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CATION-DEPENDENT PERICYCLIC REACTIONS OF PHOTOCHROMIC CROWN ETHERS

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Abstract. The review describes the photochromism of crown-ether systems based on pericyclic reactions. The photochromic transformations and the observed spectral changes or changes in physical or chemical behavior are related to the modification of the system geometry and electron distribution. A novel approach to the modification of photochromic systems includes the exploration of the complex formation process in crown ether containing photochromic systems. The results obtained show that the introduction of crown-ether moieties into dye molecules affords compounds that can change their spectral and photochromic properties upon complex formation. The approach offers the possibility of synthesizing new photochromic substances characterized by enhanced photostability, high sensitivity, and a broad range of operating wavelengths. Yet another important feature of the novel systems is reversible change in the capacity of a photochromic host molecule for association with guests upon irradiation. The researches believe that the novel photochromic systems can now be regarded as being promising for traditional applications (photochromic ophthalmic lenses or camera filters, reversible holographic systems, cosmetics) and for molecular electronics, biomimetic chemistry, and optical information storage.

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1. Introduction

Photochromism is a reversible transformation of a single chemical species between two states, the absorption spectra of which are clearly different, the transition in at least one direction being induced by electromagnetic radiation.¹ Photochromic systems may be classified into six major groups according to the reaction types: triplet-triplet absorption, *trans-cis*-isomerization, pericyclic reactions, tautomerization, dissociation, and electron transfer (redox photochromism).² The widest and the most important group is that based on pericyclic reactions; it has proved to be an especially suitable basis for photochromic systems;³ it is used in practice (photochromic lenses) and has potential industrial applications.⁴

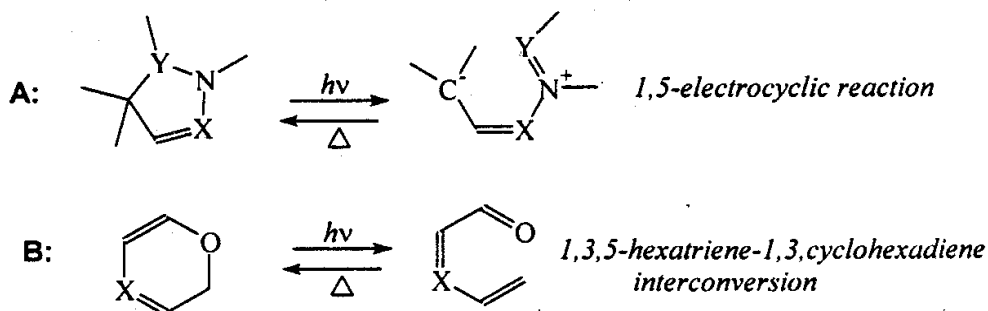
The incorporation of an ionophore into a photochromic system affords a substance that optically responds to the presence of cations in solution. In addition, since binding of cations is sensitive to the ligand environment, the binding constant can be controlled effectively by employing photochromic systems which change in the light.⁵ Photochromic crown ethers constitute a new class of artificial receptors in which the recognition of metal cations induces a conformational change in the receptor framework accompanied by signaling (coloration). Examples of potential applications utilizing the physical or chemical changes that accompany the observed shift of the absorption maxima include:⁶

- photoswitching extraction of metal cations;
- optoelectronic systems;
- photoswitching transport through membranes;
- optical information storage;
- photochemical switchable enzymatic systems;
- nonlinear optical devices.

This review surveys studies devoted to the pericyclic reactions of organic photochromic compounds incorporating crown ether fragments. The development of these photochromic systems is aimed at improving the photostability, increasing the sensitivity and obtaining a broader range of operating wavelengths. Incorporation of a crown ether moiety, which is able to bind metal ions into the chromophore skeleton, can help to tune the photochromic properties by using complex formation.

2. Electrocyclic reactions

Of different classes of pericyclic reactions, electrocyclic reactions have proved to be especially suitable as a basis for photochromic systems.⁶ Of numerous possible electrocyclization reactions, only two reactions shown in Scheme 1 have been applied by now in photochromic crown ethers.



Scheme 1

It was not until quite recently that the first type of reaction A has been successfully used in effective photochromic systems dihydroindolizines.² The $4n+2$ systems whose photochromism results from the electrocyclic 1,3,5-hexatriene-1,3-cyclohexadiene interconversion (reaction B) comprise spirobenzopyrans, spironaphthoxazines, chromenes, fulgides, and diarylethylenes.⁶

2.1. Dihydroindolizines

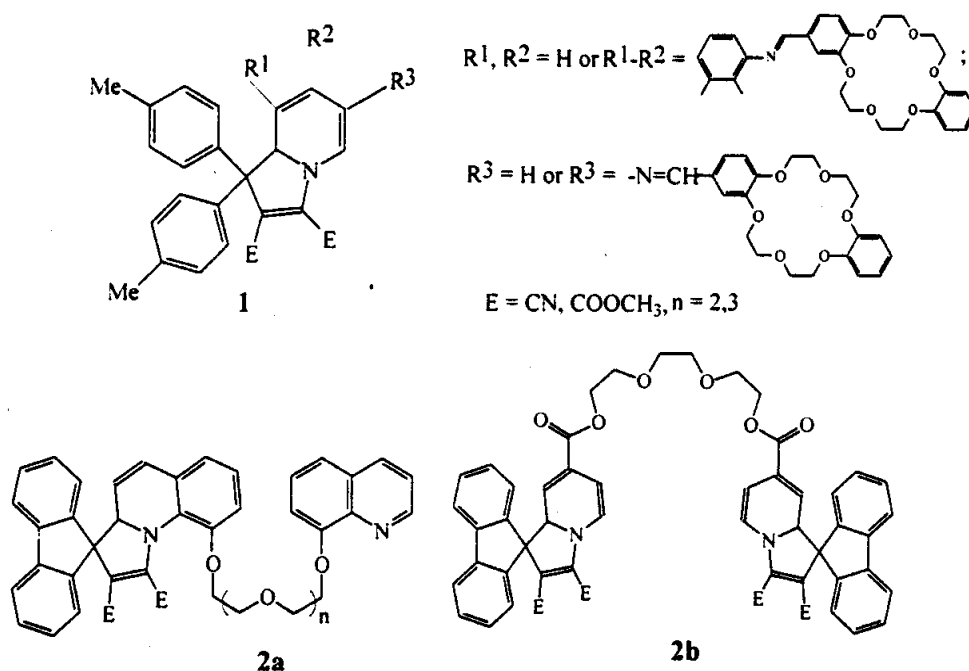
The photochromism of dihydroindolizines (DHI) was discovered only in 1979.⁷ New molecules based on a pentaatomic, six-electron $(4n+2)\pi$ system can undergo ring opening to give a zwitterionic species or neutral heteropentadienes (Scheme 1, reaction A).

The photochemical transformation of the colorless form to betaines can be induced only photochemically; however, the back reaction can be brought about thermally or photochemically. 1,5-Electrocyclization can be controlled by varying the substituents in the molecule. A new approach to fine tuning of physical properties of DHI includes the use of complex formation in crown ether-containing DHI.⁸⁻¹⁰ Data on DHI linked to podand, crown-ether or calixarene anchor groups can be found in the literature (Scheme 2).

After addition of metal cations, DHI 1 shows the following specific properties of the excited state:

- bathochromic shift (up to 40 nm for Ba^{2+}) in the UV spectra of both the colorless and betaine isomers;
- an increase of the fluorescence intensity;

c) changes in the rate of ring opening reaction; in particular, alkali metal cations decelerate and alkaline earth metal cations accelerate the photoinduced reaction. The effect depends on the selectivity of the cation binding.



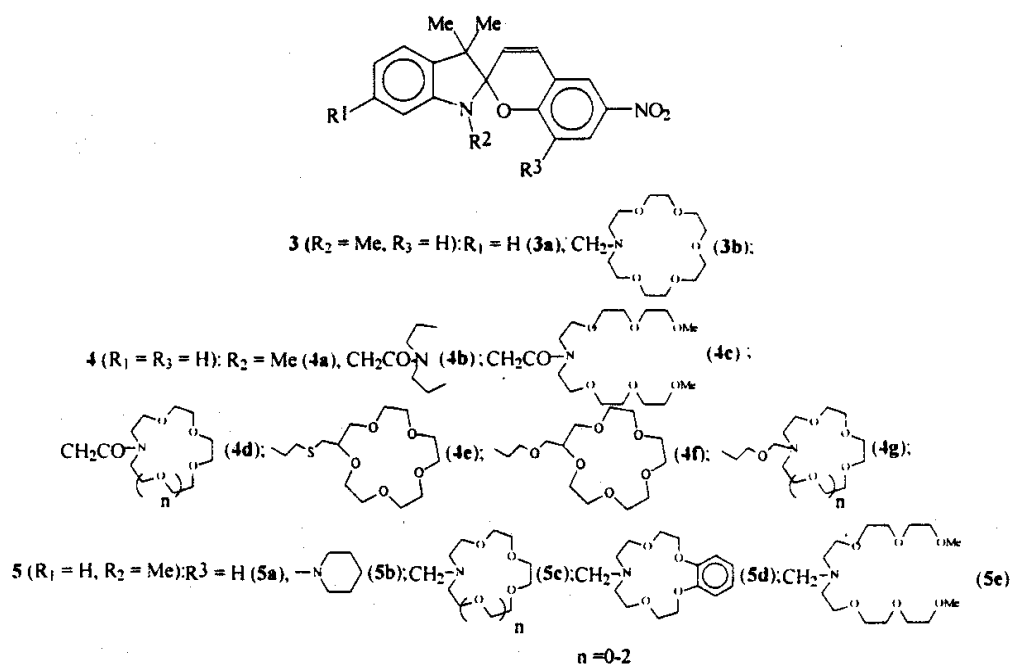
Scheme 2

In the case of DHI **2a,b**, coordination to alkaline earth metal cations was found to be weak; thus, it has only a slight influence on the spectral and photochromic properties. This may be due to the high flexibility of the podand chain in DHI **2a,b** which prevents the formation of a sufficiently stable complex with metal cations.

2.2. Spirobenzopyrans

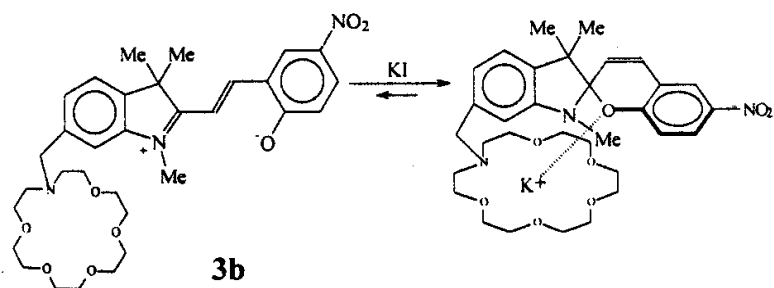
An electrocyclic ($4n+2$) reaction has been found for spirobenzopyrans. UV irradiation of the colorless spiro compounds leads to the cleavage of the C—O bond to give open-chain compounds which strongly absorb in the visible region (Scheme 1, reaction B, $X = CH$).⁶ The crowned spirobenzopyrans can modulate the cation-complexing capacity of the crown ether moiety due to photoisomerization, namely, interconversion of electrically neutral spirobenzopyran and a zwitterionic merocyanine form. In turn, complexation with cations can substantially change the spectral and photochromic characteristics of the molecules.

Spirobenzopyran derivatives containing monoazacrown ether and 15-crown-5 ether moieties and their acyclic analogues, either at the 6'-position of the indoline cycle (**3a,b**), or at the N atom (**4a-g**), or at the 8-position of the benzopyrane ring (**5a-e**) have been synthesized (Scheme 3).^{11,12}



Scheme 3

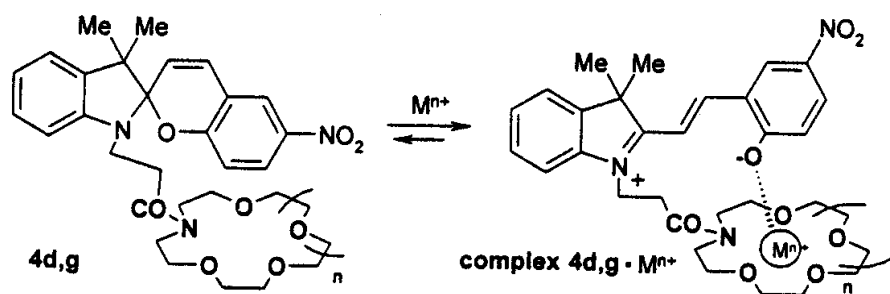
In the study of compounds **3a,b** and **4a-g**, the following results were obtained.¹¹ The absorption spectra of spiropyrans **3a** and **4a** containing no crown ether were not at all affected by alkali metal iodides. The isomerization of crown-containing compound **3b** to the colored merocyanine form was suppressed most strongly by the presence of K^+ , which is expected to be the best recognized by the crown ether ring (Scheme 4).



Scheme 4

The design of the crowned spirobenzopyrans **4b-g** was based on the fact that the strong interaction between the complexed cations and the phenoxide anion of the merocyanine form could favor the spiro-

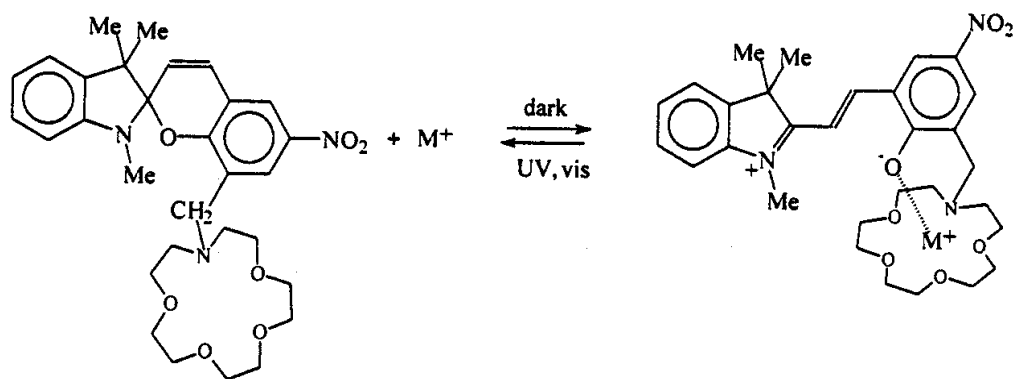
to-merocyanine isomerization. The colored complex formed by spiropyrans **4b-g** and alkali-metal cations is shown in Scheme 5.



Scheme 5

The influence of alkali-metal cations on the coloration was found to be governed by several factors: (1) the size of the crown ring; (2) the position of the recognition; (3) the electric properties of both the complexed cation and the merocyanine dipole; (4) the length of the alkyl chains linking the spiropyran moiety and the crown ether moiety. For spiropyrans containing azacrown fragments **4d,g**, selective coloration was found in compounds bearing a short linkage (CH_2CO) and aza-15-crown-5 ether (**4d**, $n=1$) in the case of Li^+ and for aza-18-crown-6 (**4d**, $n=2$) in the case of Na^+ .

Spirobenzopyran derivatives having a monoazacrown moiety such as 12-crown-4, 15-crown-5 and 18-crown-6 or their acyclic analogue at the 8-position (**5a-e**) have been studied in detail.^{12,13} Binding of alkali metal ions (Li^+ , Na^+ , and K^+) by the crown moieties leads to isomerization of the crowned spirobenzopyrans even in the dark.

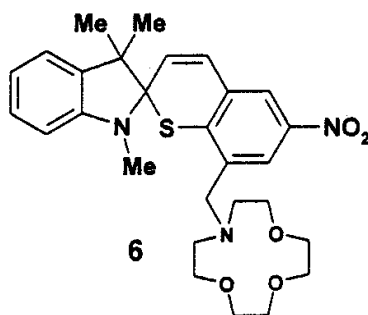


Scheme 6

The data of ^7Li and ^{23}Na NMR spectroscopy suggest that an alkali metal ion, especially Li^+ , complexed by the crown moiety in the merocyanine isomer is subject to intramolecular interaction with

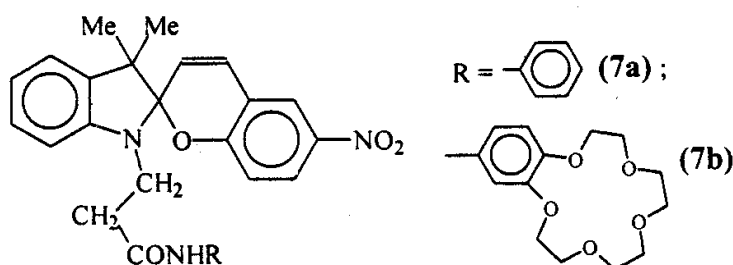
the phenoxide anion and, hence, it is bound more strongly than that in the corresponding spiropyran isomer, owing to the additional-binding-site effect. On exposure to visible light, the cation-bound merocyanine form readily reverts to the spiropyran form, releasing the metal ions to some extent. The alternating irradiation with UV and visible light or alternating switching-on and -off of the visible light causes isomerization of the crowned spiropyrans even in the presence of alkali metal ions, which, in turn, provides a tool for controlling their cation-complexing capacity (Scheme 6).

The isomerization behavior of crown containing spiropyrans **6** (Scheme 7) is very different from that of its corresponding spiropyrans **5b**, the pyran ring of which can be opened readily by Li^+ complexation even without UV-light irradiation. Thermal decoloration of the **6** solution in the presence and absence of Li^+ was followed by turning off UV light, the half life time of the merocyanine isomer increases from 5s to 2 min in presence of Li^+ .¹⁴



Scheme 7

The photochromic behavior of benzocrown ether-linked spiropyran **7b** and its analogue **7a**, which has no crown ring, was studied in a dichloromethane solution and in a poly(vinyl chloride) membrane (Scheme 8).¹⁵

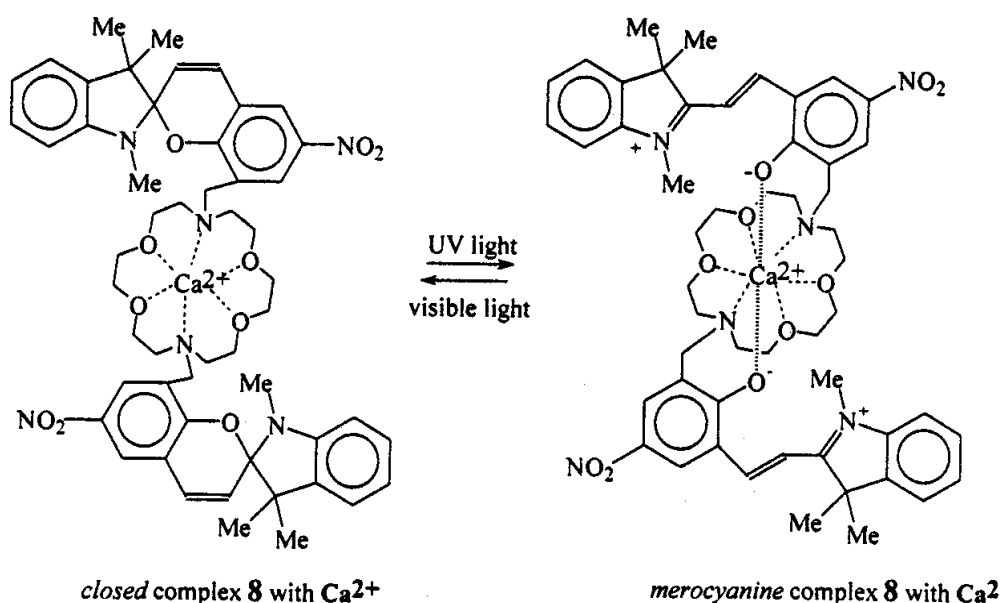


Scheme 8

A dichloromethane solution containing compound **7b** extracts alkali metal picrates from water; the binding capacity varies in the sequence $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$. The liquid extraction of alkali

metal picrates by **7b** decreases by up to 3—6% after exposure to UV light; compound **7a** does not bind these cations either before or after irradiation with light. Both spiropyrans **7a,b** show normal photochromism in membranes. In the case of **7b**, the magnitude of the photoinduced change depends on the sort and concentration of the alkali metal cation.

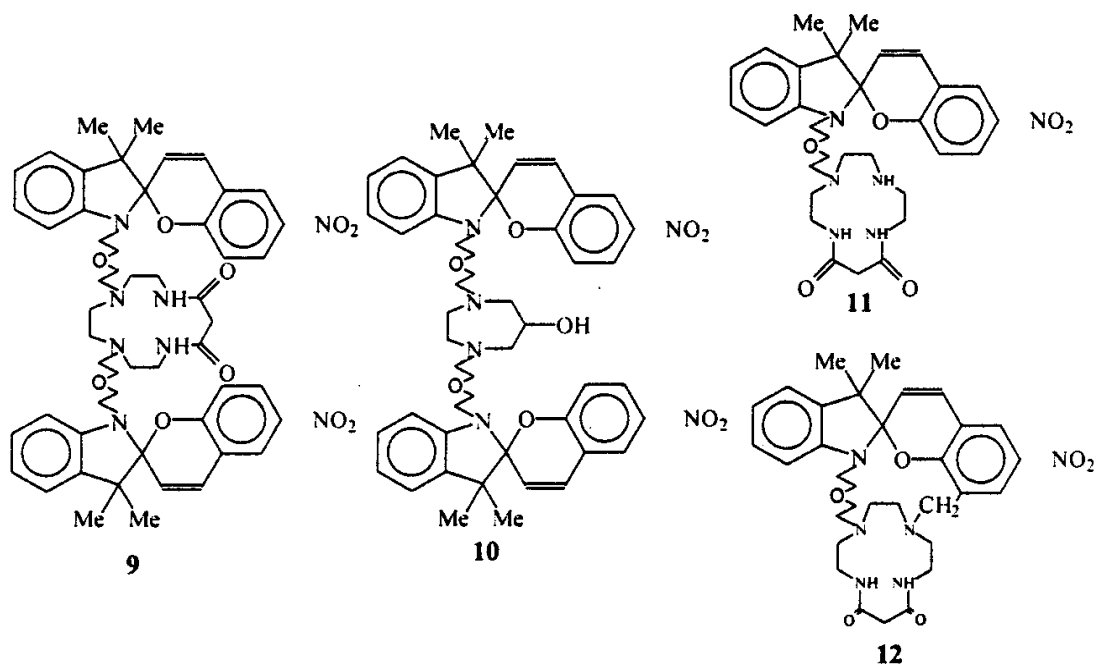
Crowned bis(spirobenzopyran) **8** was investigated in solution and compared with the corresponding derivative incorporating only one spirobenzopyran unit.¹⁶ Complexing of multicharged metal ions, especially Ca^{2+} and La^{3+} , by crowned bis(spirobenzopyran) facilitates isomerization of the spirobenzopyran moiety to the corresponding merocyanine form due to the effective intramolecular interaction between the crown-complexed cation and the two phenoxide anions in the cation complexes of the merocyanine form (Scheme 9). The isomerization of **8** to the corresponding merocyanine form induced by complexation with a cation has been studied by spectrophotometry, NMR spectroscopy, and molecular orbital calculations. The results indicate that, upon complexation with Li^+ , one of the two spirobenzopyran units in compound **8** isomerizes to the merocyanine form. The complexation of divalent and trivalent metal cations by **8** forces two spirobenzopyran units to isomerize due to the intermolecular interaction between the multicharged cation and the two phenoxide anions. Significant photoinduced switching of ionic conductivity was implemented in composite films containing compound **8** and calcium salts.



Scheme 9

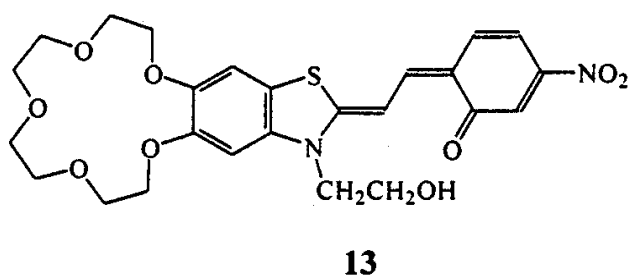
Bis(spiropyran) containing an azacrown fragment (**9**, **10**) and their monomeric analogues (**11**, **12**) showed the recognition of transition metal cations (Cu^{2+} , Co^{2+} , Ni^{2+}) accompanied by isomerization to the

corresponding merocyanine isomers (Scheme 10).¹⁷ Compounds 9 - 12 exhibit a high selectivity with respect to Co^{2+} and compound 12, with respect to Cu^{2+} .



Scheme 10

Spirobenzothiazolopyran **13**, which contains a crowned benzothiazolium fragment, has been prepared.¹⁸ It is stable as the open form (λ_{max} 488-579 nm in various solvents). Compound **13** exhibits a reversed type of photochromism. No experiments on the effect of introducing metal cations into the crown ether moiety have been reported (Scheme 11).

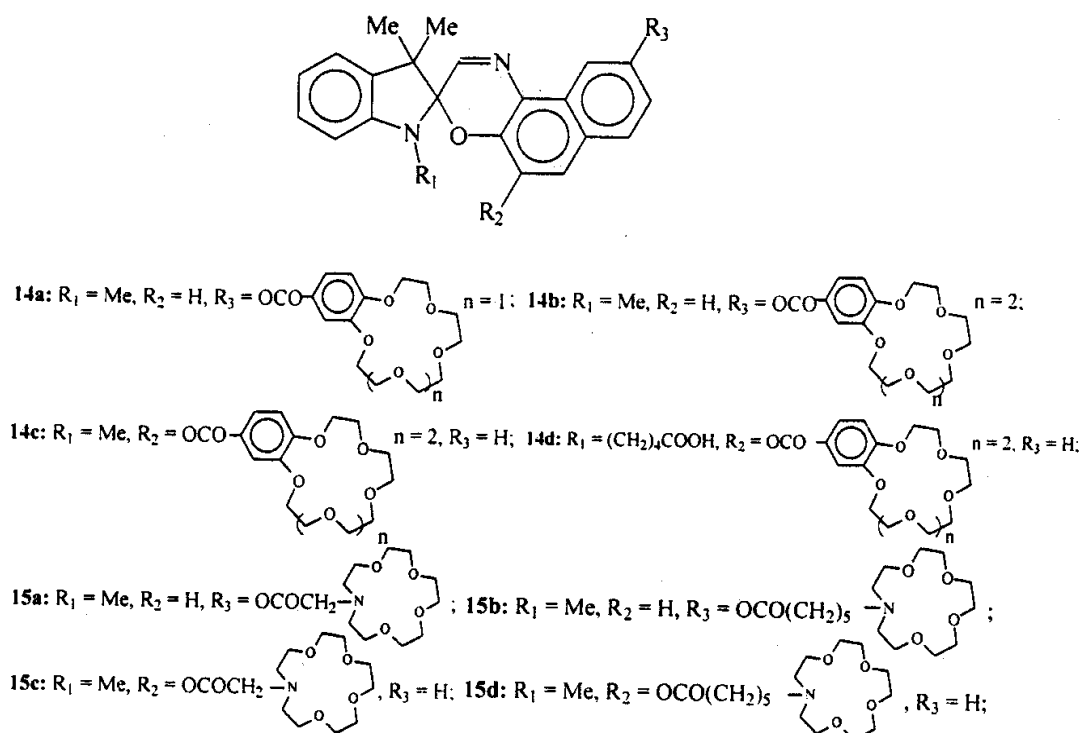


Scheme 11

2.3. Spirooxazines

Photochromic spirooxazine compounds are molecules containing 2H-[1,4]oxazine in which the number 2 carbon of the oxazine ring is involved in a spiro linkage. Photochromism of spirooxazines implies the heterolytic or homolytic cleavage and reformation of the carbon - oxygen single bond of the oxazine ring (Scheme 1, reaction B, X = N).

Methods for the synthesis of new spironaphthoxazines containing benzo-15(18)-crown-5(6) (**14a-d**) and aza-15-crown-5 (**15a-d**) moieties in two different positions (5' and 9') have been developed (Scheme 12).¹⁹⁻²¹



Scheme 12

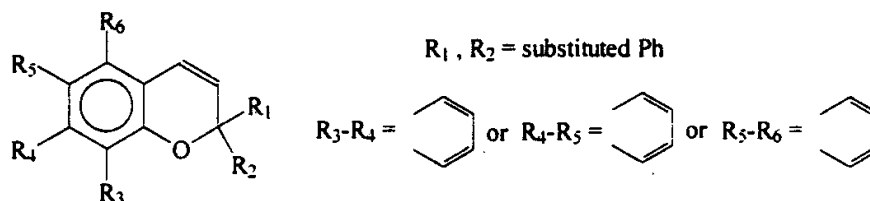
The structure and the position of the crown-containing fragments in spiro compound are important factors influencing the stability of the merocyanine form. Thus, investigations into spiroindolinonaphthoxazines bearing a benzo-15(18)-crown-5(6) moiety in different positions (**14a-d**) showed that the rigid structure of the spacer prevents the formation of an additional coordination bond between the oxygen atom of the merocyanine form (MF) of the dye and the metal cation in the crown-ether cavity, which results in substantial stabilization of the MF.¹⁹

The investigation of the series of compounds **15a-d** showed that the introduction of a flexible spacer into position 5' of a spiro compound shows the significant influence of complex formation on the

kinetics of decoloration of the MF of the spiro compound. A comparative study of the spectral properties of crown-ether-containing and crown-ether-free compounds indicated that complexation follows two competing routes, involving both free metal cations and those linked to the crown fragment.^{20,21}

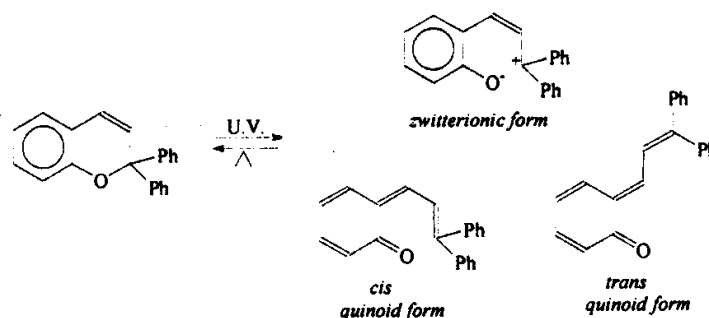
2.4. Benzo and naphthopyrans (chromenes)

The general structure of benzo and naphthopyrans in which R_1 and R_2 are not joined to form a spiro heterocyclic group, is shown in Scheme 13.²²



Scheme 13

The photochromism of benzo and naphthopyrans is believed to involve rupture of the oxygen—carbon bond of the pyran ring ($4n+2$ electrocyclic reaction), as shown in Scheme 14.²³

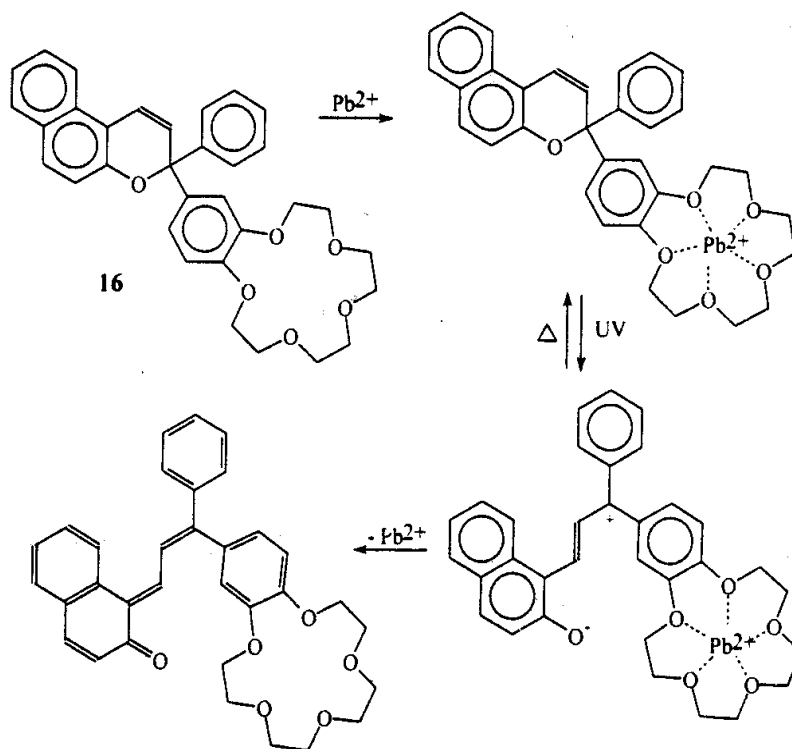


Scheme 14

A reasonable level of room-temperature photochromism requires that the pyran be substituted at the 2-position with conjugate substituents such as phenyl. The color of the open forms can be varied over a broad range of the visible spectrum by introducing substituents into the naphthyl moiety or into the aromatic groups present in the 2-position of the pyran ring.²⁴

As regards crown-ether-containing compounds of this series, a report devoted to the photoreversible binding of Pb^{2+} by a crowned photochromic naphthopyran 16 has been published.²⁵ It was reported that binding of Pb^{2+} to a benzo-15-crown-5 ether occurs in the dark and is followed by liberation of Pb^{2+} from the crown ether on exposure to the UV light. This reversible phenomenon may be

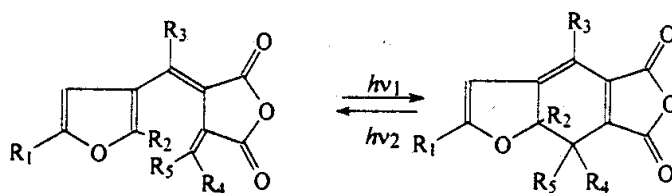
due to the pronounced geometry change which accompanies cleavage of the carbon—oxygen ring during absorption of UV light, and/or to the change in the affinity to Pb^{2+} caused by the fact that the electron density of the crown-ether oxygen participates in the stabilization of the newly formed carbocation charge (Scheme 15).



Scheme 15

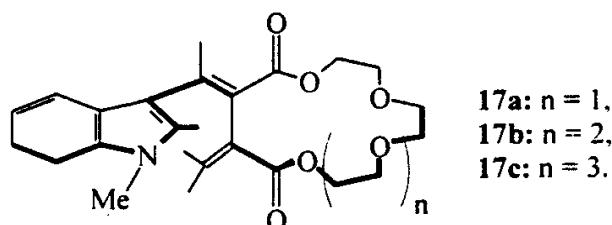
2.5. Fulgides

The fulgides belong to a class of photochromic compounds for which the thermal reversal or decoloration of the colored species is forbidden.²⁶ Therefore, the transformation is largely driven photochemically, as illustrated in Scheme 16. In this class of compounds, the photochromic transformation includes 1,5-hydrogen shift following a photochemical valence isomerization.



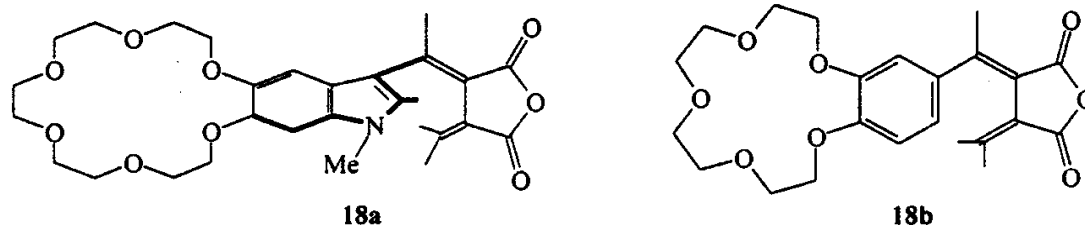
Scheme 16

The cyclic crowned fulgenates, corresponding to 14-crown-4 (**17a**), 17-crown-5 (**17b**), and 20-crown-6 (**17c**) were synthesized and the association constants with Li^+ , Na^+ , K^+ , were determined for colorless and colored isomers.²⁷ The following features are worth noting: (1) the association constant with Na^+ is the greatest for **17b**, and that for K^+ is the greatest for **17c**. The association of the open form is stronger than that of the cyclic form. The complexes exhibit no photocoloration (Scheme 17).



Scheme 17

The indolylfulgide **18a** containing a benzo-18-crown-6 moiety has been synthesized; its photochromic properties are being studied (Scheme 18).²⁷



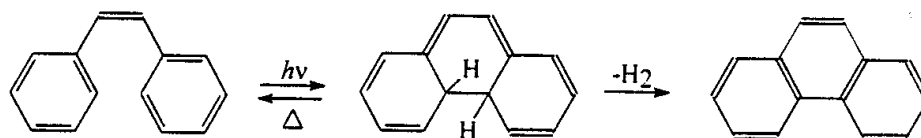
Scheme 18

It has been found²⁸ for novel benzo-15-crown-5-modified fulgide **18b** that the absorption spectra of the initial and colored forms shift hypsochromically by up to 50 nm upon complex formation with alkali and alkaline earth metal cations. The decoloration rate evidently decreases upon selective cation binding.

2.6. Diarylethylenes with heterocyclic groups

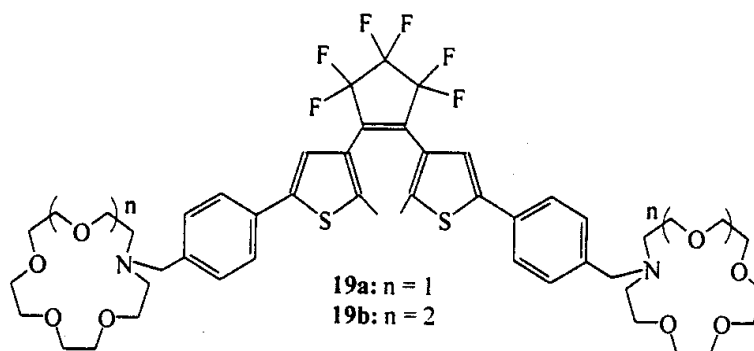
Styrene is well known to undergo a *trans-cis* photoisomerization upon irradiation with UV light.^{29,30} In addition to this isomerization, stilbene shows a photocyclization reaction to produce

dihydrophenanthrene. Although in the presence of air, the dihydrophenanthrene irreversibly converts to phenanthrene upon hydrogen abstraction with oxygen, it returns termally to the initial stilbene in the absence of oxygen (Scheme 19).



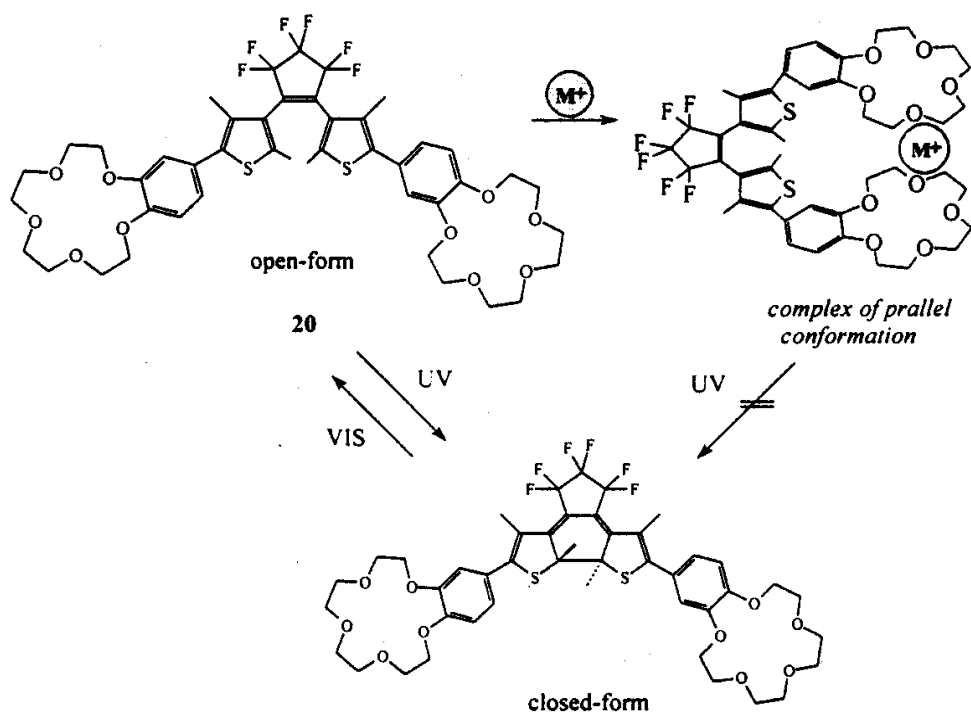
Scheme 19

The synthesis and behavior of novel bis(azacrown ether)-containing diarylethylenes **19a,b** were described in³¹ (Scheme 20). The experiments on the extraction of metal picrates demonstrated selectivity of **19a** toward Na^+ and **19b** toward K^+ and Rb^+ . The open form exhibits higher capacity for cation binding (by 5-10%) than the cyclic form. The conformational flexibility of the system in the open form permits the crown ethers to act in concert in the binding of a metal cation ("biscrown effect").



Scheme 20

The quantum yield of the photocyclization of 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene having two benzo-15-crown-5 ethers **20** was decreased by the addition of K^+ and Rb^+ perchlorates.^{32a,b} The phenomenon was explained by the formation of photochemically inert complex having a parallel conformation upon the intramolecular interaction of the two crown moieties with the metal ions (Scheme 21):

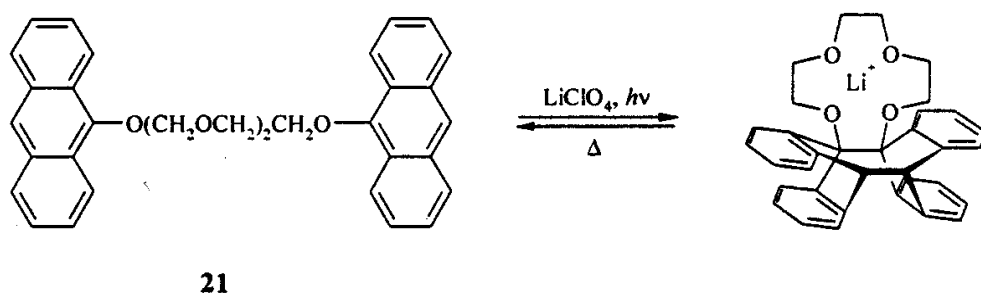


Scheme 21

3. Cycloaddition reactions

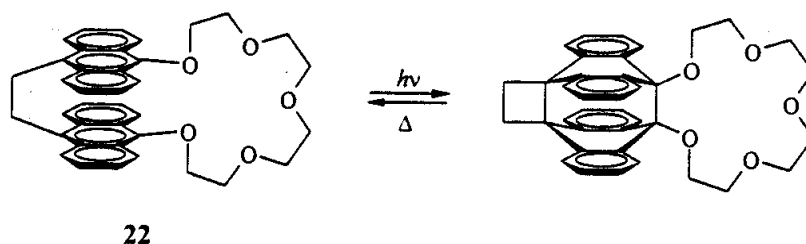
3.1. [4+4] Photocycloaddition reactions

Cycloaddition is yet another important class of pericyclic reactions, which provides a basis for photochromic molecules. Examples are provided by [4+4] cycloaddition of dianthracene derivatives. Photodimerization of anthracene can also be employed as a photochemical switch for photosensitive crown ethers. Photoirradiation of **21** in the presence of Li^+ gives the photocycloisomer (Scheme 22).³³ The compound is fairly stable with Li^+ but readily reverts to the open form when the metal cation has been removed from the ring.



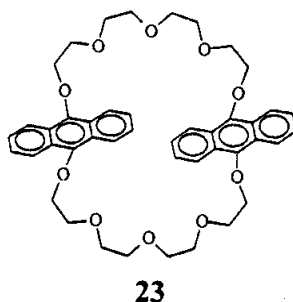
Scheme 22

Yamashita et al.³⁴ have synthesized compound **22** in which intermolecular photodimerization of anthracene is completely suppressed. The cyclic form of the compound showed excellent Na⁺ selectivity (Scheme 23).



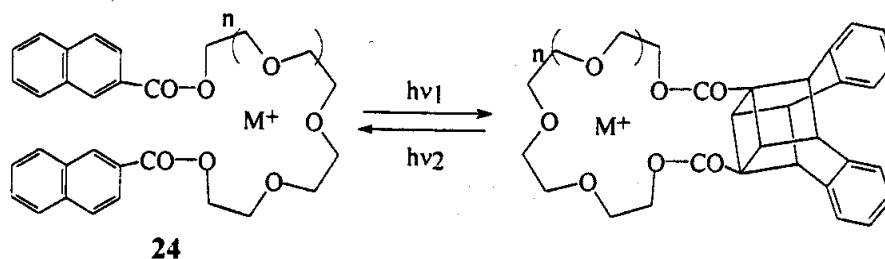
Scheme 23

In compound **23**, two anthracenes are linked by two polyether chains (Scheme 24).³⁵ Intramolecular photodimerization proceeds rapidly in the presence of Na⁺ as the template metal cation.



Scheme 24

Photochemical dimerization of naphthalene end-labeled poly(ethylene glycol) oligomers in methanol in the presence of alkali metal and lanthanide cations (**24 a-f**) has been investigated.³⁶ Photoirradiation of the compounds resulted in a cubane-like dimer, the quantum yield of photodimerization being affected by alkali metal cations (Scheme 25).



Scheme 25

Table 1. The relative quantum yield of photodimerization of **24** in methanol in the presence of alkali metal chlorides; [Ligand] = 2.70×10^{-5} mol dm⁻³; [metal chloride] = 1.14×10^{-4} mol dm⁻³

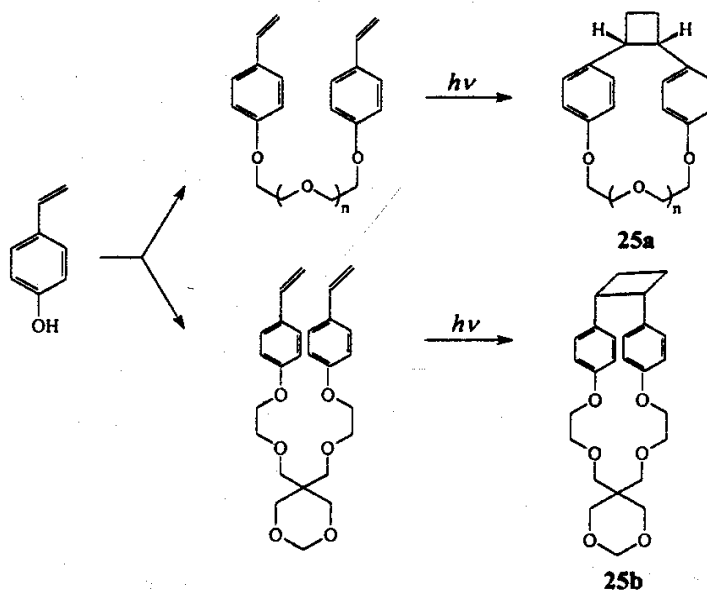
n	Relative quantum yield				
	Metal-free	Li ⁺	Na ⁺	K ⁺	Cs ⁺
4	0.34	1.00	1.31	1.16	1.12
10	1.45	1.00	1.03	1.28	1.37

The process also shows dependence on the chain length (Table 1). All the results indicate that the polyether chain of the compounds is involved in the complex formation with the cations. Thus, the orientation of the terminal chromophores makes the dimerization reaction dependent on the cation size and the polyether length.

The reversibility of photodimerization is excellent, but the synthesis of anthracene- or naphthalene-containing crown ethers is fairly difficult and, therefore, these compounds are of limited utility.

3.2. [2+2] Photocycloaddition reactions

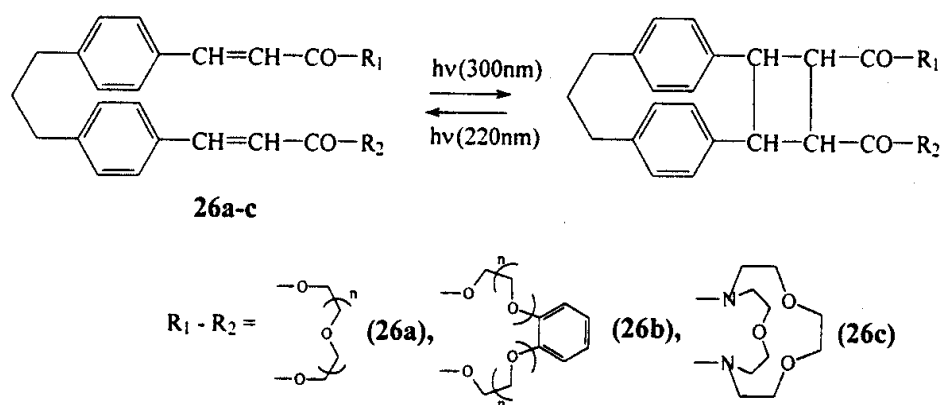
Photocycloaddition can be used to prepare a new kind of crown ethers containing face-to-face oriented aromatic systems, which might modify their properties. The examples of this type of crown ether are few in number.^{37,38} A new crown compounds **25a,b** fused in a cyclophane skeleton was prepared by intramolecular [2+2] photocycloaddition (Scheme 26).^{39a,b}



Scheme 26

The photophysical investigation of the cycloaddition revealed that it is an efficient reaction with a high quantum yield. The addition of an alkali metal ion increases the yield of the cycloadduct due to the template effect.

Cyclobutanecrown ethers formed by intramolecular [2+2] photocycloaddition have received considerable attention in view of the purpose in question.^{40a-d} However, the above-mentioned reaction was found to be irreversible. The possibility of photoreversible cleavage of the cyclobutanecrown ethers has been reported.^{41a-c} Irradiation of a solution of the crown ethers **26a-c** in acetonitrile with light (300 nm) gave intramolecular [2+2] photocycloadducts in an excellent yield (above 90%) (Scheme 27). Subsequently, cyclobutanes were transformed into the initial compound upon irradiation with 220-nm UV light. The yield of the reversible reaction was much lower (up to 30%) because of side reactions.

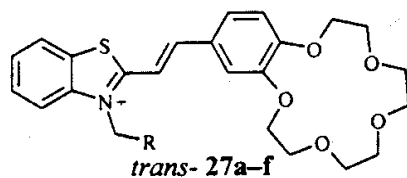


Scheme 27

The stereochemistry of the major product of concerted [2+2]-photocycloaddition (PCA) of alkenes, which involves the lowest singlet excited state of one of the two reacting molecules, is determined by taking into account the orbital symmetry and orbital overlap.⁴² In solution, these intermolecular transformations are characterized by low quantum yields, since the reactants undergo a bimolecular reaction, while the excited state is rapidly deactivated, due to the occurrence of competing processes, first of all, *trans-cis*-photoisomerization. The intermolecular PCA reactions normally have low regio- and stereoselectivities because the reacting molecules can have different mutual arrangements.

A promising tool for controlling the regio- and stereoselectivity of PCA as well as the efficiency may be provided by assembling alkenes into a supramolecular structure with pre-organization of reactants such that that the spatial arrangement of molecules would be favorable for the formation of only one cyclobutane isomer in a high yield.

This idea was realized using crown ether styryl dyes (CESD) **25a-f** (Scheme 28).⁴³

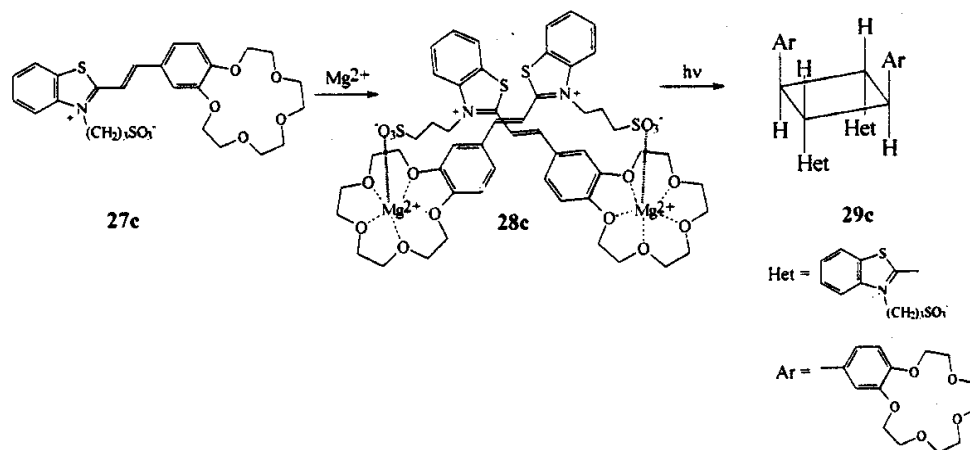


a R = Me (anion ClO₄⁻), **b** R = (CH₂)₂SO₃⁻, **c** R = (CH₂)₃SO₃⁻, **d** R = (CH₂)₄SO₃⁻,

e R = *o*-C₆H₄SO₃⁻, **f** R = *p*-C₆H₄SO₃⁻

Scheme 28

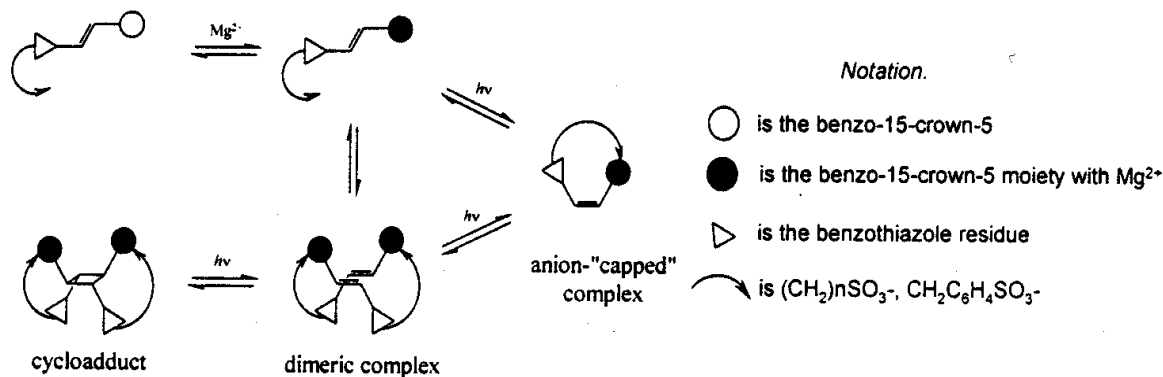
The compounds **27c-f** having betaine structures form supramolecular dimers with a crossed arrangement of molecules (*anti*-head-to-tail) in the presence of Mg²⁺ ions, due to the intramolecular interaction between the sulfo group of one of the molecules and a Mg²⁺ ion located in the crown-ether cavity of the other molecule.⁴⁴ It was shown that photoirradiation of solutions of dimer **27c** results in stereospecific PCA giving only one of the 11 possible derivatives of cyclobutane **27c**, which is expected in conformity with the concerted superficial (*s,s*) addition of the reactants (Scheme 29).⁴⁵⁻⁴⁸ It is noteworthy that neither *trans-27a-f* without alkaline earth metal cations nor complexes of *trans-27a,b* with Mg²⁺, Ca²⁺, Ba²⁺ undergo PCA even in saturated solutions. Transition from spacers with flexible polymethine chains to *N*-substituents in which the sulfo group is rigidly arranged in space, makes it possible to influence the efficiency of these photochemical reactions and also to change the route of transformation of CESD.



Scheme 29

The CESD **27c-f** are able to form anion-“capped” complexes (Scheme 30) upon *E-Z*-photoisomerization owing to the interaction of the sulfo group of the *N*-substituent (spacer) with a metal cation in the crown-ether cavity. However, the data obtained confirmed the previous conclusion that the

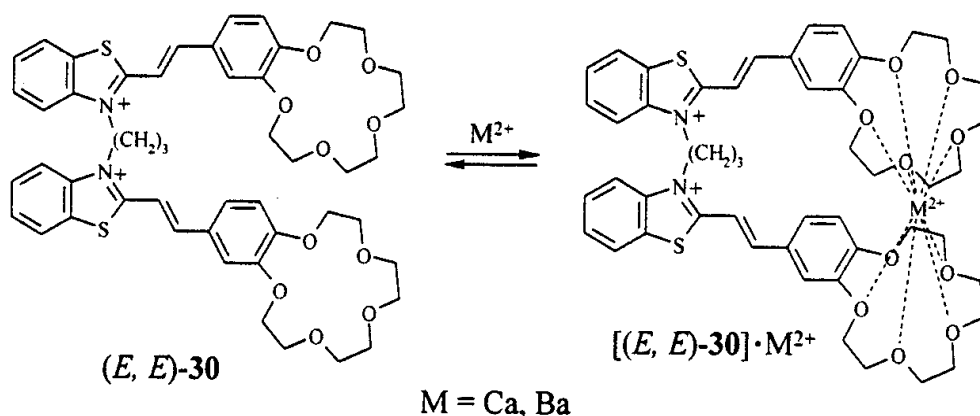
Z-isomer of **27b** is unable to form an anion-“capped” complex. It should be noted that the influence of the spacer structure on the stability of the complexes is much more pronounced in the case of *Z*-isomers. This refers most of all to CESD with conformationally rigid spacers. The ratio of the stability constants of the anion-“capped” complexes (*Z*-**27f**)·Mg²⁺ and (*Z*-**27e**)·Mg²⁺ is about 500.



Scheme 30

It can be suggested that the variation of the structure of CESD would make it possible to change the supramolecular spatial structure of the dimer in a desired direction and thus to control the efficiency of interaction and stereochemistry of the final product of PCA.⁴⁹

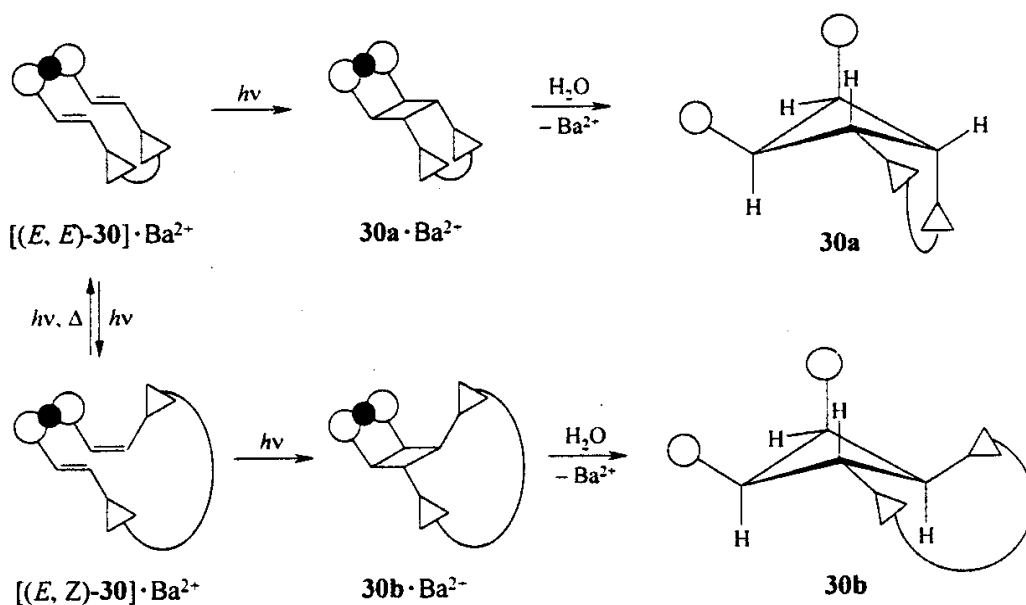
Bis-crown-containing styryl dye (*E,E*)-**28a** having the structure and properties of molecular pincers has been synthesised. In acetonitrile solution, dye (*E,E*)-**28** is able to form intramolecular sandwich complexes with Ca²⁺ and Ba²⁺ cations (Scheme 31).^{50, 51}



Scheme 31

The spontaneous assembly of bisCESD **30** and metal cations with large ionic radii into sandwich complexes, which results in stacking and head-to-head alignment of unsaturated dye fragments, can

become a new method for controlling the efficiency and stereoselectivity of intramolecular PCA with the formation of cyclobutanes. Indeed, in the case of the Ba^{2+} complexes of bisCESD **30**, prolonged photolysis of a photostationary mixture of the geometric isomers led to complete consumption of the dye.



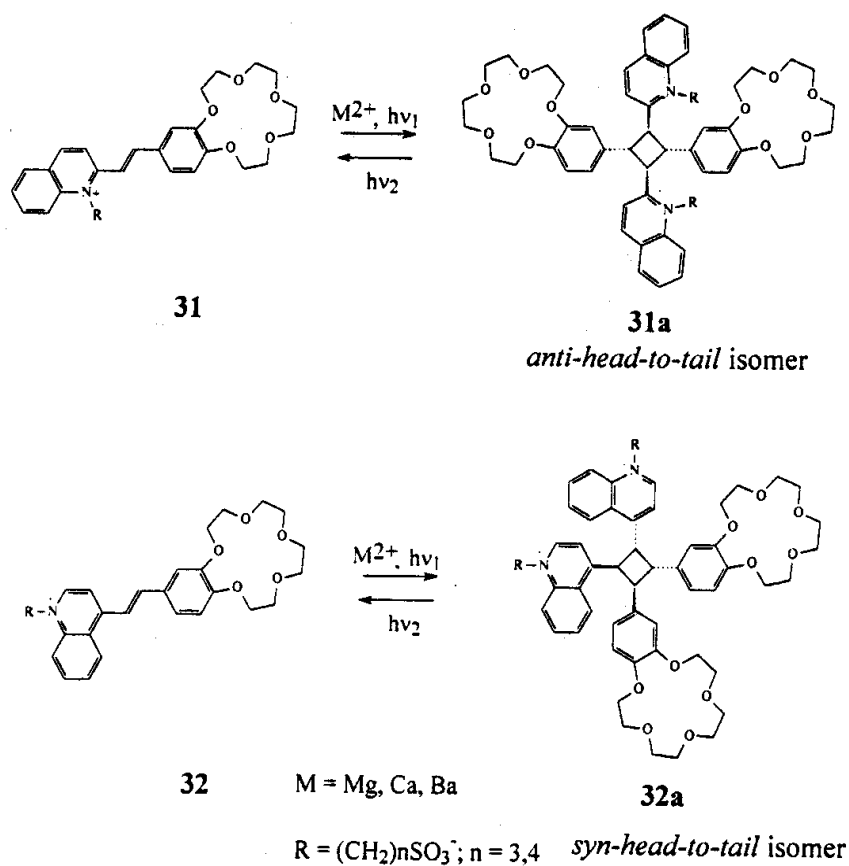
Notation. \bigcirc is the benzo-15-crown-5-ether moiety; \bullet is Ba^{2+} ; --- is $(\text{CH}_2)_3$; \triangleleft is the benzothiazole residue;

Scheme 32

The analysis of 2D COSY and NOESY NMR spectra of the PCA products showed the presence of two isomeric crown-containing cyclobutane derivatives **30a** and **30b** (Scheme 32) in 17 : 83 ratio.

Isomeric chromogenic 15-crown-5-ethers of the quinoline series **31** and **32** were shown to undergo PCA in acetonitrile to give cyclobutane derivatives **31a** and **32a** only in the presence of $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$.⁵² The modification of the heterocyclic residue from 2-methylquinoline to 4-methylquinoline appears to change in principle the PCA route (Scheme 33). The overall quantum yield in the PCA of **31** was 0.0007. In the case of the PCA of **32**, the high quantum yield (0.15) was found, which indicates that the degree of dimerization of the complexes of this dye remains rather high even in a very dilute solution and that the spatial structure of dimeric complexes is probably rather favourable for PCA.

A molecular-mechanics procedure for the computer simulation of PCA of CESD complexes with metal cations has been proposed.⁵³⁻⁵⁵ This procedure allows prediction of the stereochemistry of the cyclobutane derivatives expected in conformity with the calculated predominant conformation of the dimeric supramolecular complexes.



Scheme 33

4. Conclusion

The intense research efforts made by several groups of investigators interested in photochromic crown ethers convincingly demonstrated that photochromic crown ethers represent a novel class of photochromic molecules suited for some possible applications. A substantial influence of complex formation on the spectral characteristics of the molecules and on the kinetics of phototransformation can be expected. In turn, the conformational transformations of molecules that accompany the photoreaction sharply influence the ability of molecules to bind metal cations. This implies that photocontrolled complex formation is possible in this type of system. The results obtained were extended to novel series of photochromic systems. The important objectives for the future research include:

- synthesis of new compounds,
- more extensive and more detailed investigation of their physico-chemical properties in order to find structure—property correlations, and
- modification of already known systems by incorporating them physically or chemically into liquid crystals or polymers in order to develop new effective materials based on the novel photochromic molecules.

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