Benzoaza-15-crown-5 ethers: synthesis, structure, and complex formation with metal and ethylammonium ions

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Benzoaza-15-crown-5 ethers containing one or two nitrogen atoms in different positions of the macrocycle and bearing different substituents at these atoms were synthesized. The structures of azacrown ethers and their metal complexes were studied by X-ray diffraction. The stability constants of the complexes of azacrown ethers with Na⁺, Ca²⁺, Ba²⁺, Ag⁺, Pb²⁺, and EtNH₂⁺ ions were determined by ¹H NMR titration in MeCN-d₂. In free benzoazacrown ethers containing secondary nitrogen atoms bound to the benzene ring, as well as in N-acetyl derivatives, the N atoms are sp²-hybridized and have a planar geometry. The nitrogen lone pairs on the p orbitals are efficiently conjugated to the benzene ring or the carbonyl fragment of the acetyl group, which is unfavorable for the complex formation. In addition, the formation of complexes with benzoazacrown ethers containing secondary nitrogen atoms is hindered because the hydrogen atoms of the NH groups are directed to the center of the macrocyclic cavity. In benzoazacrown ethers bearing N-alkyl substituents or secondary nitrogen atoms distant from the benzene ring, the N atoms show a substantial contribution of the sp³-hybridized state and have a pronounced pyramidal configuration, which promotes the complex formation. The lead and calcium cations form the most stable complexes due to the high affinity of Pb^{2+} ions for O,N-containing ligands, a high charge density on these ions, and the better correspondence of the cavity size of the 15-membered macrocycles to the diameter of the Ca^{2+} ion. An increase in the stability of the complexes is observed mainly in going from monoazacrown ethers to diazacrown ethers containing identical substituents at the N atoms and in the following series of substituents: $C(O)Me < H < Me < CH_2CO_2Et$. In the case of the CH_2CO_2Et substituents, the carbonyl oxygen atom is also involved in the coordination to the cation. The characteristic features of the complexing ability of N-alkylbenzomonoaza-15-crown-5 ethers bearing the nitrogen atom conjugated to the benzene ring show that macrocyclic ligands having this structure are promising as selective and efficient complexing agents for metal cations.

Key words: benzoazacrown ethers, complex formation, metal cations, ethylammonium ion, stability constants, X-ray diffraction study, ¹H NMR spectroscopy.

The discovery of cyclic polyethers in the late 1960s¹ has stimulated the vigorous development of the chemistry of macrocyclic ligands due to the pronounced ability of crown ethers to selectively bind metal and ammonium cations. This ability lied at the basis of the use of these compounds for the determination, extraction, and separation of metal cations, in the ion transport through mem-

branes, in ion-selective electrodes, as phase-transfer catalysts, *etc.*² The replacement of one or several oxygen atoms in crown ethers by nitrogen atoms leads to a change in the selectivity with respect to metal ions and, as a rule, to an increase in stability of the complexes. The synthesis of azacrown compounds was described in detail in reviews.³⁻⁵

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Azacrown ethers containing the nitrogen atom conjugated to the benzene ring are of particular interest because this structural feature allows the use of these compounds for the design of molecular optical sensors with a substantial shift of absorption and/or fluorescence and a stronger optical response to the complex formation compared to the related compounds containing the O atom conjugated to a chromophoric moiety. Chromogenic N-phenylazacrown ethers (see, for example, Refs 6-8) have been studied in most detail. However, these compounds have a substantial drawback in that the stability constants of their complexes with metal cations are low. This is due to the efficient conjugation of the nitrogen lone pair of phenylazacrown ethers to chromophores, which hinders the switching of this lone pair to the formation of a coordination bond with a cation, resulting in the complex formation. The efficient conjugation leads to sp²-hybridization of the nitrogen atom due to which the N atom and three substituents at this atom are in the same plane, resulting in the additional hindrance to the formation of complexes with metal and ammonium cations, which requires considerable conformational rearrangements of the macroheterocycle.9

Benzannulated derivatives of azacrown ethers can have substantial advantages as complexing agents over N-phenylazacrown ethers due to the higher conformational rigidity of the macrocycle and the possibility of a weakening of the conjugation of the nitrogen lone pair to the benzene ring for steric reasons. However, benzoazacrown ethers containing the nitrogen atom bound to the benzene ring are poorly known in spite of their relatively simple structures.⁵

Earlier, we have developed¹⁰ a procedure for the synthesis of formyl and nitro derivatives of N-methylbenzoazacrown ethers 1a-f by the stepwise transformation of the macrocycle of benzocrown ethers 2 (for example, of **2b,c**) and have shown¹¹⁻¹³ that these compounds have the ability to efficiently bind calcium cations. This ability is comparable to that of benzocrown ethers and is substantially higher than the binding ability of N-phenylazacrown ethers containing the macrocycle of the same size and bearing the same substituent in the benzene ring. The high binding ability of benzoazacrown ethers **1a-f** is determined by steric interactions between the methyl and methylene groups at the nitrogen atom containing an alkoxy substituent in the *ortho* position. This leads to a partial decrease in the conjugation of the lone pair of this N atom to the benzene ring and the pronounced pyramidal geometry of the N atom favorable for the involvement of the nitrogen lone pair in the coordination bond with metal cations. The multidentate binding of metal cations is additionally facilitated by the fact that macroheterocycle 1 prefers to have a crown conformation, in which the lone pairs of most of heteroatoms are directed to the center of the macrocyclic cavity, *i.e.*,

ligands **1a-f** are preorganized to form inclusion complexes.



1: X = CHO (**a**-**c**), NO₂ (**d**-**f**); *n* = 0 (**a**, **d**), 1 (**b**, **e**), 2 (**c**, **f**) **2**, **3:** X = H (**a**), CHO (**b**), NO₂ (**c**)

A quantitative comparison of the complexation properties of benzoazacrown ethers depending on the number and positions of nitrogen atoms in the macrocycle and the estimation of the influence of the substituents at the nitrogen atoms on these properties are of considerable interest. These data can provide insight into the most promising macrocyclic ligands for the use of their structural fragments in efficient and selective molecular chemosensors with a strong optical response to the formation of complexes with metal and ammonium cations.

In the present study, we report the synthesis and structural features of benzoaza-15-crown-5 ethers 4-7 containing the unsubstituted benzene ring and their metal complexes, which were characterized by X-ray diffrac-



4-7: R = H(a), Me (b), C(O)Me (c), CH₂CO₂Et (d) 5: R' = H(a, c), Me (b)

tion. The structures and the complexing ability of these compounds with respect to metal and ethylammonium cations were studied by ¹H NMR spectroscopy. For comparison, we determined the corresponding characteristics of model compounds 2a and 3a with the same size of the macrocycle and of some related compounds.

Results and Discussion

Synthesis of benzoazacrown ethers. Benzoazacrown ethers 4a and 5a were synthesized by the condensation of 2-aminophenol or o-phenylenediamine with halogen derivatives of tetraethylene glycol in the presence of bases under high dilution conditions to prevent the formation of oligomerization products (Scheme 1). Only trace amounts of the target product 4a were obtained (in 1.6% vield) upon heating of a mixture of 2-aminophenol and 1,11-diiodo-3,6,9-trioxaundecane in MeCN in the presence of Na_2CO_3 . The careful chromatographic separation of the reaction mixture allowed us to isolate also a byproduct, which proved to be the o-hydroxy derivative of N-phenylaza-12-crown-4 ether 8 (in 2.8% yield). Apparently, under the conditions of the synthesis, the basicity of Na_2CO_3 is too low to provide the efficient deprotonation of the hydroxy group of 2-aminophenol or the intermediate aza podand, which is the open-chain analog of the azacrown ether. This results in the strong resinification of the reaction mixture and in the partial closure of the aza podand to form the more strained 12-membered ring 8. On the contrary, the condensation of *o*-phenylenediamine with 1,11-diiodo-3,6,9-trioxaundecane under these conditions afforded benzodiazacrown ether 5a in 25% yield. This fact confirms the conclusion that the amino group in the aniline derivative is relatively reactive toward diiodoalkane. Benzomonoazacrown ether 4a was synthesized in 8% yield by the condensation of 2-aminophenol with 1,11-dichloro-3,6,9-trioxaundecane in an waterbutanol solution in the presence of NaOH. It should be noted that compounds 4a, 5a, and 8 have been described previously;^{14–17} however, the yields of these products have not been reported or their yields were lower than those obtained in our work.

Benzomonoazacrown ether **6a** and its *N*-methyl derivative **6b** are commercially available products. The synthesis of benzodiazacrown ether **7a** by the reduction of the corresponding macrocyclic diamide was documented.¹⁸ *N*,*N*'-Dimethyl derivative **7b** has been synthesized previously by sonication of compound **7a** with methyl iodide¹⁹ or by the reduction of the corresponding bisurethane.²⁰ In the present study, we suggest the synthesis of compounds **7a,b** by the condensation of two acyclic precursors, *viz.*, 1,2-bis(2-iodoethoxy)benzene and terminal diamines (see Scheme 1), by analogy with the method developed in our earlier work for the synthesis of formyl derivatives of benzodiazacrown ethers.²¹





X = O (4a), NH (5a); R = H (7a), Me (7b); Y = Cl, I

The synthesis of compounds 4b-d, 5b,c, 6c,d, and 7c,d is presented in Scheme 2. The *N*-methyl derivatives of azacrown ethers 4b and 5b were synthesized by the reactions of compounds 4a and 5a, respectively, with methyl iodide in the presence of NaH in dry THF. The methylation of diamine 5a afforded double alkylation product 5b in almost quantitative yield. The mono-N-methylation product of compound 5a was not detected by TLC monitoring of the course of the reaction. Apparently, this intermediate is more reactive toward MeI than the starting compound 5a due probably to the influence of the tertiary amino group in the *ortho* position with respect to the NH group. It should be noted that N, N'-dimethyl derivative 5b can be theoretically formed as *trans* and/or cis isomers, in which the methyl substituents are located on opposite sides or on the same side of the macrocycle, respectively. Under ambient conditions, the exchange between the isomers of **5b** is unlikely due to steric hindrance to the rotation of the N(Me)CH₂ group about the N- C_{Ar} bond caused by the second bulky N(Me)CH, group in the ortho position. The ¹H NMR spectroscopic data provide evidence that compound 5b is formed as one isomer because the spectra of the free ligand and its complexes with metal cations show only one set of signals for protons (except for the complexes with Pb^{2+} due to the slow exchange; see below). The cis structure of this isomer was established by the X-ray diffraction study of the complex of compound 5b with barium perchlorate.



X = O(4b,c), NMe (5b), NH (5c)

The *N*-acetyl derivatives of benzoazacrown ethers 4c-7c were synthesized by heating the corresponding secondary amines in acetic anhydride. In the case of benzodiazacrown ether 5a, the acylation was carried out in benzene. This allowed us to introduce only one *N*-acetyl group due apparently to considerable steric hindrance to the acylation of the NH group in crown ether 5c caused by the bulky N(Ac)CH₂ moiety in the *ortho* position. Compounds 4a, 6a, and 7a were modified by ester side groups to form azacrown ethers 4d, 6d, and 7d, respectively, through the *N*-alkylation with ethyl bromoacetate in the presence of a base.

X-ray diffraction study. Azacrown ethers 4a,c, 5a,c, 6a-c, 7a, and 8 were prepared as single crystals and were studied by X-ray diffraction. The structures of these compounds are shown in Figs 1 and 2. For convenience of the comparison of the geometric parameters, we used the

same atomic numbering scheme that differs from the IUPAC nomenclature. The asymmetric units of 4a and 6a contain two independent molecules of azacrown ethers, which differ in the conformation of the polyether chain. Since the structures of most of the compounds under study were determined with high accuracy, their main geometric parameters can be compared. The exception is compound **6a**, whose crystals are characterized by high mosaicity. However, the geometric characteristics of the latter compound show the same tendencies as those observed for the other structures. It should be noted that the crystallographic parameters of compounds 5a and 7a determined at 240 K and at room temperature, respectively, have been described previously.^{22,23} The structural motifs of these compounds determined in the present study are similar to those described in the literature; however, we cooled the single crystals to

Scheme 2



Fig. 1. Molecular structures of compounds 4a (two independent molecules), 4c, 5a,c, and 8. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen bonds are indicated by dashed lines.

120 K with the aim of improving the accuracy of X-ray diffraction data.

In the benzene rings of all benzoazacrown ethers, the C(1)-C(6) bond shared by the rings of the bicyclic system is somewhat elongated (the average value is 1.410(3) Å),

whereas the opposite C(3)-C(4) bond is the shortest one (the average value is 1.369(4) Å) compared to the other bonds of the benzene ring (the average values are 1.390(3)-1.397(3) Å). This bond length distribution undoubtedly reflects the steric repulsion between the *ortho*

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Fig. 2. Molecular structures of compounds **6a** (two independent molecules), **6b,c**, and **7a** \cdot H₂O. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen bonds are indicated by dashed lines.

substituents at the C(1) and C(6) atoms, which should also lead to an increase in the C(6)–C(1)–N/O and C(1)–C(6)–N/O bond angles and, consequently, to a decrease in the C(2)–C(1)–N/O and C(5)–C(6)–N/O bond angles. However, we observed the opposite situation. Thus, the bond angles at the C(1) and C(6) atoms exocyclic with respect to the benzene ring show a pronounced tendency to an increase in the case of the C(2)–C(1)–N/O and C(5)–C(6)–N/O bond angles (on the average, by 125.0(2)°) and to a decrease in the case of the C(6)–C(1)–N/O and C(1)–C(6)–N/O bond angles (on the average, by 115.3(2)°) for compounds **4a**, **6a**–c, and **7a** (Table 1). This deformation of the bond angles compared to the ideal value (120°) characteristic of most of benzocrown ethers results in a decrease in the distance between the N and/or O atoms in the *ortho* positions and is attributed to the fact that the lone pairs of these heteroatoms on the p orbitals are efficiently conjugated to the benzene ring.^{24,25} The conjugation is favored also by the conformation of the C(2)–C(1)–N/O–C and C(5)–C(6)–N/O–C fragments, such that these torsion angles are relatively small (–20.5–17.4°), *i.e.*, are close to zero, which is the ideal value for the conjugation. The presence of conjugation is evidenced also by the predominantly sp²-hybridized state of the N and O atoms characterized by the bond angles at these atoms close to 120°, as well as by shortened $N/O{-}C_{\rm Ar}$ bonds compared to $N/O-C_{Alk}$ bonds. An analogous, but a less pronounced tendency for the deviation of the above-mentioned parameters from the ideal values is observed in diazacrown ether 5a due apparently to the steric interaction between the hydrogen atoms of two NH groups in the ortho positions. In amide 4c and phenylazacrown ether 8, the deviations of the bond angles from the ideal value (120°) are observed only for one of the carbon atoms of the benzene ring (C(6) in 4c and C(1) in 8). In amide 4c, the O(1) atom bound to the C(6) atom is evidently conjugated to the benzene ring, which is favored by the small C(5)-C(6)-O(1)-C(7) torsion angle (-8.0°). The amide N(1) atom in compound 4c is sp²-hybridized, and the sum of the bond angles at this atom is $360.0(1)^{\circ}$. However, the N(1) atom is involved in the conjugation not to the benzene ring but to the carbonyl group. Thus, the AcNC₂ fragment is planar, and the dihedral angle between this plane and the plane of the benzene ring is 80.0° . The fact that the nitrogen atom in compound 4c is not involved in the conjugation to the benzene ring is evidenced also by a considerable elongation of the $N-C_{Ar}$ bond compared to the corresponding bonds in the other azacrown ethers. The similar geometry is observed also in amide 5c, in which the angle between the

planes of the $AcN(1)C_2$ fragment and the benzene ring is 82.0°. The second nitrogen atom in amide **5c** is efficiently conjugated to the benzene ring, which is seen from the geometric characteristics of the N(2) atom and its environment (see Table 1). The $AcNC_2$ fragment in amide **6c**, in which the nitrogen atom is distant from the benzene ring, is planar. The latter fact is indicative of the presence of efficient conjugation in this fragment. In the other azacrown ethers containing nitrogen atoms distant from the benzene rings (**6a,b** and **7a**), these nitrogen atoms have a pronounced pyramidal bond configuration. The sums of the bond angles at the nitrogen atoms are close to the value typical of the ideal sp³-hybridized state (328.4°).

The hydrogen atoms of the NH groups in compounds **4a**, **5a,c**, **6a**, and **7a** are directed to the center of the macrocyclic cavity and apparently form predominantly intramolecular hydrogen bonds with the nitrogen and oxygen atoms of the macrocycles. The hydrogen bond parameters are as follows: in **4a** the N(1)–H...O(1), N(1)–H...O(4), N(2)–H...O(5), and N(2)–H...O(8) distances are 2.23, 2.46, 2.24, and 2.46 Å, respectively, and the angles at the H atoms are 105–108°; in **5a** the N(1)–H...O(1) and N(2)–H...N(1) distances are 2.33 and 2.39 Å, respectively, and the corresponding angles

Table 1. Selected bond lengths (*d*), bond angles (ω), torsion angles (φ), and the sums of the bond angles at the N atoms (Σ_{ω}) in azacrown ethers **4a,c**, **5a,c**, **6a–c**, **7a** · H₂O, and **8**

Parameter	4a ^{<i>a</i>}	4c	5a	5c	6a ^a	6b	6c	7a ⋅ H ₂ O	8
Bond					d/Å				
C(1)-N/O	1.387(2), 1.378(2)	1.437(2)	1.386(1)	1.365(2)	1.394(5), 1.359(5)	1.363(1)	1.369(2)	1.369(1)	1.430(2)
C(6)—N/O	1.372(2), 1.375(2)	1.360(2)	1.403(1)	1.443(2)	1.354(5), 1.396(5)	1.359(1)	1.371(2)	1.367(1)	1.361(2)
Angle	. ,				ω/deg				
C(2)-C(1)-N/O	124.0(2), 124.0(2)	119.8(1)	122.1(1)	122.8(1)	125.0(4), 125.9(4)	125.1(1)	125.7(1)	124.2(1)	124.2(1)
C(6)-C(1)-N/O	116.7(2), 117.0(2)	120.0(1)	119.4(1)	120.3(1)	115.2(4), 115.0(4)	114.7(1)	114.5(1)	116.3(1)	116.3(1)
C(1)-C(6)-N/O	115.1(1), 114.6(2)	115.6(1)	117.7(1)	120.0(1)	115.2(4), 115.5(4)	114.1(1)	115.1(1)	115.6(1)	120.4(1)
C(5)-C(6)-N/O	124.8(2), 125.1(2)	125.2(1)	123.0(1)	118.8(1)	126.0(4), 124.6(5)	126.1(1)	125.0(1)	124.8(1)	119.4(2)
$C(1)-N/O-C_{mc}^{b}$	119.8(1), 118.9(1)	118.2(1)	122.7(1)	125.0(1)	116.2(3), 118.1(4)	117.7(1)	117.9(1)	116.3(1)	113.9(1), 116.1(1)
$C(6)-N/O-C_{mc}$	118.6(1), 118.1(1)	117.7(1)	119.3(1)	119.6(1)	117.7(4), 115.8(3)	118.6(1)	117.2(1)	117.9(1)	_
$\Sigma_{\omega}/\text{deg}$	349(2), 348(2)	360.0(1)	340.7(9), 355.6(9)	358.4(1), 359.0(13)	335(3), 320(5)	330.9(1)	359.5(1)	328.6(9), 328.7(9)	345.1(1)
Angle					φ/deg				
$C(2) - C(1) - N/O - C_{mc}$	-16.5, -20.0	80.5	30.2	-2.8	-2.6, -14.1	-13.5	5.3	-19.6	-53.2, 84.0
$C(5)-C(6)-N/O-C_{mc}$	8.1, 16.7	-8.0	-11.2	-76.1	17.4, 0.8	7.3	-20.5	13.3	_

^a For two independent molecules.

 ${}^{b}C_{mc}$ is the C atom of the macrocycle.

are 112 and 106°; in 5c the N(2)-H...O(1) distance is 2.33 Å and the angle is 149° ; in **6a** the N(1)-H...O(2)/O(3) and N(2)-H...O(6)/O(7) distances are in the range of 2.51-2.62 Å, and the angles are in the range of $98-102^{\circ}$; in 7a the N(1)-H...O(1)/O(2) and N(2)-H...O(2)/O(3)distances are in the range of 2.31–2.37 Å, and the angles are in the range of 109–111°. Evidently, the above-given geometric parameters of most of the hydrogen bonds, in particular, the angles at the H atoms, are not optimum for this type of interactions in the case of formation of one hydrogen bond; however, the angles at the H atoms in systems with a bifurcated hydrogen bond can be close to those observed in the compounds under consideration. In the crystal structures of most of the benzoazacrown ethers under study with an intramolecular hydrogen bond, the macrocycle adopts a crown-like conformation, which allows the maximum number of NH...heteroatom interactions to be formed, thus ensuring the stabilization of this conformation of the ligand.

In compound **8** containing the hydroxy group in the *ortho* position of the benzene ring with respect to the azamacrocycle, there is also the intramolecular bifurcated hydrogen bond characterized by the O(1)—H...O(2) and O(1)—H...N(1) distances of 2.26 and 2.22 Å, respectively, and the corresponding angles of 149 and 119°. Apparently, it is the presence of the hydrogen bond that is responsible for the change in the geometric parameters of phenylazacrown ether **8** compared to benzoazacrown ethers (see Table 1).

We succeeded in preparing single crystals of the complexes of benzoazacrown ethers **4b,d**, **5b**, **6a,d**, and **7b** with barium perchlorate and the complex of the formyl derivative of N, N'-dimethylbenzodiaza-15-crown-5 ether **9** with NaClO₄. These compounds were studied by X-ray diffraction. Compound **9**²¹ is a close structural analog of diazacrown ether **7b**, which differs from the latter only by the substituent in the benzene fragment of the molecule. Hence, the geometric characteristics of crown ether **9** can be considered as common for the complexes of this type of ligands with Na⁺ ions.



The structures of the complexes are shown in Figs 3 and 4. The asymmetric units of **5b** · Ba(ClO_4)₂ · 0.5H₂O, **6a** · Ba(ClO_4)₂, and **6d** · Ba(ClO_4)₂ contain two independent complexes. In one of the independent complexes **6a** · Ba(ClO_4)₂, the fragment of the polyether chain

C(13)-C(14) is disordered over two sites with occupancies of 0.90 : 0.10. In one independent complex of 5b with $Ba(ClO_4)_2$, the coordination sphere of the Ba(2) ion involves the solvent water molecule $H_2O(1W)$. The common structural feature of the crystalline complexes of benzoaza-15-crown-5 ethers with $Ba(ClO_4)_2$ is that they form dinuclear systems consisting of two metal complexes. In the dinuclear systems, two of the four perchlorate anions serve as bridges and link two barium cations through the oxygen atoms. The dinuclear systems consisting of two independent complexes are exemplified by the complexes $5b \cdot Ba(ClO_4)_2 \cdot 0.5H_2O$ and $6d \cdot Ba(ClO_4)_2$ (see Fig. 3). In the other cases, the dinuclear systems are centrosymmetric. Hence, only perchlorate anions, which are involved in the coordination spheres of the independent Ba cations, are shown. The coordination numbers of the barium cations in the complexes vary from 9 to 11. The coordination polyhedra of these cations are irregular, which is typical of Ba²⁺ cations.

Selected geometric characteristics of the metal complexes are given in Table 2. In the complexes, the lone pairs of all heteroatoms of the macrocycle are directed to the metal cation; the $M^{m+}...O-C$, $M^{m+}...N-C$, and $M^{m+}...N-H$, angles are in the ranges of 105.6(3)- $125.6(2), 97.0(2) - 116.2(2), \text{ and } 96(2) - 100(2)^{\circ}, \text{ respec-}$ tively, which is, on the whole, favorable for the interactions between the sp^2 - or sp^3 -hybridized O and N atoms and the metal cations. In the complexes with barium cations, the $M^{m+}...O_{mc}^{*}$ and $M^{m+}...N$ distances are in the ranges of 2.710(3)–2.930(2) and 2.897(4)–3.058(3) Å, respectively. In the complex $9 \cdot \text{NaClO}_4$, the corresponding parameters are 2.329(2) - 2.506(2), and 2.548(2), 2.554(3) Å. Taking into account the van der Waals radii of the O and N atoms (~1.4 and 1.5 Å, respectively), the distances between the heteroatoms of the macrocycles and the metal cations are indicative of approximately the same degree of involvement of all heteroatoms in the binding of M^{m+} . The barium cations deviate from the mean plane passing through all heteroatoms of the macrocycle by 1.60 - 1.75 Å, whereas the sodium cation in the complex with compound 9 deviates from the corresponding plane by only 0.86 Å. Undoubtedly, this difference is attributed to the smaller ionic radius of the Na⁺ ion than that of Ba^{2+} (0.95 and 1.34 Å, respectively), which allows the Na⁺ cation to move deeper into the cavity of the 15-membered macroheterocycle. In compounds 4d and 6d, the CH₂CO₂Et side chain is also involved in the coordination of the Ba²⁺ ions through the carbonyl oxygen atom. Interestingly, the Ba²⁺...O/N distances and the deviation of the cation from the mean plane of the macrocyclic system in the complexes 4d • Ba(ClO₄)₂ and 6d • Ba(ClO₄)₂ are slightly larger than

^{*} Hereinafter, the atoms of the macrocyclic moiety are denoted by the subscript mc.

those in the other complexes (see Table 2). This indicates that the ligand core is somewhat strained due to the involvement of the carbonyl oxygen atom in the coordination sphere of the metal cation. The shortest Ba²⁺...O distance (O is the neutral atom) (2.683(4) Å) is observed in the structure of **5b** · Ba(ClO₄)₂ • 0.5H₂O for the coordinated water molecule $H_2O(1W)$. A comparison of this distance with the $Ba^{2+}...O_{mc}$ distances shows that the arrangement of the oxygen atoms of the macrocyclic system in all the complexes under study is not optimum for the strongest ion-dipole interactions as a result of the limited possibility for the matching of the conformation of the



Fig. 3. Molecular structures of the complexes **4b** • Ba(ClO₄)₂, **4d** • Ba(ClO₄)₂, **5b** • Ba(ClO₄)₂ • 0.5H₂O (two independent complexes), and **6d** • Ba(ClO₄)₂ (two independent complexes). Most of the hydrogen atoms in the complexes **5b** • Ba(ClO₄)₂ • 0.5H₂O and **6d** • Ba(ClO₄)₂ are omitted for simplicity. Here and in Fig. 4, the atoms of the perchlorate anions labeled with A are related to the unlabeled atoms by the symmetry operation; thermal ellipsoids are drawn at the 50% probability level; the coordination bonds are indicated by dashed lines.

15-membered macrocyclic ligands to the coordination requirements of the barium cation.

The insufficiently high accuracy of the X-ray diffraction data for all the complexes under study did not allow us to reliably compare the bond length distribution in the benzene fragments of the complexes and the free ligands, although there is a tendency to equalize these bond lengths in the first case. The above-mentioned main characteristic features of benzocrown ethers, such as the systematic deviation of the bond angles at the C(1) and C(6) atoms exocyclic with respect to the benzene ring from the ideal value of 120° and the pronounced sp² hybridization of the O atoms conjugated to the benzene ring, are observed also in the complexes of benzoazacrown ethers with sodium and barium cations. The exception is the structure of **5b** • Ba(ClO₄)₂ • 0.5H₂O (see Table 2), in which two nitrogen atoms bound to the benzene ring in both independent ligand molecules are sp³-hybridized due to the involvement of their lone pairs in the coordination of Ba²⁺ ions, and apparently the degree of conjugation of these nitrogen atoms to the benzene ring is low (see below). In the structures of the complexes of monoazacrown ethers **6a** and **6d**, the conformation of one of the C_{Ar}-C_{Ar}-O-C fragments is indicative of a substantial disturbance of the conjugation of the O atom to the benzene ring (the corresponding torsion angles are in the range of $-62.7-56.1^{\circ}$), whereas the conformation of the structures corresponds to the retention of efficient conjugation (the torsion angles are in the range of $-20.2-19.6^{\circ}$).



Fig. 4. Molecular structures of the complexes $6a \cdot Ba(ClO_4)_2$ (two independent complexes), $7b \cdot Ba(ClO_4)_2$, and $9 \cdot NaClO_4$. Most of the hydrogen atoms in the complexes $6a \cdot Ba(ClO_4)_2$ are omitted for simplicity.

the sums of the bond an	igles at the N atoms (2	Σ_{ω}) in the complexes c	of 4b, d , 5b , 6a, d , and 7b wi	tth $Ba(CIO_4)_2$ and the co	mplex 9 • NaClO ₄		
Parameter	$4b \cdot Ba(CIO_4)_2$	$4d \cdot Ba(ClO_4)_2$	5b \cdot Ba(ClO ₄) ₂ \cdot 0.5H ₂ O ^a	$\mathbf{6a} \cdot \mathrm{Ba}(\mathrm{ClO}_4)_2^a$	$6d \cdot Ba(ClO_4)_2^a$	$7b \cdot Ba(CIO_4)_2$	9 · NaClO ₄
Bond				d/Å			
M‴O _{mc}	2./10(3)-2.829(3)	2.811(2)-2.834(2)	2.739(3) - 2.823(3), 2.739(3) - 2.827(3)	2.61(2) - 2.930(2), 2.801(2) - 2.857(2)	2.829(3) - 2.894(3), 2.837(3) - 2.910(3)	(7)-7.11(2)-7.854(2)	(7)9005.7—(7)675.7
M ^{m+} N	2.919(3)	3.031(3)	2.915(3), 2.968(3), 2 807(4) 2 050(4)	2.938(3), 2.038(3),	3.058(3),	2.991(2), 3.020(2)	2.548(2), 2.554(3)
M ^{<i>m</i>+} O=C	Ι	2.774(2)	$2.683(4)^{b}$		2.752(3), 2.752(3), 2.750(3)	I	I
C(1)-N/O	1.445(5)	1.443(4)	1.461(5),	1.377(3),	1.388(5),	1.378(3)	1.375(3)
C(6)—N/O	1.387(4)	1.372(4)	1.453(6) 1.450(6),	1.375(3) 1.379(4),	1.385(5) 1.383(5),	1.379(3)	1.349(3)
$\Delta M^{m+}/ m \AA$	1.62	1.75	1.448(5) 1.66,	1.380(3) 1.60,	1.390(5) 1.71,	1.66	0.86
Angle			1.60	1.63 0/deg	1.71		
M^{m+} O- C_{Ar}	114.7(2)	111.4(2)	I	119.4(2), 123.5(2), 121.5(2), 121.5(2)	123.1(2), 123.2(2), 118.1(2), 120.6(2)	114.8(1), 115.7(1)	112.7(2), 113.3(2)
M ^{m+} O-C _{Alk}	111.3(2)-124.7(3)	109.9(2)-125.6(2)	108.2(3) - 125.2(3), 105.6(3) - 124.4(3),	106.9(15) - 117.9(2), 121.5(2), 112.2(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 121.5(2), 12	110.5(2) - 119.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110.5(2), 110	117.4(1)—122.3(2)	112.2(2)-117.0(2)
M ^{<i>m</i>+} N–C/H	106.1(3)-108.6(2)	102.2(2)-111.7(2)	97.0(2) - 113.5(3),	100(2) - 113.0(2), 113.0(2), 100(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2), 113.0(2	106.5(2) - 113.2(2)	106.0(1)-112.5(1)	104.6(2)-111.7(2)
	173 0/11	1212 101	99.9(3)—116.2(2)	96(2)—115.4(2)	105.8(2)—112.6(2)	1077 301	175 0/31
	(+)0.071	(c)c:+71	120.6(4), 120.6(4)	123.5(3), 123.5(3)	125.2(4), 125.2(4)	120.4(2)	(c)6.c71
C(6)-C(1)-N/O	117.6(4)	117.2(3)	121.2(4),	117.0(3), $116.3(3)$	117.3(4), 115.173)	114.8(2)	113.7(2)
C(1)-C(6)-N/O	115.1(3)	115.8(3)	120.2(4),	115.0(3),	115.2(3),	114.4(2)	114.0(2)
			122.0(4)	115.4(3)	117.4(4)		
C(5) - C(6) - N/0	124.2(4)	123.2(3)	120.7(4), 119.2(4)	124.8(3), 124.4(3)	124.9(4), 121.4(4)	125.3(2)	125.6(3)
$C(1)-N/O-C_{mc}$	109.3(3)	110.5(2)	108.5(3),	$114.5(2), 130.7(15)^c$	116.2(3),	118.9(2)	117.8(2)
		110 5/21	108.8(3)	119.5(2)	116.8(3)		
	(6)1./11	(6)0.011	109.9(3), 109.4(3)	11/.0(2), 116.1(2)	11/.0(3), 116.4(3)	11/.9(2)	119.1(2)
Σ_{ω}/deg	333.8(3)	336.3(3)	329.8(3), 330.6(3), 379.9(3), 331.7(3)	331(2), 333(2)	329.4(3), 330.7(3)	327.9(2), 328.2(2)	331.1(3), 331.3(2)
Angle				φ/deg			
C(2)-C(1)-N/0-C	2 _{mc} -104.5	106.8	-87.3,	$-55.0, -1.5^{c}$	56.1, 1 0	-7.3	-0.2
C(5)-C(6)-N/O-C	Jmc 11.3	-17.9	-00.0 74.5.	47.0 19.6,	-5.0.	7.4	0.7
			76.0	-20.2	-62.7		

^a For two independent molecules. ^b The Ba(2)...O(1W) bond. ^c For two conformations.

Apparently, this feature is associated with the fact that the N atom is far distant from the benzene ring in ethers **6a** and **6d**, resulting in the necessity of a more substantial conformational rearrangement of the macrocycle for the involvement of all its heteroatoms in the coordination to the barium cation.

The conformational changes of the macrocycle in compound 6a upon the formation of the complex with $Ba(ClO_4)_2$ is shown in Fig. 5. It can be seen that the largest conformational rearrangement is observed in the region of the nitrogen atoms due to the necessity of the reorientation of the nitrogen lone pairs toward the barium cation that is located above the center of the macrocyclic cavity. It should be emphasized that the hydrogen atoms of the NH groups, which are directed to the center of the macrocyclic cavity and form hydrogen bonds with the oxygen atoms in the free ligand, are directed away from the center of the macrocyclic cavity in the complex $6a \cdot Ba(ClO_4)_2$. Therefore, the formation of metal complexes leads to the cleavage of the intramolecular NH...heteroatom hydrogen bonds, which should decrease the stability of these complexes compared to the complexes with the related ligands containing tertiary nitrogen atoms (see below).

In all the complexes under study, the nitrogen atoms of crown ethers have a pronounced pyramidal configuration close to the ideal sp³-hybridized state. The sums of the bond angles at the N atoms vary in the range of $327.9(2)-336.3(3)^{\circ}$ (see Table 2). A comparison of the sums of the bond angles at the N atoms in the structures of **4b** • Ba(ClO₄)₂ and **4d** • Ba(ClO₄)₂, in which the nitrogen atom is bound to the benzene ring, with the corresponding parameters of the related *N*-methylbenzoaza-15-crown-5 ethers **1b** and **1e** (351.4(1) and 349.4(3)°,



Fig. 5. Superposition of the structures of benzoaza-15-crown-5 ether **6a** (two independent molecules) and **6a** • Ba(ClO_4)₂ (two independent complexes) based on the benzene rings. The perchlorate anions and the hydrogen atoms are omitted (except for the H atoms of the NH groups). The coordination bonds are indicated by dashed lines.



Fig. 6. Superposition of the structures of compounds $1b_{,e}$ and the complexes $4b \cdot Ba(ClO_4)_2$ and $4d \cdot Ba(ClO_4)_2$ based on the benzene rings. The perchlorate anions and the hydrogen atoms are omitted. The coordination bonds are indicated by dashed lines.

respectively)^{13,26} and a comparison of the N– C_{Ar} bond lengths in the complexes of compounds **4b,d** (1.445(5) and 1.443(4) Å) and free crown ethers **1b,e** (1.389(2) and 1.386(5) Å) clearly show that the nitrogen atoms are more sp³-hybridized and their conjugation to the benzene ring in the metal complexes is weaker. The differences in the conformations of the macroheterocycles in all four compounds are insignificant (Fig. 6), which indicates that the *N*-alkyl derivatives of benzomonoaza-15-crown-5 ethers containing the nitrogen atom conjugated to the benzene ring are largely preorganized for the formation of complexes with metal cations.

¹H NMR spectroscopic studies. One of the characteristic features of the spectral behavior of free benzoazacrown ethers is that the rotation of the acetyl group around the N-COMe bond in amide 6c is slow on the ¹H NMR time scale (500 MHz) with the result that all eight CH₂ groups of the formally symmetric macrocycle appear to be nonequivalent due to the anisotropic effect of the C=O group. The ¹H NMR spectrum of diamide 7cis more complex in the region of signals of methylene groups of the macrocycle due to the slow rotation of two N-acetyl fragments and shows also three signals of methyl groups at $\delta 2.0$ with an integral intensity ratio of 1:1.9:1.7. Three C=O stretching vibrations are observed at 1620–1640 cm⁻¹ in the IR spectrum of solid diamide 7c (see the Experimental section). Apparently, all the above-mentioned signals correspond to three theoretically possible conformers of 7c containing NCOMe fragments in different orientations with respect to the benzene ring. The ¹H NMR spectra of amides 4c and 5c are complex and consist of strongly overlapping signals with high multiplicity for 16 nonequivalent protons of the

methylene groups of the macrocycle. This fact indicates that these compounds exist in solution predominantly in one conformation, which is most likely identical to those found in the crystals of these compounds, as confirmed by the correlations between the upfield shifts (by ~0.35 ppm) of the signals of the methyl groups of amides **4c** and **5c** compared to the corresponding signals of amides **6c** and **7c** and by the presence of the methyl groups in the shielding region of the benzene rings in crystalline amides **4c** and **5c** (see Fig. 1). Apparently, the presence of acetyl groups at the nitrogen atoms in benzoaza-15-crown-5 ethers containing N atoms bound to the benzene rings leads to the steric strain in the macrocyclic moieties, which substantially restricts their conformational transformations.

The ¹H NMR spectroscopic studies of benzoazacrown ethers 4–7 and model compounds 2a,b and 3a in MeCN-d, showed that the signals for most of protons of these ligands are strongly shifted downfield ($\Delta \delta_{H}$) upon the addition of an excess of metal (Na, Ca, Ba, Ag^I, or Pb^{II}) or ethylammonium perchlorates. This behavior is characteristic of inclusion complexes in which the M^{m+} ion is bound to all heteroatoms of the macrocycle (Scheme 3) due to the hydrogen bonding and/or ion-dipole interactions, resulting in the shift of the electron density from all atoms of the ligand toward the cation (the electron-withdrawing effect of the cation). The common tendency is that the $\Delta \delta_{\rm H}$ values are larger in the case of doubly charged cations than those for monovalent cations. In the case of the doubly charged cations under study, the largest downfield shifts ($\Delta \delta_{\rm H}$ up to 0.75 ppm) were observed for the complexes with Ca²⁺ and Pb²⁺ ions evidently due to the high charge density on these metal cations and the high affinity of lead(II) cations for N and O atoms. Silver(I) cations, unlike the other metal cations under study, form complexes with ligands 3–7, in which the largest $\Delta \delta_{H}$ values are observed for the signals of the groups bound to the nitrogen atoms. Undoubtedly, this is evidence that the N atoms make a larger contribution to the binding of the silver cation than the O atoms due to the high affinity of the soft Ag⁺ ion for the soft nitrogen atoms compared to the hard oxygen atoms.²⁷



X, Y, Z, Q = O, NR; M^{m+} is the metal or ethylammonium ion (m = 1, 2)



Fig. 7. Plots of the changes in $\Delta\delta_{\rm H}$ ($\Delta\delta_{\rm H} = \delta_{\rm H}$ (**5b**-NaClO₄) – $\delta_{\rm H}$ (**5b**)) *vs.* the ratio of the concentrations of NaClO₄ and **5b** ($C_{\rm Na}/C_{\rm 5b}$) for the signals of all protons of compound **5b** in MeCN-d₃.

The exceptions are the signal for protons of the CH₂N and MeN groups of azacrown ethers 3-5 containing nitrogen atoms bound to the benzene ring, which show upfield shifts to -0.24 ppm upon the addition of some salts. The largest upfield shifts are observed in the presence of Na⁺ ions, which have the lowest charge density among the metal cations under study (except for Ag⁺) and, at the same time, form relatively stable complexes with azacrown ethers (see below). Figure 7 exemplifies the changes in the $\Delta \delta_{H}$ values for the signals for protons of benzodiazacrown ether 5b depending on the ratio of the concentrations of NaClO₄ and **5b** (C_{Na}/C_{5b}) . Unlike the monotonic downfield shift of the signals for most of protons with increasing ratio $C_{\rm Na}/C_{\rm 5b}$, the signals of the CH₂N and MeN groups are gradually shifted to higher fields. It should be noted that the shape of the dependences $\Delta \delta_{\rm H} - (C_{\rm Na}/C_{\rm 5b})$ is indicative of the relatively low stability constant of the complex $5b \cdot Na^+$ ($K_1 < 10^5 \text{ L mol}^{-1}$), because $\Delta \delta_{H}$ do not reach the maximum values even in the presence of a threefold excess of Na⁺ ions.

This abnormal behavior of the signals of the methyl and methylene groups bound to the nitrogen atom is apparently attributed to a change in the geometry of the N atom and the conformational rearrangement of macrocycles 3-5 upon the binding of cations. The reorientation of the lone pairs of all heteroatoms toward the center of the macrocyclic cavity occupied by a metal or ethylammonium cation leads to a substantial weakening of the conjugation of the nitrogen lone pairs to the benzene ring, the deviations of the substituents at the N atoms from the plane of the benzene ring being evidently larger than those in the free ligands (see above). Larger deviations of the N substituents lead to their shift from the deshielding region of the benzene ring to the shielding region, resulting in the upfield shifts of the signals for the protons of the above-mentioned substituents.

Smaller upfield shifts are observed also for the signals of the CH₂N groups upon the formation of complexes of Na⁺, Ba²⁺, and EtNH₃⁺ ions with benzoazacrown ethers **6** and **7** ($\Delta\delta_{\rm H}$ up to -0.04 and -0.16 ppm, respectively). Undoubtedly, in this case a decrease in $\Delta\delta_{\rm H}$ compared to the analogous effects in the complexes of compounds **3–5** is associated with the smaller influence of the conformational changes of the macrocycles in compounds **6** and **7**, in which the nitrogen atoms are distant from the benzene ring. Therefore, the positions of the signals for protons of azacrown ethers in the NMR spectra are determined by two opposite effects, such as the electron-withdrawing effect of the cation and the change in the position of the crown ether moieties with respect to the benzene ring upon the complex formation.

The fact that the complex formation causes changes in the positions of the CH₂N and MeN groups with respect to the plane of the benzene ring in compounds, in which the nitrogen atom is bound to the benzene ring, was confirmed by comparing the X-ray diffraction and NOESY data for compounds 4b,d and their complexes with the earlier results^{13,26} for the structurally related N-methylbenzomonoaza-15-crown-5 ethers **1b.e**. The NOESY spectra of free compounds 4b,d show much more intense cross-peaks between the NCH₂(substituent) (or NMe) group and the ortho proton of the benzene ring compared to the cross-peaks from the analogous interaction involving the NCH_{2.mc} group, which is indicative of the close proximity of the first two fragments and is in good agreement with the X-ray diffraction and NOESY data for compounds **1b**,e, in which the shortest NMe...HC_a and NCH₂...HC_a distances are 2.20 (in both structures) and 4.09, 4.19 Å, respectively. The nitrogen lone pairs in azacrown ethers **1b**, e are efficiently conjugated to the benzene ring, and the sums of the bond angles at these atoms are 351.4(1) and $349.4(3)^\circ$, which indicates that the N atoms are in the state intermediate between the sp^2 and sp^3 hybridization. Therefore, the geometry of the nitrogen atoms and the conformations of the macrocyclic moieties in free compounds 4b,d and 1b,e are apparently very similar. In the complexes $4\mathbf{b}, \mathbf{d} \cdot \mathbf{M}^{m+}$, the nitrogen atoms are almost fully sp³-hybridized (see Table 2) and the deviations of the N-substituents from the dishielding plane of the benzene ring are larger than the corresponding characteristics of the free ligands. This is clearly seen upon the superposition of the structures of compounds 1b,e and the complexes of **4b,d** with $Ba(ClO_4)_2$ (see Fig. 6). Thus, the $C_{Ar} - C_{Ar} - N - C_{mc}$ and $C_{Ar} - C_{Ar} - N - C$ (substituent) torsion angles in 1b,e are $-139.0, -140.6^{\circ}$ and 6.5,1.2° respectively, whereas the corresponding angles in **4b,d** • Ba(ClO₄), are -104.5, -106.8 and 19.9, 19.9° .

The formation of the complexes of N,N'-dimethylbenzodiazacrown ether **5b** apparently also leads to the disturbance of the conjugation of its nitrogen atoms to the benzene ring, as evidenced by larger downfield shifts of the signals for protons of the benzene ring in the complexes compared to the free ligands (see, for example, Fig. 7) and the virtually sp³-hybridized state of the N atoms in the complex with barium perchlorate (see Table 2). The deviations of the *N*-methyl and *N*-methylene groups from the plane of the benzene ring in the complexes of **5b** are apparently still larger than those in the complexes with monoazacrown ethers **4b,d**. This is confirmed by the X-ray diffraction data for the crystalline complex **5b** · Ba(ClO₄)₂ • 0.5H₂O (see Fig. 3), in which the $C_{Ar}-C_{Ar}-N-CH_2$ and $C_{Ar}-C_{Ar}-N-Me$ torsion angles are in the ranges of $-87.3-76.0^{\circ}$ and $-47.4-40.1^{\circ}$, respectively.

In addition, one of characteristic features of the complex formation of the azacrown ethers under study is that the complexes of compounds 4b,d, 5a,b, 6a,b,d, 7a,d, and 8 with Ca^{2+} and Ba^{2+} ions have a high kinetic stability, resulting in a substantial broadening of the signals for protons of the macroheterocycle (up to the nonequivalence of the analogous methylene groups in the formally symmetric structures) or even in the nonequivalence of the geminal protons of the methylene groups as a result of the conformational exchange slow on the ¹H NMR time scale. In addition to the above-mentioned effects, most of the complexes with Pb2+ ions are characterized also by the slow ligand exchange between the free state and different types of the complexes, which is determined by the exceptionally high affinity of these cations for N,O-containing macrocyclic ligands. These effects often attend the high thermodynamic stability of the complexes. In most cases, this fact was confirmed by the quantitative study of the stability of the complexes of the above-mentioned compounds with Ca²⁺, Ba²⁺, and Pb²⁺ ions. In the case of compound 7b, the above-mentioned broadening and the nonequivalence of the signals for protons were observed in the presence of all the cations under study. This is indirectly indicative of the high affinity of the ligands having this structure for cations of different nature (and, as a consequence, of the low selectivity of these ligands). On the contrary, the formation of the complexes of amide azacrown ethers 6c and 7c with Ca^{2+} ions leads to an increase in the rate of conformational exchange compared to the free ligands (see above), resulting in the coalescence of the signals for the equivalent protons.

The quantitative determination of the stability of the complexes of benzoazacrown ethers **4**–7 and model crown ethers **2a,b**, **3a**, and **8** with metal perchlorates (Na, Ca, Ba, Ag^I, and Pb^{II}) and EtNH₃ClO₄ in MeCN-d₃ was carried out by the ¹H NMR titration. In most cases, the changes in the chemical shifts of protons of the ligands (L) depending on the ratio of the concentrations of M^{m+} and L are well described by the model with account for the equilibrium

$$L + M^{m+} \stackrel{K_1}{\longrightarrow} L \cdot M^{m+}, \tag{1}$$

where $K_1/L \mod^{-1}$ is the stability constant of the complex of the composition 1 (L) : 1 (M^{*m*+}). In some cases, good results were obtained when the equilibriums (1) and (2) were taken into account

$$\mathsf{L} \cdot \mathsf{M}^{m+} + \mathsf{L} \underbrace{\overset{K_2}{\longleftarrow}}(\mathsf{L})_2 \cdot \mathsf{M}^{m+}, \tag{2}$$

where $K_2/L \mod^{-1}$ is the stability constant of the sandwich complex of the composition 2 (L) : 1 (M^{*m*+}). In the cases higher than the upper limit of applicability of the direct titration ($K_1 \ge 10^5 \text{ L mol}^{-1}$), we used the competitive ¹H NMR titration (see the Experimental section). The stability constants ($\log K_1$ and $\log K_2$) are given in Tables 3 and 4.

Table 3. Stability constants (*K*) of the complexes of crown ethers **2a,b**, **3a**, **4a,b**, **5b**, **6a,b**, and **7b** with metal and ethylammonium perchlorates^{*a*}

Ligand	ligand $\log K_1 (\log K_2)^b$					
	Na ⁺	Ca ²⁺	Ba ²⁺	Ag^+	Pb ²⁺	EtNH ₃ ⁺
2a	~5 4.8 ^c	5.6 ^c	5.4 (5.1) ^c	<0.5	d	2.4
2b	3.5	4.3	4.4 (4.2)	-	>5 6.2 (4.2) ^e	2.2
3a	2.8	4.4	4.0	0.8	>5 7.3 ^f	1.8
4 a	1.4	4.6	3.1 (2.4)	<0.5	>5 7.8 (4.2) ^e	0.9
4b	5.0 ^g	7.3 ^g	5.4 ^g	2.3	7.9 ^e	3.0
5b	3.4	6.2 ^g	4.4	3.6	d	2.0
6a 6b	3.3 5.7 ^g	6.5 ^g 7.1 ^g	3.8 5.6 ^g	3.3 4.4	d	2.7 3.9
7b	7.1 ^g	8.2 ^g	7.1 ^g	7.0 ^{<i>h</i>}	d	>5 5.6 ^h

^{*a*} The ¹H NMR titration in MeCN-d₃, 30 °C.

 ${}^{b}K_{1}/L \text{ mol}^{-1} = [L \cdot M^{m+}]/([L] \cdot [M^{m+}]), K_{2}/L \text{ mol}^{-1} = [(L)_{2} \cdot M^{m+}]/([L] \cdot [L \cdot M^{m+}]); \text{ the error of the determination of the stability constants is <math>\pm 20\%$ for the direct titration and $\pm 30\%$ for the competitive titration.

^c Competitive with 2b.

^d The ligand exchange is slow on the ¹H NMR time scale and hinders the accurate measurement of $\Delta\delta_{\rm H}$ values.

^e Competitive with **3a**.

^{*f*} Competitive with **2c**; the direct titration in the **2c**-Pb(ClO₄)₂ system gave $\log K_1 = 4.5$, $\log K_2 = 5.0$.

^g Competitive with 2a.

^h Competitive with **6b**.

Table 4. Stability constants (*K*) of the complexes of crown ethers **4c,d**, **5a,c**, **6c,d**, **7a,c,d**, and **8** with $Ca(ClO_4)_2^a$

Ligand	$\log K_1 (\log K_2)^b$	Ligand	$\log K_1 (\log K_2)^b$
4c	2.8 (2.3)	6d	8.1 ^c
4d	8.0^{c}	7a	7.9 ^c
5a	4.2	7c	2.9 (3.7)
5c	2.4 (2.2)	7d	8.6 ^c
6c	2.5 (2.3)	8	3.3 (3.5)

^{*a*} The ¹H NMR titration in MeCN-d₃, 30 °C.

^b $K_1/L \mod^{-1} = [L \cdot Ca^{2+}]/([L] \cdot [Ca^{2+}]), K_2/L \mod^{-1} = [(L)_2 \cdot Ca^{2+}]/([L] \cdot [L \cdot Ca^{2+}]);$ the error of the determination of the stability constants is $\pm 20\%$ for the direct titration and $\pm 30\%$ for the competitive titration.

^c Competitive with 2a.

A comparison of the stability constants of the complexes of benzoazacrown ethers 4a and 6a containing secondary nitrogen atoms, N-methyl derivatives 4b-7b, and model compounds 2a,b and 3a with all metal and ethylammonium cations showed that the stability of the complexes of most of the compounds increases in the series $EtNH_{3}^{+} < Na^{+} \le Ba^{2+} < Ca^{2+} < Pb^{2+}$ (see Table 3). This order of changes in the stability constants correlates with the downfield shifts $\Delta \delta_{H}$ upon the complex formation and is attributed to the high affinity of Pb²⁺ ions for O- and O,N-macrocyclic ligands and a strengthening of ion-dipole interactions in host-guest complexes due to an increase in the surface charge density in the abovegiven sequence of the cations (except for Pb^{2+}), as well as to the better correspondence between the cavity size of the 15-membered macrocycles and the diameters of the Na⁺ and Ca²⁺ ions.

Exceptions from this rule are the complexes with Ag^+ ions, whose position in the series of stability of the complexes with crown ethers depends on the number of nitrogen atoms and their position in the macrocycle. Benzocrown ethers **2a** and **4a** are virtually incapable to bind Ag^+ ions, whereas the stability of the complexes of diazacrown ethers **5b** and **7b** with Ag^+ is comparable to that of the related complexes with Na⁺ and Ba²⁺ ions. Undoubtedly, this complexing ability is determined by the high affinity of the soft Ag^+ ion for sp³-hybridized nitrogen atoms and, on the contrary, by the low affinity for hard oxygen atoms.²⁷

The regularities of the formation of more stable complexes with the cations under study were found in the following series of crown ethers: $4a < 3a \le 2b \approx 5b \le 6a \le$ $2a \le 4b \le 6b < 7b$. Therefore, the stability of the complexes increases as the oxygen atoms in benzo-15-crown-5 ether are successively replaced by NMe groups. It should be noted that benzoazacrown ethers containing nitrogen atoms distant from the benzene ring form more stable complexes than the isomers containing nitrogen atoms bound to the benzene ring. This fact is associated with the electron-withdrawing effect of the benzene ring, resulting in a decrease in the electron-donating ability of heteroatoms bound to this ring, as well as with a substantial contribution of the sp²-hybridized state of these N atoms, resulting in the involvement of their lone pairs in the efficient conjugation to the π system of the benzene ring and, consequently, their switching to the coordination of cations is hindered. Let us note the exception from this rule observed for diazacrown ether 5b, consisting in that the stability of its complexes is low even than that of monoazacrown ether 4b. Apparently, the methyl groups in the cis positions at the nitrogen atoms in ether 5b cause steric hindrance to the location of cations in the macrocyclic cavity and can also facilitate the fixation of the macrocycle in the conformation, which is not optimum for the complex formation.

The complexes of all benzoazacrown ethers containing secondary nitrogen atoms are less stable than the complexes of their *N*-methyl derivatives. This is evidence for the presence of an intramolecular NH...heteroatom hydrogen bond in the former compounds (see above), which hinders the location of cations in the macrocyclic cavity and the conformational changes of the macrocycle necessary for the reorientation of the lone pairs of all heteroatoms toward the cation.

It should be emphasized that, in some cases, it was impossible to determine the stability constants of the complexes with Pb^{2+} ions due to very high values and the above-mentioned exchange slow on the ¹H NMR time scale between the free ligand and several types of complexes having, apparently, the composition 1 (L) : 1 (Pb²⁺) or 2 (L) : 1 (Pb²⁺). Each of these complexes gives a complex set of overlapping signals indicative of the nonequivalence of the geminal protons of all methylene groups in the macrocycle.

It is important that the stability of the complexes of N-methylbenzomonoazacrown ether 4b containing the nitrogen atom bound to the benzene ring with metal and ethylammonium cations is comparable to or even higher than the stability of the corresponding complexes of benzo-15-crown-5 ether and is substantially higher than the stability of the complexes of N-phenylaza-15-crown-5 ether. The selectivity of the complex formation of compound 4b is higher than that of isomeric monoazacrown ether **6b** and diazacrown ether **7b**, although the latter two compounds form more stable complexes. Therefore, azacrown ethers containing one nitrogen atom bound to the benzene ring and bearing an N-alkyl substituent are characterized by the best complexing ability of all the compounds under study. Hence, macrocyclic ligands of type 4b are promising for the design of efficient and selective molecular optical sensors containing the nitrogen atom conjugated to a chromogen, which will lead to the

shift of absorption and ensure a strong spectral response to the complex formation.

To compare the stability of the metal complexes of the other crown ethers, we examined the complex formation with Ca²⁺ ions. These ions form complexes with all the ligands under consideration, which are easily detectable by ¹H NMR spectroscopy (see Table 4). The stability constants of the Ca²⁺ complexes with benzoazacrown ethers of amide type 4c-7c appeared to be the lowest among all the compounds under study ($\log K_1 = 2.4 - 2.9$). This is undoubtedly a consequence of the fact that the acetyl group has a strong electron-withdrawing effect on the nitrogen atom bound to this group, which hinders the involvement of the nitrogen lone pair in the coordination to the cation. Interestingly, sandwich complexes of the composition 2 (L) : 1 (Ca²⁺), whose stability is comparable to that of the related 1:1 complexes, were found in the systems (4c-7c)-Ca²⁺. Apparently, the formation of the sandwich complexes is attributed to a decrease in the cavity size of 15-membered benzoazacrown ethers due to the planar geometry of the sp²-hybridized nitrogen atoms, as was confirmed by the X-ray diffraction data for compounds 4c-6c (see Figs 1 and 2 and Table 1). A decrease in the size of the macrocyclic cavity results apparently in that the deep penetration of Ca²⁺ ions into the cavity of the azamacrocycle is impossible and, consequently, the second ligand molecule can be coordinated at the free side of the cation in the complex of the composition 1 (L) : 1 (Ca²⁺). The formation of the complexes of the composition 1:1 and 2:1 with Ca^{2+} ions was observed also for N-phenylazacrown ether 8 with a small cavity size of the 12-membered macrocycle.

The opposite effect on the stability of the complexes was observed in the presence of the N-substituents CH₂CO₂Et in benzoazacrown ethers. Thus, the stability constants of the complexes of benzoazacrown ethers 4d, 6d, and 7d with Ca²⁺ ions increase to $\log K_1 = 8.0 - 8.6$, and the stability of these complexes is higher than that of the related complexes of N-methyl derivatives 4b, 6b, and **7b**. As in the case of compounds **4b**-**7b**, the tertiary nitrogen atoms in 4d, 6d, and 7d are evidently predominantly sp³-hybridized and are more prone to donating lone pairs for the formation of coordination bonds with cations than azacrown ethers 4a-7a containing secondary N atoms. In addition, the presence of the oxygen donor atoms in the ethoxycarbonylmethyl group creates an additional binding region of M^{m+} . The metal cations are coordinated through the carbonyl oxygen atom, as was confirmed by the X-ray diffraction data for the complexes $4\mathbf{d} \cdot \text{Ba}(\text{ClO}_4)_2$ and $6\mathbf{d} \cdot \text{Ba}(\text{ClO}_4)_2$ (see Fig. 3) and the results of IR spectroscopic studies of the solid metal complexes, which show low-frequency shifts of C=O stretching bands in the spectra of the metal complexes down to 21 cm⁻¹ compared to the free ligands (see the Experimental section). However, it should be noted

that the contribution of the additional coordination of the cation by carbonyl groups to the stability of the complexes is relatively low. This may be associated with the coordination saturation of the Ca^{2+} ion even in the complexes of *N*-methyl derivatives **4b**, **6b**, and **7b** or with the steric strain in the macrocyclic moiety upon the coordination of the cation by C=O groups (see the above discussion of the X-ray diffraction data).

To conclude, let us note that some metal complexes of azacrown ethers can be prepared in the solid state by the crystallization in an appropriate solvent system. Most of the complexes prepared by this method have the composition 1 (L) : 1 (M^{m+}), as was confirmed by elemental analysis. In most cases, the most complete precipitation and the formation of high-quality crystals stable during storage were achieved with the use of barium perchlorate. The above-mentioned tendency to the formation of dinuclear systems and the relatively low hygroscopicity of barium salts can be responsible for the formation of structured precipitates by the complexes of 15-membered azamacrocycles with Ba(CIO₄)₂.

To sum up, we synthesized benzoaza-15-crown-5 ethers containing different numbers of nitrogen atoms in different positions in the macrocycle with respect to the benzene ring and bearing the following N substituents: H, Me, C(O)Me, or CH₂CO₂Et. The quantitative study of the complexing ability of the benzoazacrown ethers for the metal and ethylammonium cations showed that the most stable complexes are formed by the compounds containing nitrogen atoms with N-alkyl substituents distant from the benzene ring. However, the selectivity of complex formation appeared to be higher for the crown ether containing the nitrogen atom bound to the benzene ring and the N-methyl substituent. In addition, the stability of the complexes of this compound is comparable to or even higher than that of the complexes of benzocrown ether and is substantially higher than the stability of the corresponding complexes of phenylazacrown ether with the same size of the macrocycle. Due to this feature, the ligands having this structure can be considered as ionophoric blocks for the design of promising selective molecular optical sensors with a strong spectral respons to the complex formation.

Experimental

The melting points (uncorrected) were measured in capillaries on a Mel-Temp II instrument. The mass spectra were obtained on Varian MAT 311A and Finnigan MAT 8430 instruments using a direct inlet system; the ionization energy was 70 eV. The high-resolution mass spectra were measured on a Finnigan MAT 8430 instrument using perfluorokerosene as the standard. The elemental analysis was carried out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). The IR spectra were recorded on Shimadzu IR-435 and Bruker ISF-113V instruments in Nujol or in films on KBr. The TLC monitoring was carried out on DC-Alufolien Aluminiumoxid 60 F_{254} neutral (Typ E) and Kieselgel 60 F_{254} (Merck) plates. The column chromatography was performed on Al₂O₃ (Aluminium oxide 90 active neutral, 0.063–0.200 mm or Aluminium oxide 150, basic (type T), 0.063–0.200 mm, Merck) and SiO₂ (Kieselgel 60, 0.063–0.100 mm, Merck). The ¹H NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 MHz) in DMSO-d₆ at 25–30 °C using the residual signals of the solvent as the internal standard ($\delta_{\rm H}$ 2.50). The chemical shifts and the spin-spin coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. The assignment of the signals for protons was made based on twodimensional homonuclear ¹H–¹H COSY and NOESY spectra.

2-Aminophenol, o-phenylenediamine, and ethyl bromoacetate (Aldrich, Merck) were used without additional purification. 1,11-Dichloro-3,6,9-trioxaundecane, 1,11-diiodo-3,6,9trioxaundecane, 1,5-diamino-3-oxapentane, N,N'-dimethyl-1,5-diamino-3-oxapentane, benzo-15-crown-5 ether (2a), 4'-formylbenzo-15-crown-5 ether (2b), N-phenylaza-15-crown-5 ether (3a), benzo-7-aza-15-crown-5 ether (6a), and N-methylbenzo-7-aza-15-crown-5 ether (6b) are commercially available products purchased from the A. V. Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine (Odessa). 1,2-Bis(2-iodoethoxy)benzene²⁸ and N,N'-dimethyl-(4'-formylbenzo)-4,10-diaza-15-crown-5 ether (9)²¹ were synthesized according to known procedures. The salts NaClO₄, $Ca(ClO_4)_2$, and $Ba(ClO_4)_2$ (Aldrich) were dried in vacuo at 200 °C. Ethylammonium perchlorate was prepared by the neutralization of a 70% aqueous ethylamine solution with a 70% aqueous HClO₄ solution (Aldrich) and dried in vacuo at 60 °C. The salts $AgClO_4 \cdot H_2O$ and $Pb(ClO_4)_2 \cdot 3H_2O$ (Aldrich) were used without additional purification.

2,3,5,6,8,9,12,13-Octahydro-11H-1,4,7,10,13-benzotetraoxaazacyclopentadecyne (4a) and 2-(1,4,7-trioxa-10-azacyclododecen-10-yl)phenol (8). A. A mixture of 2-aminophenol (8.6 g, 0.079 mol), 1,11-dichloro-3,6,9-trioxaundecane (18.3 g, 0.079 mol), and *n*-butanol (125 mL) was stirred at room temperature under a nitrogen atmosphere for 6 h and then refluxed for 30 h. After cooling, a solution of NaOH (6.3 g, 0.16 mol) in water (6 mL) was added, and the reaction mixture was refluxed with stirring for 20 h. The precipitate was filtered off, and the filtrate was concentrated *in vacuo* and extracted with chloroform (3×20 mL). The combined extracts were washed with a 5% NaOH solution and thoroughly concentrated *in vacuo*. The dry residue was extracted with hot isooctane $(8 \times 30 \text{ mL})$, and the combined extracts were concentrated in vacuo. The residue was chromatographed on SiO₂ with elution by a benzene-AcOEt gradient mixture $(0 \rightarrow 33\%)$. The product was additionally purified by chromatography on Al₂O₃ (neutral) with elution by a benzene-AcOEt gradient mixture $(0 \rightarrow 17\%)$. Product **4a** was obtained as a pale-pink powder, m.p. 98-100 °C (cf. lit. data¹⁵: m.p. 100-102 °C), in a yield of 1.73 g (8%). ¹H NMR, δ : 3.11 (m, 2 H, CH₂N); 3.53–3.60 (m, 8 H, 4 CH₂O); 3.67 (m, 2 H, C<u>H₂CH₂N); 3.72</u> (m, 2 H, CH₂CH₂OAr); 4.01 (m, 2 H, CH₂OAr); 4.97 (br.s, 1 H, NH); 6.55 (d, 1 H, H(14), J = 7.9 Hz); 6.56 (m, 1 H, H(16); 6.79 (m, 1 H, H(15)); 6.80 (d, 1 H, H(17), J = 7.7 Hz). IR (in Nujol), v/cm^{-1} : 3440 (N-H).

B. A mixture of 2-aminophenol (2.29 g, 0.021 mol), 1,11-diiodo-3,6,9-trioxaundecane (5.00 mL, 0.023 mol), anhydrous Na_2CO_3 (11.1 g, 0.105 mol), and dry MeCN (250 mL) was refluxed with stirring for 30 h. The reaction mixture was filtered off, the filtrate was concentrated in vacuo, and the residue was chromatographed first on SiO₂ (a benzene-AcOEt gradient mixture, $0\rightarrow 50\%$) and then on Al₂O₃ (neutral) (a benzene-AcOEt gradient mixture, $0 \rightarrow 17\%$). Two fractions were collected. The first fraction was concentrated, and crown ether 4a was obtained in a yield of 88 mg (1.6%) as a crystalline gray powder, m.p. 101-102 °C (cf. lit. data¹⁴: m.p. 102 °C). The second fraction was additionally chromatographed on SiO₂ with elution by a benzene–AcOEt gradient mixture $(0\rightarrow 33\%)$. Product 8 was obtained as a pinkish powder, m.p. 73 °C (from a CH₂Cl₂hexane mixture; cf. lit. data¹⁴: m.p. 90 °C), in a yield of 155 mg (2.8%). ¹H NMR, δ: 3.07 (m, 4 H, 2 CH₂N); 3.44 (m, 4 H, 2 CH₂CH₂N); 3.53 and 3.63 (both m, 4 H each, 4 CH₂O); 6.74 (td, 1 H, H(4), J = 7.7 Hz, J = 1.2 Hz); 6.76 (dd, 1 H, H(6),J = 7.9 Hz, J = 1.2 Hz; 6.93 (td, 1 H, H(5), J = 7.7 Hz, J = 1.3 Hz); 7.16 (dd, 1 H, H(3), J = 7.8 Hz, J = 1.3 Hz); 8.49 (s, 1 H, OH). IR (in Nujol), v/cm⁻¹: 3290 (O–H). MS, *m*/z (*I*_{rel} (%)): 267 $[M]^+$ (37), 179 (25), 166 (21), 148 (52), 147 (23), 134 (43), 122 (41), 121 (94), 120 (100), 119 (45).

1,2,3,5,6,8,9,11,12,13-Decahydro-4,7,10,1,13-benzotrioxadiazacyclopentadecyne (5a). A mixture of o-phenylenediamine (1.36 g, 0.013 mol), 1,11-diiodo-3,6,9-trioxaundecane (3.00 mL, 0.014 mol), anhydrous Na₂CO₃ (6.68 g, 0.063 mol), and dry MeCN (150 mL) was refluxed with stirring for 30 h. The reaction mixture was filtered off, the filtrate was concentrated in vacuo, water (100 mL) was added, and the mixture was extracted with chloroform (4×15 mL). The combined extracts were concentrated in vacuo, and the residue was chromatographed first on Al_2O_2 (basic) (a benzene-AcOEt mixture (10 : 1) as the eluent) and then on SiO₂ (a benzene–AcOEt mixture (5:1) as the eluent). The product was purified by the extraction with boiling hexane (8×20 mL). The combined extracts were concentrated to ~50 mL and then cooled to -10 °C. The precipitate that formed was filtered off and dried in air. Product 5a was obtained as colorless crystals, m.p. 108–110 °C (cf. lit. data¹⁴: m.p. 110 °C), in a yield of 0.84 g (25%). ¹H NMR, δ : 3.12 (m, 4 H, 2 CH₂N); 3.55 and 3.60 (both m, 4 H each, 4 CH₂O); 3.69 (t, 4 H, $2 CH_2 CH_2 N$, J = 5.0 Hz); 4.10 (t, 2 H, 2 NH, J = 5.5 Hz); 6.52 (m, 2 H, H(14), H(17)); 6.61 (m, 2 H, H(15), H(16)). IR (in Nujol), v/cm^{-1} : 3350 (N-H).

3,4,5,6,9,10,11,12-Octahydro-2H,8H-1,7,13,4,10-benzotrioxadiazacyclopentadecyne (7a). A solution of 1,2-bis-(2-iodoethoxy)benzene (4.04 g, 9.7 mmol) in a mixture of MeCN (25 mL) and benzene (6 mL) and a solution of 1,5-diamino-3-oxapentane (1.11 g, 10.6 mmol) in MeCN (25 mL) were simultaneously added dropwise with vigorous stirring under reflux to a mixture of anhydrous Na₂CO₂ (5.13 g, 0.048 mol) and dry MeCN (100 mL) for 30 min. Then the mixture was refluxed for 30 h. The precipitate was filtered off, the filtrate was concentrated in vacuo, and the residue was chromatographed on Al₂O₃ (neutral) with elution by a benzene-MeCN-propan-2-ol mixture (5:4:1). The fraction containing the product was concentrated in vacuo, and the residue was extracted with hot heptane (3×50 mL). The combined extracts were cooled to -10 °C, and the precipitate was filtered off and dried in air. Product 7a was obtained as a white powder, m.p. 92-94 °C (cf. lit. data¹⁸: m.p. 97–100 °C), in a yield of 0.41 g (16%). ¹H NMR, δ : 2.71 (t, 4 H, 2 CH₂N, J = 4.6 Hz); 2.86 (t, 4 H, $2 CH_{2}CH_{2}OAr, J = 4.7 Hz$; $3.51 (t, 4 H, 2 CH_{2}O, J = 4.6 Hz)$; 4.01 (t, 4 H, 2 CH₂OAr, J = 4.7 Hz); 6.88 (m, 2 H, H(14),

H(17)); 6.97 (m, 2 H, H(15), H(16)). IR (in Nujol), v/cm^{-1} : 3331 (N—H). MS, m/z (I_{rel} (%)): 266 [M]⁺ (1), 180 (89), 179 (96), 166 (66), 148 (81), 136 (54), 88 (61), 74 (55), 71 (53), 70 (62), 56 (100).

4,10-Dimethyl-3,4,5,6,9,10,11,12-octahydro-2H,8H-1,7, 13,4,10-benzotrioxadiazacyclopentadecyne (7b). A solution of *N*,*N*'-dimethyl-1,5-diamino-3-oxapentane (0.20 mL, 1.4 mmol) in MeCN (7 mL) was added with vigorous stirring to a mixture of 1,2-bis(2-iodoethoxy)benzene (0.53 g, 1.3 mmol), anhydrous K₂CO₃ (0.70 g, 5.1 mmol), and dry MeCN (40 mL). The reaction mixture was refluxed for 11 h. The precipitate was filtered off, the filtrate was concentrated in vacuo, and the residue was chromatographed on Al₂O₃ (basic) with elution by a MeCN-EtOH gradient mixture (to 20% of the latter solvent). The fraction containing the product was concentrated in vacuo, the residue was extracted with hot hexane $(2 \times 40 \text{ mL})$, and the combined extracts were concentrated in vacuo. Product 7b was obtained as a yellowish viscous oil (cf. lit. data¹⁹: b.p. 170–180 °C (0.3 Torr)) in a yield of 0.23 g (61%). ¹H NMR, δ: 2.25 (s, 6 H, 2 Me); 2.61 (t, 4 H, 2 CH₂N, J = 5.9 Hz); 2.77 (t, 4 H, $2 CH_2 CH_2 OAr, J = 4.7 Hz$; 3.59 (t, 4 H, 2 CH₂O, J = 5.9 Hz); 3.97 (t, 4 H, 2 C<u>H</u>₂OAr, J = 4.7 Hz); 6.86 (m, 2 H, H(14), H(17)); 6.93 (m, 2 H, H(15), H(16)). MS, $m/z (I_{rel} (\%))$: 294 [M]⁺ (2), 211 (14), 194 (36), 193 (100), 185 (28), 180 (15), 136 (11), 102 (15), 88 (44), 72 (11), 58 (30).

13-Methyl-2,3,5,6,8,9,12,13-octahydro-11H-1,4,7,10,13benzotetraoxaazacyclopentadecyne (4b). Methyl iodide (125 µL, 2.0 mmol) was added to a mixture of azacrown ether 4a (54 mg, 0.2 mmol), NaH (a 60% dispersion in Nujol, 160 mg, 4.0 mmol), and dry THF (6 mL). The reaction mixture was heated with stirring at 65 °C until the starting compound 4a was consumed (40 min, TLC monitoring). Then water (30 mL) was added to the reaction mixture, the mixture was extracted with chloroform (3×15 mL), the organic extracts were concentrated in vacuo, and the residue was chromatographed on Al₂O₃ (basic) using benzene and then a benzene-AcOEt mixture (2:1) as the eluent. Product 4b was obtained as a yellowish oil in a yield of 54 mg (96%). ¹H NMR, δ: 2.70 (s, 3 H, Me); 3.03 (t, 2 H, CH_2N , J = 7.5 Hz); 3.54–3.62 (m, 8 H, 4 CH_2O); 3.79 (m, 2 H, $C\underline{H}_{2}CH_{2}OAr$); 3.82 (t, 2 H, $C\underline{H}_{2}CH_{2}N$, J = 7.5 Hz); 4.05 (m, 2 H, CH₂OAr); 6.79–6.89 (m, 4 H, H(14), H(15), H(16), H(17)). MS, *m*/*z* (*I*_{rel} (%)): 281 [M]⁺ (47), 150 (23), 149 (23), 148 (31), 137 (20), 136 (100), 135 (74), 121 (31), 66 (18), 52 (23).

1,13-Dimethyl-1,2,3,5,6,8,9,11,12,13-decahydro-4,7,10,1,13benzotrioxadiazacyclopentadecyne (5b). A mixture of azacrown ether 5a (57 mg, 0.21 mmol), NaH (a 60% dispersion in Nujol, 170 mg, 4.3 mmol) and dry THF (6 mL) was heated with stirring at 65 °C for 5 min. Then methyl iodide (133 µL, 2.1 mmol) was added, and the mixture was heated until the starting compound 5a was consumed (50 min, TLC monitoring). Then water (30 mL) was added to the reaction mixture, the mixture was extracted with chloroform (3×25 mL), the organic extracts were concentrated in vacuo, and the residue was chromatographed on Al₂O₃ (basic) using benzene and then a benzene-AcOEt mixture (7:3) as the eluent. Product **5b** was obtained as a yellowish oil in a yield of 58 mg (92%). ¹H NMR, δ : 2.68 (s, 6 H, 2 Me); 3.23 (t, 4 H, 2 CH₂N, J = 6.3 Hz); 3.48 and 3.53 (both m, 4 H each, 4 CH₂O); $3.\overline{61}$ (t, 4 H, 2 CH₂CH₂N, J = 6.3 Hz); 6.84–6.91 (m, 4 H, H(14), H(15), H(16), H(17)). MS, m/z $(I_{rel} (\%)): 294 [M]^+ (66), 176 (25), 175 (100), 162 (20), 161 (44),$ 160 (33), 147 (22), 146 (69), 133 (25), 57 (16).

13-Acetyl-2,3,5,6,8,9,12,13-octahydro-11H-1,4,7,10,13benzotetraoxaazacyclopentadecyne (4c). A mixture of azacrown ether 4a (160 mg, 0.60 mmol) and acetic anhydride (2 mL) was heated at 100 °C (an oil bath) for 6 h. The reaction mixture was concentrated in vacuo. The residue was chromatographed on SiO₂ using AcOEt and then an AcOEt-EtOH mixture (5:1) as the eluent. Product **4c** was obtained as a white powder, m.p. 118-120 °C, in a yield of 176 mg (95%). Found (%): C, 62.39; H, 7.60; N, 4.30. C₁₆H₂₃NO₅. Calculated (%): C, 62.12; H, 7.49; N, 4.53. ¹H ŇMŘ, δ: 1.63 (s, 3 H, Me); 3.06 (ddd, 1 H, C<u>H</u>H'N, J = 13.1 Hz, J = 9.4 Hz, J = 6.2 Hz); 4.43 (m, 2 H, CH₂O); 3.47-3.57 (m, 6 H, 3 CH₂O); 3.62 (m, 2 H, CH₂CHH'N); 3.71 (m, 2 H, CH₂CHH'OAr); 4.13 (dt, 1 H, C<u>H</u>H'OAr, J = 11.6 Hz, J = 3.1 Hz); 4.18 (ddd, 1 H, CHH'N, J = 13.1 Hz, J = 9.5 Hz, J = 6.8 Hz); 4.25 (m, 1 H, CH<u>H</u>'OAr); 6.99 (td, 1 H, H(15), J = 7.7 Hz, J = 0.9 Hz); 7.13 (dd, 1 H, H(17), J = 7.9 Hz, J = 0.9 Hz); 7.25 (dd, 1 H, H(14), J = 7.7 Hz J = 1.6 Hz); 7.33 (td, 1 H, H(16), J = 7.9 Hz, J = 1.6 Hz). IR (in Nujol), v/cm⁻¹: 1651 (C=O). MS, m/z $(I_{rel} (\%))$: 309 [M]⁺ (12), 148 (46), 136 (42), 135 (56), 134 (45), 122 (60), 121 (41), 120 (64), 109 (52), 59 (50), 58 (100).

1-Acetyl-1,2,3,5,6,8,9,11,12,13-decahydro-4,7,10,1,13benzotrioxadiazacyclopentadecyne (5c). A mixture of diazacrown ether 5a (329 mg, 1.24 mmol), acetic anhydride (0.35 mL), and benzene (20 mL) was heated at 80 °C (an oil bath) for 4 h. Then MeOH (1 mL) was added. The reaction mixture was kept for 2 h and concentrated in vacuo. The residue was chromatographed on SiO₂ with elution by a benzene-AcOEt gradient mixture $(0\rightarrow 65\%)$. Product **5c** was obtained as a white powder, m.p. 78-79 °C, in a yield of 168 mg (44%). Found (%): C, 60.67; H, 7.99; N, 8.76. C₁₆H₂₄N₂O₄•0.5H₂O. Calculated (%): C, 60.55; H, 7.94; N, 8.83. ¹H NMR, δ: 1.67 (s, 3 H, Me); 2.94 (br.dt, 1 H, CHH'NCO, J = 13.8 Hz, J = 5.1 Hz); 3.17 (dtd, 1 H, CHH'NH, J = 13.2 Hz, J = 6.5 Hz, J = 2.8 Hz); 3.32 (m, 1 H, CHH'NH); 3.39 (ddd, 1 H, CHH'CHH'NCO, J = 10.3 Hz, J = 8.3 Hz, J = 5.5 Hz); 3.42-3.63 (m, 10 H, 5 CH₂O); 3.68 (m, 1 H, C<u>H</u>H'CHH'NH, J = 10.3 Hz, J = 6.4 Hz, J = 2.7 Hz; 4.53 (ddd, 1 H, CH<u>H</u>'NCO, J = 13.9 Hz, J = 8.2 Hz, J = 5.8 Hz); 5.11 (br.t, 1 H, NH, J = 5.4 Hz); 6.64 (td, 1 H, H(16), J = 7.5 Hz, J = 0.9 Hz); 6.74 (dd, 1 H, H(14),J = 8.1 Hz, J = 0.9 Hz; 7.04 (dd, 1 H, H(17), J = 7.7 Hz, J = 1.4 Hz); 7.17 (td, 1 H, H(15), J = 7.7 Hz, J = 1.4 Hz). IR (in Nujol), v/cm^{-1} : 3380 (N–H), 1657 (C=O). MS, $m/z (I_{rel} (\%))$: 308 [M]⁺ (38), 293 (64), 291 (89), 163 (89), 147 (89), 145 (45), 133 (69), 132 (39), 121 (44), 119 (100).

7-Acetyl-2,3,6,7,8,9,11,12-octahydro-5H-1,4,10,13,7-benzotetraoxaazacyclopentadecyne (6c). A mixture of azacrown ether 6a (205 mg, 0.77 mmol) and acetic anhydride (2 mL) was heated at 100 °C (an oil bath) for 6 h. The reaction mixture was thoroughly concentrated in vacuo at 90 °C. Product 6c was obtained as a white powder, m.p. 85-87 °C, in a yield of 240 mg (100%). Found (%): C, 62.36; H, 7.70; N, 4.33. C₁₆H₂₃NO₅. Calculated (%): C, 62.12; H, 7.49; N, 4.53. ¹H NMR, 5: 2.00 (s, 3 H, Me); 3.42 (t, 2 H, CH_2N , J = 5.9 Hz); 3.50 (t, 2 H, CH_2N , J = 6.6 Hz); 3.62 (t, 2 H, CH_2CH_2N , J = 5.9 Hz); 3.71 (m, 2 H, C<u>H</u>₂CH₂OAr); 3.77 (t, 2 H, C<u>H</u>₂CH₂N, J = 6.6 Hz); 3.78 (m, 2 H, CH₂CH₂OAr); 4.03 (m, 4 H, 2 CH₂OAr); 6.87 (m, 2 H, H(14), H(17)); 6.94 (m, 2 H, H(15), H(16)). IR (in Nujol), v/cm⁻¹: 1657 (C=O). MS, m/z (I_{rel} (%)): 309 [M]⁺ (9), 265 (21), 156 (32), 136 (100), 121 (31), 100 (79), 99 (36), 88 (27), 86 (88), 70 (38), 56 (64).

4,10-Diacetyl-3,4,5,6,9,10,11,12-octahydro-2H,8H-1,7, 13,4,10-benzotrioxadiazacyclopentadecyne (7c). A mixture of diazacrown ether 7a (149 mg, 0.56 mmol) and acetic anhydride (2 mL) was heated at 100 °C (an oil bath) for 6 h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed on SiO₂ using a benzene-MeCN mixture (1 : 1) and then a benzene-EtOH mixture (5:1) as the eluent. Product 7c was obtained as a white powder, m.p. 102-104 °C, in a yield of 167 mg (85%). Found (%): C, 61.80; H, 7.61; N, 7.97. C₁₈H₂₆N₂O₅. Calculated (%): C, 61.70; H, 7.48; N, 8.00. ¹H NMR, δ: 2.025, 2.034, 2.048 (3 s, 1.3 H, 2.5 H, 2.2 H, 2 Me); 3.53–3.62 (m, 5.4 H, 2.7 CH₂); 3.69 (m, 2.4 H, 1.2 CH₂); 3.73 (m, 2.7 H, 1.35 CH₂); 3.78 (m, 1.5 H, 0.75 CH₂); 4.09 (m, 2.5 H, 1.25 CH₂OAr); 4.15 (m, 1.5 H, 0.75 CH₂OAr); 6.86–6.93 (m, 2 H, H(14), H(17)); 6.93-7.00 (m, 2 H, H(15), H(16)). IR (in Nujol), v/cm⁻¹: 1640, 1633, 1621 (C=O). MS, m/z $(I_{rel} (\%)): 350 [M]^+ (12), 268 (43), 253 (28), 235 (25), 234 (23),$ 71 (16), 69 (18), 59 (33), 58 (100), 57 (35), 55 (18).

Ethyl 2,3,5,6,8,9,11,12-octahydro-13H-1,4,7,10,13-benzotetraoxaazacyclopentadecyn-13-ylacetate (4d). A mixture of benzoazacrown ether 4a (107 mg, 0.40 mmol), ethyl bromoacetate (49 µL, 0.44 mmol), anhydrous Na₂CO₃ (51 mg, 0.46 mmol), and dry MeCN (4 mL) was refluxed with stirring for 60 h. Then MeCN (20 mL) was added, the precipitate was filtered off, the filtrate was concentrated in vacuo, and the residue was chromatographed on Al_2O_3 (basic) with elution by a benzene-EtOAc mixture (2 : 1). Product 4d was obtained as a pale-yellow oil in a yield of 130 mg (93%). ¹H NMR, δ: 1.17 (t, 3 H, Me, J = 7.1 Hz); 3.34 (t, 2 H, CH₂CH₂N, J = 6.3 Hz); 3.52, 3.56, 3.58, and 3.62 (all m, 2 H each, CH₂O); 3.72 (t, 2 H, CH_2CH_2N , J = 6.3 Hz); 3.79 (m, 2 H, CH_2CH_2OAr); 4.05 (s, 2 H, CH₂CO₂); 4.06 (m, 2 H, CH₂OAr); 4.07 (q, 2 H, CH₂Me, J = 7.1 Hz); 6.80 (br.d, 1 H, H(14), J = 4.7 Hz); 6.80–6.85 (m, 2 H, H(15), H(16)); 6.88 (br.d, 1 H, H(17), J = 7.4 Hz). IR (in film), v/cm⁻¹: 1740 (C=O). MS, $m/z (I_{rel} (\%))$: 353 [M]⁺ (1), 280 (46), 149 (26), 148 (60), 134 (73), 122 (35), 120 (59), 71 (29), 59 (34), 58 (100), 57 (43). High-resolution MS, Found: m/z 353.1834 [M]⁺. C₁₈H₂₇NO₆. Calculated: M = 353.1838.

Ethyl 2,3,5,6,8,9,11,12-octahydro-7H-1,4,10,13,7-benzotetraoxaazacyclopentadecyn-7-ylacetate (6d). A mixture of benzoazacrown ether 6a (201 mg, 0.75 mmol), ethyl bromoacetate (100 µL, 0.90 mmol), anhydrous K₂CO₃ (416 mg, 0.46 mmol), and dry MeCN (10 mL) was refluxed with stirring for 20 h. Then benzene (30 mL) was added, the precipitate was filtered off, the filtrate was concentrated in vacuo, and the residue was chromatographed on Al₂O₃ (neutral) with elution by a benzene-MeCN mixture (5:1). Product 6d was obtained as a colorless substance, m.p. 50-52 °C, in a yield of 203 mg (76%). Found (%): C, 61.38; H, 7.67; N, 3.87. C₁₈H₂₇NO₆. Calculated (%): C, 61.17; H, 7.70; N, 3.96. ¹H NMR, 5: 1.17 (t, 3 H, Me, J = 7.2 Hz); 2.78 (t, 4 H, (CH₂C<u>H₂)₂N, J = 6.0 Hz);</u> 3.41 (s, 2 H, CH₂CO₂); 3.61 (t, 4 H, (C<u>H₂CH₂)</u>, N, J = 6.0 Hz); 3.72 (m, 4 H, 2 CH₂CH₂OAr); 4.02 (m, 4 H, CH₂OAr); 4.05 (q, 2 H, C<u>H</u>₂Me, J = 7.2 Hz); 6.86 (m, 2 H, H(14), H(17)); 6.93 (m, 2 H, H(15), H(16)). IR (in film), v/cm⁻¹: 1735 (C=O). MS, *m*/*z* (*I*_{rel} (%)): 353 [M]⁺ (14), 280 (68), 109 (20), 85 (21), 84 (23), 69 (25), 59 (42), 58 (100), 57 (33), 56 (46), 55 (31).

4,10-Bis(ethoxycarbonylmethyl)-2,3,5,6,8,9,11,12-octahydro-4*H*,10*H*-1,7,13,4,10-benzotrioxadiazacyclopentadecyne (7d). A solution of benzodiazacrown ether 7a (0.60 g, 2.3 mmol), ethyl bromoacetate (0.55 mL, 5.0 mmol), and dry Et_3N

Compound	4a	4c	5a	5c
Molecular formula	C ₁₄ H ₂₁ NO ₄	C ₁₆ H ₂₃ NO ₅	C ₁₄ H ₂₂ N ₂ O ₃	C ₁₆ H ₂₄ N ₂ O ₄
M/g mol ⁻¹	267.32	309.35	266.34	308.37
Crystal system	Orthorombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$Pca2_1$	C2/c	$P2_1/n$	$P2_{1}2_{1}2_{1}$
a/Å	20.1308(6)	24.774(4)	8.4832(4)	8.3151(7)
b/Å	8.4639(3)	8.1343(11)	17.2639(8)	9.3885(8)
c/Å	16.4133(6)	18.038(2)	9.9592(5)	20.4825(18)
α/deg	90	90	90	90
β/deg	90	118.517(3)	109.0300(10)	90
γ/deg	90	90	90	90
$V/Å^3$	2796.58(16)	3194.0(8)	1378.84(11)	1599.0(2)
Ζ	8	8	4	4
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.270	1.287	1.283	1.281
<i>F</i> (000)	1152	1328	576	664
μ (Mo-K α)/mm ⁻¹	0.093	0.095	0.090	0.092
Crystal dimensions/mm	0.36×0.28×0.22	0.26×0.23×0.18	$0.22 \times 0.20 \times 0.18$	$0.42 \times 0.36 \times 0.32$
θ Scan mode/range, deg	ω/2.02-29.00	ω/2.67-29.00	ω/2.36-29.00	ω/2.39-28.99
Ranges of indices of	$-24 \le h \le 26,$	$-33 \le h \le 27,$	$-8 \le h \le 11,$	$-11 \le h \le 10,$
measured reflections	$-9 \le k \le 11,$	$-11 \le k \le 11,$	$-17 \le k \le 23,$	$-12 \le k \le 5,$
	$-13 \le l \le 22$	$-23 \le l \le 24$	$-13 \le l \le 9$	$-14 \le l \le 27$
Number of measured reflections	15701	9369	8959	7805
Number of independent	5416	4183	3673	4033
reflections	$(R_{\rm int} = 0.0287)$	$(R_{\rm int} = 0.0352)$	$(R_{\rm int} = 0.0197)$	$(R_{\rm int} = 0.0220)$
Number of reflections with $I > 2\sigma(I)$	4769	3028	2995	3561
Number of refined parameters	513	291	261	295
R factors based on	$R_1 = 0.0332,$	$R_1 = 0.0506,$	$R_1 = 0.0364,$	$R_1 = 0.0346$,
reflections with $I > 2\sigma(I)$	$wR_2 = 0.0788$	$wR_2 = 0.1143$	$wR_2 = 0.0933$	$wR_2 = 0.0785$
based on all reflections	$R_1 = 0.0419$,	$R_1 = 0.0742,$	$R_1 = 0.0473,$	$R_1 = 0.0435,$
	$wR_2 = 0.0826$	$wR_2 = 0.1227$	$wR_2 = 0.0982$	$wR_2 = 0.0823$
Goodness-of-fit on F^2	1.052	1.012	1.059	1.050
Residual electron density $(\min/\max)/e \cdot Å^{-3}$	-0.186/0.202	-0.269/0.344	-0.198/0.315	-0.188/0.216

Table 5. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of **4a**,**c** and **5a**,**c**

(0.76 mL, 5.5 mmol) in anhydrous THF (50 mL) was kept at room temperature for 7 days. Then the solvent was evaporated in vacuo. Benzene (50 mL) was added to the residue. The mixture was washed with water (4×15 mL), the solvent was evaporated in vacuo, and the residue was extracted with boiling heptane (3×40 mL). After evaporation of the extracts in vacuo, diester 7d was obtained as a slightly yellowish viscous oil in a yield of 0.92 g (90%). ¹H NMR, δ : 1.18 (t, 6 H, 2 Me, J = 7.1 Hz); 2.83 (t, 4 H, 2 CH₂N, *J* = 6.1 Hz); 3.01 (t, 4 H, 2 CH₂N, *J* = 4.8 Hz); 3.44 (s, 4 H, 2 \overline{CH}_2CO_2); 3.54 (t, 4 H, 2 \overline{CH}_2O , J = 6.1 Hz); 3.95 (t, 4 H, 2 C<u>H</u>₂OAr, J = 4.8 Hz); 4.06 (q, 4 H, 2 C<u>H</u>₂Me, J = 7.1 Hz; 6.84 (m, 2 H, H(14), H(17)); 6.90 (m, 2 H, H(15), H(16)). IR (in film), v/cm⁻¹: 1734 (C=O). MS, m/z (I_{rel} (%)): 438 [M]⁺ (3), 365 (85), 265 (93), 250 (40), 192 (47), 160 (100), 146 (55), 124 (41), 130 (88), 100 (46), 56 (59). High-resolution MS, Found: m/z 438.2364 [M]⁺. C₂₂H₃₄N₂O₇. Calculated: M = 438.2366.

Complexes of aza crown ethers with metal perchlorates were precipitated by the slow saturation of a solution of a mixture of NaClO₄, Ba(ClO₄)₂, or Pb(ClO₄)₂ • $3H_2O$ (~20–60 µmol)

and a 5% excess of azacrown ether in MeCN (3-5 mL) with benzene vapor at room temperature. The precipitates were separated by decantation and dried *in vacuo* at 80 °C.

Complex 3a · 4Ba(ClO₄)₂. The yield was 71%, colorless crystals, m.p. >272 °C (with decomp.). Found (%): C, 11.97; H, 1.84; N, 0.81. $C_{16}H_{25}Ba_4Cl_8NO_{36}$. Calculated (%): C, 11.72; H, 1.54; N, 0.85.

Complex 4a · Ba(ClO₄)₂ · 0.25C₆H₆. The yield was 93%, colorless crystals, m.p. >255 °C (with decomp.). Found (%): C, 29.92; H, 3.80; N, 2.10. $C_{15.5}H_{22.5}BaCl_2NO_{12}$. Calculated (%): C, 29.88; H, 3.64; N, 2.25. IR (in Nujol), v/cm⁻¹: 3391 (N–H).

Complex 4a • Pb(ClO₄)₂. The yield was 66%, colorless crystals, m.p. 291–292 °C (with decomp.). Found (%): C, 25.15; H, 3.20; N, 2.14. $C_{14}H_{21}Cl_2NO_{12}Pb$. Calculated (%): C, 24.97; H, 3.14; N, 2.08.

Complex 4b · Ba(ClO₄)₂. The yield was 88%, colorless crystals, m.p. 339–340 °C (with decomp.). Found (%): C, 29.11; H, 3.69; N, 2.28. $C_{15}H_{23}BaCl_2NO_{12}$. Calculated (%): C, 29.17; H, 3.75; N, 2.27.

Compound	6a	6b	6c	7a ⋅ H ₂ O
Molecular formula	C ₁₄ H ₂₁ NO ₄	C ₁₅ H ₂₃ NO ₄	C ₁₆ H ₂₃ NO ₅	C ₁₄ H ₂₄ N ₂ O ₄
M∕g mol ^{−1}	267.32	281.34	309.35	284.35
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	$P2_1$	Pbca	$P\overline{1}$	Pbcn
a/Å	10.6366(8)	16.6030(16)	8.0215(4)	36.9551(12)
b/Å	8.5150(5)	8.3768(8)	9.2735(5)	9.0727(3)
c/Å	15.8098(8)	21.075(2)	10.8191(5)	9.2441(3)
α/deg	90	90	90.031(2)	90
β/deg	105.328(2)	90	95.766(2)	90
γ/deg	90	90	98.946(2)	90
$V/Å^3$	1380.97(15)	2931.1(5)	790.88(7)	3099.39(18)
Ζ	4	8	2	8
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.286	1.275	1.299	1.219
<i>F</i> (000)	576	1216	332	1232
μ (Mo-K α)/mm ⁻¹	0.094	0.092	0.096	0.089
Crystal dimensions/mm	$0.26 \times 0.20 \times 0.16$	0.36×0.28×0.18	0.20×0.16×0.14	0.24×0.22×0.18
θ Scan mode/range, deg	ω/3.11-30.26	ω/1.93-29.00	ω/1.89—28.99	ω/2.20-29.00
Ranges of indices of	$-14 \le h \le 14,$	$-22 \le h \le 22,$	$-10 \le h \le 10,$	$-47 \le h \le 50,$
measured reflections	$-12 \le k \le 11,$	$-11 \le k \le 11,$	$-12 \le k \le 12,$	$-8 \le k \le 12,$
	$-22 \le l \le 22$	$-28 \le l \le 28$	$-14 \le l \le 13$	$-12 \le l \le 10$
Number of measured reflections	12172	23325	5186	17057
Number of independent	7575	3892	3853	4081
reflections	$(R_{\rm int} = 0.0474)$	$(R_{\rm int} = 0.0461)$	$(R_{\rm int} = 0.0182)$	$(R_{\rm int} = 0.0221)$
Number of reflections with $I > 2\sigma(I)$	6181	2980	3024	3393
Number of refined parameters	351	273	291	278
<i>R</i> factors based on	$R_1 = 0.1383$,	$R_1 = 0.0404,$	$R_1 = 0.0413$,	$R_1 = 0.0394$,
reflections with $I > 2\sigma(I)$	$wR_2 = 0.3365$	$wR_2 = 0.1082$	$wR_2 = 0.0992$	$wR_2 = 0.0982$
based on all reflections	$R_1 = 0.1558$,	$R_1 = 0.0562,$	$R_1 = 0.0570$,	$R_1 = 0.0492,$
	$wR_2 = 0.3555$	$wR_2 = 0.1164$	$wR_2 = 0.1049$	$wR_2 = 0.1027$
Goodness-of-fit on F^2	1.434	1.082	1.057	1.038
Residual electron density $(min/max)/e \cdot Å^{-3}$	-0.423/2.458	-0.212/0.441	-0.192/0.288	-0.163/0.266

Table 6. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of 6a-c and $7a \cdot H_2O$

Complex 4d · Ba(ClO₄)₂. The yield was 64%, colorless crystals, m.p. 282–283 °C (with decomp.). Found (%): C, 31.14; H, 3.94; N, 2.07. $C_{18}H_{27}BaCl_2NO_{14}$. Calculated (%): C, 31.35; H, 3.95; N, 2.03. IR (in Nujol), v/cm⁻¹: 1722 (C=O).

Complex 5b • Pb(ClO₄)₂. The yield was 73%, colorless crystals, m.p. 259–261 °C (with decomp.). Found (%): C, 27.67; H, 3.85; N, 4.09. $C_{16}H_{26}Cl_2N_2O_{11}Pb$. Calculated (%): C, 27.43; H, 3.74; N, 4.00.

Complex 6a · Ba(ClO₄)₂. The yield was 81%, colorless crystals, m.p. 312–313 °C (with decomp.). Found (%): C, 28.01; H, 3.34; N, 2.26. $C_{14}H_{21}BaCl_2NO_{12}$. Calculated (%): C, 27.86; H, 3.51; N, 2.32. IR (in Nujol), v/cm⁻¹: 3312 (N–H).

Complex 6b · NaClO₄. The yield was 35%, white powder, m.p. 160–163 °C. Found (%): C, 44.71; H, 5.71; N, 3.49. $C_{15}H_{23}CINNaO_8$. Calculated (%): C, 44.62; H, 5.74; N, 3.47.

Complex 6b · Ba(ClO₄)₂. The yield was 90%, white powder, m.p. 293–296 °C (with decomp.). Found (%): C, 29.11;

H, 3.71; N, 2.24. $C_{15}H_{23}BaCl_2NO_{12}$. Calculated (%): C, 29.17; H, 3.75; N, 2.27.

Complex 6d · Ba(ClO₄)₂. The yield was 85%, colorless crystals, m.p. 289–290 °C (with decomp.). Found (%): C, 31.38; H, 3.87; N, 2.04. $C_{18}H_{27}BaCl_2NO_{14}$. Calculated (%): C, 31.35; H, 3.95; N, 2.03. IR (in Nujol), v/cm⁻¹: 1716 (C=O).

Complex 7b · Ba(ClO₄)₂. The yield was 94%, white powder, m.p. 313–314 °C (with decomp.). Found (%): C, 30.51; H, 4.19; N, 4.54. $C_{16}H_{26}BaCl_2N_2O_{11}$. Calculated (%): C, 30.47; H, 4.16; N, 4.44.

Complex 7d · NaClO₄. The yield was 53%, yellowish powder, m.p. 62–64 °C. Found (%): C, 47.24; H, 6.09; N, 5.04. $C_{22}H_{34}ClN_2NaO_{11}$. Calculated (%): C, 47.11; H, 6.11; N, 4.99. IR (in Nujol), v/cm⁻¹: 1732 (C=O).

Complex 7d · Ba(ClO₄)₂. The yield was 74%, yellowish powder, m.p. >115 °C (with decomp.). Found (%): C, 34.19; H, 4.47; N, 3.58. $C_{22}H_{34}BaCl_2N_2O_{15}$. Calculated (%): C, 34.11; H, 4.42; N, 3.62. IR (in Nujol), v/cm⁻¹: 1713 (C=O).

X-ray diffraction study. Crystals of free azacrown ethers were grown by the slow evaporation of their solutions in a CH_2Cl_2 —hexane mixture at room temperature. The crystalline

Compound	$4\mathbf{b} \cdot \mathrm{Ba}(\mathrm{ClO}_4)_2$	$4\mathbf{d} \cdot \mathrm{Ba}(\mathrm{ClO}_4)_2$	$7\mathbf{b} \cdot \mathrm{Ba}(\mathrm{ClO}_4)_2$	8
Molecular formula	C ₁₅ H ₂₃ BaCl ₂ NO ₁₂	C ₁₈ H ₂₇ BaCl ₂ NO ₁₄	C ₁₆ H ₂₆ BaCl ₂ N ₂ O ₁₁	C ₁₄ H ₂₁ NO ₄
M/g mol ⁻¹	617.58	689.65	630.63	267.32
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\overline{1}$
<i>a</i> /Å	8.7311(14)	15.0987(9)	9.4114(5)	6.4366(4)
b/Å	15.935(3)	8.5917(5)	17.2171(9)	10.2180(7)
c/Å	15.306(2)	20.4014(12)	14.4367(7)	11.4097(7)
α/deg	90	90	90	67.697(2)
β/deg	98.990(4)	110.939(2)	100.5700(10)	86.696(2)
γ/deg	90	90	90	82.179(2)
$V/Å^3$	2103.4(6)	2471.8(3)	2299.6(2)	687.80(8)
Ζ	4	4	4	2
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.950	1.853	1.822	1.291
<i>F</i> (000)	1224	1376	1256	288
μ (Mo-K α)/mm ⁻¹	2.206	1.894	2.018	0.094
Crystal dimensions/mm	$0.46 \times 0.04 \times 0.04$	$0.42 \times 0.22 \times 0.08$	$0.28 \times 0.22 \times 0.18$	$0.14 \times 0.12 \times 0.10$
θ Scan mode/range, deg	ω/1.86-28.00	ω/2.11-28.00	ω/1.86-30.57	ω/1.93-28.99
Ranges of indices of	$-11 \le h \le 11,$	$-17 \le h \le 19,$	$-13 \le h \le 13,$	$-8 \le h \le 6,$
measured reflections	$-21 \le k \le 21,$	$-11 \le k \le 11,$	$-24 \le k \le 24,$	$-13 \le k \le 9,$
	$-20 \le l \le 15$	$-26 \le l \le 26$	$-20 \le l \le 20$	$-15 \le l \le 8$
Number of measured reflections	15540	13970	22843	4078
Number of independent	5074	5946	7053	3304
reflections	$(R_{\rm int} = 0.0562)$	$(R_{int} = 0.0406)$	$(R_{\rm int} = 0.0243)$	$(R_{\rm int} = 0.0196)$
Number of reflections with $I > 2\sigma(I)$	3778	4513	6566	2268
Number of refined parameters	372	434	393	257
R factors based on	$R_1 = 0.0355,$	$R_1 = 0.0324,$	$R_1 = 0.0286,$	$R_1 = 0.0465,$
reflections with $I \ge 2\sigma(I)$	$wR_2 = 0.0814$	$wR_2 = 0.0690$	$wR_2 = 0.0590$	$wR_2 = 0.1108$
based on all reflections	$R_1 = 0.0614,$	$R_1 = 0.0537,$	$R_1 = 0.0313,$	$R_1 = 0.0731,$
	$wR_2 = 0.0907$	$wR_2 = 0.0757$	$wR_2 = 0.0599$	$wR_2 = 0.1216$
Goodness-of-fit on F^2	1.042	1.017	1.201	1.035
Residual electron density $(min/max)/e \cdot Å^{-3}$	-0.753/1.051	-1.108/1.326	-0.590/0.664	-0.241/0.219

Table 7. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of $4\mathbf{b} \cdot \text{Ba}(\text{ClO}_4)_2$, $4\mathbf{d} \cdot \text{Ba}(\text{ClO}_4)_2$, $7\mathbf{b} \cdot \text{Ba}(\text{ClO}_4)_2$, and $\mathbf{8}$

complexes of benzoazacrown ethers with barium and sodium perchlorates were prepared by the slow saturation of solutions of the ligands and the salts in MeCN with benzene vapor as described above.

Single crystals of azacrown ethers or their metal complexes were mounted on a Bruker SMART-CCD diffractometer under a cold nitrogen stream (T = 190(2) K for **7b** · Ba(ClO₄)₂ and 120.0(2) K for the other crystals). The X-ray diffraction data sets were collected using Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator). The X-ray data were processed with the use of the SAINT program.²⁹ For the crystals of all metal complexes, absorption corrections were applied using the SADABS method. All structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms at the carbon atoms were positioned geometrically and refined isotropically for **4a,c**, **5a,c**, **6b,c**, **7a** · H₂O, **8**, **4b** · Ba(ClO₄)₂, **4d** · Ba(ClO₄)₂, **5b** · Ba(ClO₄)₂ · 0.5H₂O, **7b** • Ba(ClO₄)₂, and **9** • NaClO₄, using a riding model for **6a** and **6d** • Ba(ClO₄)₂, or using a mixed scheme (isotropically and using a riding model) for **6a** • Ba(ClO₄)₂. The hydrogen atoms of the NH groups in molecules **4a**, **5a**,**c**, **6a**, **7a** • H₂O, and **6a** • Ba(ClO₄)₂, the hydrogen atom of the OH group in molecule **8**, and the hydrogen atoms of the solvent water molecules in **7a** • H₂O and **5b** • Ba(ClO₄)₂ • 0.5H₂O were located from difference Fourier maps and refined isotropically (with restraints on the N-H bond length in **4a** and **6a**).

The structure of 6a was characterized by the relatively high R factors because of high crystal mosaicity, which is apparently the inherent property of this compound. We succeeded in choosing only a few crystals with a relatively low content of an impurity component, as evidenced by the high residual electron density even for the best-quality sample. Nevertheless, in spite of the low accuracy of the structure solution, it can be stated with assurance that the structural motif and the main geometric parameters of both independent molecules 6a are reliable for a

Compound	$5\mathbf{b} \cdot \mathrm{Ba}(\mathrm{ClO}_4)_2 \cdot 0.5\mathrm{H}_2\mathrm{O}$	$6a \cdot Ba(ClO_4)_2$	6d · Ba(ClO ₄) ₂	9 ⋅ NaClO ₄
Molecular formula	C ₁₆ H ₂₇ BaCl ₂ N ₂ O _{11.5}	C ₁₄ H ₂₁ BaCl ₂ NO ₁₂	C ₁₈ H ₂₇ BaCl ₂ NO ₁₄	C ₁₇ H ₂₆ ClN ₂ NaO ₈
M/g mol ⁻¹	639.64	603.56	689.65	444.84
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	$P2_1/c$
a/Å	10.0303(8)	11.9951(7)	20.6668(7)	9.4634(8)
b/Å	10.3858(8)	14.0697(8)	10.8212(4)	25.232(2)
c/Å	23.6537(19)	15.3256(8)	22.9762(9)	9.3834(9)
α/deg	82.597(4)	115.317(2)	90	90
β/deg	79.106(4)	92.818(2)	107.8800(10)	112.588(3)
γ/deg	71.101(4)	113.811(2)	90	90
$V/Å^3$	2283.1(3)	2060.7(2)	4890.2(3)	2068.7(3)
Ζ	4	4	8	4
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.861	1.945	1.873	1.428
<i>F</i> (000)	1276	1192	2752	936
μ (Mo-K α)/mm ⁻¹	2.036	2.250	1.915	0.252
Crystal dimensions/mm	$0.12 \times 0.08 \times 0.06$	0.28×0.26×0.12	$0.50 \times 0.40 \times 0.04$	$0.46 \times 0.28 \times 0.08$
θ Scan mode/range, deg	ω/2.08-28.00	ω/1.93-28.00	$\omega/2.39 - 28.00$	ω/2.84-29.00
Ranges of indices of	$-13 \le h \le 13,$	$-15 \le h \le 15,$	$-27 \le h \le 27,$	$-12 \le h \le 8,$
measured reflections	$-13 \le k \le 13,$	$-18 \le k \le 18,$	$-13 \le k \le 14,$	$-34 \le k \le 33,$
	$-31 \le l \le 31$	$-20 \le l \le 20$	$-29 \le l \le 27$	$-12 \le l \le 12$
Number of measured reflections	27045	14184	27392	11920
Number of independent	10655	9243	11578	5355
reflections	$(R_{\rm int} = 0.0466)$	$(R_{\rm int} = 0.0218)$	$(R_{\rm int} = 0.0523)$	$(R_{\rm int} = 0.0755)$
Number of reflections with $I > 2\sigma(I)$	8295	7781	8100	2841
Number of refined parameters	802	672	649	367
<i>R</i> factors based on	$R_1 = 0.0429$.	$R_1 = 0.0332$.	$R_1 = 0.0392.$	$R_1 = 0.0660$.
reflections with $I > 2\sigma(I)$	$wR_2 = 0.1117$	$wR_2 = 0.0973$	$wR_2 = 0.0845$	$wR_2 = 0.1216$
based on all reflections	$R_1 = 0.0559$,	$R_1 = 0.0386$,	$R_1 = 0.0707$	$R_1 = 0.1457$,
	$wR_2 = 0.1203$	$wR_2 = 0.1009$	$wR_2 = 0.0922$	$wR_2 = 0.1421$
Goodness-of-fit on F^2	1.048	1.104	0.957	0.930
$\frac{\text{Residual electron density}}{(\text{min/max})/\text{e}\cdot\text{\AA}^{-3}}$	-2.003/2.180	-0.945/1.888	-1.429/2.476	-0.381/0.522

Table 8. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for the crystals of $5b \cdot Ba(ClO_4)_2 \cdot 0.5H_2O$, $6a \cdot Ba(ClO_4)_2$, $6d \cdot Ba(ClO_4)_2$, and $9 \cdot NaClO_4$

comparison with the corresponding parameters of the other free benzoazacrown ethers and the discussion of conformational changes caused by the formation of the complex with $Ba(CIO_4)_2$.

All calculations were carried out with the use of the SHELXTL-Plus program package.³⁰ The crystallographic characteristics and the X-ray diffraction data collection and refinement statistics are given in Tables 5–8. The atomic coordinates and other experimental data were deposited with the Cambridge Crystallographic Data Centre;* the CCDC numbers 671441 (4a), 671443 (4c), 671445 (5a), 671447 (5c), 671449 (6a), 671450 (6b), 671451 (6c), 671453 (7a \cdot H₂O), 671454 (8), 671442 (4b \cdot Ba(ClO₄)₂), 671444 (4d \cdot Ba(ClO₄)₂), 671445 (5b \cdot Ba(ClO₄)₂, 0.5H₂O), 671448 (6a \cdot Ba(ClO₄)₂), 671452 (6d \cdot Ba(ClO₄)₂), 683509 (7b \cdot Ba(ClO₄)₂), and 671455 (9 \cdot NaClO₄).

¹H NMR titration. In the experiments, MeCN-d₃ was used as the solvent (the water content <0.05%, FGUP RNTs Prikladnaya khimiya, St. Petersburg). The compositions and the stability constants of the complexes of benzoazacrown ethers with the salts $M^{m^+}(ClO_4^-)_m$ were determined by analyzing the changes in the positions of the signals for protons of the ligands (L) depending on the concentration of the salt in the case of direct titration or the concentration of the competitive ligands (L^c) in the case of competitive titration. In the case of direct titration, the concentration of the salts was varied from 0 to 0.015-0.08 mol L⁻¹, the total concentration of L being unchanged (~ $5 \cdot 10^{-3}$ mol L⁻¹). In the case of competitive titration, the concentrations of L and the salts remained unchanged $(\sim 5 \cdot 10^{-3} \text{ and } 6 \cdot 10^{-3} \text{ mol } L^{-1}$, respectively), and the concentration of L^c was varied from 0 to 0.03-0.1 mol L⁻¹. The crown ethers, whose signals in the spectrum overlap with the signals of L only slightly and for which the stability constants of the corresponding complexes with these ligands were determined, were used as L^c. The ligands L^c are given in Tables 3 and 4. The $\Delta\delta_{H}$

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values were measured with an accuracy of 0.001 ppm. The stability constants of the complexes were calculated with the use of the HYPNMR program. 31

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