chem.*, 2005, **29**, 182.
12. Y. Ohashi, *Acta Crystallogr., Sect. A*, 1998, **54**, 842.
13. H. Hosomi, S. Ohba, K. Tanaka, and F. Toda, *J. Am. Chem. Soc.*, 2000, **122**, 1818.
14. I. Turowska-Tyrk, *J. Phys. Org. Chem.*, 2004, **17**, 837.
15. H. Nalanishi, W. Jones, J. M. Thomas, and K. Honda, *Bull. Chem. Soc. Jpn*, 2002, **75**, 2383.
16. S. P. Gromov and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 641 [*Russ. Chem. Bull.*, 1997, **46**, 611 (Engl. Transl.)].
17. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, I. I. Baskin, A. V. Buevich, E. N. Andryukhina, M. V. Alfimov, D. Johnels, U. G. Edlund, J. K. Whitesell, and M. A. Fox, *J. Org. Chem.*, 2003, **68**, 6115.
18. A. I. Vedernikov, N. A. Lobova, E. N. Ushakov, M. V. Alfimov, and S. P. Gromov, *Mendeleev Commun.*, 2005, **15**, 173.
19. A. I. Vedernikov, S. K. Sazonov, P. S. Loginov, N. A. Lobova, M. V. Alfimov, and S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 29.
20. A. I. Vedernikov, S. P. Gromov, N. A. Lobova, L. G. Kuz´mina, Yu. A. Strelenko, J. A. K. Howard, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1896 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1954].
21. S. P. Gromov, A. I. Vedernikov, N. A. Lobova, L. G. Kuz´mina, S. N. Dmitrieva, O. V. Tikhonova, and M. V. Alfimov, Pat. RF 2278134; *Byul. izobret.* [*Inventor Bull.*], 2006, No. 17 (in Russian).
22. L. G. Kuz´mina, A. I. Vedernikov, N. A. Lobova, A. V. Churakov, J. A. K. Howard, M. V. Alfimov, and S. P. Gromov, *New J. Chem.*, 2007, **31**, 980.
23. L. G. Kuz´mina, A. I. Vedernikov, S. K. Sazonov, N. A. Lobova, P. S. Loginov, J. A. K. Howard, M. V. Alfimov, and S. P. Gromov, *Kristallografiya*, 2008, **53**, № 2 [*Crystallogr. Repts*, 2008, **53** (Engl. Transl.)].
24. J. L. R. Williams, R. E. Adel, J. M. Carlson, G. A. Reynolds, D. G. Borden, and J. A. Ford, *J. Org. Chem.*, 1963, **28**, 387.
25. A. K. Yatsimirskii, *Itogi nauki i tekhniki. Bioorganicheskaya khimiya* [*Advances in Science and Technology, Ser. Bioorganic Chemistry*], VINITI, Moscow, 1990, **17**, 148 (in Russian).
26. T. Steiner, *Acta Crystallogr., Sect. B*, 1998, **54**, 456.
27. D. A. Dickie, D. Abeysekera, I. D. VcKenzie, H. A. Jenkins, and J. C. Clyburne, *Cryst. Eng.*, 2003, **6**, 79.
28. T. Sakurai, *J. Nucl. Sci. Technol.*, 1996, **33**, 266.
29. R. Grünwald and H. Tributsch, *J. Phys. Chem. B*, 1997, **101**, 2564.
30. S. P. Gromov, D. E. Levin, K. Ya. Burshtein, V. E. Krasnovskii, S. N. Dmitrieva, A. A. Golosov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 999 [*Russ. Chem. Bull.*, 1997, **46**, 959 (Engl. Transl.)].
31. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, V. A. Soldatenkova, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1192 [*Russ. Chem. Bull.*, 1997, **46**, 1143 (Engl. Transl.)].
32. H. Görner and H. Gruen, *J. Photochem.*, 1985, **28**, 329.
33. S. P. Gromov, A. I. Vedernikov, Yu. V. Fedorov, O. A. Fedorova, E. N. Andryukhina, N. E. Shepel´, Yu. A. Strelenko, D. Johnels, U. G. Edlund, J. Saltiel, and

* CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223 33 6033; e-mail: deposit@ccdc.cam.ac.uk). The data can also be obtained from the authors.

M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1524 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1569].
34. M. V. Alfimov, S. P. Gromov, O. B. Stanislavskii, E. N. Ushakov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1449 [*Russ. Chem. Bull.*, 1993, **42**, 1385 (Engl. Transl.)].
35. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, A. V. Buevich, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2225 [*Russ. Chem. Bull.*, 1995, **44**, 2131 (Engl. Transl.)].
36. O. A. Fedorova, Yu. V. Fedorov, A. I. Vedernikov, S. P. Gromov, O. V. Yescheulova, M. V. Alfimov, M. Woerner, S. Bossmann, A. Braun, and J. Saltiel, *J. Phys. Chem. A*, 2002, **106**, 6213.
37. D. Donati, M. Fiorenza, and P. S. Fautoni, *J. Heterocycl. Chem.*, 1979, **16**, 253.
38. S. K. Kearsley, *Studies in Organic Chemistry. 32. Organic Solid State Chemistry*, Ed. G. R. Desiraju, Elsevier, Amsterdam, 1987, **32**, 69.
39. M. V. Alfimov, A. V. Churakov, Yu. V. Fedorov, O. A. Fedorova, S. P. Gromov, R. E. Hester, J. A. K. Howard, L. G. Kuz´mina, I. K. Lednev, and J. N. Moore, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2249.
40. O. A. Fedorova, Yu. V. Fedorov, A. I. Vedernikov, O. V. Yescheulova, S. P. Gromov, M. V. Alfimov, L. G. Kuz´mina, A. V. Churakov, J. A. K. Howard, S. Yu. Zaitsev, T. I. Sergeeva, and D. Möbius, *New J. Chem.*, 2002, **26**, 543.
41. S. P. Gromov, A. I. Vedernikov, E. N. Ushakov, L. G. Kuz´mina, A. V. Feofanov, V. G. Avakyan, A. V. Churakov, Yu. S. Alaverdian, E. V. Malysheva, M. V. Alfimov, J. A. K. Howard, B. Eliasson, and U. G. Edlund, *Helv. Chim. Acta*, 2002, **85**, 60.
42. S. P. Gromov, S. A. Sergeev, S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, L. G. Kuz´mina, A. V. Churakov, J. A. K. Howard, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 530 [*Russ. Chem. Bull.*, 1999, **48**, 525 (Engl. Transl.)].
43. E. N. Andryukhina, M. M. Mashura, O. A. Fedorova, L. G. Kuz´mina, J. A. K. Howard, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1650 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1700].
44. A. K. Sheinkman and L. G. Piotrkovskaya, *Metody polucheniya khimicheskikh reaktivov i preparatov* [*Methods for the Synthesis of Chemical Reagents and Preparations*], IREA, Moscow, 1965, Vol. 13, 29 (in Russian).
45. O. A. Fedorova, E. N. Andryukhina, A. V. Lindeman, S. S. Basok, T. Yu. Bogashchenko, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 302 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 319].
46. F. Cherioux, P. Audebert, and P. Hapiot, *Chem. Mater.*, 1998, **10**, 1984.
47. *SAINT, Version 6.02A*, Bruker AXS Inc., Madison (Wisconsin, USA), 2001.
48. *SHELXTL-Plus, Version 5.10*, Bruker AXS Inc., Madison (Wisconsin, USA), 1997.

Received May 30, 2007;
in revised form July 25, 2007