Full Articles

Recoordination of a metal ion in the cavity of a crown compound: a theoretical study
1. Conformers of arylazacrown ethers and their complexes with Ca^{2+} cation

A. Ya. Freidzon, A. A. Bagatur´yants, S. P. Gromov, and M. V. Alfimov*

Center of Photochemistry, Russian Academy of Sciences,
7a ul. Novatorov, 117421 Moscow, Russian Federation.
Fax: +7 (095) 936 1255. E-mail: sanya@photonics.ru

Photoinduced recoordination of Ca^{2+} complexes of the photochromic azacrown ethers is studied by the density functional method. The study included model arylazacrown ethers containing various acceptor groups in the aromatic ring in the *para* position to the azacrown ether moiety and a real azacrown-containing styryl dye. It is found that both free azacrown ethers and their complexes can adopt two types of conformations: (1) axial conformations, in which the aromatic ring axis passing through the crown ether nitrogen N_{cr} and the opposite atom of the aromatic ring is perpendicular to the root-mean-square (RMS) plane of the crown ether (least-squares fitted plane for all the crown ether atoms), and (2) equatorial conformations, in which the aromatic ring axis only slightly deflects from the RMS plane of the crown ether. In the equatorial conformers, the metal cation is coordinated only to the O atoms of the azacrown ether cycle, the metal—nitrogen bond is broken, and N_{cr} is conjugated with the aromatic ring. In the axial conformers, the metal cation is additionally coordinated to N_{cr}. It is found that the presence of an acceptor group bearing a formal positive charge decreases the relative energy of the equatorial conformer and favors metal—nitrogen bond dissociation, which results in the recoordination of the metal cation. However, a long distance between the charged group and N_{cr} has the reverse effect. The photoinduced recoordination observed in the alkaline-earth metal complexes of the photochromic azacrown ethers is explained by the transitions between the axial and equatorial conformers facilitated by the charge transfer in the excited state of the complex.

Keywords: arylazacrown ethers, azacrown-containing dyes, complexes with Ca^{2+}, photoinduced recoordination, quantum-chemical calculations, density functional theory.

Absorption spectra of the alkaline-earth metal complexes of azacrown-containing styryl dyes exhibit a long-wavelength shoulder, which cannot be attributed to the residual absorption of the free ligand.[1,2] It was supposed that these spectral features are caused by the recoordination of the metal cation in the crown ether cavity.

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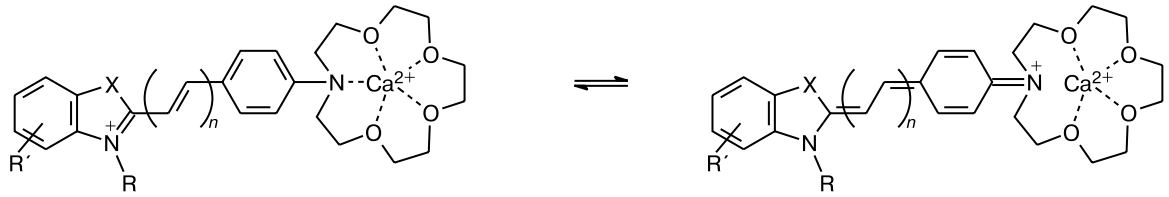
Scheme 1



1a,b

1a: X = S, R = Et, R′ = H, *n* = 1; **1b:** X = CMe_2, R = Me, R′ = 4,6-Me_2, *n* = 2

This means that, in the ground state, dye **1a** exists in solution in two forms, namely, a "benzenoid" form, where the cation is coordinated to the four crown ether oxygen atoms and one nitrogen N_{cr}, and a "quinoid" form, where the metal—nitrogen bond is absent (Scheme 1). Because photoexcitation decreases the electron density on N_{cr}, we can expect the equilibrium in the excited state to be shifted toward the latter structure. This is supported by high similarity of the patterns of the time-resolved UV spectra[3,4] of free ligand **1b** and its excited-state metal complex. The fluorescence spectra of the alkaline-earth metal complexes of these dyes exhibit the bands of both locally excited parent compound and its recoordinated product.[3,4] Apparently, the complex form without the metal—nitrogen bond makes the dominant contribution to the fluorescence spectra; therefore, complexation causes only a slight shift of the fluorescence bands of dyes **1a,b**. Excited-state recoordination of the dye complex proceeds rapidly by the intramolecular mechanism. However, the details of the recoordination process and the nature of the potential barrier separating the two conformers of the dye are to be elucidated.

The structure of azacrown ethers and their complexes implies two different types of conformations (Figs. 1 and 2). These are the axial conformations (**Ax**), in which the aromatic ring axis passing through N_{cr} and the opposite atom of the aromatic ring is perpendicular to the root-mean-square (RMS) plane of the crown ether (least-squares fitted plane for all the crown ether atoms), and the equatorial conformations (**Eq**), in which the aromatic ring axis only slightly deflects from the RMS plane of the crown ether. We supposed that it is these conformational changes that are responsible for the rearrangement in the coordination sphere of the metal cation. The lone electron pair (LP) of the crown ether nitrogen can either be directed inwards the crown ether cavity (toward the cation in the **Ax** conformer of the complex), which facilitates the metal—nitrogen bonding, or be perpendicular to the RMS plane of the crown ether (at a large angle to the metal—nitrogen direction in the equatorial conformers).

X-ray diffraction data for the free dyes **1** show that the crown ether moieties in the dyes can adopt both types of conformation. The styryl dye **1a**[5] adopts only one, **Eq** conformation, whereas two crystallographically independent molecules of the butadienyl dye **1b**[6] adopt two different axial conformations of the crown ether moiety (**Ax1** and **Ax2**) differing only in arrangement of the OCH_2CH_2 links. The **Ax2** conformation is most frequently

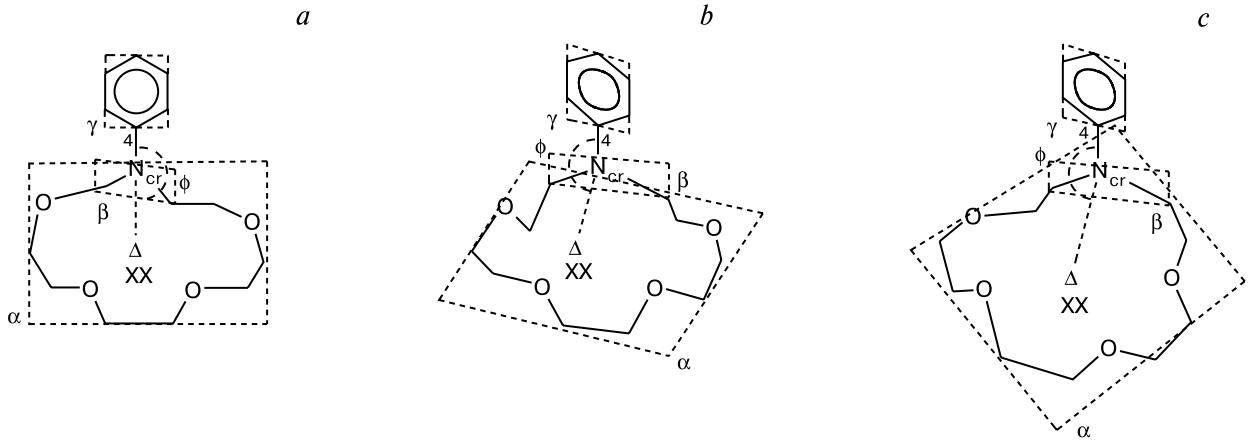


Fig. 1. Conformers of the free arylazacrown ethers: **Eq** (*a*), **Ax1** (*b*), and **Ax2** (*c*); XX is the center of mass of the crown ether macrocycle; ϕ is the angle C(4)—N_{cr}—XX; α is the root-mean-square plane of the crown ether; β is the $N_{cr}(CH_2)_2$ plane passing through the C(7), N_{cr}, and C(8) atoms; and γ is the aromatic ring plane.

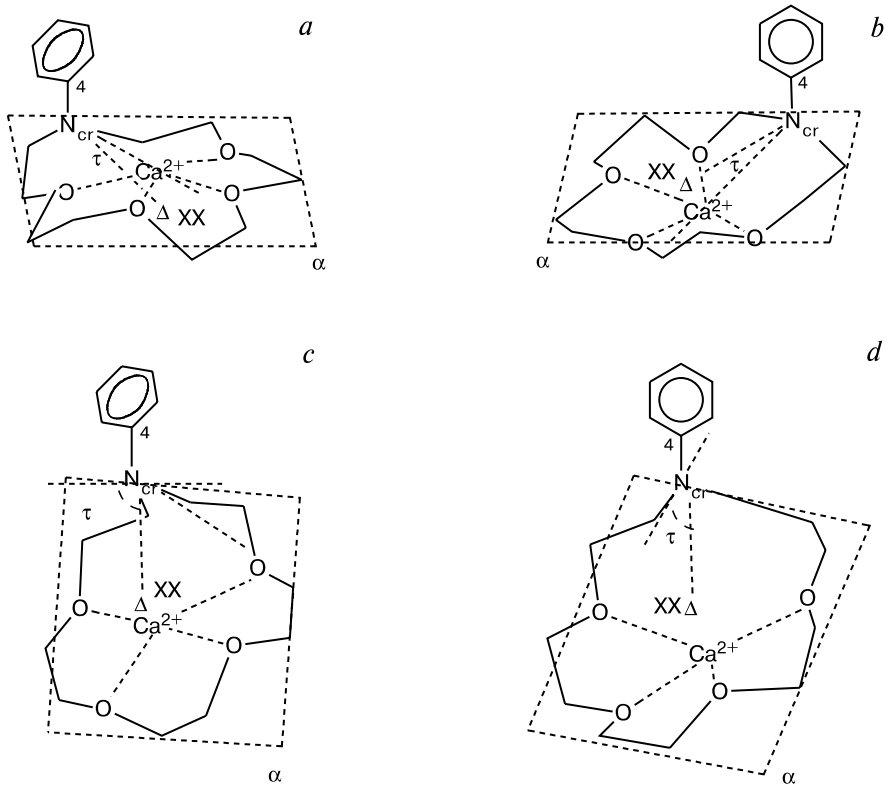


Fig. 2. Conformers of the arylazacrown ether complexes with Ca^{2+}: **Ax1** (*a*), **Ax2** (*b*), **Eq1** (*c*), and **Eq2** (*d*); XX is the center of mass of the crown ether macrocycle without metal cation; α is the root-mean-square plane of the crown ether; τ is the angle between the normal to the plane passing through the C(7), C(8), and C(4) atoms and the N_{cr}—Ca line.

observed in the other known crystal structures of the substituted aza-15-crown-5 ethers with a sp^2-hybridized carbon bonded to N_{cr}. In all the structures of the free substituted aza-15-crown-5 ethers of this type, N_{cr} has a virtually planar environment. At the same time, the experimental structures of the metal complexes of the substituted aza-15-crown-5 ethers exhibit only axial conformations, in which N_{cr} has a pyramidal environment.

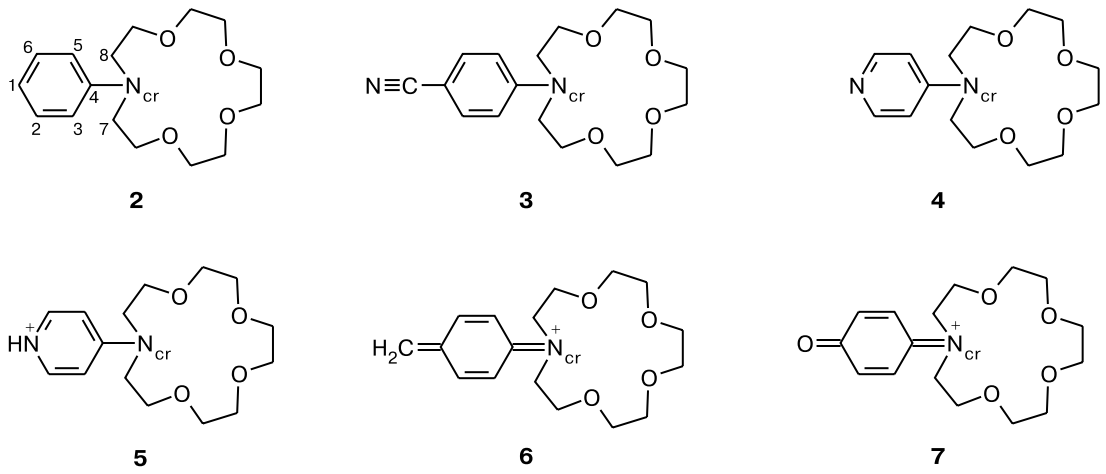
Recently,[7] we obtained very good results in calculating the geometries and energies of 18-crown-6 complexes with heavy metals using the DFT approach with the triple-zeta quality basis set, the Vosko—Wilk—Nusair parameterization of the local density part (LDA),[8] the Becke (Becke88) nonlocal gradient corrections to the exchange part,[9] and the Perdew—Wang (DFT/BPW91) nonlocal corrections to the correlation part of the exchange—correlation potential.[10] Preliminary DFT calculations of the same compounds with the Perdew—Burke—Ernzerhof functional (PBE)[11] gave close results. This allowed us to use the DFT/PBE method in studies of the conformations of azacrown ethers and their complexes with metal ions.

In this paper, various conformers of some arylazacrown ethers and their complexes with Ca^{2+} were studied by the density functional method. The possibility of various types of coordination of the metal ion in the crown ether cavity was also investigated in relation to the conformation of the crown ether moiety.

Calculation Procedure

Calculations with full geometry optimization of the model compounds, azacrown-containing styryl dye, and their complexes with Ca^{2+} were performed by the DFT/PBE method using an original triple-zeta quality basis set implemented in the PRIRODA program.[12] The orbital basis sets of contracted Gaussian-type functions of the size (5s1p)/[3s1p] for H, (11s6p2d)/[6s3p2d] for C, O, and N, and (17s13p)/[12s9p] for Ca were used in conjunction with the density-fitting basis sets of uncontracted Gaussian-type functions of the size (5s1p) for H, (10s3p3d1f) for C, O, and N, and (18s3p2d) for Ca. The electron density distribution in the calculated complexes was analyzed in terms of the Mulliken charges, which can be useful in qualitative analysis of the charge transfer effects.

The molecule of the dye **1** comprises more than 60 atoms, and half of them are non-hydrogen ones. Therefore, we studied the conformers of its crown ether moiety using three models of the "benzenoid" form and three models for its "quinoid" form of the dye. The first group of compounds included *N*-phenylaza-15-crown-5 ether **2** (13-phenyl-1,4,7,10-tetraoxa-13-azacyclopentadecane), *N*-(4-cyanophenyl)aza-15-crown-5 ether **3** (4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzonitrile), and



2 **3** **4**

5 **6** **7**

N-(4-pyridyl)aza-15-crown-5 ether **4** (13-(4-pyridyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane). The second group comprised *N*-(4-pyridyl)aza-15-crown-5 ether **5** with the protonated pyridine nitrogen (4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)pyridinium) as well as 4-methylene-2,5-cyclohexadieneimine **6** and quinoneimine **7** quaternized by the azacrown ether moiety (13-(4-methylene-2,5-cyclohexadienyliden)-1,4,7,10-tetraoxa-13-azoniacyclopentadecane and 13-(4-oxo-2,5-cyclohexadienyliden)-1,4,7,10-tetraoxa-13-azoniacyclopentadecane, respectively). The protonated structure **5** bears the formal positive charge on the pyridine nitrogen, whereas the quinoid structures **6** and **7** have the formal positive charge on N_{cr}. In addition, we studied the complexes of the model crown ethers **2**—**7** with Ca^{2+}.

For the styryl dye **1a** and its complex with Ca^{2+}, we studied only the conformers of the azacrown ether moiety observed in the model compounds, whereas the geometry and conformation of the conjugated moiety of the dye corresponded to the experimental structure[5] (Table 1). Full geometry optimization of this structure resulted in only minor changes in the bond lengths and bond angles of the conjugated moiety as compared to the experiment.

The geometric parameters of the free model crown ethers, real azacrown-containing dye, and their complexes with Ca^{2+} were compared with the X-ray diffraction data for the free *N*-phenylaza-15-crown-5 ether (PhN15C5),[13] its triaquacomplex with Ca^{2+},[13] and TrN15C5·Ca^{2+} (Tr is 2-troponyl)[14] from the Cambridge Structural Database.[15] In addition, we used the experimental structures of styryl and butadienyl dyes **1a**[5] and **1b**,[6] respectively.

Let us introduce some notation, which will be used in the geometry analysis of the azacrown ethers and their complexes from here on. The atomic numbering scheme is shown above taking compound **2** as an example. Denote the RMS plane of the crown ether as α and the center of mass of the crown ether macrocycle as XX (see Fig. 1), and the XX—N_{cr}—C(4) angle as ϕ. For the free azacrown ethers, the angle ϕ shows whether the conformation is axial or equatorial (see Fig. 1). Since the metal cation in the azacrown ether complexes usually does not lie exactly in the crown ether plane, the conformations of these complexes can also be characterized by the C(4)—N_{cr}—Ca angle (see Fig. 2). When the cation and the *N*-substituent lie on one side of the plane α, the C(4)—N_{cr}—Ca angle is smaller than ϕ; otherwise, ϕ is smaller than the angle C(4)—N_{cr}—Ca. The angle τ between the N_{cr}—Ca line and the normal to the plane passing through the C(7), C(8), and C(4) atoms, characterizes the deflection of the LP at N_{cr} from the N_{cr}—Ca direction. Noticeable (>40°) deflection indicates that metal—nitrogen bond is broken.

Table 1. Selected experimental and calculated geometric parameters of the arylazacrown ethers studied in this work

Structure	Conformer	$r(N_{cr}—C(4))$ /Å	ϕ[a]	ψ[b]	θ[c]
			deg		
PhN15C5[d]	**Ax2**[13]	1.403	127.5	0.14	4.3
1a	**Eq**[5]	1.368	170.8	0.13	7.6
1b	**Ax1**[6]	1.375	125.0	0.76	16.6
	Ax2[6]	1.381	123.9	0.41	10.9
1a	**Eq**	1.361	179.8	0.00	1.5
	Ax1	1.363	119.0	0.05	11.2
	Ax2	1.363	124.6	0.24	8.7
2	**Eq**	1.391	179.7	0.01	3.7
	Ax1	1.395	121.6	0.62	15.8
	Ax2	1.393	126.3	0.77	12.1
3	**Eq**	1.381	179.9	0.00	3.1
	Ax1	1.384	118.9	0.20	13.0
	Ax2	1.382	124.7	0.48	9.4
4	**Eq**	1.380	180.0	0.00	2.8
	Ax1	1.383	117.1	0.24	11.7
	Ax2	1.381	121.0	0.51	9.1
5	**Eq**	1.345	179.9	0.00	1.1
	Ax1	1.347	119.4	0.01	9.8
	Ax2	1.346	124.9	0.18	7.6
6	**Eq**	1.343	179.9	0.00	0.3
	Ax1	1.342	116.2	0.01	10.2
	Ax2	1.342	121.8	0.09	6.5
7	**Eq**	1.339	179.8	0.00	2.3
	Ax1	1.333	117.4	0.00	11.3
	Ax2	1.336	118.2	0.00	2.1

[a] XX—N_{cr}—C(4) is the angle between the center of mass of the crown ether macrocycle and the *N*-substituent.
[b] Pyramidalization of N_{cr} (see text).
[c] The angle between the $N_{cr}(CH_2)_2$ plane and the aromatic ring plane.
[d] *N*-Phenylaza-15-crown-5 ether.

The degree of conjugation of the LP at N_{cr} with the aromatic ring can be assessed from the pyramidalization of this atom (ψ), calculated as the difference between 360° and the sum of the bond angles C(7)—N_{cr}—C(8), C(8)—N_{cr}—C(4), and C(7)—N_{cr}—C(4) (for a trigonal pyramid, ψ 0; for ammonium ion, which is a regular tetrahedron with the N atom at the center, $\psi = 31.5°$). Another important parameter characterizing the conjugation is the angle θ between the $N_{cr}(CH_2)_2$ plane (plane β passing through the C(7), N_{cr}, and C(8) atoms) and the aromatic ring plane (plane γ in Figs. 1 and 2). When this angle is small (in our case, at most 30—35°), the conjugation exists.

Results and Discussion

Free azacrown ethers. Crown ethers have many conformers with similar energies and low barriers between them. Three of the found conformers of arylaza-15-crown-5 ethers correspond to the experimental structures found by X-ray diffraction. These structures were studied by DFT, because their calculated geometric parameters can be compared with the experimental data.[5,6,13] Selected experimental and PBE/TZ calculated geometric parameters of the free model crown ethers and dye **1a** are given in Table 1.

The relative errors in the bond lengths calculated by PBE/TZ are generally at most 2%. Only for **7** the errors reach 4% in the conjugated ring bonds (relative to the experimental PhN15C5 structure). This is due to the fact that compounds **6** and **7** are distinctly quinoid with the C(2)—C(3) and C(5)—C(6) bonds in the conjugated ring and the N—C(4) bond much shorter than the others. For compound **6** (the conjugated ring bonds are 1.36 and 1.45 Å, $r(N_{cr}—C(4)) = 1.34$ Å), this difference is slightly smaller than for **7** (1.35 and 1.47 Å for the ring bonds and 1.33—1.34 Å for N_{cr}—C(4)). In the calculated conformers of the dye **1a**, this difference is much smaller, 1.38 and 1.43 Å for the conjugated ring bonds and 1.36 Å for the N_{cr}—C(4) bond (*cf.* the experimental data[5,6] 1.38 and 1.41 Å for the conjugated ring bonds and 1.37—1.38 Å for N_{cr}—C(4)), that is, the "quinoid" nature is only slightly pronounced. In the "benzenoid" structures **2**—**4**, the carbon—carbon bonds of the aromatic ring are ~1.40 Å, and the N_{cr}—C(4) bond is 1.38—1.39 Å. The protonated structure **5** exhibits a "quinoid" nature: the carbon—carbon bond lengths of the conjugated ring are 1.37 and 1.44 Å and N_{cr}—C(4) is 1.35 Å. In the experimental structure of the free azacrown ether[13] (which is, obviously, "benzenoid") the carbon—carbon bond lengths in the aromatic ring are 1.397 Å and N_{cr}—C(4) is 1.403 Å. The geometry of the conjugated ring does not depend on the conformation of the crown ether moiety.

In all the studied free azacrown ethers **1a—7** as well as in the experimental structures of the free dyes **1a,b**[5,6] and phenylazacrown ether[13], the environment of N_{cr} is virtually planar ($\psi = 0—1°$) and this atom is conjugated with the aromatic ring.

Complexes with Ca^{2+}. As in the case of the free azacrown ethers, the calculated C—C, C—O, and C—N_{cr} bond lengths in the complexes are close to their experimental values.[13,14] The largest errors were obtained for the Ca—N_{cr} (7%) and Ca—O (4%) bond lengths. Apparently, this is due to the fact that our calculations were carried out without inclusion of interaction between the cation and additional ligands and counter-ions and the crystal effects. Both axial and equatorial conformers were located in calculations of the Ca^{2+} complexes of the model crown ethers. In the axial structures, the cation is coordinated to the four O atoms and N_{cr}, whereas in the equatorial conformers, it is coordinated only to the four O atoms. Since Ca^{2+} in the aza-15-crown-5 cavity does not lie exactly in the RMS plane of the macrocycle, the cation and the aromatic ring in the axial conformer can lie either on one side or on the opposite sides of the crown ether ring (**Ax1** and **Ax2** conformers, respectively). Both axial-type conformers were observed among the crystal structures of arylaza-15-crown-5 ether complexes with various cations and *N*-substituents. In particular, the conformation of PhN15C5 · Ca^{2+} [13] is **Ax2**, and that of TrN15C5 · Ca^{2+} [14] is **Ax1** additionally stabilized through the interaction between the cation and the O atom of the troponyl ligand. The Cambridge Structural Database gives no structures of equatorial conformers of aza-15-crown-5 ether complexes.

In addition to the N_{cr}—Ca distance, the presence of the metal—nitrogen bond is governed by the direction of the LP at N_{cr}, which is characterized by the angle τ (see Fig. 2). The conformer is referred to as **Ax1**, **Ax2**, or **Eq** based on the C(4)—N_{cr}—Ca and ϕ angles. The calculated and experimental geometric parameters of the complexes with Ca^{2+} cation are given in Table 2.

In general, the **Ax1** conformer can be described as follows: the cation is coordinated to all heteroatoms of the crown ether, the N_{cr}—Ca distance is relatively short, and the LP at N_{cr} is directed towards the cation. The cation and the aromatic ring lie on one side of the crown ether ring; the environment of N_{cr} is pyramidal, the angle θ is rather large (see Table 2), though it does not reach the maximum value (90°) because of the influence of the metal cation. Owing to this fact, the **Ax1** conformers can exhibit two very similar structures with the angles θ opposite in sign. There is no conjugation of N_{cr} with the aromatic ring.

The equatorial conformers **Eq1** found for all complexes with Ca^{2+} are characterized by very large C(4)—N_{cr}—Ca and ϕ angles (160—180°), large N_{cr}—Ca distance (3.8—4.2 Å), and noticeable (60—80°) deflection of the LP at N_{cr} from the N_{cr}—Ca direction. As mentioned above, the cation is coordinated only to the four O atoms and "protrudes" from the α plane. The environment of N_{cr} is virtually planar, and the angle θ is rather small, which indicates conjugation of N_{cr} with the

Table 2. Selected experimental and calculated geometric parameters of the studied complexes

Compound	Conformer	*r*/Å			Angle/deg				
		Ca—O	Ca—N_{cr}	N_{cr}—C(4)	τ^a	ϕ^b	Ca—N_{cr}—C(4)	ψ^b	θ^b
TrN15C5·Ca^{2+}	**Ax1**[14]	2.513	2.749	1.434	3.4	136.4	102.5	20.2	62.1
PhN15C5·Ca^{2+}	**Ax2**[13]	2.476	2.723	1.460	21.8	106.8	129.6	26.4	87.0
1a·Ca^{2+}	**Ax1**	2.440	2.622	1.463	5.4	139.4	111.7	24.6	66.1
	Ax2	2.408	2.596	1.470	21.5	111.5	128.9	25.2	89.5
	Eq1	2.398	3.996	1.415	80.3	166.2	171.9	0.9	23.7
2·Ca^{2+}	**Ax1**	2.446	2.560	1.447	15.1	114.3	88.2	14.8	47.9
	Ax1	2.460	2.580	1.447	15.4	119.2	88.2	15.3	−48.3
	Ax2	2.418	2.535	1.471	14.5	102.4	121.4	23.7	89.0
	Eq1	2.398	3.786	1.458	83.6	160.2	176.6	4.2	35.6
3·Ca^{2+}	**Ax1**	2.454	2.597	1.441	14.8	118.1	88.8	15.0	46.8
	Ax1	2.441	2.577	1.441	14.3	114.7	88.8	14.5	−46.7
	Ax2	2.418	2.553	1.469	15.4	102.9	122.4	23.9	88.8
4·Ca^{2+}	**Ax1**	2.455	2.615	1.434	16.5	117.1	87.0	13.9	44.0
	Ax2	2.418	2.548	1.469	14.7	102.4	121.7	24.1	88.8
	Eq1	2.399	3.821	1.423	79.5	164.4	172.8	1.3	22.9
5·Ca^{2+}	**Ax1**	2.416	2.955	1.429	14.8	147.8	121.5	22.8	55.4
	Ax2	2.400	2.805	1.458	29.6	119.6	137.4	25.7	88.3
	Eq2	2.408	4.015	1.382	59.4	136.7	156.6	4.6	23.6
	Eq1	2.407	4.219	1.380	77.6	166.9	167.8	0.05	12.4
6·Ca^{2+}	**Ax1**	2.416	3.122	1.404	11.0	142.0	114.8	15.4	47.6
	Eq2	2.410	4.073	1.372	58.9	134.6	154.6	2.8	19.6
	Eq1	2.407	4.103	1.372	59.3	159.8	149.9	0.04	11.3
7·Ca^{2+}	**Ax1**	2.425	3.981	1.355	16.9	140.7	112.9	2.8	21.9
	Eq2	2.418	4.207	1.352	58.5	132.0	152.3	1.14	11.7
	Eq1	2.414	4.220	1.354	61.3	160.2	151.6	0.01	8.7

[a] The angle between the N_{cr}—Ca line and the normal to the plane passing through the C(7), C(8), and C(4) atoms (see text).
[b] See footnotes[a–c] to Table 1.

aromatic ring and the absence of the metal—nitrogen bond.

The conformations obtained when the cation and the aromatic ring lie on the opposite sides of the RMS plane of the crown ether are different for the complexes with and without positive charge in their *N*-substituents (that is, for "benzenoid" complexes of compounds **2**—**4** with Ca^{2+} and "quinoid" complexes of compounds **5**—**7** with Ca^{2+}). In the first group of complexes, the cation is coordinated to all heteroatoms of the crown ether, the cation and the aromatic ring lie on the opposite sides of the RMS plane of the crown ether, and the LP at N_{cr} is directed toward the cation. The C(4)—N_{cr}—Ca and ϕ angles are at most 125°. The environment of N_{cr} is pyramidal, and the angle θ is close to 90°. There is no conjugation between N_{cr} and the aromatic ring. We refer to this conformation as **Ax2**. In the second group, the metal—nitrogen distance is as long as in the **Eq1** conformation, the deflection of LP at N_{cr} from the N_{cr}—Ca direction is ~60°, the environment of N_{cr} is virtually planar, and the angle θ is relatively small. The angles C(4)—N_{cr}—Ca and ϕ are somewhat larger than that in the **Ax1** and **Ax2** conformers of the first group of complexes, though they are not so large as those in the **Eq1** conformers. The metal—nitrogen bond is absent, and N_{cr} is conjugated with the aromatic ring. According to these parameters, this conformer is closer to the **Eq1** structures; therefore, the corresponding conformation is referred to as **Eq2**.

Calculations of complex **5**·Ca^{2+} revealed two local energy minima corresponding to the **Ax2** and **Eq2** structures with the cation and the aromatic ring arranged on the opposite sides of the RMS plane of the crown ether. Apparently, the lower-lying conformer **Eq2** can be transformed into **Ax2** by rotating the aromatic ring around the C(4)—N_{cr} bond and changing the position and configuration of the $N_{cr}(CH_2CH_2)_2$ group relative to the cation and the aromatic ring with only slight repositioning of the cation and the $O(CH_2)_2$ links. In the **Eq2** conformer, the environment of N_{cr} is virtually planar (ψ = 4.6°), θ = 24°, and *r*(Ca—N_{cr}) = 4 Å. In the **Ax2** structure lying 6.6 kcal mol^{-1} higher, *r*(Ca—N_{cr}) = 2.8 Å, the environment of N_{cr} is pyramidal (ψ = 26°), and θ = 88°.

In other model complexes, the local minimum of energy corresponds to either the **Ax2** or **Eq2** conformer and never to both conformers.

The formation and breakage of the metal—nitrogen bond in the Ca^{2+} complexes of arylazacrown ethers can be monitored by the changes in various geometric param-

eters of the complexes (see Table 2). In particular, in the axial structures of all complexes, the N_{cr}—Ca distance is much shorter and the deflection of LP at N_{cr} from the N_{cr}—Ca direction is less than in the equatorial conformers. In all equatorial conformers, pyramidalization of N_{cr} is small ($\psi = 0$—$4°$), whereas in both axial conformers, it is rather large (14—26°). In the **Ax2** conformers of Ca^{2+} complexes of compounds **2**—**5**, the angle θ between the $N_{cr}(CH_2)_2$ plane and the aromatic ring is close to 90°, and in the **Ax1** conformers of Ca^{2+} complexes of **2**—**6**, it is 44—55°. In these cases, the conjugation of the amino group with the aromatic ring is broken. In the other cases, the angle θ is at most 25° (the exception is the equatorial conformer of complex **2**·Ca^{2+} ($\theta = 35°$)), which indicates the conjugation of the amino group and the aromatic ring. This conjugation is present in both equatorial conformers of those complexes where these conformers were found. The angles ψ and θ change in parallel from structure to structure.

Correlations between the parameters ψ and τ of the axial and equatorial conformers of the Ca^{2+} complexes of the model crown ethers and dye **1a** and the N_{cr}—Ca distance are shown in Fig. 3. The patterns for other geometric parameters are very similar. The structures of the complexes can be divided into two groups. The first group with the shorter N_{cr}—Ca distance (2.5—3.2 Å) corresponds to the axial conformers. The second group with the longer N_{cr}—Ca distance (3.8—4.3 Å) corresponds to the equatorial conformers. The C(4)—N_{cr}—Ca angle in the first group lies in the range 87—121°. The exceptions are the **Ax1** conformer of complex **7**·Ca^{2+}, in which the angle of 113° corresponds to the **Ax1** conformation but the N_{cr}—Ca distance (3.98 Å) is too long, and the **Ax2** structure of **5**·Ca^{2+}, in which $r(N_{cr}—Ca) = 2.81$ Å but the C(4)—N_{cr}—Ca angle is too large (137°). In the second group, the C(4)—N_{cr}—Ca angle lies between 150 and 177°. The angle ϕ in the equatorial conformers lies within 130—167°. In the axial conformers, this angle lies within 100—120°; the exceptions are the **Ax1** conformers of the complexes of compounds **5**—**7** with Ca^{2+}, where this angle increases to 140—147° owing to the repulsion between the positively charged *N*-substituent and the metal cation. The angle τ correlates with the C(4)—N_{cr}—Ca and ϕ angles and lies within 5—30° for the axial conformers and within 60—80° for the equatorial ones (the exception is the axial conformer of complex **7**·Ca^{2+}, for which $\tau = 17°$, but the N_{cr}—Ca distance is too long). In the **Ax1** conformers, the torsion angle Ca—N_{cr}—C(4)—C(5) lies in the range 113—126° (the longer the N_{cr}—Ca distances, the smaller the angles), while in the **Ax2** conformers it is ~180°. Similarly, the angle θ in the **Ax1** conformers lies within 44—55° and is ~90° in the **Ax2** conformers (the aromatic ring is markedly rotated with respect to the crown ether). In the axial conformers, pyramidalization of N_{cr} is rather large, 14—23° (*cf.* $\psi = 26°$ in the experimental structure of PhN15C5·Ca^{2+} [13]) and the N_{cr}—C(4) bond length is 1.40—1.47 Å. This means that the metal—nitrogen bond exists and N_{cr} is not conjugated with the aromatic ring in the axial conformers. In the equatorial conformers, the torsion angle Ca—N_{cr}—C(4)—C(5) lies between 90 and 103° (in some cases, it cannot be determined because Ca—N_{cr}—C(4) atoms are virtually collinear), the angle θ lies within 8—24° (the exception is the equatorial conformer of complex **2**·Ca^{2+} with $\theta = 36°$), and the environment of N_{cr} is virtually planar ($\psi = 0$—$5°$). This means that the aromatic ring and N_{cr} are conjugated and the metal—nitrogen bond is absent in the equatorial conformers. The N_{cr}—C(4) bond length in this case lies within 1.35—1.38 Å, which corresponds to the length of the conjugated C—N_{cr} bond; the exceptions are the equatorial conformers of complexes **2**·Ca^{2+} and **4**·Ca^{2+}, in which these bonds are only slightly shorter than those in the axial conformers.

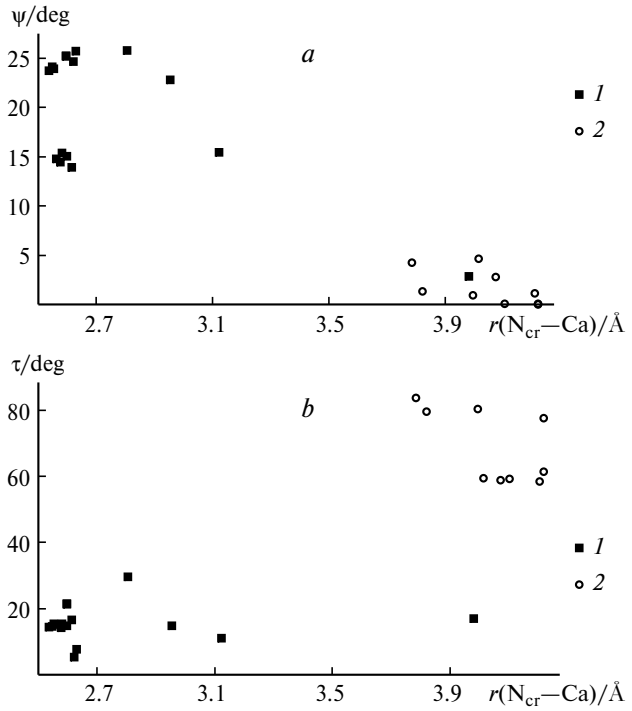


Fig. 3. Correlation between geometric parameters of the axial (*1*) and equatorial (*2*) complexes of the arylazacrown ethers with Ca^{2+} and the N_{cr}—Ca distance: pyramidalization of N_{cr}, ψ, (*a*) and deflection, τ, of the LP at N_{cr} from the N_{cr}—Ca direction (*b*).

Complexation with Ca^{2+} causes the C—C bonds in the conjugated ring to change only slightly compared to the free azacrown ethers. Only in some cases (**1a**, **3**—**5**), the "quinoid" nature of the ring becomes less pronounced. The N_{cr}—C(4) bond length changes depending on the conformation adopted by the complex. Thus, this bond elongates from 1.38 Å in the free crown ethers **2**—**4** to

1.44—1.47 Å in the complexes **2**·Ca^{2+} and **3**·Ca^{2+} and in the **Ax1** and **Ax2** conformers of complex **4**·Ca^{2+} (only to 1.42 Å in the **Eq1** conformer of **4**·Ca^{2+}). For complex **1a**·Ca^{2+}, this bond length increases to 1.46—1.47 Å in **Ax1** and **Ax2** conformers and to 1.42 Å in the **Eq1** conformer (*cf.* 1.36 Å in the free dye). In **5**·Ca^{2+}, this bond elongates to 1.43 and 1.46 Å in the **Ax1** and **Ax2** structures, respectively, and only to 1.38 Å in the **Eq1** and **Eq2** conformers (*cf.* 1.35 Å in the free crown ether). In complex **6**·Ca^{2+}, this bond elongates to 1.40 Å in the axial and 1.37 Å in both equatorial conformers (*cf.* 1.34 Å in the free crown ether). In **7**·Ca^{2+}, this change is very small: $r(N_{cr}—C(4))$ = 1.34 Å in the free crown ether and 1.35 Å in the complex. In the experimental PhN15C5 structures, this bond elongates[13] from 1.403 Å in the free crown ether to 1.460 Å in the complex. The shortening of the N_{cr}—C(4) bond in the equatorial conformers virtually down to its length in the free crown ether indicates the conjugation of N_{cr} with the aromatic ring and, therefore, breakage of the metal—nitrogen bond.

Relative energies of the conformers of the free azacrown ethers. The energies of the conformers of the free azacrown ethers lie within a short range (Table 3). For instance, the relative conformation energies of compounds **2**—**4** are at most 0.5 kcal mol^{-1}, and the **Eq** conformer is not the lowest-lying one. As we found earlier,[7] these values are within the limits of error of the computational method employed. The energies of the **Ax2** conformers of compounds **5**—**7** are 2.5—4.7 kcal mol^{-1} higher than the corresponding global minima, namely, **Ax1** in **5** and **Eq** in **6** and **7**. The **Ax2** conformer of the dye **1a** lies 1.4 kcal mol^{-1} higher than the lowest-energy conformer (**Eq**).

Complexation energies. In calculating the conformation energies of the complexes **2**·Ca^{2+} and **4**·Ca^{2+} we found equatorial (**Eq1**) conformers with the relative energies of 32 and 28 kcal mol^{-1}, respectively. This means that these conformations are inaccessible in the ground state. No equatorial conformers of complex **3**·Ca^{2+} were located. For these three complexes, **Ax1** is the lowest-lying conformer (the energy of **Ax2** is 3.3—4.0 kcal mol^{-1} higher). For the Ca^{2+} complexes of compounds **5**—**7**, we found two low-lying equatorial conformers; one of them (**Eq2**) corresponds to the global minimum. The energies of the other conformers of these complexes are also low, 0.5—3.0 kcal mol^{-1} for **Ax1** and 0.9—1.8 kcal mol^{-1} for **Eq1**. For the complex **5**·Ca^{2+}, we found the **Ax2** conformer with a relative energy of 6.6 kcal mol^{-1}. The relative energy of the only equatorial conformer **Eq1** of the complex **1a**·Ca^{2+} is intermediate, 18 kcal mol^{-1}. The calculated relative energies of different conformers of the complexes are given in Table 4.

Table 3. Relative energies (E_{rel}) of different conformers of arylazacrown ethers **1a**—**7**

Crown ether	E_{rel}/kcal mol^{-1}		
	Eq	**Ax1**	**Ax2**
1a	0.00	0.12	1.44
2	0.46	0.50	0.00
3	0.13	0.00	0.02
4	0.27	0.30	0.00
5	0.77	0.00	2.49
6	0.00	0.53	3.07
7	0.00	1.71	4.66

Table 4. Relative energies (E_{rel}) of different conformers of complexes of compounds **1a**—**7** with Ca^{2+}

Complex	E_{rel}/kcal mol^{-1}			
	Ax1	**Ax2**	**Eq2**	**Eq1**
1a·Ca^{2+}	0.00, 0.94*	2.14	Not found	18.10
2·Ca^{2+}	0.00, 0.80*	4.05	Not found	32.21
3·Ca^{2+}	0.72, 0.00*	3.35	Not found	Not found
4·Ca^{2+}	0.00	3.61	Not found	28.31
5·Ca^{2+}	0.45	6.56	0.00	1.81
6·Ca^{2+}	1.95	Not found	0.00	1.45
7·Ca^{2+}	2.95	Not found	0.00	0.85

* Data for the **Ax1** conformers with the angles θ opposite in sign.

Thus, the calcium complexes of the model crown ethers with positively charged *N*-substituents tend to form equatorial conformers. In the axial conformers, the Mulliken charge on N_{cr} ($q(N_{cr})$) is −(0.1—0.2) for **Ax1** and −0.5 for **Ax2**. The exceptions are both axial conformers of complex **1a**·Ca^{2+}, for which $q(N_{cr})$ = −0.4. In the equatorial conformers, this parameter changes its sign and increases to 0.1—0.2. The exception is the complex **7**·Ca^{2+}, in which $q(N_{cr})$ = 0.1 for the axial conformer and 0.2 for the equatorial conformer. This is probably due to the high electronegativity of the substituent in the *para*-position to N_{cr} in compound **7**. According to our calculations, the formation of the axial conformers of the complexes of compounds **1a**—**5** with Ca^{2+} causes $q(N_{cr})$ to decrease, whereas it changes only slightly in the equatorial conformers of these complexes and in all conformers of **7**·Ca^{2+}. The decrease in $q(N_{cr})$ weakens the repulsion and facilitates the bonding of N_{cr} with Ca^{2+}.

Figure 4 shows distinct partition of the calculated structures of both free crown ethers and their complexes into two groups corresponding to the axial and equatorial conformers (represented by pyramidalization ψ and angle θ) depending on $q(N_{cr})$.

Free dyes **1** bear a formal positive charge; therefore, their cationic complexes can also adopt two types of conformations. However, a long distance between the charged group and the crown ether moiety as well as the substan-

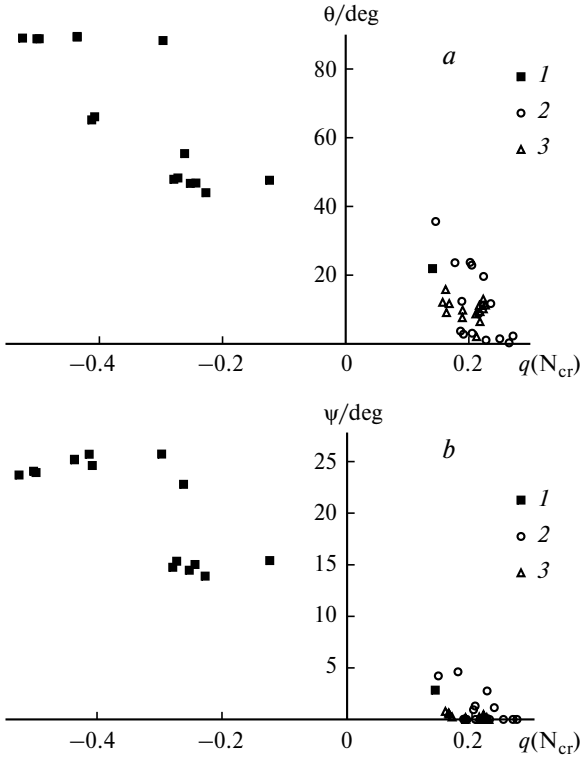


Fig. 4. Correlation between geometric parameters of the axial (*1*) and equatorial (*2*) complexes of the arylazacrown ethers with Ca^{2+} and free arylazacrown ethers (*3*) and the charge at N_{cr}: angle θ between the aromatic ring plane and plane β (*a*) and pyramidalization of N_{cr}, ψ, (*b*).

tial charge delocalization make manifestation of this effect in the ground state less probable. Apparently, this is also the reason for nearly equal $q(N_{cr})$ values in the **Ax1** and **Ax2** conformers of complex **1a** · Ca^{2+}.

Since the attraction between N_{cr} and the metal cation in the complexes of the model crown ethers with (formally) positively charged *N*-substituent is weakened (or, in some cases, changed by repulsive interaction), the formation energies of these complexes (20—40 kcal mol^{-1}) are regularly lower than those of the complexes with neutral crown ethers (150—190 kcal mol^{-1}). In this case, the dye **1a** is also characterized by intermediate energies (80—100 kcal mol^{-1}) (Table 5). This is also related to the electron density transfer to N_{cr} on complexation.

The complexation energies account for the absence of equatorial conformations in the crystal structures of the metal complexes of aza-15-crown-5 ethers established by X-ray analysis. First, these conformations are typical solely of the crown ethers with the positively charged *N*-substituents. Second, the rather low complexation energies make the complexes unstable, especially taking into account their interaction with additional ligands and counter-ions.[7] However, the situation can be different in the excited state, and an equatorial conformer may be more stable than the axial ones toward dissociation into the excited azacrown ether and the cation.

Table 5. Formation energies (E_f) of different conformers of complexes **1a**—**7** with Ca^{2+}

Complex	$-E_{rel}$/kcal mol^{-1}			
	Ax1	**Ax2**	**Eq2**	**Eq1**
1a · Ca^{2+}	98.94, 98.00*	96.79	Not found	80.84
2 · Ca^{2+}	189.99, 189.18*	185.94	Not found	157.77
3 · Ca^{2+}	174.92, 175.64*	172.29	Not found	Not found
4 · Ca^{2+}	178.88	175.27	Not found	150.57
5 · Ca^{2+}	44.73	38.62	45.18	43.38
6 · Ca^{2+}	38.93	Not found	40.88	39.43
7 · Ca^{2+}	18.61	Not found	21.56	20.71

* Data for the **Ax1** conformers with the angles θ opposite in sign.

A decrease in the bonding energy of the cation in the equatorial conformer facilitates its release in the electron excitation of the azacrown ether. This opens up the possibilities of photocontrol of the cation binding in the cavity of photochromic azacrown ethers.

* * *

Our theoretical study of various conformers of the Ca^{2+} complexes of arylazacrown ethers showed that the macrocycle can coordinate the metal cation in different manner depending on the conformation type of the crown ether moiety. It was found that in the equatorial conformers, the metal cation is coordinated only to the O atoms of the azacrown ether cycle, the metal—nitrogen bond is broken, and N_{cr} is conjugated with the aromatic ring. In the axial conformers, the metal cation is additionally coordinated to N_{cr}. This demonstrates that, in principle, recoordination in the metal complexes of azacrown-containing dyes is possible. Redistribution of the electron density in the conjugated system under electron excitation can contribute to the conformational change in the crown ether moiety from the axial conformation to the equatorial one, which results in the recoordination of the metal cation in the macrocycle cavity. Thus, we can control cation binding through irradiation of the dye.

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