Crown-containing spirooxazines and spiropyrans
1. Synthesis and the anion-"capped" complexes of photochromic aza-15-crown-5 ethers with flexible spacers

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Methods for the synthesis of new spironaphthooxazines containing an aza-15-crown-5 fragment in two different positions (5' and 9') were developed. The spectral and photochemical properties of these compounds suggest that two competitive complexation processes occur with alkaline-earth or rare-earth metal cations differing in efficiency and selectivity. A metal cation occupies the optimum position in the crown-ether cavity with respect to the donor oxygen atom of the merocyanine form of the dye and thus can affect more strongly its spectral and photochemical properties than in the case of intermolecular interaction.

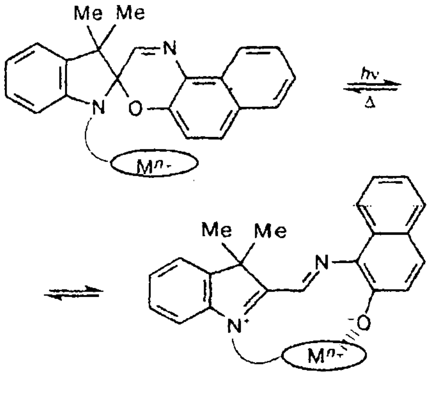
Key words: crown-containing spironaphthooxazines, synthesis, complexation, photochromic properties.

Earlier, we showed that the introduction of a crown-ether fragment into a molecule of a styryl dye affords compounds that can change their spectral and photochemical properties upon complexation.[1] They are promising in the elaboration of chemical sensors, in molecular electronics, and in information recording and reproduction systems. Another example of currently known photochromic crown ethers is crown-containing spiropyrans and spirooxazines.[2-5] It was found that a metal cation added to spiro compounds whose *N*-substituent includes a crown-ether fragment can additionally coordinate with the oxygen atom of a merocyanine-form (MF) dye in the cavity of the crown ether (anion-"capped" complex, Scheme 1).

The structure and position of the crown-containing fragment in a spiro compound are important factors influencing the stability of the anion-"capped" complex. Thus, investigations into spiroindolinonaphthooxazines bearing a benzo-15(18)-crown-5(6) fragment in different positions showed[6] that the rigid structure of a spacer prevents the formation of an anion-"capped" complex, and the addition of metal ions to a solution of such a compound almost does not change its photochromic properties. Note that in the papers cited[2-6] complexation is discussed without considering a possible interaction of the oxygen atom of the MF of the spiro compounds with free metal cations present in the solution. This process competes with the formation of an anion-"capped" complex and can also affect significantly the photochromic properties of the molecule.

Thus, it was necessary to develop the molecular design of spironaphthooxazines differing in the position of a crown-ether fragment. Studies of such compounds would allow one to determine the conditions under which either of the above-mentioned competitive processes of complexation occurs and estimate their contribution to the changes in the photochromic properties of a spiro compound.

Scheme 1



anion-"capped" complex

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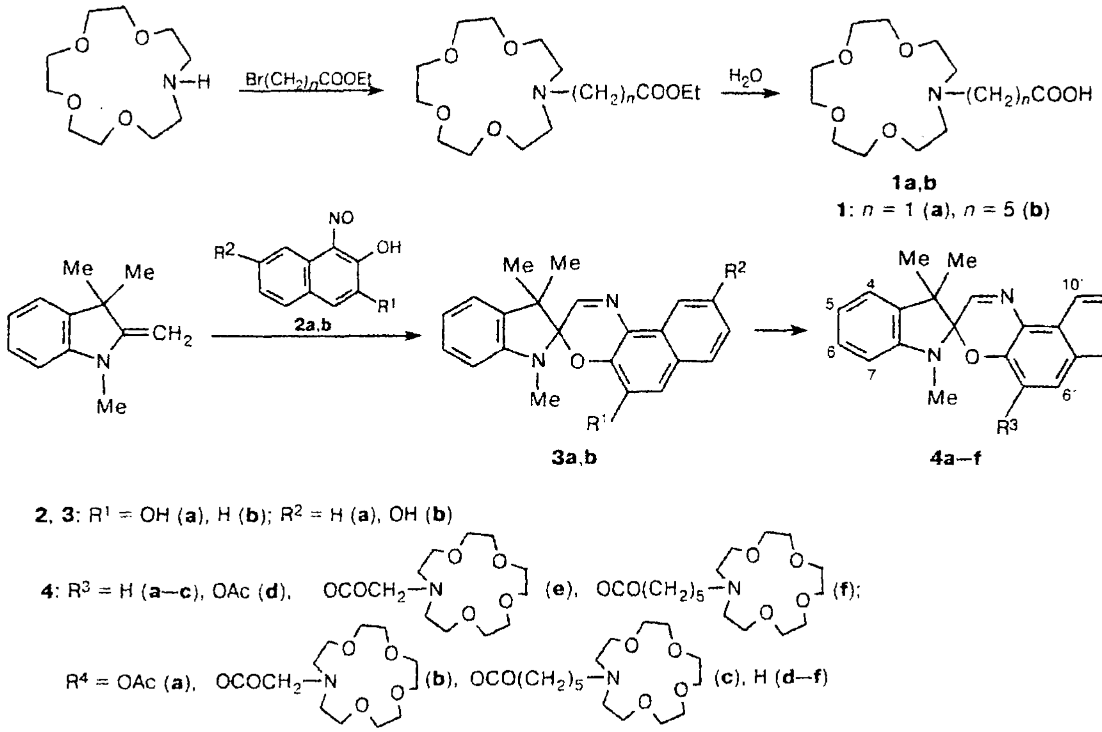
Scheme 2



Synthesis of crown-containing spironaphthooxazines

We synthesized crown-containing spironaphthooxazines (CSN) **4b,c,e,f** and their analogs **4a,d** containing no azacrown-ether fragment (Scheme 2).

Previously unknown crown-containing amino acids **1a,b** were synthesized in two steps. Alkylation of aza-15-crown-5 with ethyl bromoacetate and ethyl 6-bromohexanoate in the presence of Na_2CO_3 or Et_3N yields the corresponding crown-containing esters, which were hydrolyzed *in situ*.

2,3-Dihydroxy-1-nitrosonaphthalene (**2a**) and 2,7-dihydroxy-1-nitrosonaphthalene (**2b**) were obtained according to the known procedures.[7–9] Spiroindolinonaphthooxazines **3a,b** were synthesized by condensation of 1,3,3-trimethyl-2-methylideneindolenine with compounds **2a,b**.[6]

Compound **4b** was used to search for optimum approaches to the synthesis of CSN (Scheme 3).

Spironaphthooxazine **3b** does not react with *N*-(chlorocarbonylmethyl)aza-15-crown-5 (**5**) in the presence of dimethylaniline at room temperature. The reaction of pentachlorophenol with acid **1a** in THF in the presence of dicyclohexylcarbodiimide (DCC) gave pentachlorophenyl ester **6** in 20% yield. Addition of an equimolar amount of 4-pyrrolidinopyridine (PP) increased the yield of ester **6** to 53%. Condensation of the hydroxy compound **3b** with ester **6** can be carried out without isolation and purification of the latter (see Experimental). The reaction product **4b** (the reaction was carried out in the presence of PP) was obtained in 26% yield (method *A*). In other runs where ester **6** was purified before use, the yield of the reaction product also did not exceed 30% (method *B*).

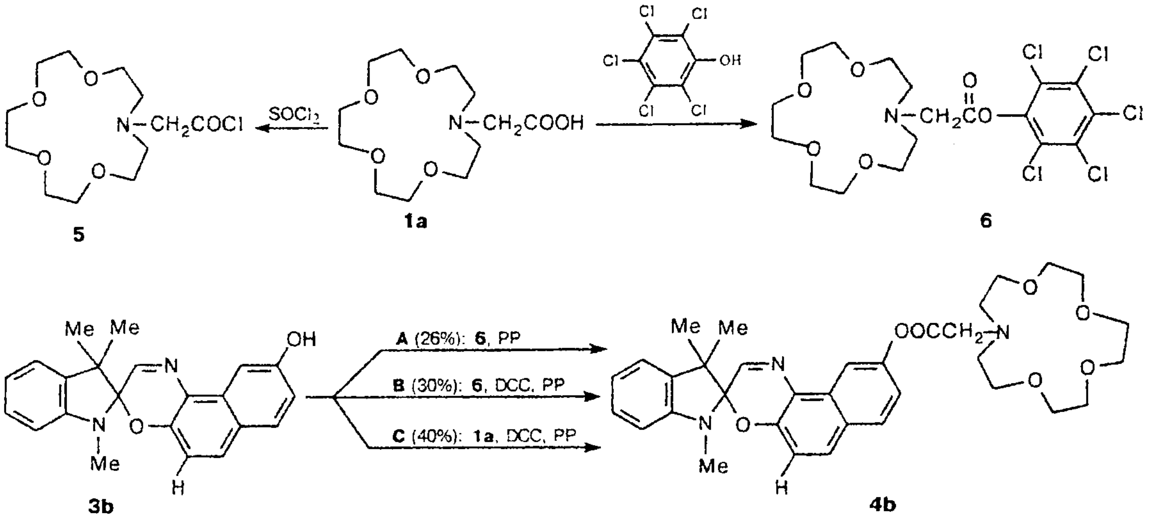
Higher yields of the target product **4b** were achieved by the reaction of acid **1a** with hydroxy derivative **3b** in the presence of PP and DCC (the carbodiimide method[8]), necessary for activation of the carboxyl component. The reaction is carried out at room temperature because the reaction mixture is resinified even upon brief heating at 40 °C. The optimization of the reactant ratio and the reaction time affords product **4b** in up to 40% yield (method *C*). The ester bond in **4b** is easily hydrolyzed, and an attempt to purify this compound by column chromatography on SiO_2 resulted in its hydrolysis with recovery of the starting compound **3b**.

The carbodiimide method proved to be the simplest and most efficient for the synthesis of unknown spironaphthooxazines containing the aza-15-crown-5 fragment in positions 5′ and 9′. The yields of compounds **4a,c—f** amounted to 90%.

The structures of compounds **1a,b**, **3a**, **4a—f**, and **6** were determined by ^1H NMR spectroscopy and mass spectrometry and confirmed by data from elemental analysis (Tables 1 and 2).

Under electron impact, the molecular ions of *N*-carboxyalkyl derivatives of aza-15-crown-5 ethers **1a,b** are

Scheme 3



unstable (see Table 2). The mass spectrum of acid **1b** contains a peak for the $[M - OH]^+$ ion. For both compounds **1a,b**, the main peak at *m/z* 232 is due to cleavage of the C—C bond in the β-position to the side-chain nitrogen atom, which is characteristic of amino acids. The structure of CSN **4b** is supported by the corresponding peak of the molecular ion. The intensity of the molecular ion peak of **4f** is very low, and the spectrum of **4c** exhibits no peak of the molecular ion, but contains intense peaks due to splitting of the substituted aza-15-crown-5 fragment (*m/z* 328). Further fragmentation involves elimination of dihydroxynaphthalene from spironaphthooxazine (*m/z* 185)

Table 1. Properties of compounds **1a,b**, **3a,b**, **4a—f**, and **6**

Compound	M.p./°C	Yield (%)	Molecular formula (*M*)	Molecular ion, *m/z*	Found/Calculated (%) C	H	N
1a	—[a]	88	$C_{12}H_{23}NO_6$ (277)	233[c]	—	—	—
1b	—[a]	95	$C_{16}H_{31}NO_6$ (333)	316[d]	—	—	—
3a	103—07	16	$C_{22}H_{20}NO_2 \cdot 0.5 \cdot H_2O$ (344)		75.11 74.77	5.71 5.99	6.18 7.93
3b	210—212[b] (decomp.)	54	$C_{22}H_{20}N_2O_2$ (344)		76.27 76.72	5.83 5.85	8.13 8.89
4a	180—182 (decomp.)	28	$C_{24}H_{22}N_2O_3$ (386)		75.11 74.59	6.09 5.74	7.26 7.25
4b	—[a]	40	$C_{34}H_{41}N_3O$ (603)	603	—	—	—
4c	—[a]	89	$C_{38}H_{49}N_3O_7$ (659)	344[e]	—	—	—
4d	—[a]	36	$C_{24}H_{22}N_2O_3$ (386)	386	—	—	—
4e	95—98	57	$C_{34}H_{41}N_3O_7 \cdot H_2O$ (603)		65.88 65.68	7.03 6.97	6.72 6.76
4f	—[a]	90	$C_{38}H_{49}N_3O_7$	659			
6	88—90	53	$C_{18}H_{22}Cl_5NO_6$ (523)				

[a] Oil.
[b] *Cf.* Ref. 7.
[c] $[M - CO_2]^+$.
[d] $[M - OH]^+$.
[e] $[M - C_{10}H_{20}NO_4(CH_2)_5COOH]^+$.

Table 2. Mass spectra of compounds **1a,b** and **4b,c,d,f** and the ^{1}H NMR spectra of compounds **1a,b**, **3a,b**, **4a—f**, and **6**

Compound	m/z (I_{rel} (%))[a]	^{1}H NMR (DMSO-d_6), δ (J/Hz)
1a	233 $[M - CO_2]^+$ (17), 232 (100), 202 (35),172 (11), 156 (16), 144 (54),114 (52), 100 (36), 86 (15), 82 (44), 56 (28)	2.90 (m, 4 H, 2 CH_2N); 3.37 (s, 2 H, CH_2N); 3.54 (m, 16 H, 8 CH_2O)
1b	316 $[M - OH]^+$ (17), 233 (13), 232 (100), 202 (19), 172 (21), 114 (18), 100 (21), 87 (14), 86 (15), 74 (13), 58 (15) $[M - OH]^+$ = 316.21185/316.21222[b]	1.25 (m, 2 H, CH_2); 1.45 (m, 4 H, 2 CH_2); 2.18 (m, 2 H, $COCH_2$); 2.52 (m, 2 H, CH_2N); 2.72 (m, 4 H, 2 CH_2N); 3.55 (m, 16 H, 8 CH_2O)
3a		1.24 (s, 3 H, 3-Me); 1.26 (s, 3 H, 3-Me); 2.72 (s, 3 H, NMe); 6.66 (d, 1 H, H-4 or H-7, J = 7.6); 6.82 (t, 1 H, H-5 or H-6, J = 7.4); 7.10 (m, 3 H, H-5 or H-6, H-4 or H-7, H-6′); 7.30 (m, 2 H, H-8′, H-9′); 7.62 (d, 1 H, H-7′, J = 7.5); 7.85 (s, 1 H, CH=N); 8.33 (d, 1 H, H-10′, J = 8.8); 9.94 (br.s, 1 H, OH)
3b		1.15 (s, 3 H, 3-Me); 1.17 (s, 3 H, 3-Me); 2.69 (s, 3 H, NMe); 6.63, 6.85 (2 d, 2 H, H-4 and H-7, J = 7.7 and J = 7.1); 6.81 (d, 1H, H-7′, J = 8.8); 6.95 (dd, 1 H, H-8′, J = 8.8 and J = 2.3); 7.15 (m, 2 H, H-5, H-6); 7.63 (d, 1 H, H-6′, J = 9.3); 7.68 (d, 1 H, H-5′, J = 9.3); 7.73 (d, 1 H, H-10′, J = 2.3); 7.80 (s, 1 H, CH=N); 9.92 (br.s, 1 H, OH)
4a		1.26 (s, 3 H, 3-Me); 1,28 (s, 3 H, 3-Me); 2.34 (s, 3 H, COMe); 2.69 (s, 3 H, NMe); 6.66 (d, 1 H, H-4 or H-7, J = 7.7); 6.84 (t, 1H, H-5 or H-6, J = 7.3); 7.15 (m, 4 H, H-4 or H-7, H-5 or H-6, H-7′, H-8′); 7.83 (d, 1 H, H-5′, J = 9.1); 7.87 (s, 1 H, CH=N); 7.92 (d, 1 H, H-6′, J = 9.1); 8.14 (s, 1 H, H-10′)
4b	603 $[M]^+$ (17), 342 (16), 341 (61), 325 (46), 233 (13), 232 (100), 160 (19), 159 (61), 158 (25), 144 (25), 56 (9) $[M]^+$ = 603.2982/603.2942[b]	1.28 (s, 3 H, 3-Me); 1.29 (s, 3 H, 3-Me); 2.72 (s, 3 H, NMe); 2.95 (m, 4 H, 2 NCH_2); 3.62 (m, 16 H, 8 CH_2O); 3.81 (s, 2 H, $COCH_2$); 6.66 (d, 1 H, H-4 or H-7, J = 7.7); 6.83 (t, 1 H, H-5 or H-6, J = 7.2); 7.13 (m, 3 H, H-4 or H-7, H-5 or H-6, H-7′); 7.21 (dd, 1 H, H-8′, J = 8.7 and 2.4); 7.83 (d, 1 H, H-5′, J = 9.0); 7.87 (s, 1 H, CH=N); 7.92 (d, 1 H, H-6′, J = 8.0); 8.14 (d, 1 H, H-10′, J = 2.3)
4c	344 $[M-C_{10}H_{20}NO_4(CH_2)_5COOH]^+$ (5), 342 (9), 328 (37), 313 (20), 232 (7), 185 (76), 159 (63), 158 (100), 145 (16), 144 (51), 130 (22), 115 (17)	1.47 (s, 3 H, 3-Me); 1.49 (s, 3 H, 3-Me); 1.50 (m, 4 H, 2 CH_2); 1.80 (m, 2 H, CH_2); 2.36 (m, 2 H, $COCH_2$); 2.60 (m, 2 H, NCH_2); 2.73 (t, 4 H, 2 NCH_2, J = 6.3); 2.80 (s, 3 H, NMe); 3.60 (m, 16 H, 8 CH_2O); 6.84 (d, 1 H, H-4 or H-7, J = 7.8); 7.03 (t, 1 H, H-5 or H-6, J = 7.0); 7.24 (m, 3 H, H-7′, H-4 or H-7, H-5 or H-6); 7.30 (dd, 1 H, H-8′, J = 8.7 and 2.3); 7.90 (d, 1 H, H-5′, J = 8.9); 7.95 (s, 1 H, CH=N); 8.07 (d, 1 H, H-6′, J = 8.9); 8.21 (d, 1 H, H-10′, J = 2.3)
4d [c]	386 $[M]^+$ (4), 329 (13), 185 (39), 175 (78), 160 (91), 159 (73), 158 (74), 157 (60), 145 (70), 144 (71), 130 (69), 115 (66)	1.32 (s, 3 H, 3-Me); 1.38 (s, 3 H, 3-Me); 1.98[d] (s, 3 H,COMe); 2.66 (s, 3 H, NMe); 6.60, 7.14 (2 d, 2 H, H-4 and H-7, J = 7.7 and 7.2); 6.90, 7.20 (2 t, 2 H, H-5 and H-6, J = 7.2 and 7.7); 7.47 (m, 1 H, H-8′); 7.53 (s, 1 H, H-6′); 7.60 (m, 1 H, H-9′); 7.81 (d, 1 H, H-7′, J = 8.4); 7.88 (s, 1 H, CH=N); 8.53 (d, 1 H, H-10′, J = 8.4)
4e		1.20 (m, 6 H, 2 Me); 2.71 (s, 3 H, NMe); 3.50 (m, 22 H, $COCH_2$, 8 CH_2O, 2 NCH_2); 6.64 (d, 1 H, H-4 or H-7, J = 8.0); 6.82 (t, 1 H, H-5 or H-6, J = 6.8); 7.15 (m, 2 H, H-4 or H-7, H-5 or H-6); 7.46 (m, 1 H, H-8′); 7.60 (m, 1 H, H-9′); 7.69 (s, 1 H, H-6′); 7.84 (m, 1 H, H-7′); 7.95 (s, 1 H, CH=N); 8.46 (d, 1 H, H-10′, J = 8.6)
4f[c]	659 $[M]^+$ (<1), 328 (36), 160 (26), 159 (69), 158 (100), 157 (31), 145 (24), 144 (73), 143 (23), 130 (21), 115 (24)	1.25 (m, 2 H, CH_2); 1.32 (s, 3 H, 3-Me); 1.36 (s, 3 H, 3-Me); 1.42 (m, H, CH_2); 1.57 (m, 2 H, CH_2); 2.22 (t, 2 H, $COCH_2$); 2.40 (m, 2 H, NCH_2); 2.64 (m, 7 H, NMe, 2 NCH_2); 3.56 (m, 16 H, 8 OCH_2); 6.58, 7.12 (2 d, 2 H, H-4′ and H-7, J = 7.7 and 6.9); 6.87, 7.18 (2 t, 2 H, H-5 and H-6, J = 7.4 and J = 7.6); 7.46 (m, 1 H, H-8′); 7.51 (s, 1 H, H-6′); 7.79 (m, 1 H, H-9′); 7.29 (d, 1 H, H-7′, J = 8.2); 7.86 (s, 1 H, CH=N); 8.52 (d, 1 H, H-10′, J = 8.4)
6		2.90 (t, 4 H, 2 CH_2N, J = 5.8); 3.56 (m, 16 H, 8 CH_2O); 3.97 (s, 2 H, $COCH_2$)

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[a] The molecular ion peak and ten of the most intense peaks are given.
[b] Data from high-resolution mass spectrometry: found/calculated.
[c] ^{1}H NMR spectra recorded in MeCN-d_3.
[d] The signal overlaps with a signal for the water present in the solvent.

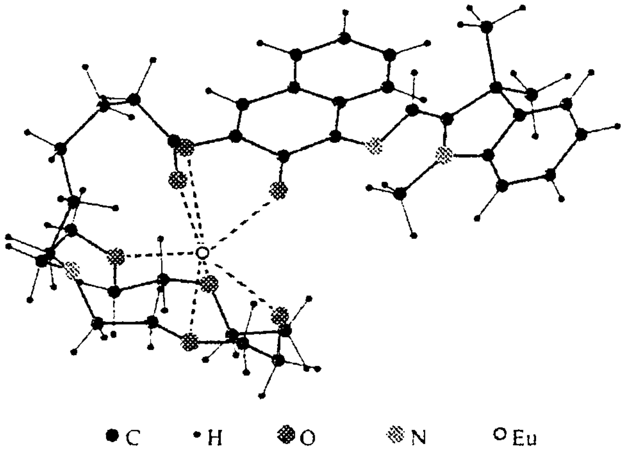


Fig. 1. Structural model of the MF of complex [**4f** · Eu^{3+}].

to give the most intense peak in the spectrum (*m/z* 158), which corresponds to dihydroindole.

Molecular modeling of CSN complexes

A model analysis of the structures of CSN complexes with Mg^{2+} and Eu^{3+} cations was performed with the use of the GenMol method.[10] The following procedure was used for calculations. First, the geometry of each CSN molecule was optimized, and then a cation was introduced into the molecule by docking and the structure of the resulting complex was calculated. In this case, the stability of the complexes was defined as the energy of interaction (E_i) between a metal cation and a free ligand, which is the sum of noncovalent interactions (van der Waals and Coulomb ones). This gave the following E_i values:

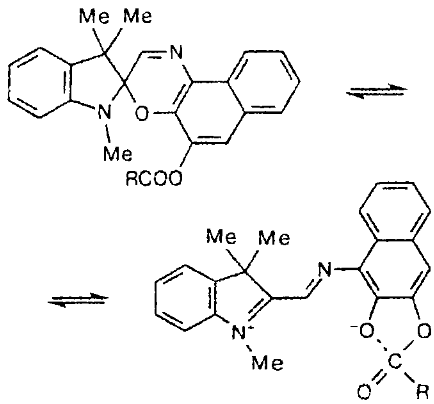
CSN	**4b**	**4c**	**4e**	**4f**
E_i (kcal mol^{-1})	−134	−125	−136	−142

The more stable complex corresponds to the more negative E_i value. The complexation between CSN **4a—f** and the Mg^{2+} cation involves the oxygen atom of the spacer carbonyl group and the heteroatoms of the crown-ether fragment. The metal cation charge value influences the strength and structure of the resulting complex. According to our calculation, complexation between **4f** and Eu^{3+} gives a stable complex in which the trivalent cation is coordinated by the oxygen atoms of the spacer ester group, the oxygen atom of MF, and the heteroatoms of the crown-ether macrocycle (Fig. 1).

Spectral and photochemical studies of CSN and their complexes

When irradiated, compounds **4a—f** are reversibly converted to the colored MF, which are capable of transforming spontaneously into the original spiro forms.

Scheme 4



The presence of the crown-ether fragment in position 9′ of the system does not change markedly the spectral pattern of the spiro and merocyanine forms of compounds **4b,c** nor the thermodynamic equilibrium between these forms, but increases the thermal relaxation rate constant (*K*) for the colored forms of these compounds by a factor of ~2 (Table 3). The observed changes in the constant *K* may be evidence of steric interactions in **4b,c**, which prevent *cis-trans*-isomerization of the open form and reduce the number of possible MF conformations of these compounds.

Unlike 9′-substituted spironaphthooxazines, in the case of 5′-substituted compounds **4d—f**, the equilibrium is shifted towards MF. This is evidenced by a low-intensity absorption band of MF in the visible region and may be associated with the participation of the carbonyl group in the stabilization of the merocyanine form of the dye[11] (Scheme 4).

When Mg, Ca, and Ba perchlorates were added to solutions of **4a—c** in MeCN at the concentration ratio C_L/C_M = 1/1 (C_L and C_M are the concentrations of ligand and salt, respectively), the spectral and kinetic parameters of these compounds did not change markedly. A gradual increase in the concentration of the metal anion gradually changes the spectral pattern. At the concentration ratio C_L/C_M = 1 : 100, a long-wavelength band ($\Delta\lambda_{max}$) is slightly shifted bathochromically in the absorption spectra of MF (by 5 nm for **4c** and by 15 nm for **4b**) (Fig. 2) (see Table 3).

The addition of Mg^{2+}, Ca^{2+}, and Ba^{2+} cations to solutions of compounds **4a—c** also leads to lower *K* values (see Table 3). For compounds **4a,c**, the relative changes in *K* are virtually the same, while in the case of **4b** the effect is more strongly pronounced (see Table 3). In an attempt to explain the results obtained, we assumed that the introduction of the metal cations into solutions of **4a—c** in MeCN allows the processes illustrated in Scheme 5 to occur. The formation of complexes **A** for compounds containing no crown-ether

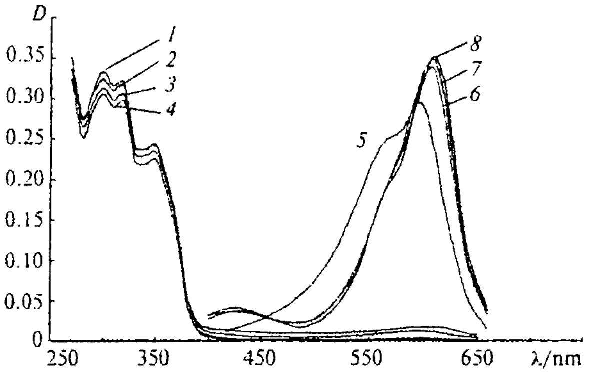


Fig. 2. Electronic absorption spectra of the spiro form (*1*) of **4b** and its complexes with Mg^{2+} (*2*), Ca^{2+} (*3*), and Ba^{2+} (*4*) ions and the merocyanine form (*5*) of compound **4b** and its complexes with Mg^{2+} (*6*), Ca^{2+} (*7*), and Ba^{2+} (*8*) ions in MeCN. $C_L = 5 \cdot 10^{-4}$ mol L^{-1}; [L]/[M] = 1 : 100.

fragment was noted earlier.[12] According to these data on the molecular modeling, crown-containing compounds **4b,c** should exist in the form of complex **B**, whose structure is the most thermodynamically stable.

In the case of crown-free spironaphthooxazine **4a**, the formation of complex **A** upon addition of metal ions lowers the ground state energy of the MF of the molecule and, consequently, increases the potential barrier to thermal relaxation and extends the lifetime of the MF.

When alkaline-earth metal ions are added to solutions of CSN **4b,c**, they first bind to the crown-ether fragment (see Scheme 5, complex **B**). A larger effect of the metal ions on the thermal relaxation rate constant of the MF of **4b**, with a short methylene chain (as compared to that in the case of **4c**), correlates with the above calculations on the strength of the resulting complex **B** formed by these compounds. Involvement of the CO oxygen atom in the formation of complex **B** redistributes the π-electron density over the MF chromophore conjugation chain, thus additionally stabilizing it.

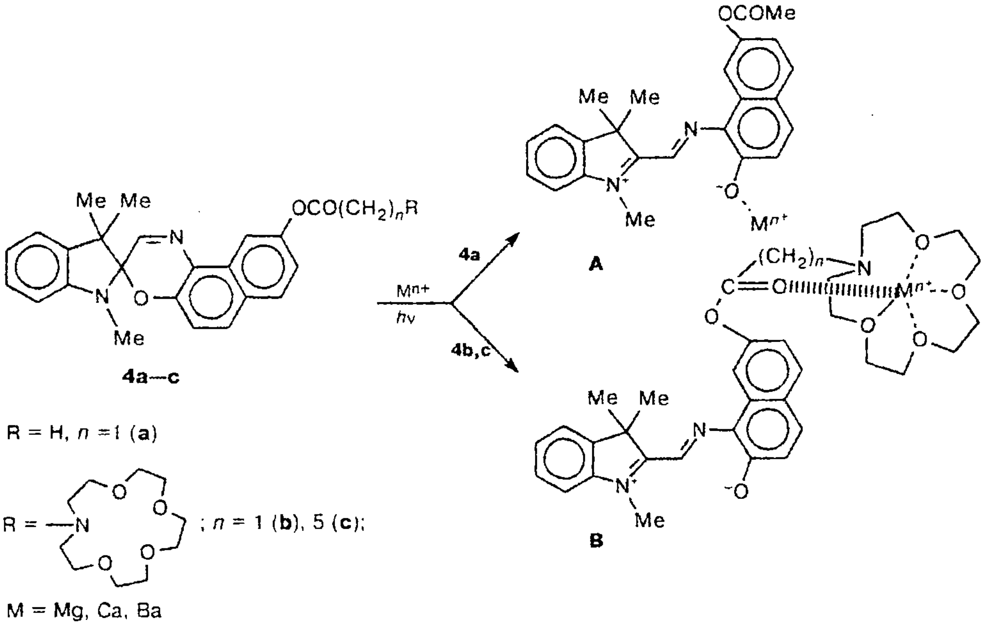
Introduction of $Mg(ClO_4)_2$ into solutions of **4d—f** in MeCN shifts the equilibrium towards the MF, the shift magnitude depending on the concentration of the salt added. In the range of low concentrations of Mg^{2+} (C_L/C_M = 1 : 1), the electronic absorption spectra of crown-containing compounds **4e,f** exhibit much more intense bands of the colored form as compared to crown-free compound **4d** (see Table 3). The observed changes in the spectral pattern may be due to different natures of the complexes at high and low C_L/C_M values. Scheme 6 shows possible structures of the resulting complexes of spiro compounds **4d—f** with metal cations with consideration of the above data on molecular modeling and the literature data.[11,12]

Table 3. Spectral and photochemical properties of compounds **4a—f** and their complexes with Mg^{2+}, Ca^{2+}, and Ba^{2+} ions in MeCN

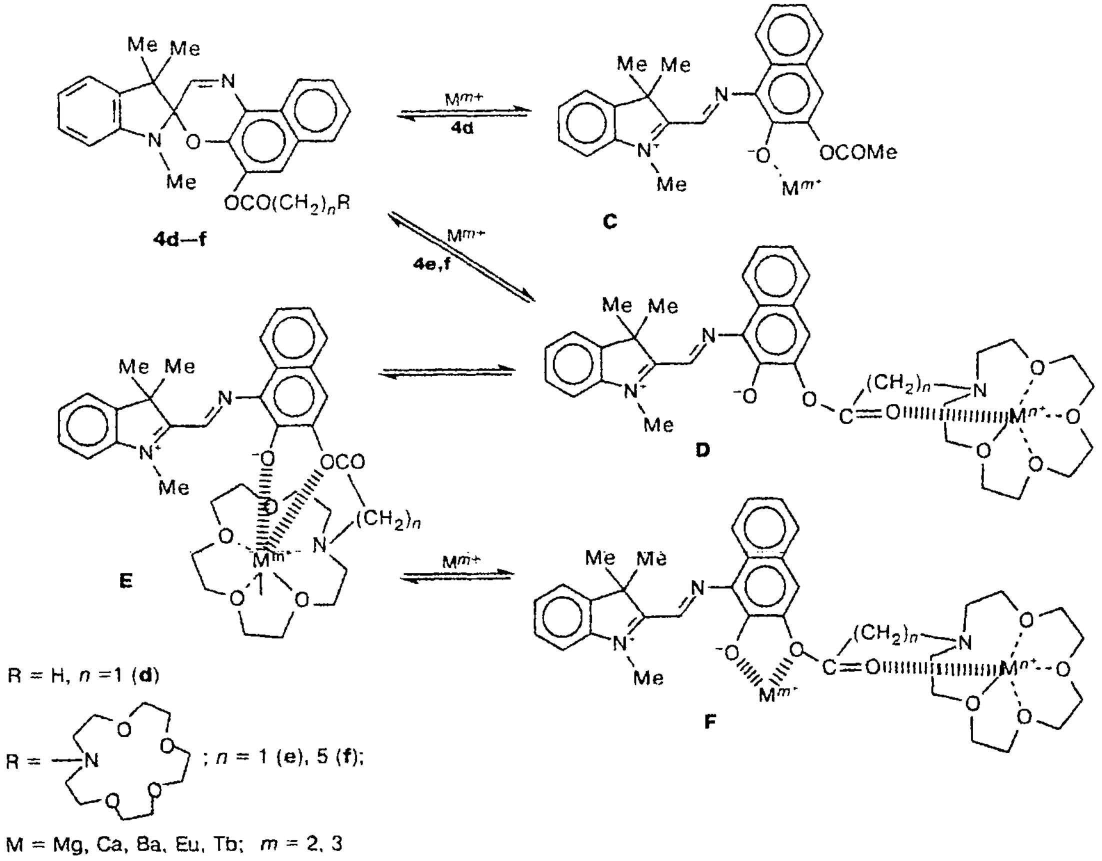
Compound	M^{n+}	[L]/[M]	λ	Δλ	$\varepsilon_0 \cdot 10^{-4}$	$\varepsilon/\varepsilon_0$	K/s^{-1}	K/K^0
			nm					
4a	—		597		0		0.53	1.0
	Mg^{2+}	1 : 100	596	−1	0		0.10	0.19
	Ca^{2+}	1 : 100	597	0	0		0.13	0.24
	Ba^{2+}	1 : 100	598	+1	0		0.38	0.72
4b	—		595		0		1.10	1.0
	Mg^{2+}	1 : 100	607	+12	0		0.060	0.055
	Ca^{2+}	1 : 100	607	+12	0		0.040	0.036
	Ba^{2+}	1 : 100	610	+15	0		0.20	0.18
4c	—		595		0		0.96	1.0
	Mg^{2+}	1 : 100	597	+2	0		0.20	0.21
	Ca^{2+}	1 : 100	598	+3	0		0.24	0.25
	Ba^{2+}	1 : 100	599	+4	0		0.66	0.69
4d	—		595		0.05	1.0	0.35	1.0
	Mg^{2+}	1 : 1	594	−1	0.13	2.5	0.10	0.29
	Mg^{2+}	1 : 10	592	−3	0.30	6.0	0.04	0.11
4e	—		597		0.02	1.0	0.46	1.0
	Mg^{2+}	1 : 1	597	0	0.11	6.0	0.12	0.26
	Mg^{2+}	1 : 10	597	0	0.18	9.0	0.045	0.10
4f	—		595		0.02	1.0	0.45	1.0
	Mg^{2+}	1 : 1	575	−20	0.39	20.0	0.35	0.78
	Mg^{2+}	1 : 10	587	−8	0.3	15.0	0.15	0.33
	Mg^{2+}	1 : 100	590	−5	0.5	25.0	0.06	0.13

Note. $\Delta\lambda = \lambda_{Ml} - \lambda_l$ is the relative shift of the absorption band of the colored form upon complexation; $\varepsilon/\varepsilon_0$ is the change in the intensity of a long-wavelength absorption band of the MF upon complexation; K is the thermal relaxation constant of the MF; K/K^0 is the change in the thermal relaxation constant upon complexation.

Scheme 5



Scheme 6



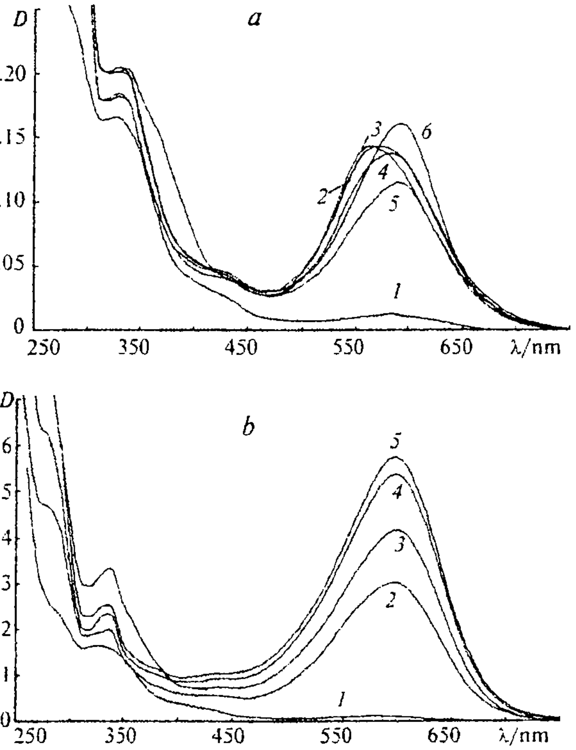


Fig. 3. Electronic absorption spectra of the MF of compound **4f** (*1*) and its complexes with Mg^{2+} (*a*) and Eu^{3+} (*b*) ions in MeCN. $C_L = 5 \cdot 10^{-4}$ mol L^{-1}; [L]/[M] = 1 : 0.5 (*2*), 1 : 2 (*3*), 1 : 5 (*4*), 1 : 20 (*5*), and 1 : 50 (*6*).

A markedly larger shift of the equilibrium towards the MF in the case of crown-containing compounds **4e,f** at C_L/C_M = 1 : 1 may be explained by the formation of an anion-"capped" complex **E**. As a result, the energy of the MF ground state is lowered, which allows its thermal occupation. It follows from the experimental results and molecular modeling that the magnitude of the effect observed depends on the length of the spacer methylene chain connecting the photochromic and ionophoric parts of the molecule. Presumably, compound **4f** forms a structure in which the crown-linked Mg^{2+} cation and the MF oxygen atom are closer to each other than in the case of **4e**, having a short spacer. The influence of complexation involving free Mg^{2+} ions and an MF oxygen atom (the formation of complex **C**) on the spectral characteristics of the crown-free compound **4d** is much less pronounced under these conditions (see Table 3).

The effect of the concentration of Mg^{2+} ions on the spectral pattern was studied with compound **4f** as an example (Fig. 3). It was shown that the transformation of the anion-"capped" complex **E**, which exists at low metal concentrations, into complex **F**, formed in the reaction of MF with free Mg^{2+} cations at high concentrations of the latter, is accompanied by a change in the shape of an absorption band of MF.

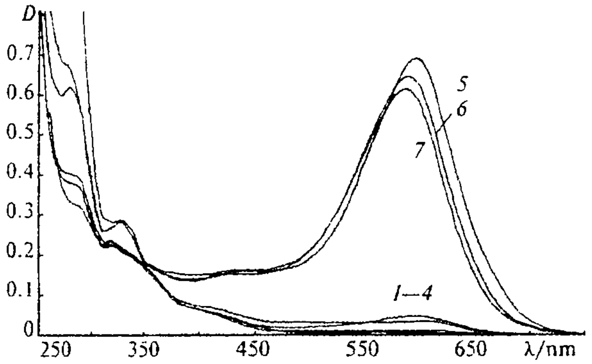


Fig. 4. Electronic absorption spectra of the MF of compound **4d** (*1*) and its complexes with Ba^{2+} (*2*), Ca^{2+} (*3*), Mg^{2+} (*4*), La^{3+} (*5*), Eu^{3+} (*6*), and Tb^{3+} (*7*) ions in MeCN. $C_L = 2 \cdot 10^{-4}$ mol L^{-1}; [L]/[M] = 1 : 100.

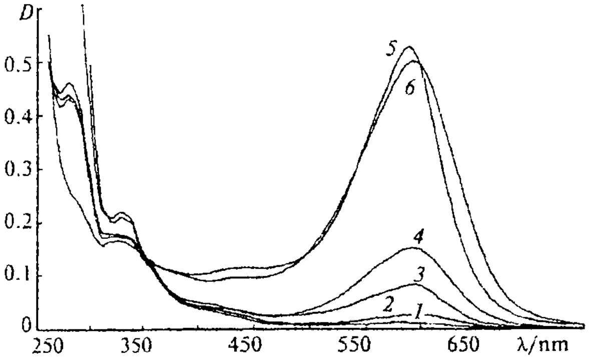


Fig. 5. Electronic absorption spectra of the MF of compound **4f** (*1*) and its complexes with Ba^{2+} (*2*), Ca^{2+} (*3*), Mg^{2+} (*4*), La^{3+} (*5*), and Eu^{3+} (*6*) ions in MeCN. $C_L = 2 \cdot 10^{-4}$ mol L^{-1}; [L]/[M] = 1 : 100.

The addition of $Mg(ClO_4)_2$ to solutions of compounds **4d—f** affects the constant K of the thermal decolorization of the MF (see Table 3). However, the observed changes in K are different for **4d—f**, which may be due to the different natures of the resulting complexes. In the presence of metal cations, thermal relaxation of the merocyanine forms existing as complexes **C** (in the case of **4d**), **F** (**4e**), and the anion-"capped" complex **E** (**4f**) is observed. The constant of formation of the anion-"capped" complex **E** for compound **4f**, obtained by spectrophotometric titration,[13] is more than two orders of magnitude higher than that for complex **C** formed by free metal cations with the MF.

These results suggest that the crown-ether fragment can provide (owing to a more favorable position of a metal cation in the cavity of the macrocycle with respect to the donor centers of the molecule) a stronger effect of the cation on the spectral characteristics and photochemical properties of these compounds than that provided by intermolecular interaction of a photochromic molecule with a metal cation.

We studied the influence of the nature of a metal cation on the equilibrium between the colored and colorless forms of CSN **4d,f**. Solutions of $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Ba(ClO_4)_2$, $Eu(NO_3)_3$, $La(NO_3)_3$, and $Tb(NO_3)_3$ were added to a solution of a spiro compound in MeCN at the ligand : salt ratio = 1 : 100. The changes observed in the absorption spectra are shown in Figs. 4 and 5.

Absorption bands that appeared in the visible region upon addition of rare-earth element nitrates to solutions of CSN **4d,f** in MeCN are much more intense than those observed in the case of alkaline-earth metal salts (see Figs. 4 and 5). Their intensities are virtually independent of the presence or absence of a crown-ether fragment. In our opinion, this attests that complexes of CSN **4d,f** with metal ions are similar in nature. These complexes can include the same chelato groups (see Scheme 6, complexes **C** and **F**), which eliminates the effect of the crown-ether fragment on complexation.

Additionally, this assumption was confirmed by an UV spectroscopic study of solutions of CSN **4f** at different relative concentrations of added Eu^{3+} ions (Fig. 3, *b*). The fact that the complexes obtained with different amounts of the metal absorb at the same UV wavelength suggests their similar nature, which is independent of the metal concentration. High surface charge density of rare-earth metal cations[14] favors efficient complexation involving the MF oxygen atoms, *i.e.*, the formation of complex **C** at low concentrations of the metal and of complex **F** with an excess of the salt.

Thus, we proposed the method for the synthesis of new 5′- and 9′-azacrown-substituted spironaphthooxazines. It was shown that introduction of a flexible spacer into position 5′ of a spiro compound allows one to reveal a significant influence of complexation on the spectral properties and the kinetics of decolorization of the MF of the spiro compound. A comparative study of the spectral and photochemical properties of crown-containing spiroindolinonaphthooxazines synthesized by us showed that complexation occurs in two competitive ways, involving both free metal cations and those linked to the crown fragment. Also, this made it possible to estimate their efficiency and selectivity in the series of alkaline-earth and rare-earth metal cations. Investigations of these compounds are important for creating new types of photochromic materials whose spectral and photochemical properties can be controlled by complexation.

Experimental

^1H NMR spectra were recorded on Bruker AMX-200p and Bruker AMX-400 spectrometers in DMSO-d_6 and CD_3CN with Me_4Si as the internal standard; δ values were measured with an accuracy of 0.01 ppm, and spin-spin coupling constants with an accuracy of 0.1 Hz. Mass spectra were obtained with a Varian MAT-311A instrument (EI-MS, 70 eV, direct inlet of the sample). The course of the reactions was monitored by TLC on Kieselgel 60 F_{254} plates (Merck). Column chromatography was performed on silica gel 60 (70—230 mesh ASTM, Merck).

Electronic absorption spectra were measured with a Shimadzu UV-3100 spectrophotometer. The electronic absorption spectra and thermal relaxation rate constants of the colored form were obtained on a kinetic setup in the time range 0.001—1000 s (photoexcitation with UV radiation generated by a pulse xenon lamp). Measurements were performed in solutions with a concentration of compounds $C_L = 2 \cdot 10^{-4}$ mol L^{-1} at 298 K. MeCN (Aldrich, water content 0.005%) was used as a solvent. Mg, Ca, and Ba perchlorates and Eu, La, and Tb nitrates were used as complexing agents.

***N*-Carboxymethyl-1,4,7,10-tetraoxa-13-azacyclopentadecane (1a)** was obtained by analogy with the known procedure.[11] $BrCH_2CO_2Et$ (1.12 mL, 10.1 mmol), anhydrous Na_2CO_3 (1.092 g, 10.3 mmol), and 100 mL of anhydrous MeCN were added to aza-15-crown-5 (2 g, 9.13 mmol). The reaction mixture was refluxed for 24 h and then cooled. The precipitate that formed was filtered off, and the filtrate was concentrated *in vacuo*. The residue was dissolved in chloroform and washed with water. The aqueous layer was washed with $CHCl_3$, and the combined extracts were concentrated *in vacuo*. Water (40 mL) was added to the residue, and the resulting solution was refluxed for 50 h. After cooling, the aqueous solution was washed with benzene and concentrated *in vacuo*.

***N*-(5-Carboxypentyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (1b).** A solution of aza-15-crown-5 (1.095 g, 5 mmol), ethyl 6-bromohexanoate (0.89 mL, 5 mmol), and anhydrous Et_3N (1.04 mL, 7.5 mmol) in 10 mL of anhydrous THF was kept at 20—25 °C for 140 h. The crystalline precipitate that formed was filtered off, and the filtrate was concentrated *in vacuo*. Water (20 mL) was added to the residue, and the resulting solution was refluxed for 30 h. The solvent was removed *in vacuo*, and products were extracted from the residue with hot hexane.

Synthesis of 5′(9′)-hydroxy-1,3,3-trimethylspiroindolinonaphthooxazines (3a,b) (general procedure). A solution of 1,3,3-trimethyl-2-methylideneindoline (1.1 mmol) and compound **2a** (**2b**) (1 mmol) in 5 mL of anhydrous EtOH was refluxed in an inert atmosphere for 2 h. The solvent was removed *in vacuo*. In the case of **3a**, the residue was chromatographed on silica gel in 1 : 1 hexane—benzene. In the case of **3b**, a small amount of EtOH was added to the residue. The insoluble precipitate was filtered off and repeatedly washed with hot hexane and toluene.

***N*-(Pentachlorophenoxycarbonylmethyl)aza-15-crown-5 (6).** A solution of dicyclohexylcarbodiimide (0.268 g, 1.3 mmol) in 1 mL of THF was added to a solution of compound **1a** (0.332 g, 1.2 mmol), pentachlorophenol (0.399 g, 1.5 mmol), and 4-pyrrolidinopyridine (0.220 g) in 4 mL of anhydrous THF at 0 °C. The reaction mixture was kept at 20—25 °C for 1 day. The precipitate of dicyclohexylurea that formed was filtered off, and the filtrate was concentrated *in vacuo*. The residue was chromatographed on silica gel in benzene, 1 : 1 benzene—EtOAc, and EtOAc.

1,3,3-Trimethyl-9′-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)methylcarbonyloxyspiro{indolino-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine} (4b). Method *A*. A solution of DCC (0.268 g, 1.3 mmol) in 1 mL of THF was added to a solution of compound **1a** (0.332 g, 1.2 mmol), pentachlorophenol (0.399 g, 1.5 mmol), and PP (0.220 g, 1.5 mmol) in 4 mL of anhydrous THF at 0 °C. The reaction mixture was kept at 20—25 °C for 1 day. The precipitate of dicyclohexylurea that formed was filtered off, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 3 mL of anhydrous THF, and a solution of **3b** (0.120 g, 0.35 mmol) and PP (0.052 g, 0.35 mmol) in 5 mL of anhydrous THF was added. The reaction mixture was kept at 20—25 °C for 1 day, and the solvent was removed *in vacuo*. The residue was chromatographed on silica gel in benzene, 1 : 1 benzene—EtOAc, and EtOAc to give **4b** in 26% yield.

Method *B*. A solution of compound **6** (0.269 g, 0.5 mmol), compound **3b** (0.172 g, 0.5 mmol), and PP (0.072 g, 0.5 mmol) in 5 mL of dichloromethane was kept at room temperature for 1 day. The reaction mixture was concentrated *in vacuo*, and the residue was chromatographed on silica gel in benzene, 1 : 1 benzene—EtOAc, and EtOAc to give **4b** in 30% yield.

Method *C*. **Synthesis of crown-containing spironaphthooxazines (4a—f) (general procedure).** Compound **1** (4.4—6.6 mmol) (or glacial AcOH (4.4 mmol) in the case of **4a,d**), DCC (4.8 mmol), and PP (0.4 mmol) were added to a solution of spironaphthooxazines **3a,b** (4.4 mmol) in 20 mL of CH_2Cl_2. The resulting solution was kept in the dark at 20—25 °C for 3 to 5 days. The precipitate of dicyclohexylurea that formed was filtered off, and the filtrate was concentrated *in vacuo*. Products were extracted from the residue with dry ether. In the case of **4a**, the precipitate that formed was filtered off and dried. To obtain **4b,c,d—f**, the ethereal extracts were combined and filtered, and the filtrates were concentrated *in vacuo*. Compound **4d** was extracted from the residue with hexane, and the hexane extracts were combined and concentrated *in vacuo*. Compound **4b** was extracted from the residue with hot hexane, and the hexane extracts were combined and concentrated *in vacuo*.

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