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Cation-dependent pericyclic reactions of crown-containing photochromic compounds

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The review is devoted to the photochromism of pericyclic reactions of crown-containing photochromic systems. The complex formation of photochromic crown ethers with metal cations has a substantial effect on both the spectral characteristics of molecules and occurrence of photochromic reactions. A possibility to create systems with photocontrolled complex-forming properties is an attractive feature of the novel systems.

Key words: crown ethers, photochromic compounds, pericyclic reactions, electrocyclic reactions, cycloaddition, complex formation, spirodihydroindolizines, spiropyrans, spironaphthoxazines, benzo- and naphthopyrans, fulgides, dihetarylethenes, cyclophanes, styryl dyes, anthracene derivatives, substituted cyclobutane.

1. Introduction

A photochromic reaction is a reversible transformation of the substance under the light action from one isomer into another, and for this photoinduced transition to occur a great distinction between both photoisomers in spectral characteristics is necessary.[1] Photochromic reactions can be classified into six types corresponding to the transformations occurred under the light action: triplet-triplet transformations, *trans-cis*-isomerization, pericyclic reactions, tautomerism, dissociation, and photochromic transitions with electron transfer.[2] Pericyclic reactions compose the most numerous and important group of reactions on which, as it was shown, the most promising photochromic compounds for practical and potential application are based.[3,4]

At the same time, the introduction of an ionophoric fragment into the photochromic system results in the formation of optical sensors for metal cations. Changes in the structure of such a ligand, which can be induced by phototransformations, has a considerable influence on the complex-forming properties. Thus, photoisomerization can be used for controlling the complex-forming ability of ligands with the help of the light.[5]

The introduction of crown-ether fragments into photochromic molecules discovered a new approach to controlling the photochromic properties using the complex formation process. Binding of a metal cation by the ionophoric fragment of a photochromic molecule results in substantial changes in practically useful properties, such as photostability, sensitivity, and width of the operative optical region.

Thus, photochromic crown ethers represent a novel class of artificial receptors, whose reaction with a metal cation results in conformational changes in the receptor accompanied by color effects. Similar systems can be used for the following purposes[6]:

photoswitched extraction of metal cations;
molecular electronics;
photoswitched transport through membranes;
systems of optical recording of information;
artificial photocontrolled catalysis;
nonlinear optical devices.

This review is devoted to studies of pericyclic reactions of organic photochromic compounds containing crown-ether fragments. The number of studies in this area is being intensely increased. However, only electrocyclic reactions and cycloaddition of photochromic crown-containing compounds are presented in literature, this fact being related, most likely, to the greatest interest in these processes from the viewpoint of practical application.

2. Electrocyclic reactions

Photochromic systems that undergo electrocyclic reactions under the light action are the most promising and developed photochromic compounds to date. Among numerous possible electrocyclic transformations, only two types are presently used: 1,5-electrocyclic reaction (1) and phototransformation of hexa-1,3,5-triene into cyclohexa-1,3-diene (2) (Scheme 1).

Dihydroindolizines that undergo photoinduced transformation (1) have recently been synthesized and studied.[2] Electrocyclic [$4n+2$]-reactions (2) are characteristic of many compounds, including spirobenzopyrans, spironaphthoxazines, benzopyrans, fulgides, and diarylethenes.

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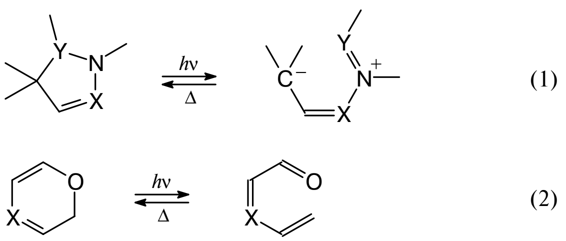
Scheme 1

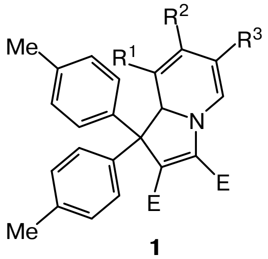


2.1. Dihydroindolizines

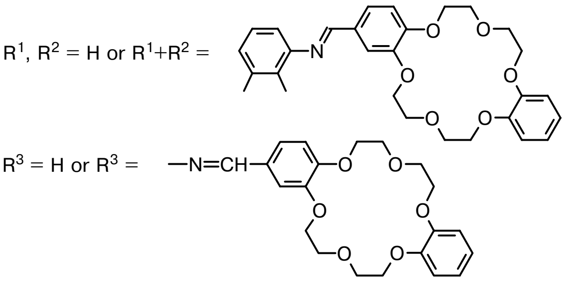
The photochromic reaction that occur in molecules of this class of compounds is the formation of colored zwitterionic compounds under irradiation.[7] This reaction occurs only photochemically, whereas the reverse transformation is possible either under the light action or thermally. The course of a 1,5-electrocyclic reaction can change when substituents of different nature are intorduced into the molecule. A novel approach to change the character of a reaction is the use of complex formation in crown-containing dihydroindolizines. Below we present dihydroindolizines **1** and **2** containing podands and crown ethers as substituents.[8—10]

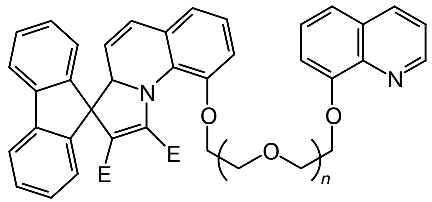
The following changes in the properties were observed upon the addition of metal cations to a solution containing dihydroindolizines: (1) the bathochromic shift by 40 nm in the UV spectra of the initial and betaine forms of the molecule; (2) an increase in the fluorescence quantum yield; and (3) a change in the photochromic reaction rate, for example, alkaline metals retard and alkali-earth metals accelerate the photoinduced reaction. The effect also depends on the selectivity of metal cation binding: the stronger the complexes that formed, the higher the influence.

In the case of compounds **2a,b**, the coordination of metal cations is weak and, hence, the influence on the spectral and photochromic properties is insignificant. It is assumed that this fact can be explained by a higher mobility of the podand chain, which prevents the formation of strong complexes.

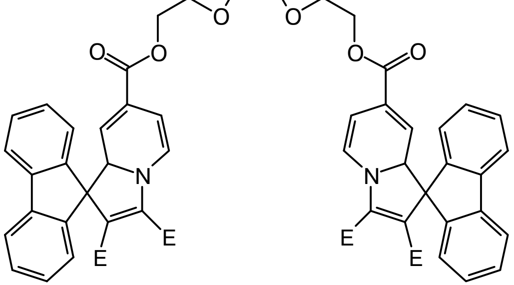


1





2a



2b

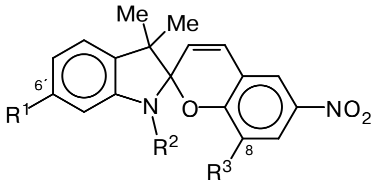
E = CN, COOMe; *n* = 2, 3

2.2. Spirobenzopyrans

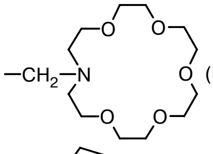
The electrocyclic [4*n*+2]-reaction occurs in spirobenzopyrans under the light to cleave the C—O bond and to form a colored structure of the merocyanine type, whose electronic absorption spectra are located in the region from 400 to 700 nm (Scheme 1, reaction (2), X = CH).[6] The spectral characteristics of the spiro- and merocyanine forms of the compound and the character of their isomerization into each other depend on the nature and positions of substituents, solvent, temperature, and other factors.

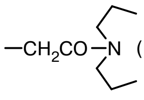
In the case of crown-containing spiropyrans, the presence of metal cations in a solution has a great effect on the photochromic properties. This fact was confirmed by results of studying spirobenzopyrans **3—5** containing monoaza-15-crown-5, 15-crown-5 fragments or acyclic analogs in position 6′ (**3a,b**) or at the nitrogen atom (**4a—g**) of the indoline ring, as well as in position 8 (**5a—e**) of the benzopyran part of the molecule.[11,12]

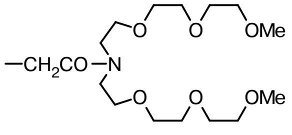
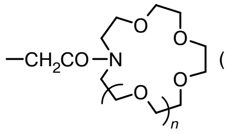
The absorption spectra of compounds **3a** and **4a** containing no crown-ether fragment remained unchanged when alkaline metal iodides were added to a solution of these compounds.[11] The photoisomerization of spiropyran **3b** to the merocyanine form in the presence of K^+ is suppressed. The potassium cation, which is well suitable in size, formed a complex with crown ether and additionally coordinated to the nearby oxygen atom of the pyran cycle, thus making this cycle more resistant toward the light (Scheme 2).

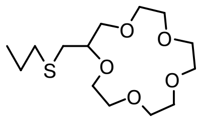
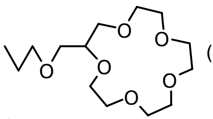


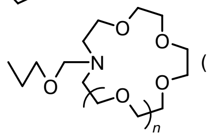
3—5

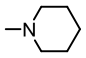
3: R^2 = Me, R^3 = H; R^1 = H (**a**),

(**b**)

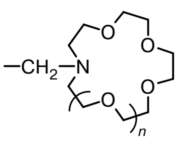
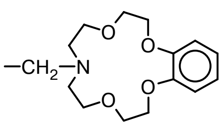
4: R^1 = R^3 = H; R^2 = Me (**a**),

(**b**),

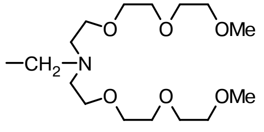

(**c**),

(**d**),


(**e**),

(**f**),


(**g**)

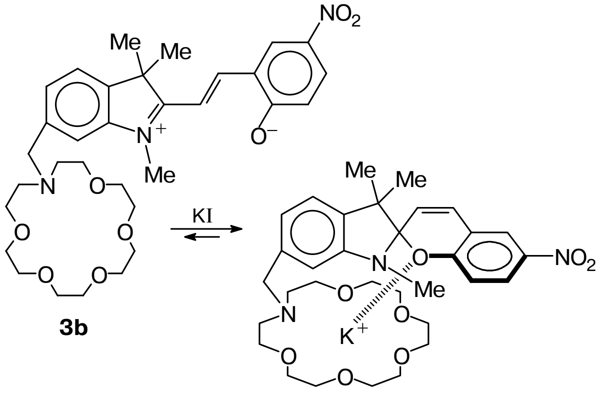
5: R^1 = H, R^2 = Me; R^3 = H (**a**),

(**b**),


(**c**),

(**d**),


(**e**)

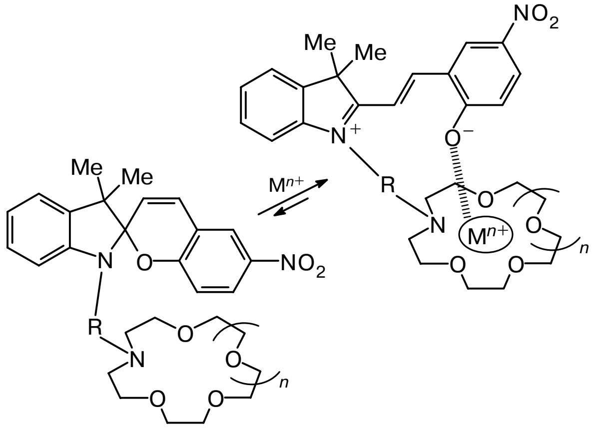
n = 0—2

Scheme 2



Molecules **4b—g** were diesigned taking into account the fact that the "crowned" metal cation is capable of forming an additional coordination bond with the phenolate oxygen atom, favoring the stabilization of the merocyanine form of the spiro compound (Scheme 3).

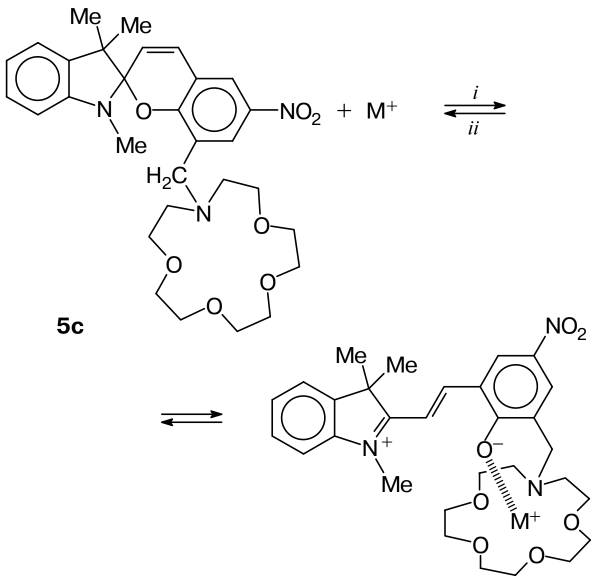
Scheme 3



Results of the study showed that the influence of metal cations is determined, in this case, by the following factors: (1) the ratio of the sizes of the crown-ether cavity to the metal cation; (2) the position of the ionophoric group; (3) the length of the alkyl chain linking the spiropyran molecule and the crown ether macrocycle; and (4) the electron properties of both the metal cation involving in complex formation and the dipole, merocyanine. For example, the selective coloring was observed for the compounds **4d,g**. For **4d** (*n* = 1) the strongest effect was observed when Li^+ was present in the solution, and for **4g** (*n* = 2) Na^+ provided the strongest effect.

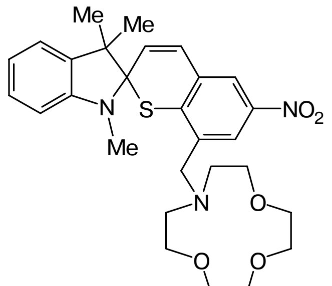
Spirobenzopyrans containing monoazacrown-ether fragments (12-crown-4, 15-crown-5, and 18-crown-6) as substituents and their acyclic analogs in position 8 of the benzopyran part of the molecule were studied in detail.[12,13] It turned out that complex formation with alkaline metals, such as Li^+, Na^+, and K^+, results in the isomerization of crown-containing spiropyran to form the open merocyanine form even in the dark. The ^{7}Li and ^{23}Na NMR spectroscopic data indicate that in the merocyanine isomer the metal cation, which is localized in the crown-ether cavity, is capable of additionally coordinating with the phenolate anion to stabilize the merocyanine form. This effect is absent in compounds containing no ionophoric fragment. Being photoirradiated, the merocyanine isomer is transformed into the closed spiro form to release the metal ion. Thus, photoirradiation can be used for the isomerization of crown-containing spiropyrans. In addition, the photochromic reaction allows a possibility of photocontrolling the complex formation process (Scheme 4).

Scheme 4



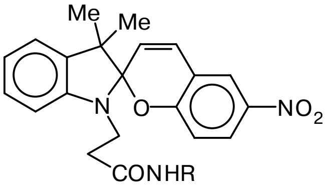
i. In the dark. *ii*. Irradiation (UV, VIS).

The behavior of crown-containing spirobenzothiapyran **6** differs from that of previously considered compound **5c**, which is readily isomerized to the merocyanine form in the presence of Li^+ even without irradiation. The photochromic transformation of **6** in the presence or absence of Li^+ occurs only under irradiation, although in the presence of the metal cation, the lifetime of the merocyanine isomer increases from 5 s to 2 min.[14]

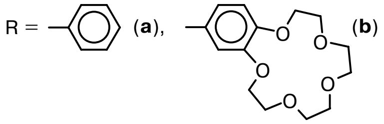


6

The photochromic behavior of spiropyran **7b** linked with benzocrown ether through the methylene chain and its analog **7a** containing no crown-ether fragment was studied in a CH_2Cl_2 solution and in the polyvinyl chloride membrane.[15]

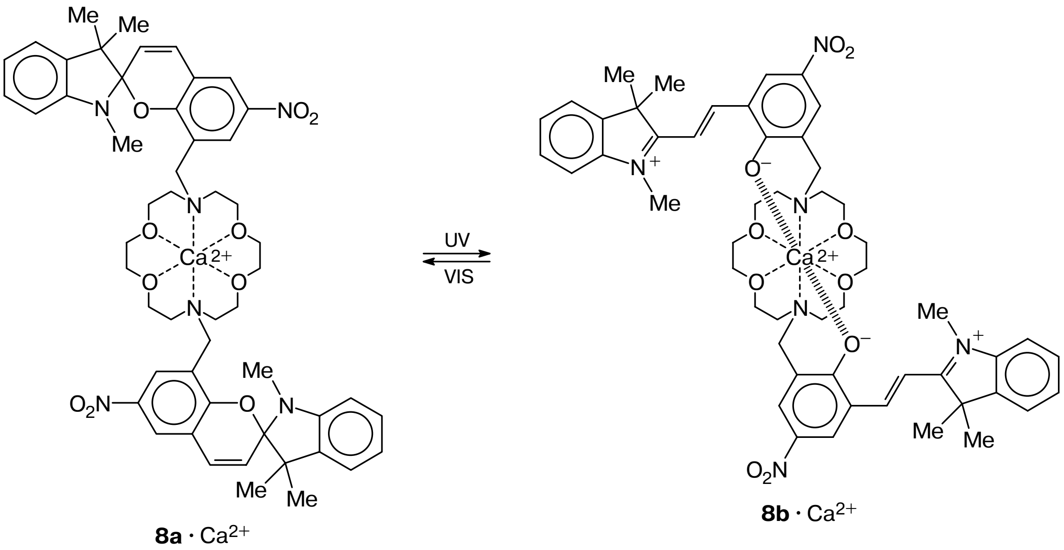


7a,b

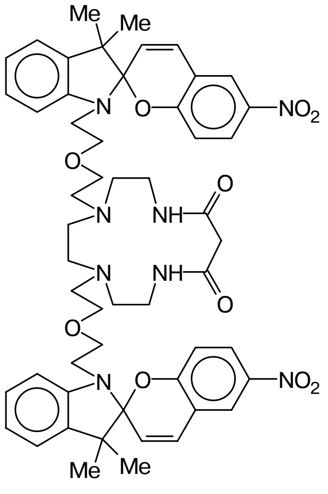


The selectivity of binding cations by spiropyran **7b** was determined in a study of the extraction of alkaline metal picrates from water to CH_2Cl_2. Alkaline metals were extracted in the following sequence: $K^+ > Na^+ > Rb^+ > Cs^+$. The liquid extraction of alkaline metals using **7b** decreased by 3—6% under irradiation. Spiro-

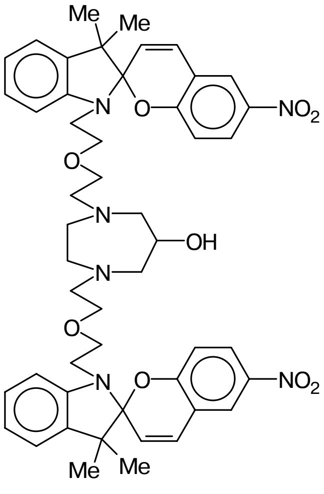
Scheme 5



8a · Ca^{2+} is the complex of closed isomer **8** with Ca^{2+}, **8b** · Ca^{2+} is the complex of merocyanine isomer **8** with Ca^{2+}.



9



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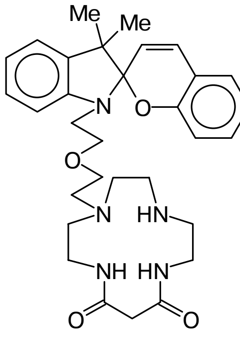

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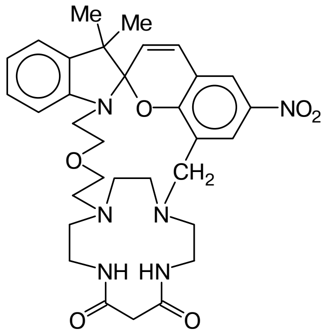


12

pyran **7a** is not bound to metal cations before and after photoirradiation. Both compounds are photochromic in a solution and in the membrane. The magnitude of photoinduced changes of compound **7b** in the membrane depends in the size of the radius of the alkaline metal cation and its concentration in a solution.

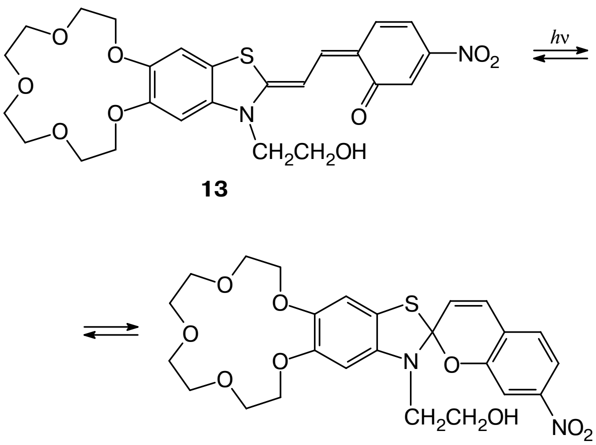
Crown-containing bis(spiropyran) **8** was compared with monospiropyran with a similar structure.[16] The cation-induced isomerization of bis(spyropyran) **8** was studied by optical absorption and NMR spectroscopies and confirmed by data of molecular mechanics calculations.[16] Complex formation with univalent alkaline cations was shown to result in the formation of the merocyanine form of only one of the bis(spiropyran) molecules **8**. The addition of bi- or trivalent cations (for example, Ca^{2+} or La^{3+}) to a solution of spiropyran results in the complete transition of the molecule to the open, merocyanine form in which the "crowned" cation forms additional coordination bonds with both phenolate groups (Scheme 5).

Composite films containing compound **8** demonstrate, in the presence of Ca^{2+}, substantial changes in the ionic conductivity under photoirradiation.

The capability of binding with the Cu^{2+}, Co^{2+}, and Ni^{2+} cations was found for bis(spiropyrans) **9**, **10** with azacrown-ether fragments and their monomeric analogs **11**, **12**. For compounds **9—11** the selectivity is highest with respect to Co^{2+}, whereas for compound **12** the highest selectivity is observed with respect to Cu^{2+}. Complex formation is accompanied by the isomerization to the corresponding merocyanine form.[17]

The synthesis of spirobenzothiazolinopyran **13**, in which the crown-ether fragment is localized in the benzothiazolium part of the molecule, was developed.[18] The compound was obtained in the open, merocyanine form (λ_{max} = 488—579 nm, depending on the solvent). Under irradiation the compound is reversibly transformed into the closed form (Scheme 6). No experiment on the influence of metal cations on the photochromic properties is reported.

Scheme 6



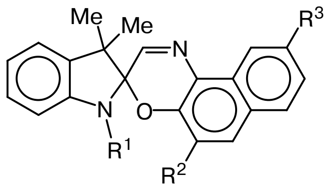
13

2.3. Spiroindolinonaphthoxazines

Photochromic molecules of spiroindolinonaphthoxazines contain the 2*H*-[1,4]oxazine cycle, and the carbon atom in position 2 of the cycle is included into the spiro structure. Photochromisms of this class of compounds is the reversible homo- or heterolytic cleavage of the C—O bond of the oxazine cycle (see Scheme 1, reaction (2), X = N).

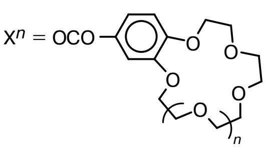
The structures of presently known spironaphthoxazines containing different crown-ether fragments in the naphthaline part of the molecule are presented below.[19—21]

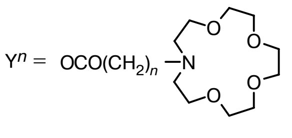
The structure and position of the crown-containing fragment are the most important factors affecting the stability of the merocyanine form and, thus, the photochromic transformations of molecules. The spectral and



14, 15

14a: R^1 = Me, R^2 = H, R^3 = X^n, n = 1
14b: R^1 = Me, R^2 = H, R^3 = X^n, n = 2
14c: R^1 = Me, R^2 = X^n, n = 2, R^3 = H
14d: R^1 = $(CH_2)_4COOH$, R^2 = X^n, n = 2, R^3 = H
15a: R^1 = Me, R^2 = H, R^3 = Y^n, n = 1
15b: R^1 = Me, R^2 = H, R^3 = Y^n, n = 5
15c: R^1 = Me, R^2 = Y^n, n = 1, R^3 = H
15d: R^1 = Me, R^2 = X^n, n = 5, R^3 = H



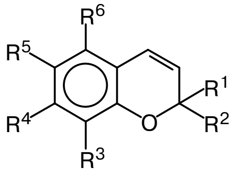


photochemical properties of compounds **15a—d** containing the azacrown-ether fragment indicate two competing processes of the complex formation of alkaline-earth and rare-earth metal cations at the crown-ether fragment and oxygen of the oxazine cycle, which differ in efficiency and selectivity. The metal cation in the crown-ether cavity can form an additional coordination bond with the oxygen atom due to the optimum arrangement of the merocyanine form of the dye toward the donating oxygen atom. This shifts the equilibrium toward the formation of the merocyanine form even in the absence of irradiation.

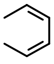
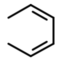
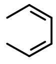
Studies of spironaphthoxazines with the benzo-15(18)-crown-5(6)-ether fragments in different positions of the naphthaline cycle (**14a—d**) showed that complex formation did not affect the photochromic transformations of the molecules. This is related, most likely, to the fact that the rigid structure of the spacer prevents the coordination of the merocyanine oxygen to the cation localized in the crown-ether cavity.

2.4. Benzo- and naphthopyrans (chromenes)

The general structure of benzo- and naphthopyrans is presented below. Theoretically, the R^1 and R^2 groups can be any except spiroheterocyclic groups (in this case, the compounds will formally belong to the class of spironaphthopyrans, which has been considered in Section 2.2).[22]

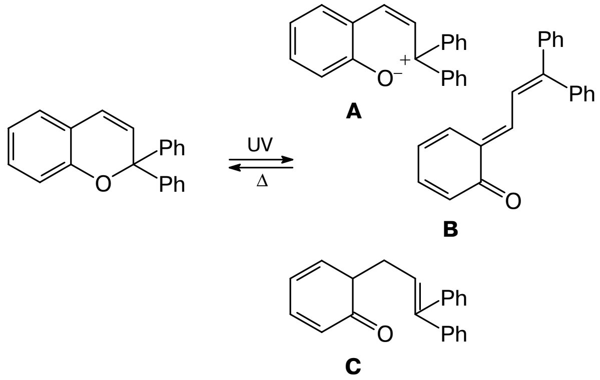


R^1, R^2 = substituted Ph,

R^3+R^4 =  , or R^4+R^5 =  , or R^5+R^6 = 

The photochromic reaction of chromenes occurs according to the type of the [4n+2]-electrocyclic reaction and represents the cleavage of the C—O bond under irradiation (Scheme 7).[23] The photoinduced colored merocyanine form is stable at room temperature if the substituents in position 2 of the pyran cycle are substituted or unsubstituted phenyl groups. The color of the open form can be varied in a wide range of the visible spectrum by the introduction of substituents in different positions of the naphthalene (or benzene) part of the molecule and in the phenyl; rings in position 2 of the pyran cycle.[24]

Scheme 7



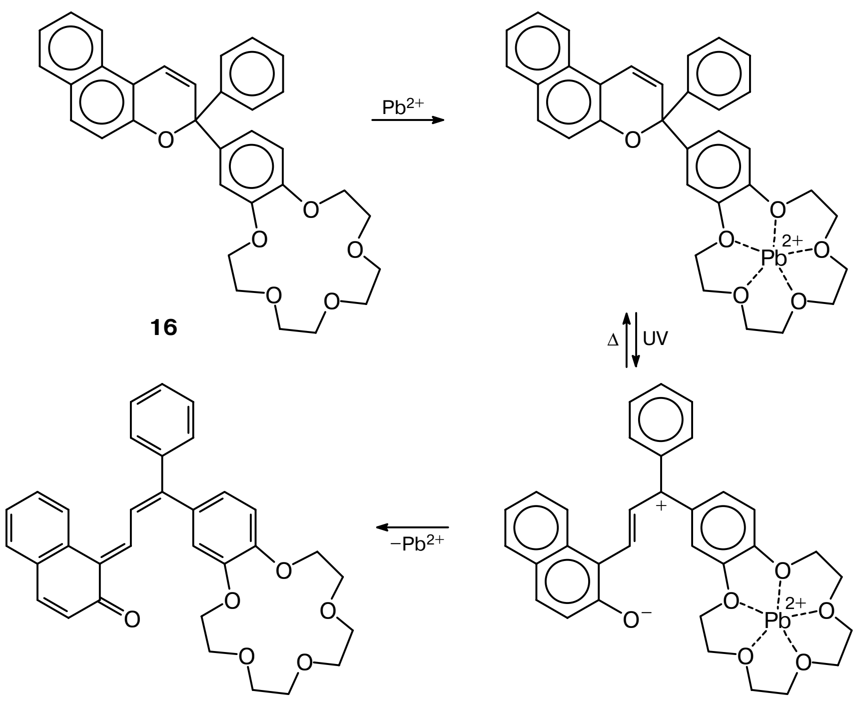
A is zwitterionic form, **B** is *trans*-quinoid form, **C** is *cis*-quinoid form.

The only example of the crown-containing compound of this class is published.[25] This report is devoted to the photocontrolled complex formation of lead cations with naphthopyran **16** (Scheme 8). It was found that Pb^{2+} can bind to the benzo-15-crown-5-ether fragment of chromene **16** in the dark; however, the cation is ejected from the crown-ether cavity under irradiation. The authors believe that irradiation induces the formation of the merocyanine isomer of chromene; betaine being one of its forms in which the positive charge is localized near the crown-ether fragment. The arrangment of the like charges near each other destabilizes the molecule resulting in the ejection of Pb^{2+} from the crown-ether cavity.

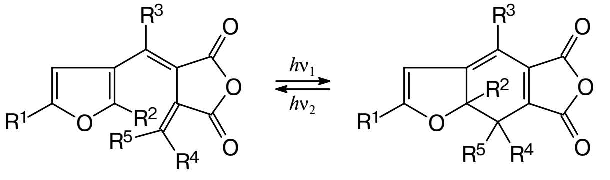
2.5. Fulgides

Fulgides under irradiation undergo photochromic transformation into a colored derivative of 7,7a-dihydrobenzofuran *via* the reaction presented in Scheme 9.[26] The specific feature of this class of compounds is that the inverse photochromic transition to the initial uncolored form is thermally forbidden due to steric hindrances.

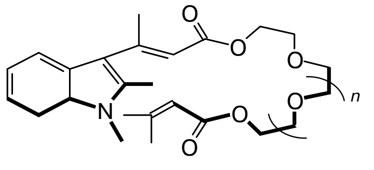
Scheme 8



Scheme 9



Crown-containing compounds **17a—c** were synthesized, and for both isomers their complex formation constants with the Li^+, Na^+, and K^+ cations were determined.[27] The ability to complex formation of the open colored form is higher than that of the uncolored form. The complexes of compounds **17a—c** are not photochromic. The selectivity of complex formation was observed: compound **17b** preferentially binds with Na^+, and **17c** with K^+.

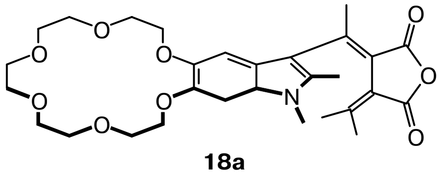


17a—c

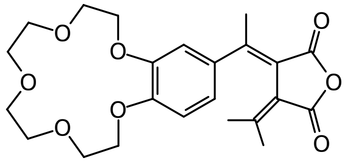
n = 1 (**a**), 2 (**b**), 3 (**c**)

The synthesis of indolylfulgide **18a** is reported,[27] however, its photochromic and complex-forming properties have not yet been investigated.

The study of the new fulgide compound **18b** showed that the absorption spectra of the initial and colored forms are shifted to the short-wave region by 50 nm during complex formation with alkaline and alkaline-earth metal cations, and the decoloring rate decreases in the presence of metal cations.[28]



18a



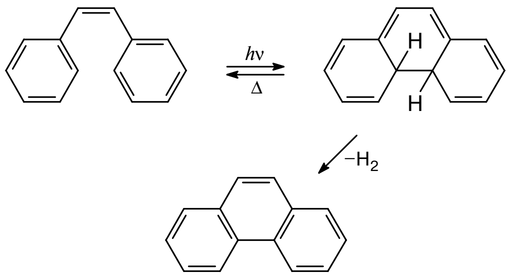
18b

2.6. Dihetarylethenes

It is known that stylbenes being irradiated undergo the reversible *trans-cis*-isomerization reaction.[29,30] A deeper transformation under irradiation is possible in addition to isomerization: photocyclization resulting in the reversible formation of dihydrophenanthrene, which, however, in the presence of air oxygen can irreversibly be oxidized to phenanthrene (Scheme 10).

As a rule, the lifetime of the cyclic dihydro form is short: it readily and rapidly returns to the primary colored state. It was also shown that the stability of the cyclic isomer increases considerably when the phenyl

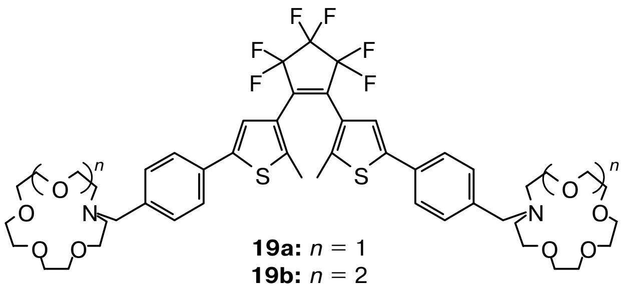
Scheme 10



groups are replaced by heterocyclic groups, *e.g.*, indoline, furan, and best of all, thiophene.

The synthesis and photochromic compounds of new bis(crown ether)-containing diarylethenes **19a,b** were described.[31] Experiments on the extraction of picrates of alkaline metals demonstrates the selectivity of **19a** to the Na^+ cation and of **19b** to the K^+ and Rb^+ cations. The open form of the compound extracts metal cations by 5—10% better than the closed form. It is assumed that in the open form, due to a greater mobility of the molecular fragments, sandwich complexes can be formed in which the metal is hold more strongly.

The quantum yield of the photocyclization of dihetarylethene **20** containing the benzo-15-crown-5-ether fragment decreases when K^+ and Rb^+ perchlorates are added to a solution (Scheme 11).[32a,b] This phenomenon can be explained by the fact that the addition of salts to a solution of dihetarylethene **20** can result in the formation of photochemically inactive sandwich complexes with the parallel arrangement of the crown-ether fragments.



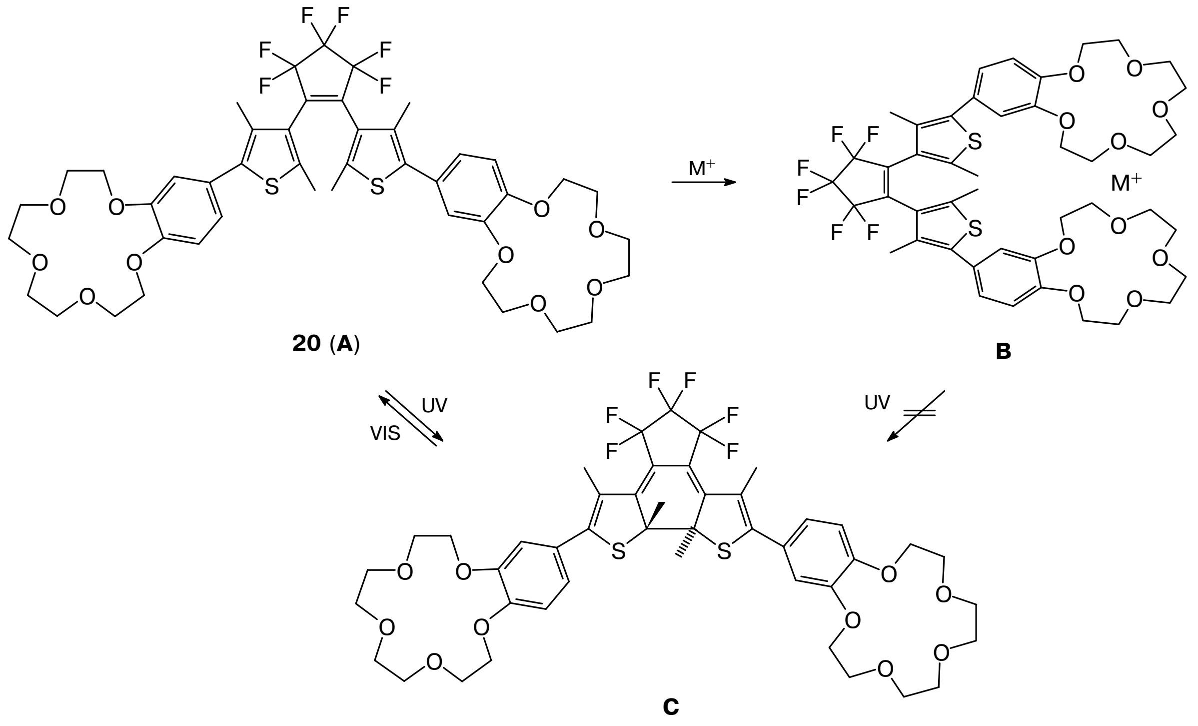
19a: $n = 1$
19b: $n = 2$

3. Cycloaddition reactions

3.1. [4+4]-Photocycloaddition

Cycloaddition is one more important class of pericyclic reactions, which can form grounds for the design of photochromic molecules. Intramolecular [4+4]-cycloaddition in compounds containing two anthracene residues seems to be a good example in this respect. The cycloaddition of anthracene can also be used for photoswitching of crown ether derivatives. For example, irradiation of the anthracene-containing podand **21**, in the presence of Li^+, gives the crown-containing cycloadduct (Scheme 12).[33] This compound in a complex with Li^+ is

Scheme 11



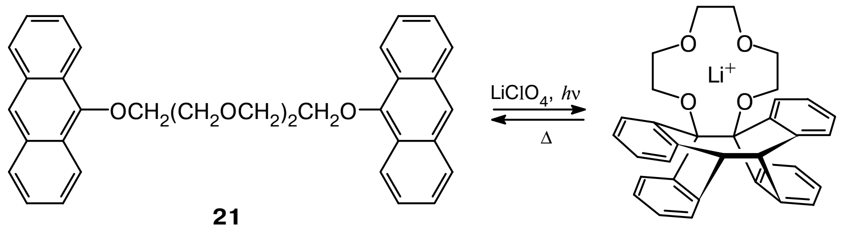
20 (**A**)

B

C

A is open form, **B** is complex with the parallel arrangement of crown-ether fragments, **C** is closed form.

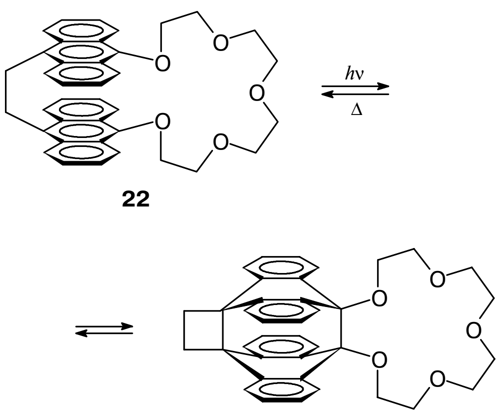
Scheme 12



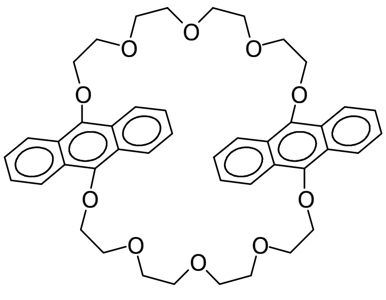
rather stable but is readily transformed into the initial open form when the metal cation is removed from the macrocycle.

Compound **22** exhibited only intramolecular photocycloaddition involving anthracene residues.[34] The obtained photocycloadduct was isolated and characterized using NMR spectroscopy. Further studies showed its capability of selective binding the Na$^+$ cation (Scheme 13).

Scheme 13



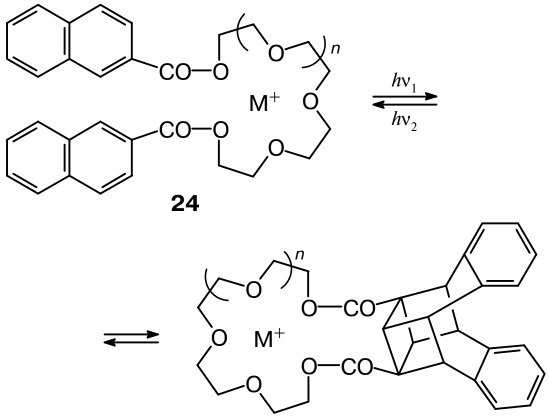
In compound **23** two anthracene residues are linked by two polyether chains.[35] In this case, intramolecular photocycloaddition is especially fast in the presence of the template Na$^+$ ion.



23

The photoinduced cycloaddition of oligomers of poly(ethylene glycols) containing naphthalene residues as terminal groups (**24**) was studied in MeOH in the presence of alkaline and rare-earth metal cations.[36] The photoirradiation of the compounds resulted in the formation of cubane-like cycloadducts, and a pronounced dependence of the quantum yield of the reaction on the nature of the alkaline metal was observed (Scheme 14). The efficiency of the reaction also depended on the polyether chain length (Table 1). All these data indicate that the polyether chain of the compounds is involved in the complex formation with the metal cation. As a result, a certain mutual orientation of the naphthalene residues necessary for efficient cycloaddition depends rather strongly on the size of the metal cation and the polyether chain length.

Scheme 14



Photoreversibility of the cycloaddition of the crown-containing anthracene derivatives is high; however, the synthesis of these compounds is complicated, which restricts possibilities of their practical use.

3.2. [2+2]-Photocycloaddition

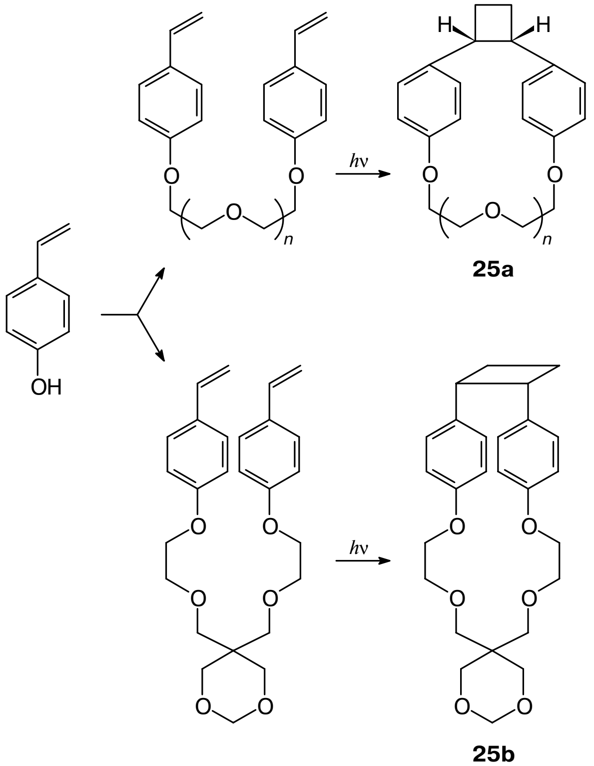
[2+2]-Cycloaddition can be used for the preparation of the new type of photoswitchable crown ethers containing benzene cycles and capable of orienting in the space opposite each other. There are a few examples of these crown ethers.[37,38] New crown-containing cyclophanes **25a,b** were obtained using intramolecular [2+2]-cycloaddition (Scheme 15).[39a,b] The photochemical study of the initial compounds showed that the cycloaddition reaction occurs in a high quantum yield. The addition of alkaline metal ions increases the yield of the cycloadduct due to the template effect.

Table 1. Relative quantum yield (η) of the photocycloaddition of **24** in MeOH in the presence of alkaline metal chlorides (MCl)*

n	η				
	24	**24** + Li^+	**24** + Na^+	**24** + K^+	**24** + Cs^+
4	0.34	1.00	1.31	1.16	1.12
10	1.45	1.00	1.03	1.28	1.37

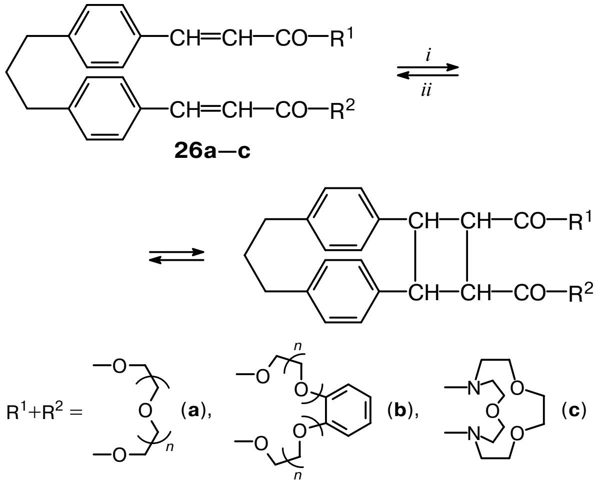
* Conditions: [**24**] = $2.70 \cdot 10^{-5}$ mol L^{-1}; [MCl] = $1.14 \cdot 10^{-4}$ mol L^{-1} (see Scheme 14).

Scheme 15



Crown-containing cyclobutanes formed due to intramolecular [2+2]-photocycloaddition (PCA) are of interest as photoswitchable complexons.[40a—d] However, the reaction mentioned above was found to be irreversible. A possibility of the photoreversible cleavage of crown-containing cyclobutanes was also demonstrated for other compounds.[41a—c] Irradiation of solutions of crown ethers **26a—c** in MeCN with λ = 300 nm resulted in the formation of the intramolecular cycloaddition products in a yield higher than 90% (Scheme 16). The initial compounds are formed when the obtained cyclobutanes are UV-irradiated with λ = 220 nm. The yields in the inverse reaction were much lower (to 30%) due to side processes.

Scheme 16

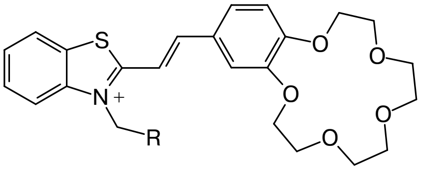


*i. h*ν (λ = 300 nm); *ii. h*ν (λ = 220 nm).

Stereochemistry of the main product of the concerted PCA reaction of alkenes, which involves the lowest excited singlet state of one of two reacting molecules, is determined taking into account orbital symmetry and orbital overlap.[42] In a solution these intermolecular reactions occur in a low quantum yield because the interaction of the reactants is a bimolecular reaction and the excited state is promptly deactivated, which is due to competing processes, first of all, *trans-cis*-photoisomerization. Intermolecular PCA reactions are characterized, as a rule, by low regio- and stereoselectivities because the reacting molecules can have different mutual orientations.

A promising tool for controling the regio- and stereoselectivities and efficiency of PCA can be proposed: spontaneous self-assembling of alkenes to form a supramolecular structure with such a pre-organization of reactants at which the mutual spatial orientation of molecules favors the formation of only one cyclobutane isomer in a high yield.

This idea was accomplished for crown-containing styryl dyes (CSD) **27a—f**.[43]

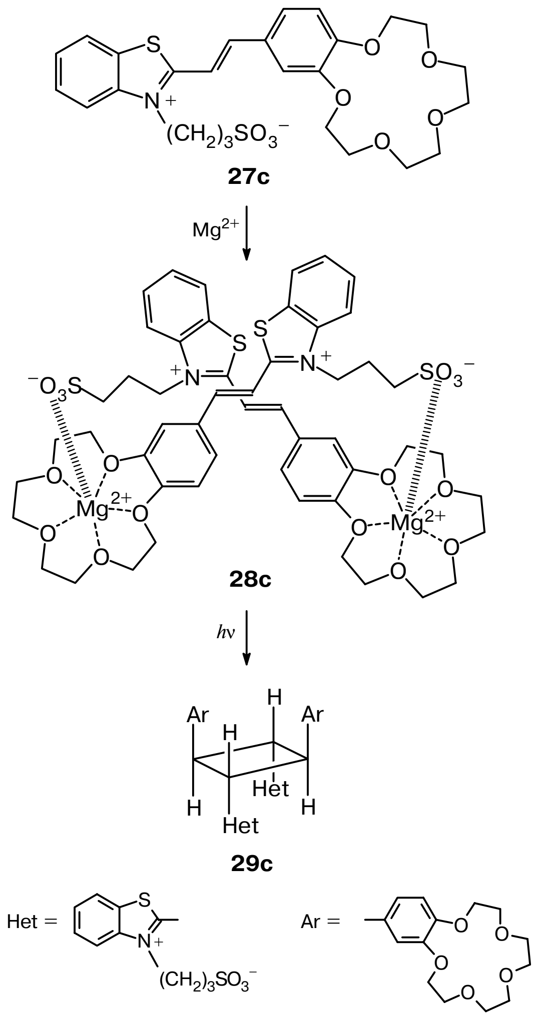


trans-**27a—f**

R = Me (counterion ClO_4^-) (**a**), $CH_2SO_3^-$ (**b**), $(CH_2)_2SO_3^-$ (**c**), $(CH_2)_3SO_3^-$ (**d**), *o*-$C_6H_4SO_3^-$ (**e**), *p*-$C_6H_4SO_3^-$ (**f**)

Compounds **27c—f** with the betaine structure in the presence of Mg^{2+} ions form supramolecular structures with the crossed arrangement of the molecules (*anti*-"head-to-tail") due to the intermolecular interaction of the sulfo group of one molecule and the Mg^{2+} ion in the crown cavity of another molecule.[44] It has been shown[45—48] that, when solutions of dimer **27c** are irradiated, the stereospecific PCA occurs and results

Scheme 17



exclusively in the formation of only one of 11 possible derivatives of cyclobutane **29c**, which is expected according to the concerted supraface-supraface (s,s) addition of the reactants (Scheme 17). Note that *trans*-**27a—f** in the absence of alkaline-earth metal cations and complexes of *trans*-**27a,b** with Mg^{2+}, Ca^{2+}, or Ba^{2+} do not enter the PCA reaction even in saturated solutions. The transition of spacers with the flexible polymethylene chains with different lengths to *N*-substituents with the rigidly spatially oriented sulfo group allows one to expect an increase in the efficiency of these photoreactions and to influence on the choice of the route of CSD transformation.

Crown-containing styryl dyes **27c—f** are capable of forming anion-"capped" complexes in *trans*-*cis*-isomerization due to the interaction of the sulfo group of the *N*-substituent (spacer) with the metal cation in the crown-ether cavity (Scheme 18). The data obtained also reveal reasons for which the *Z*-isomer **27b** cannot give a stable anion-"capped" complex. Note that the influence of the spacer structure on the stability of the complexes is much more pronounced in the case of *Z*-isomers. This concerns first CSD with conformationally rigid spacers. For example, the ratio of the stability constants of anion-"capped" complexes (*Z*-**27f**) · Mg^{2+} to (*Z*-**27e**) · Mg^{2+} is ~ 500.

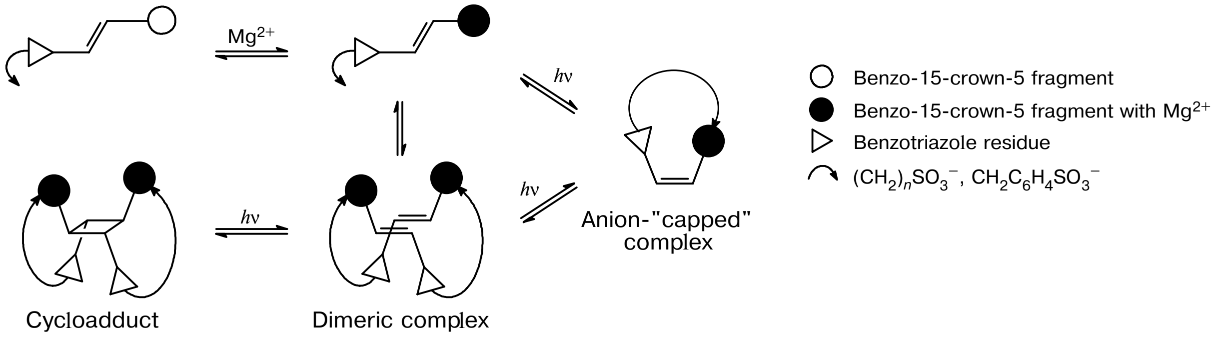
It could be assumed that the variation of the CSD structure allows one to change the spatial structure of the supramolecular dimeric complex in the desired direction and to control thus the efficiency of the interaction and stereochemistry of the final PCA product.[49]

With this purpose we synthesized the biscrown-containing styryl dye (*E,E*)-**30** with the structure and properties of a molecular pincer. Dye (*E,E*)-**30** with the Ca^{2+} and Ba^{2+} cations in a solution of MeCN forms intramolecular sandwich complexes (Scheme 19).[50,51]

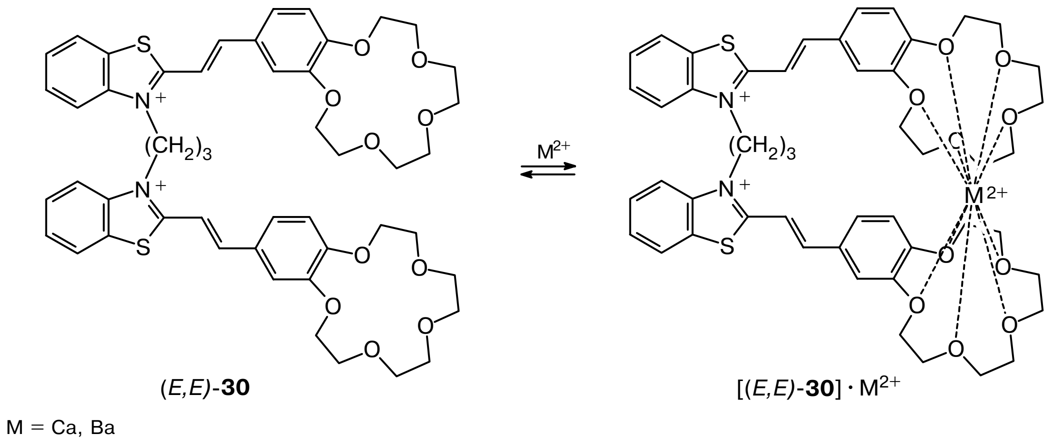
Spontaneous self-assembling of bis-CSD **30** and metal cations with a large ion radius to sandwich complexes, which results in the stacking interaction of unsaturated fragments of the dye arranged according to the "head-to-head" type, gives one more method for controling the efficiency and stereoselectivity of intramolecular PCA with the formation of cyclobutanes. Indeed, in the case of the Ba^{2+} complexes with bis-CSD **30**, a prolonged photolysis of a photostationary mixture of the geometric isomers results in the complete consumption of the dye.

Two isomeric crown-containing cyclobutane derivatives **30a** and **30b** in a ratio of 17 : 83 were observed among the photoproducts using ^1H NMR spectroscopy

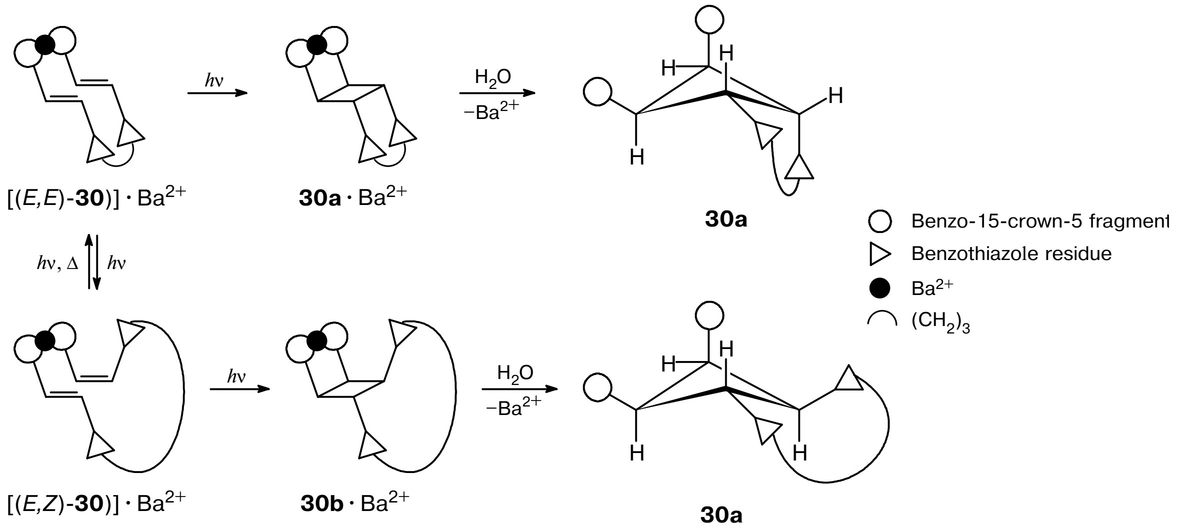
Scheme 18



Scheme 19



Scheme 20



with two-dimensional COSY and NOESY procedures (Scheme 20).

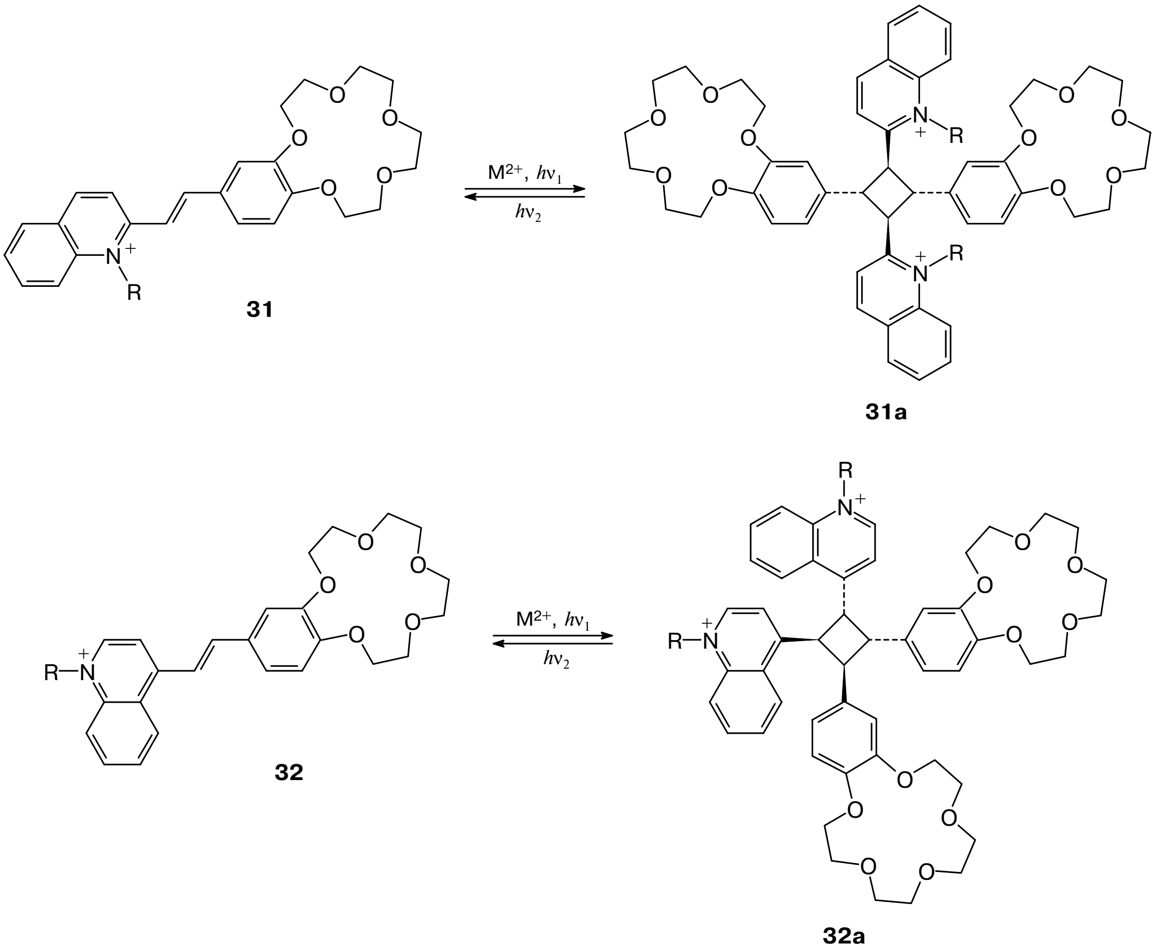
It has been shown[52] that isomeric chromogenic 15-crowns-5 of the quinoline series in MeCN enter the PCA reaction to form cyclobutane derivatives only in the presence of $Mg(ClO_4)_2$ or $Ca(ClO_4)_2$. Going from the dye containing the 2-substituted quinoline residue to the dye containing the 4-substituted quinoline residue fundamentally changes the direction of the PCA reaction (Scheme 21). The quantum yield of dye **31** is low being equal to 0.0007. In the case of the PCA of **32**, the quantum yield is much higher, which indicates that the degree of dimerization of complexes of this dye remains high even in very dilute solutions and that the steric structure of the dimeric complexes is likely favorable for PCA.

The molecular mechanics method were used to study the PCA of the CSD complexes with metal cations.[53—55] This approach makes it possible to predict stereochemistry of cyclobutane derivatives according to the calculated predominant conformations of dimeric supramolecular complexes.

4. Conclusion

The results of studies by several research groups demonstrated that photochromic crown ethers are a new class of photochromic molecules for which several promising applications can be assumed. For these compounds we can expect a substantial influence of complex formation on the spectral characteristics of molecules and kinetics of phototransformations. By contrast, conformational transformations of molecules, which accompany the photoreaction, strongly affect the capability of molecules of binding metal cations. This implies that photocontrolled complex formation becomes possible

Scheme 21



M = Mg, Ca, Ba; R = $(CH_2)_nSO_3^-$; n = 3, 4.

Note: **31a** is isomer *anti*-"head-to-tail," **32a** is isomer *syn*-"head-to-head."

for systems of this type. The obtained results can be extended to new series of photochromic systems. The most important purposes of future studies can be the synthesis of new compounds; more diverse and detailed investigations of their physicochemical properties in order to find structure—property relationships; and the modification of the already known systems for their physical or chemical incorporation into liquid crystals with the purpose for creating new useful materials based on new photochromic molecules.

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