Russian Chemical Bulletin, International Edition, Vol. 53, No. 7, pp. 1417—1427, July, 2004

New methodology for the synthesis of benzoazacrown ethers by transformation of the macrocycle of benzocrown ethers*

S. P. Gromov,*[*] *S. N. Dmitrieva, A. I. Vedernikov, and M. V. Churakova

Photochemistry Center, Russian Academy of Sciences,
7A ul. Novatorov, 119421 Moscow, Russian Federation.
Fax: +7 (095) 936 1255. E-mail: gromov@photonics.ru

The review summarizes the results of studies aimed at constructing new promising macrocyclic ligands that bind metal and ammonium ions. A new approach to the synthesis of formyl and nitro derivatives of 1-aza-2,3-benzocrown ethers possessing considerable synthetic potential is described. The review presents a radically new methodology for the synthesis of such benzoazacrown ethers based on stepwise transformations of the macrocycle of readily accessible benzocrown ethers. The main structural factors and necessary conditions enabling stepwise transformations of the macrocycle of crown ethers into azacrown ethers were revealed. For the first time, the ability of *N*-methylbenzoazacrown ethers to form complexes was found, which is much superior to that of widely used *N*-phenylazacrown ethers and benzocrown ethers with the same size of the macrocycle.

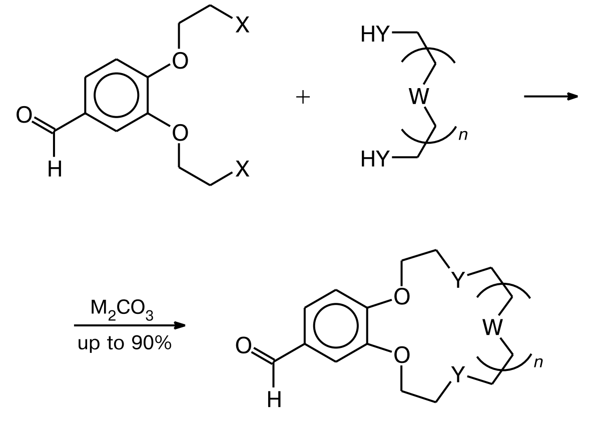
Key words: crown ethers, benzocrown ethers, ring opening, podands, ring closure, benzoazacrown ethers.

Introduction

The ability of crown ethers to form stable complexes with metal ions, organic cations, and neutral polar molecules is their the most important property. This forms the basis for the use of crown ethers as selective ligands coordinated to metal cations, including their use for extraction,[1,2] in ion-selective electrodes,[3] photosensitive systems,[4—9] *etc.*

In organic chemistry of macroheterocyclic compounds, the main attention is being given to the construction of the macrocycle of crown ethers.[10—12] The main approach is based on the synthesis of macrocyclic compounds from two fragments (the so-called 1 + 1 condensation). Earlier, this method, *viz.*, condensation of the corresponding benzaldehyde derivatives with dithiols or diamines in the presence or absence of alkali metal carbonates, has been used[13—15] for the preparation of formyl derivatives of benzothiacrown and benzodiazacrown ethers (Scheme 1). Other methods for the synthesis of macroheterocyclic compounds were studied to a much lesser extent.

Scheme 1



1—4

X = Cl, I; M = Li, Na, K, Cs

n = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**)

	1a—d	**2c**	**3c**	**4b,c**
Y	S	S	NH	NMe
W	O	S	O	O

Benzocrown ethers can also be synthesized by introduction of substituents into the benzene ring[16—18] or their modifications[19] as well as by alkylation of nitrogen atoms of the macroheterocycle.[15] For example, formylbenzocrown ethers **1**, **4**, and **5** (Scheme 2) were synthesized by metallation of the corresponding bromo derivatives with *n*-butyllithium followed by the reaction of the organolithium derivatives that formed with DMF.[16—18]

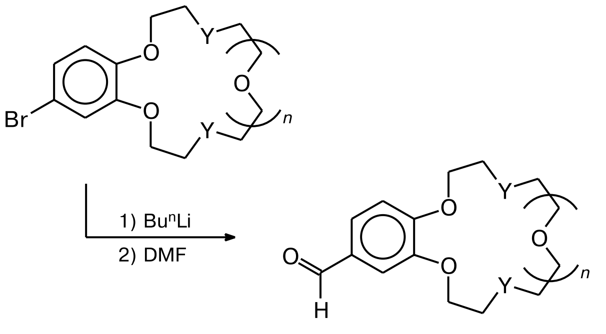
---

[*] Materials were presented at the Russian-French Symposium "Supramolecular Systems in Chemistry and Biology" (Kazan, September 22—25, 2003).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1362—1372, July, 2004.

1066-5285/04/5307-1417 © 2004 Springer Science+Business Media, Inc.

Scheme 2



1, **4**, **5**

5b,c: Y = O; *n* = 1 (**b**), 2 (**c**)

From the viewpoint of the use of crown-ether fragments as components of photosensitive ligands, crown ethers in which the nitrogen atom is conjugated with a chromophore are of particular interest. Such azacrown ethers are characterized by much longer-wavelength absorption than crown ether derivatives, which is of particular importance in photometric and fluorescence analysis, for photocontrolled extraction and membrane ion transport, and in the construction of photosensitive molecular devices. Presently, *N*-phenylazacrown ether derivatives are most widely used for these purposes (see, for example, Refs. 20—29). However, a substantial drawback of these compounds is that they have low constants of complex formation with metal ions.

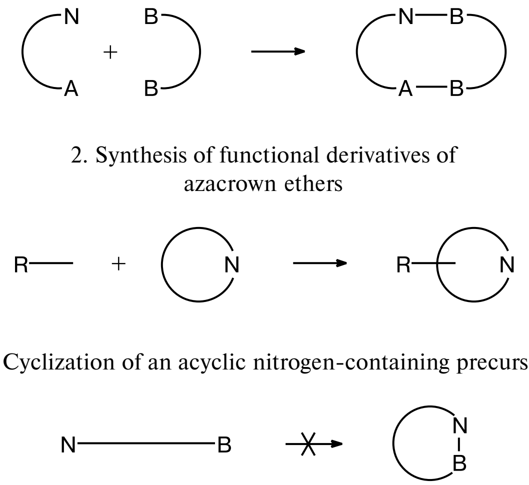
In this respect, benzoannelated derivatives of azacrown ethers may have essential advantages. However, 1-aza-2,3-benzocrown ether derivatives belong to a poorly studied type of crown ethers. Although they are structurally simple, functional derivatives of these compounds are practically inaccessible.

Examples of the synthesis of 1-aza-2,3-benzocrown ethers are scarce. These compounds were prepared mainly by condensation of two acyclic fragments (Scheme 3), their yields generally being lower than 10—20%.[30—33] Some functional derivatives of benzoazacrown ethers were also synthesized by acylation of the nitrogen atom in the macrocycle and by electrophilic substitution in the benzene ring.[31,33] No methods for the synthesis of benzoazacrown ethers by cyclization of the appropriate acyclic precursors were documented because the starting compounds are practically inaccessible.

Formyl and nitro derivatives of benzoazacrown ethers are of especial interest for the application in the synthesis of photosensitive compounds. However, their synthesis has not been described in the literature.

It is known that various derivatives of heterocycles that are accessible with difficulty can be prepared from more readily accessible precursors by ring transformations. These methods are based on the ring opening and the use of the acyclic compounds that formed in the synthesis of new heterocycles.[34—37]

Scheme 3


1. Construction of azacrown ethers from two fragments

2. Synthesis of functional derivatives of azacrown ethers

3. Cyclization of an acyclic nitrogen-containing precursor

We were the first to extend this methodology to nitrogen-containing macroheterocyclic compounds.[38,39] In this case, the general scheme for the synthesis is as follows (Scheme 4): under the action of N-nucleophiles, the starting crown ethers afford nitrogen-containing acyclic intermediates, which further cyclize to form the target azacrown ethers. This scheme is applicable to the synthesis of benzoazacrown ethers starting from benzocrown ether derivatives containing electron-withdrawing substituents, which activate the macrocycle opening in benzocrown ethers under the action of amines. The nitrogen-containing podands* thus prepared can be transformed into the target benzoazacrown ethers after the replacement of the hydroxy group with better leaving groups.

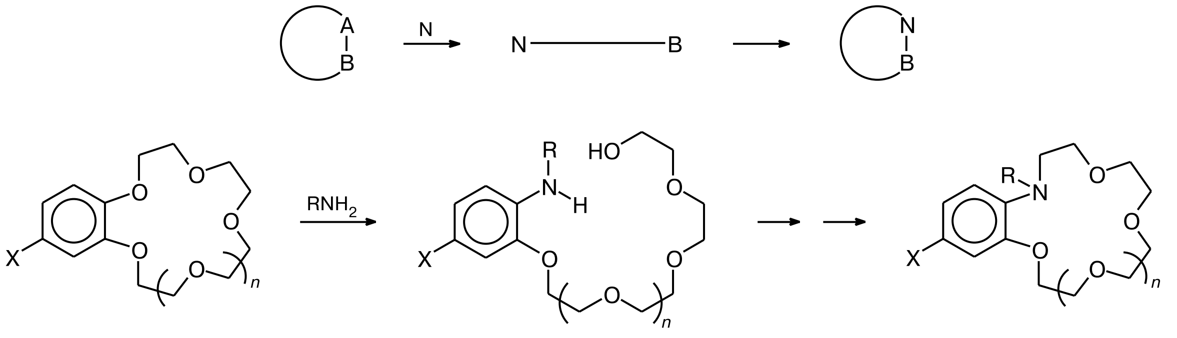
Synthesis of formyl derivatives of benzoazacrown ethers

The development of methods for the synthesis of formyl derivatives of benzoazacrown ethers, which are most valuable for the preparation of photosensitive crown ethers, was begun from the studies of aminolysis of readily accessible formyl derivatives of benzocrown ethers containing different combinations of oxygen, sulfur, and nitrogen atoms in the macrocycle. Opening of the macrocycle in compounds **1**, **5**, and **6** can be performed by heating these compounds with a mixture of an aliphatic amine and alkylammonium chloride (Scheme 5).[40,41] Nitrogen-containing podands **7—11** were synthesized according to this method in yields up to 96%. Apparently,

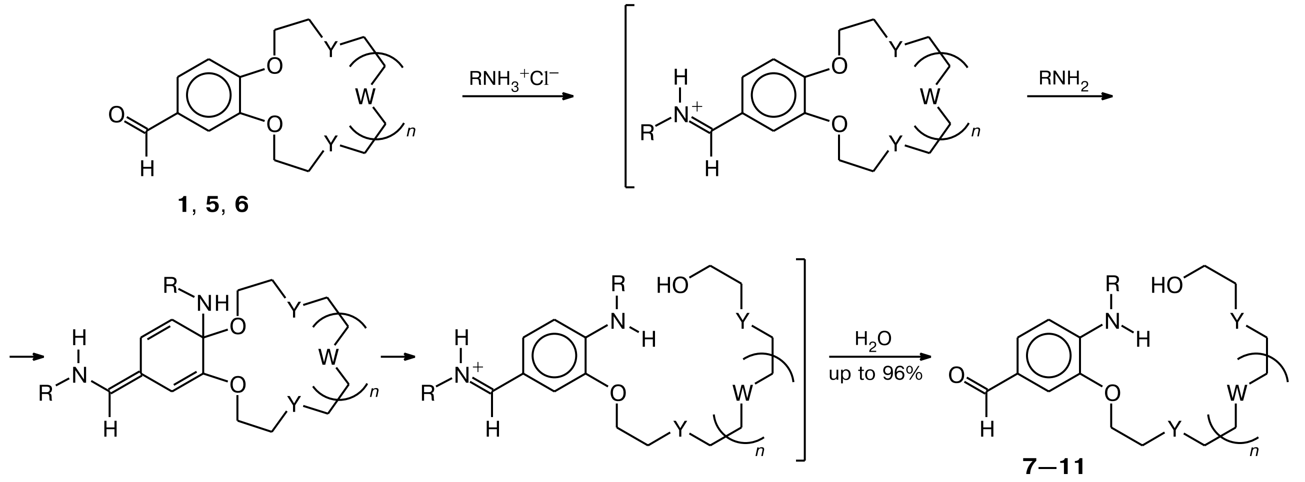
---

* Podands are open-chain analogs of crown ethers.

Scheme 4



Scheme 5



	6b	**7a—c**	**8b**	**9b**	**10b,c**	**11b**
Y	O	O	O	O	S	O
W	NMe	O	O	O	O	NMe
R	—	Me	Et	Pr^n	Me	Me

n = 0 (**a**), 1 (**b**), 2 (**c**)

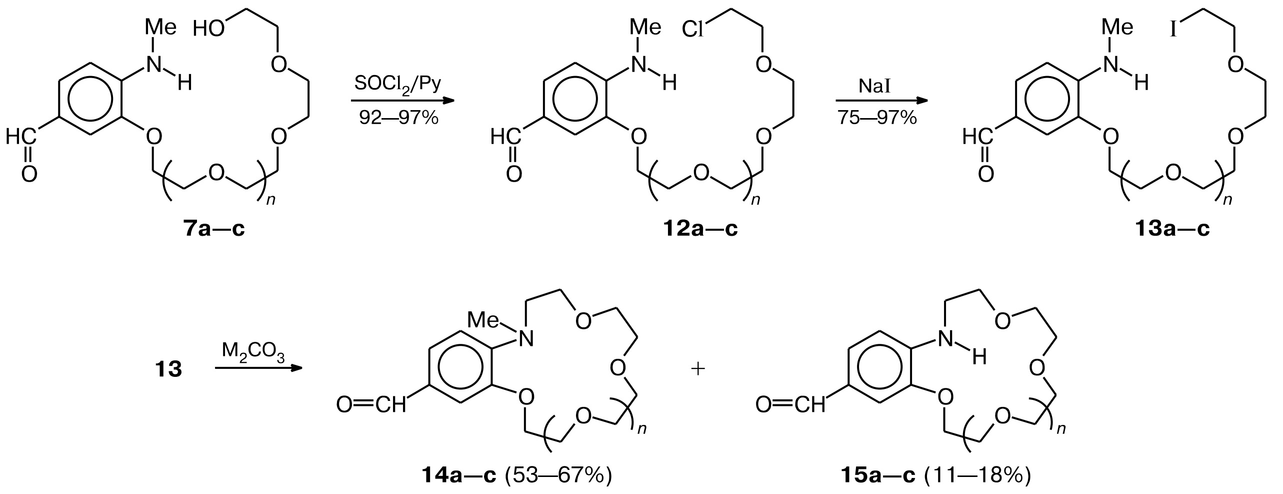
the reaction proceeds *via* an intermediate iminium salt. The efficiency of this reaction is influenced by the template effect of the alkylammonium salt used.

Cyclization of the nitrogen-containing podands requires the replacement of the hydroxy group with better leaving groups, for example, with the Cl and I atoms (Scheme 6).[42,43] Cyclization of iodo derivatives **13** was studied in the absence of bases as well as under the action of weak bases.[43] In the presence of a weak base, the reactions afford azacrown ethers, with *N*-methyl derivative **14** substantially predominating (see Scheme 6). In the absence of a base, the reactions produce predominantly or even exclusively the *N*-demethylated derivative of benzoazacrown ether **15**. The drawback of this method of cyclization is that the reaction requires a long period of time (the reaction is not completed even in 150 h).

The use of strong bases, such as sodium hydride (Scheme 7), and the iodine atom as a leaving group made it possible to complete this reaction in 30 min and prepare *N*-methyl derivatives of benzoazacrown ethers **14** in high yields.[44]

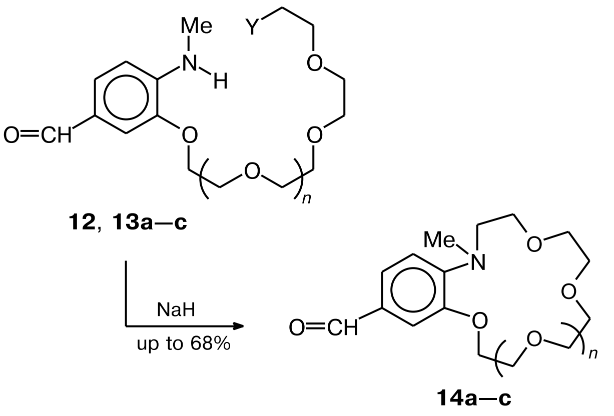
These results led us to the conclusion that the reaction can proceed by two mechanisms depending on the conditions used.[43] In the absence of strong bases, the reaction occurs apparently *via* an intermediate macrocyclic cation (path *a*), which is transformed into *N*-demethylated benzoazacrown ether **15** or *N*-methyl derivative **14** upon elimination of the methyl group or proton abstraction, respectively (Scheme 8). The reaction in the presence of a strong base produces presumably the reactive arylamide anion (path *b*), which rapidly and readily undergoes cyclization to the final product.

Scheme 6



n = 0 (**a**), 1 (**b**), 2 (**c**); M = Li, Na, K, Rb, Cs

Scheme 7



Y = Cl, I; *n* = 0 (**a**), 1 (**b**), 2 (**c**)

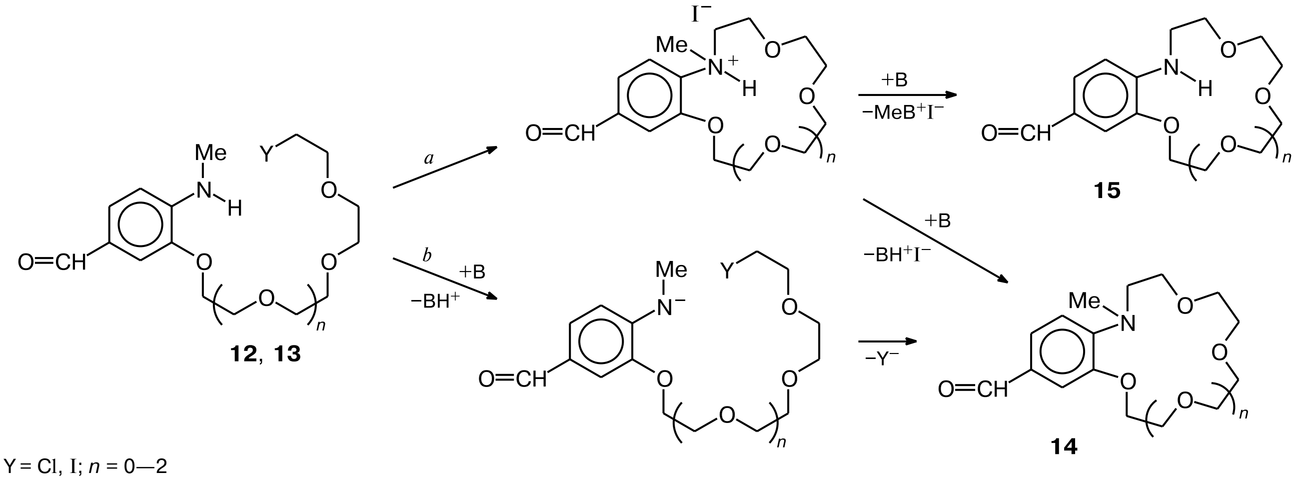
The proposed mechanism of this reaction is supported by the fact that refluxing of the starting *N*-methyl derivative **14c** with dilute acetic acid afforded *N*-demethylated product **15c** (Scheme 9).[43]

Synthesis of nitro derivatives of benzoazacrown ethers

When developing a procedure for the synthesis of nitro derivatives of benzoazacrown ethers, we used accessible nitro derivatives of benzocrown ethers **16** as the starting compounds. Under the action of methylamine, these compounds underwent opening of the macrocycle to form nitrogen-containing podands **17** in nearly quantitative yields (Scheme 10).[45]

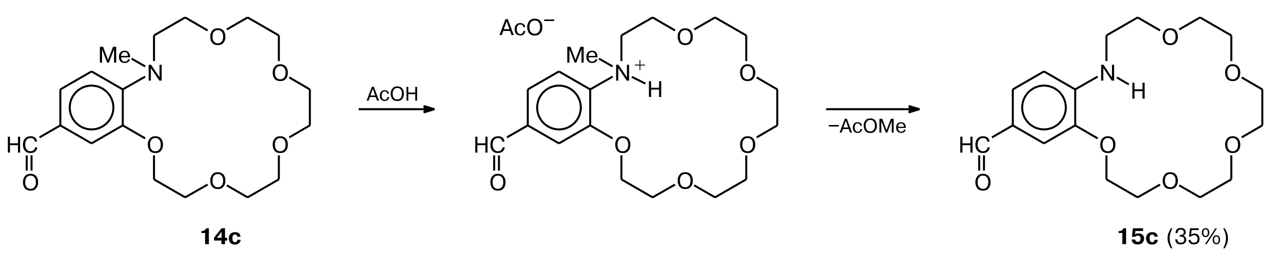
It was found that the efficiency of the macrocycle opening in the reactions with aliphatic amines depends

Scheme 8

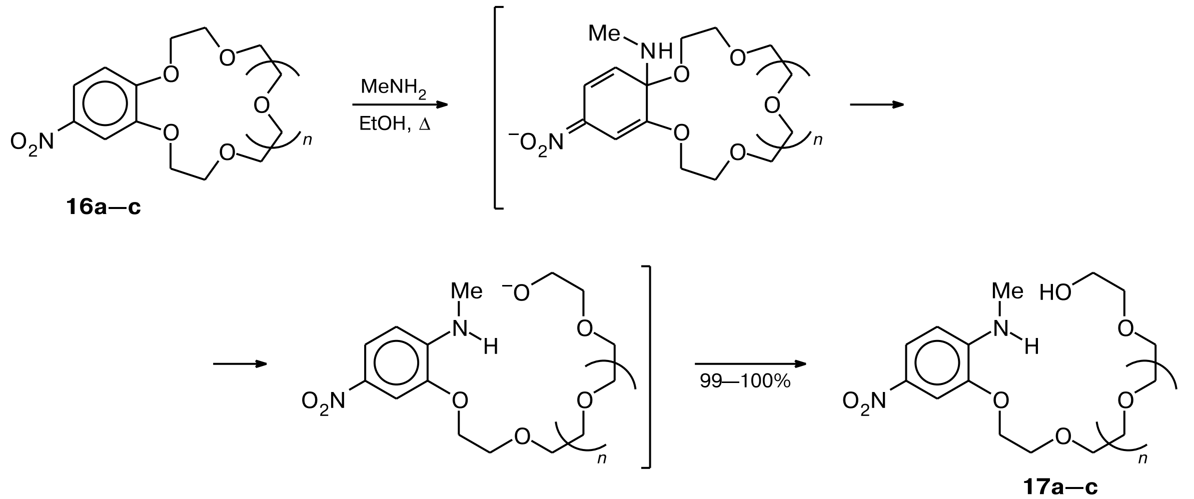


Y = Cl, I; *n* = 0—2

Scheme 9

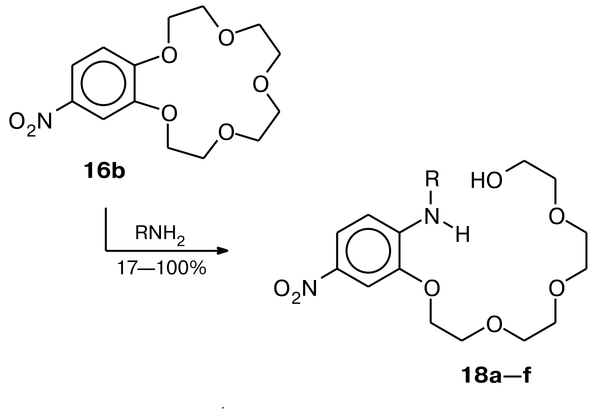


Scheme 10



$n = 0$ (**a**), 1 (**b**), 2 (**c**)

Scheme 11

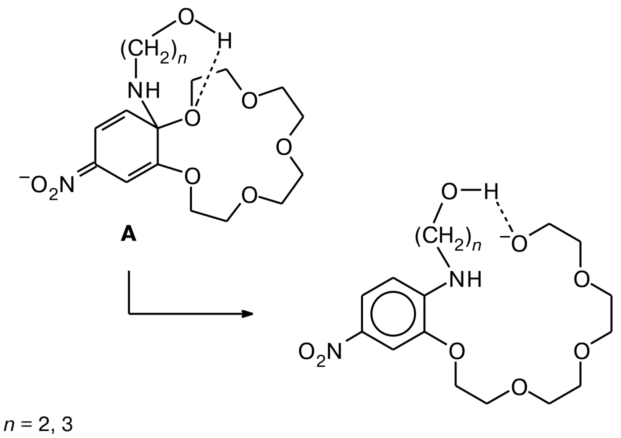


18: R = Et (**a**), $\mathrm{Pr^n}$ (**b**), $\mathrm{Pr^i}$ (**c**), CH_2Ph (**d**), $(CH_2)_2OH$ (**e**), $(CH_2)_3OH$ (**f**)

on the length of the alkyl fragment, the degree of its branching, and the nature of substituents in the amine.[46] For example, the use of alkylamines RNH_2 other than methylamine leads to a gradual decrease in the conversion of nitrobenzo-15-crown-5 ether **16b** into podands **18** as the length of the alkyl fragments and the degree of their branching increase: from 97% for **18a** to 19% for **18c** (Scheme 11). Attempts to prepare the corresponding podand using *tert*-butylamine failed.

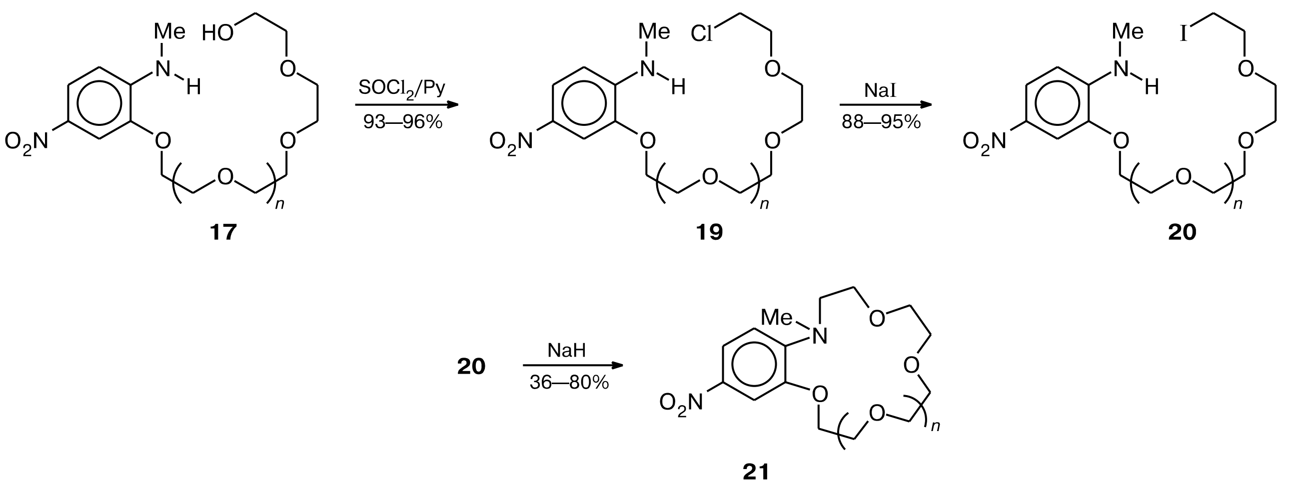
Nitrogen-containing podands **18e** and **18f** bearing the terminal hydroxy group were synthesized in virtually quantitative yields. Apparently, this is associated with the for-

Scheme 12



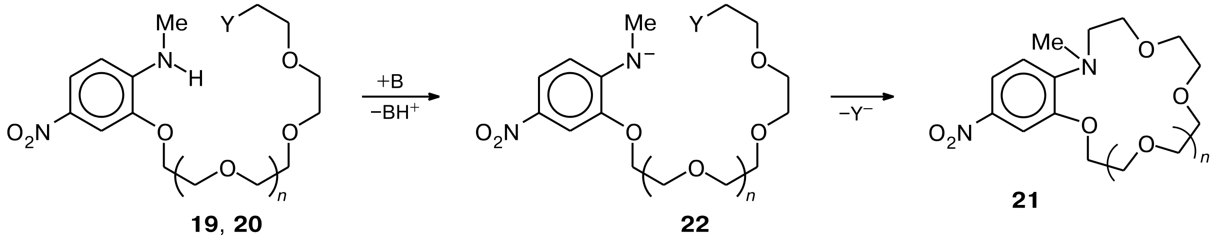
$n = 2, 3$

Scheme 13



$n = 0—2$

Scheme 14



Y = Cl, I; $n = 0—2$

mation of an intramolecular hydrogen bond in the intermediate σ-complex **A** (Scheme 12), which substantially facilitates the macrocycle opening.

By analogy with the synthesis of the related formyl derivatives,[47] azapodands **17** were transformed into halogeno derivatives **19** and **20** by replacement of the hydroxy group successively with the better leaving chlorine and iodine atoms (Scheme 13). Cyclization of the latter under the action of sodium hydride for 0.5—2 h gave the target benzoazacrown ethers **21**.[48,49]

Such a short time of cyclization suggests that deprotonation of compounds **19** and **20** with strong bases occurs apparently *via* intermediate reactive arylamide anion **22**, which is prone to intramolecular cyclization (Scheme 14).

Structures and complex formation of benzoazacrown ethers

Study of compounds **14** and **15** by NMR spectroscopy demonstrated that the NOE spectra of *N*-methyl derivatives **14** show an intense cross-peak, which corresponds to the interaction of the methyl group with the proton in the *ortho* position with respect to the amino group (Fig. 1)

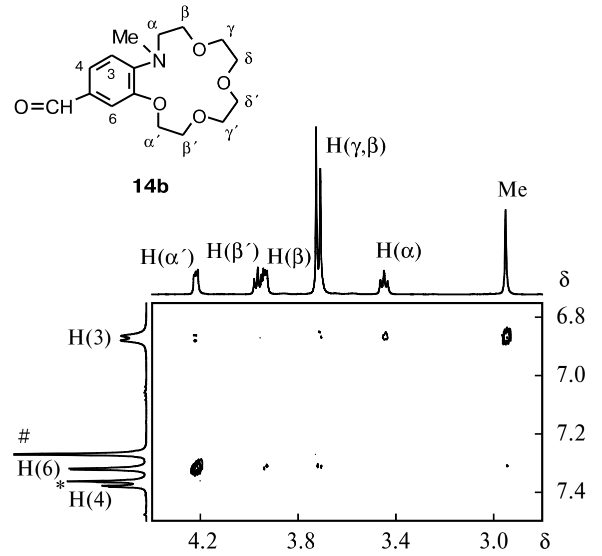


Fig. 1. The NOE spectrum of formyl-*N*-methylbenzoaza-15-crown-5 **14b**.

and is indicative of their spatial proximity. In addition, the signal for this proton in the ^{1}H NMR spectrum is substantially shifted downfield compared to its position in the spectra of the starting azapodands **7**. This is evidence that the conjugation between the donor nitrogen atom and the benzene ring is disturbed and, correspondingly, the substituents at the nitrogen atom deviate from the plane of the benzene ring. In contrast, it is the protons of the N-CH$_2$ group and the hydrogen atom in the *ortho* position with respect to the amino group in N-demethylated derivatives **15** that are in proximity. Presumably, the hydrogen atom bound to the nitrogen atom in the latter compounds is directed inwards.

These observations were confirmed by the results of X-ray diffraction study, which demonstrated that the N-CH$_2$ and N-CH$_3$ groups in N-methyl derivative **14a** form angles of about 40 and 10°, respectively, with the plane of the benzene ring (Fig. 2),**[43]** and the conjugation between the nitrogen atom and the benzene ring is substantially disturbed. As a result, the lone electron pair of the nitrogen atom can be efficiently donated for the formation of the coordination bond with the metal cation. In the case of N-demethylated derivative **15c**, the hydrogen atom at the nitrogen atom is directed strictly inwards.**[43]** Presumably, this arrangement of the hydrogen atom prevents the complex formation with metal cations.

According to the results of X-ray diffraction study of nitro derivative **21b** (Fig. 3, *a*),**[49]** the angles of inclination of the N-CH$_3$ and N-CH$_2$ groups with respect to the plane of the benzene ring are virtually identical to those observed in the corresponding formyl derivative. Hence, the nitrogen atom in **21** is as accessible to the complex

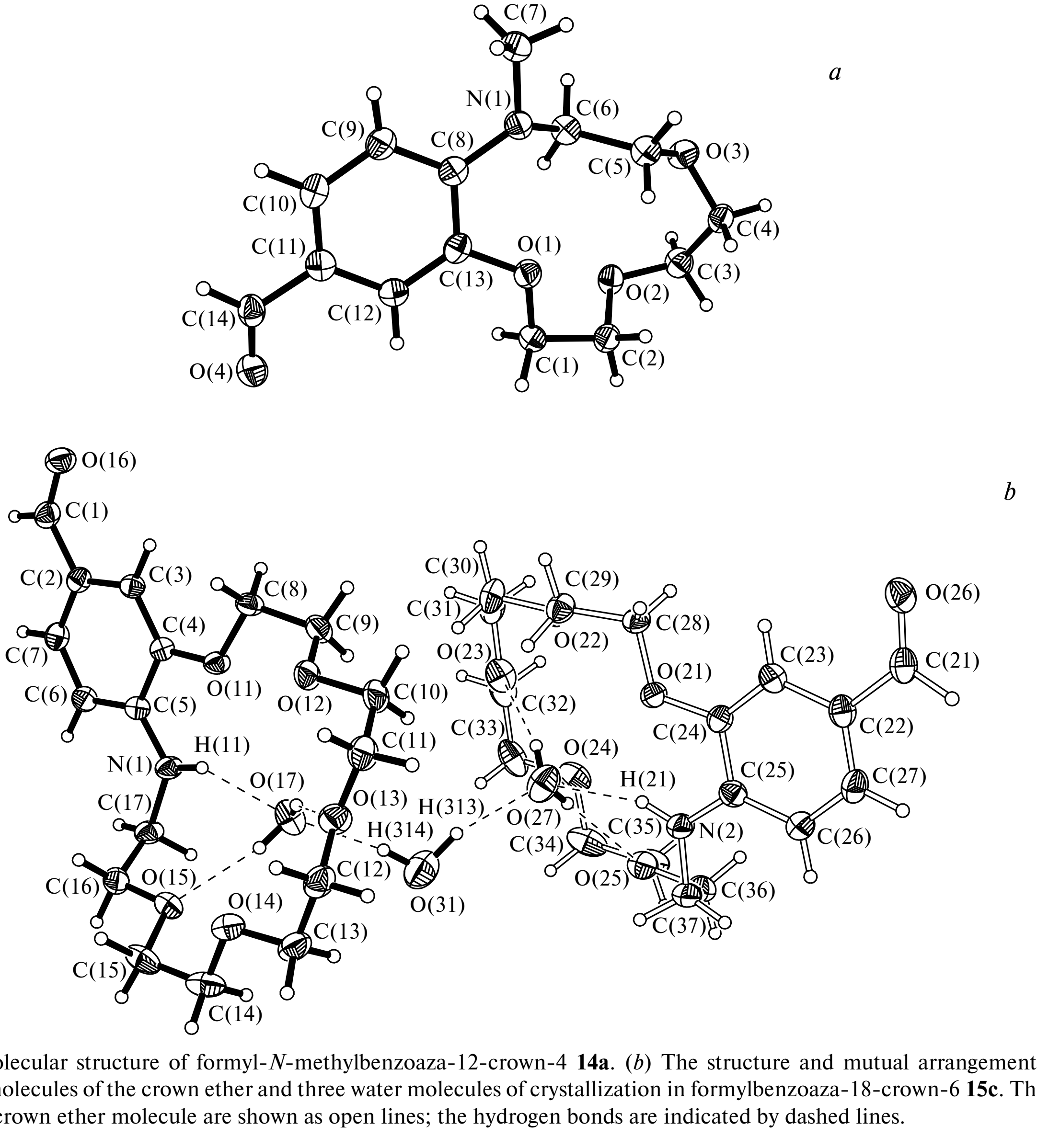


Fig. 2. (*a*) Molecular structure of formyl-N-methylbenzoaza-12-crown-4 **14a**. (*b*) The structure and mutual arrangement of two independent molecules of the crown ether and three water molecules of crystallization in formylbenzoaza-18-crown-6 **15c**. The bonds in the second crown ether molecule are shown as open lines; the hydrogen bonds are indicated by dashed lines.

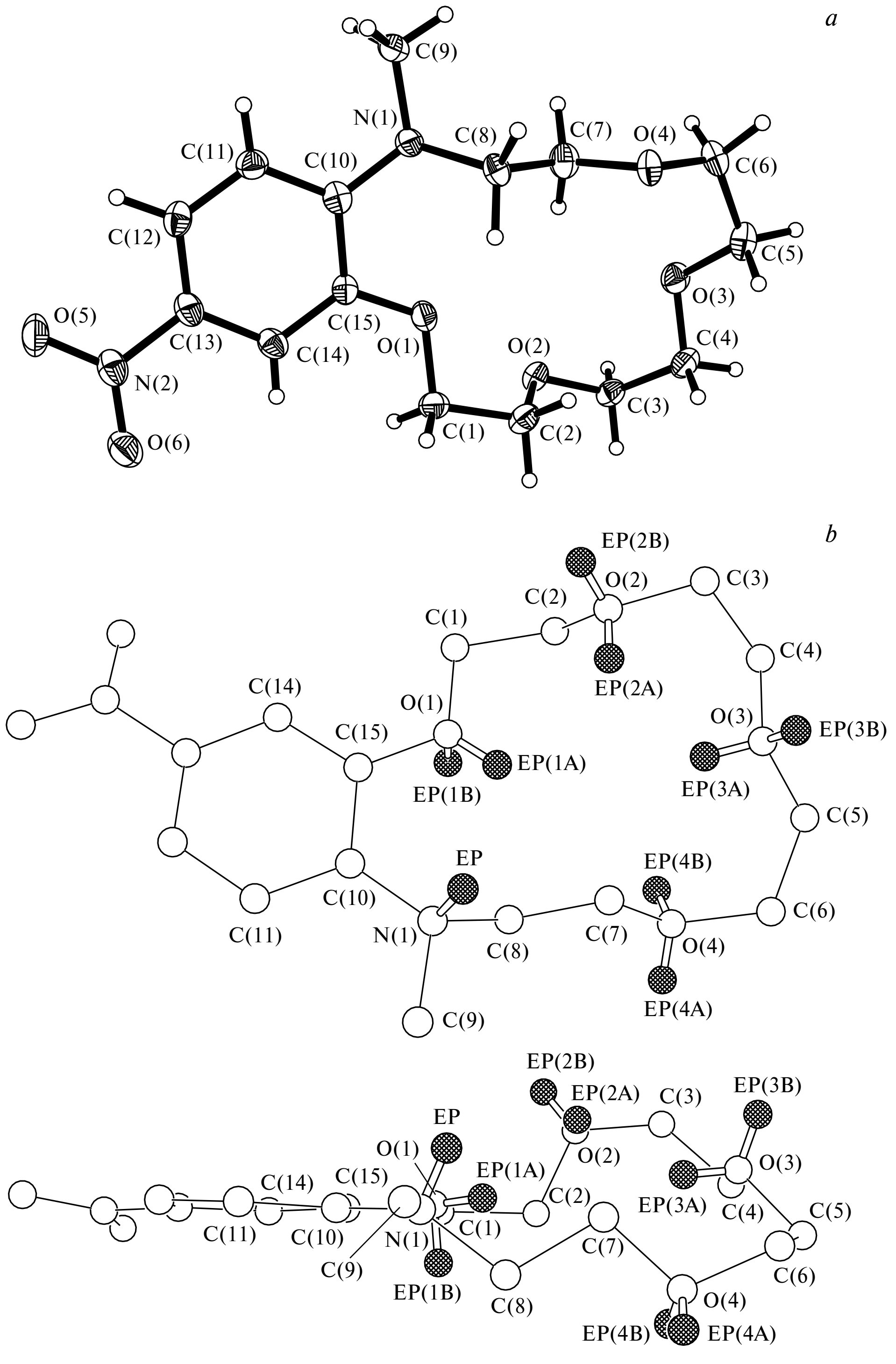


Fig. 3. (*a*) Molecular structure of nitro-*N*-methylbenzoaza-15-crown-5 **21b**. (*b*) The orientation of the lone electron pairs (LEP) of the heteroatoms of the macrocycle; frontal and side views (LEPs are labeled EP with a number corresponding to the oxygen atom number).

formation with metal cations as that in formyl derivatives **14**. Based on the results of X-ray diffraction study, the spatial arrangement of the lone electron pairs of the nitrogen atom and the oxygen atoms, which can be involved in complex formation, was found by calculation methods (Fig. 3, *b*). It appeared that these lone pairs are oriented predominantly toward the center, which is located above the mean plane of the macrocycle. There-

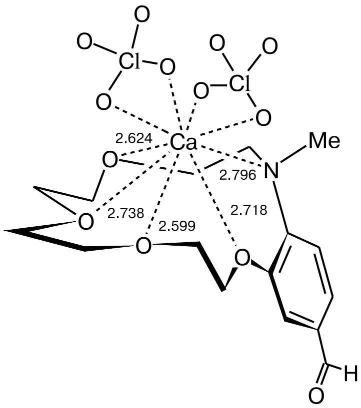


Fig. 4. Structure of the complex of formyl-*N*-methylbenzoaza-15-crown-5 **14b** with $Ca(ClO_4)_2$ calculated by the DFT/PBE method.

fore, it can be hypothesized that benzoazacrown ethers **14** and **21** are preorganized to form partially inclusion complexes with metal cations.

Quantum-chemical study of the complex formation of formylbenzoazacrown ethers with calcium perchlorate demonstrated that the calcium cation and the counterions in the complex of *N*-methyl derivative **14b** are actually located above the plane of the macrocycle (Fig. 4).[50]

The stability constants of the complexes with the Ca^{2+} ion were calculated for a series of compounds using ^1H NMR titration and the HYPNMR program[51] (Table 1). Based on the dependence of the change in the chemical shifts of the protons of the ligands on the amount of $Ca(ClO_4)_2$ used, it was established that 1 : 1 complexes are formed in all cases

$$\mathrm{L} + \mathrm{Ca}^{2+} \xrightleftharpoons{K_1} (\mathrm{L\cdot Ca})^{2+},$$

where L is crown ether and K_1 (M^{-1}) is the stability constant of the 1 : 1 complex. In the case of **14b**, 2 : 1 complexes are also produced

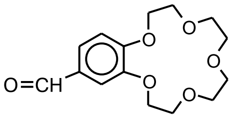
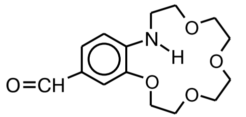
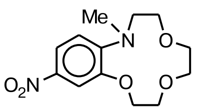
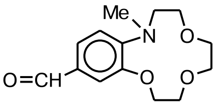
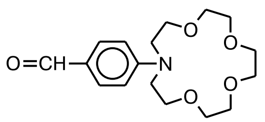
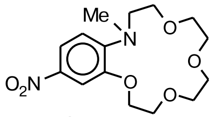
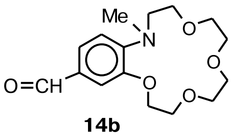
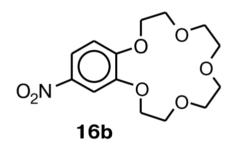
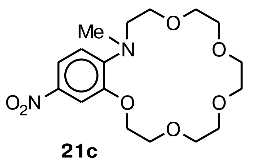
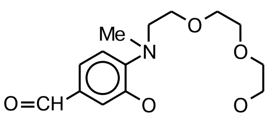
$$(\mathrm{L\cdot Ca})^{2+} + \mathrm{L} \xrightleftharpoons{K_2} (\mathrm{L_2\cdot Ca})^{2+},$$

where K_2 (M^{-1}) is the stability constant of the 2 : 1 complex.

As expected, the smallest stability constant was found for the complex of demethylated derivative of benzoazacrown ether **15b** and the largest stability constant (in the series of compounds with the same size of the macrocycle) was observed for *N*-methyl derivative **14b**. The latter constant is substantially higher than those of the corresponding complexes of *N*-phenylazacrown ether derivative (by a factor of 250) and benzocrown ether **5b** (by a factor of 10).[50]

The replacement of the formyl group in the benzene ring with the nitro group leads to a substantial decrease in the stability constant in the series of nitro derivatives **21**

Table 1. Stability constants of the complexes of formylcrown ethers (**5b**, **14a—c**, and **15b**) and nitrobenzocrown ethers (**16b** and **21a—c**) with $Ca(ClO_4)_2$*

Ligand	$\log K_1$ ($\log K_2$)	Ligand	$\log K_1$ (olgK_2)	Ligand	$\log K_1$ ($\log K_2$)
 **5b**	3.8	 **15b**	2.0	 **21a**	1.1
 **14a**	2.1		2.4	 **21b**	3.3 (2.5)
 **14b**	4.8 (2.3)	 **16b**	2.9	 **21c**	5.8
 **14c**	6.8				

---

* Data from ^1H NMR titration in CD_3CN at 30 °C.

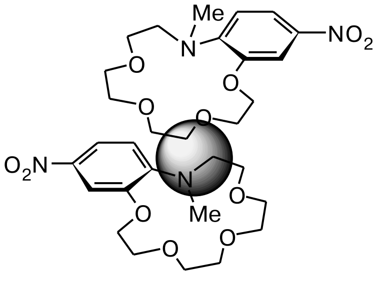
Table 2. Stability constants of the complexes of nitrobenzoaza-15-crown-5 **21b** with metal and ammonium perchlorates*

Cation	logK_1	logK_2	Cation	logK_1	logK_2
Li^+	3.1	2.7	Mg^{2+}	3.2	—
Na^+	2.7	—	Ca^{2+}	3.3	2.5
K^+	1.9	—	Ba^{2+}	4.2	1.6
NH_4^+	1.7	—			

* Data from ^1H NMR titration in CD_3CN at 30 °C.

(see Table 1). However, the higher ability of benzoazacrown ether **21b** to form complexes compared to benzocrown ether **16b** is retained.

A more detailed study of the complex formation of **21b** with alkali metal cations, alkaline-earth metal cations, and ammonium ions demonstrated (see Table 2) that the 2 : 1 complexes are formed with calcium, barium, and lithium cations. The tendency to form 2 : 1 complexes is apparently associated with preorganization of the macrocycle to yield partially inclusion complexes. In the case of ions with large ionic radii, this gives rise to sandwich complexes of type **23**.

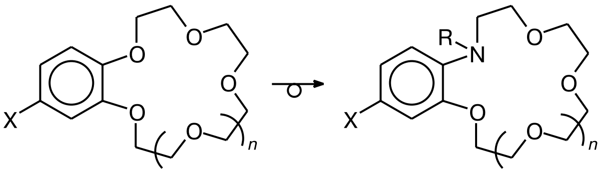


23

Conclusions

To summarize, the results presented in this review demonstrate that considerable advances were made in the chemistry of benzocrown ethers in recent years. In particular, progress was achieved in the development of fundamentals and methodology of a new approach to the synthesis of benzoazacrown ethers **24** based on stepwise transformations of the macrocycle of accessible benzocrown ethers (Scheme 15).

Scheme 15



24

The most valuable property of *N*-methyl derivatives of benzoazacrown ethers **24** (R = Me) is that the stability constants of their complexes with metal cations are much higher than the corresponding constants of the complexes of *N*-phenylazacrown ethers and even benzocrown ethers.

The formyl and nitro derivatives of benzoazacrown ethers **24** (X = CHO, NO_2) are of most interest from the synthetic standpoint. These derivatives can be transformed into compounds containing benzoazacrown ether fragments according to known methods. These can be used as selective ligands for metal cations, for extraction of metal ions from water, membrane ion transport, in ion-selective electrodes, ion-selective dyes, fluoroionophores, and as components of polymeric and Langmuir—Blodgett films.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 03-03-32177 and 03-03-32929), the Ministry of Science and Technology of the Russian Federation, the Presidium of the Russian Academy of Sciences, the Foundation for Support of National Science, and the INTAS (Grant 2001-0267).

References

1. A. T. Yordanov and D. M. Roundhill, *Coord. Chem. Rev.*, 1998, **170**, 93.
2. K. Gloe, H. Graubaum, M. Wust, T. Rambusch, and W. Seichter, *Coord. Chem. Rev.*, 2001, **222**, 103.
3. P. Buhlmann, E. Pretsch, and E. Bakker, *Chem. Rev.*, 1998, **98**, 1593.
4. A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
5. M. V. Alfimov and S. P. Gromov, in *Applied Fluorescence in Chemistry, Biology, and Medicine*, Eds W. Rettig, B. Strehmel, S. Schrader, and H. Seifert, Springer-Verlag, Berlin, 1999, 161.
6. B. Valeur and I. Leray, *Coord. Chem. Rev.*, 2000, **205**, 3.
7. S. Shinkai, in *Comprehensive Supramolecular Chemistry*, Ed. G. W. Gokel, Pergamon, Oxford, 1996, **1**, 671.
8. S. P. Gromov and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 641 [*Russ. Chem. Bull.*, 1997, **46**, 611 (Engl. Transl.)].
9. A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, and G. B. Behera, *Chem. Rev.*, 2000, **100**, 1973.
10. *Host Guest Complex Chemistry Macrocycles. Synthesis, Structures, Applications*, Eds F. Vogtle and E. Weber, Springer-Verlag, Berlin, 1985, Ch. 1.
11. K. B. Yatsimirskii, A. G. Kol´chinskii, V. V. Polishchuk, and G. G. Talanova, *Sintez makrotsiklicheskikh soedinenii* [*Synthesis of Macrocyclic Compounds*], Naukova Dumka, Kiev, 1987, p. 279 (in Russian).
12. A. A. Formanovskii, in *Makrotsiklicheskie soedineniya v analiticheskoi khimii* [*Macrocyclic Compounds in Analytical Chemistry*], Eds Yu. A. Zolotov and N. M. Kuz´min, Nauka, Moscow, 1993, Ch. 1 (in Russian).

13. O. A. Fedorova, A. I. Vedernikov, O. V. Eshcheulova, P. V. Tsapenko, Yu. V. Pershina, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1881 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1853 (Engl. Transl.)].
14. O. A. Fedorova, A. I. Vedernikov, O. V. Yescheulova, Y. V. Pershina, P. V. Tsapenko, and S. P. Gromov, *Synth. Commun.*, 2002, **32**, 1909.
15. O. A. Fedorova, A. I. Vedernikov, I. E. Baronova, O. V. Eshcheulova, E. A. Fedorchuk, K. Gloe, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 381 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 396 (Engl. Transl.)].
16. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, V. V. Samoshin, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 996 [*Russ. Chem. Bull.*, 1993, **42**, 960 (Engl. Transl.)].
17. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, V. V. Samoshin, N. S. Zefirov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 121 [*Russ. Chem. Bull.*, 1995, **44**, 116 (Engl. Transl.)].
18. M. V. Alfimov, Yu. V. Fedorov, O. A. Fedorova, S. P. Gromov, R. E. Hester, I. K. Lednev, J. N. Moore, V. P. Oleshko, and A. I. Vedernikov, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1441.
19. A. I. Vedernikov and S. P. Gromov, *Synthesis*, 2001, 889.
20. S. P. Gromov, M. V. Fomina, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1625 [*Russ. Chem. Bull.*, 1993, **42**, 1561 (Engl. Transl.)].
21. S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *Mol. Cryst., Liq. Cryst.*, 1994, **246**, 183.
22. S. P. Gromov, O. A. Fedorova, M. V. Alfimov, S. I. Druzhinin, M. V. Rusalov, and B. M. Uzhinov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2003 [*Russ. Chem. Bull.*, 1995, **44**, 1922 (Engl. Transl.)].
23. S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, M. V. Alfimov, S. P. Gromov, and O. A. Fedorova, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1995, **107**, 721.
24. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, V. A. Soldatenkova, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1192 [*Russ. Chem. Bull.*, 1997, **46**, 1143 (Engl. Transl.)].
25. M. V. Alfimov, A. V. Churakov, Y. V. Fedorov, O. A. Fedorova, S. P. Gromov, R. E. Hester, J. A. K. Howard, L. G. Kuz´mina, I. K. Lednev, and J. N. Moore, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2249.
26. S. P. Gromov, S. A. Sergeev, S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, L. G. Kuz´mina, A. V. Churakov, J. A. K. Howard, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 530 [*Russ. Chem. Bull.*, 1999, **48**, 525 (Engl. Transl.)].
27. S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, S. P. Gromov, S. A. Sergeev, and M. V. Alfimov, *J. Fluor.*, 1999, **9**, 33.
28. O. A. Fedorova, E. N. Andryukhina, A. V. Lindeman, S. S. Basok, T. Yu. Bogashchenko, and S. P. Gromov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 302 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 319 (Engl. Transl.)].
29. Yu. V. Fedorov, O. A. Fedorova, S. P. Gromov, M. B. Bobrovskii, E. N. Andryukhina, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 302 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 789 (Engl. Transl.)].
30. J. C. Lockhart, A. C. Robson, M. E. Thompson, S. D. Furtado, C. K. Kaura, and A. R. Allan, *J. Chem. Soc., Perkin Trans. 1*, 1973, 577.
31. Pat. USA 3 847 949, 1974; *Chem. Abstr.*, 1975, **82**, 73049.
32. S. A. G. Hogberg and D. J. Cram, *J. Org. Chem.*, 1975, **40**, 151.
33. J. C. Lockhart and M. E. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1977, 202.
34. H. C. van der Plas, *Ring Transformations of Heterocycles*, Academic Press, London—New York, 1973, **1**, 484; **2**, 352.
35. A. N. Kost, S. P. Gromov, and R. S. Sagitullin, *Tetrahedron*, 1981, **37**, 3423.
36. S. P. Gromov and A. N. Kost, *Heterocycles*, 1994, **38**, 1127.
37. S. P. Gromov, *Heterocycles*, 2000, **53**, 1607.
38. S. P. Gromov, A. I. Vedernikov, and S. N. Dmitrieva, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1204 [*Russ. Chem. Bull.*, 1999, **48**, 1190 (Engl. Transl.)].
39. S. P. Gromov, S. N. Dmitrieva, M. V. Churakova, and A. Yu. Turchanov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1232 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1335 (Engl. Transl.)].
40. S. P. Gromov, A. I. Vedernikov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 950 [*Russ. Chem. Bull.*, 1995, **44**, 923 (Engl. Transl.)].
41. S. P. Gromov, A. I. Vedernikov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 687 [*Russ. Chem. Bull.*, 1996, **45**, 648 (Engl. Transl.)].
42. RF Patent 2161153, 2000; *Byul. Izobr.* [*Invention Bulletin*], 2000, No. 36 (in Russian).
43. S. P. Gromov, S. N. Dmitrieva, A. I. Vedernikov, L. G. Kuz´mina, A. V. Churakov, Y. A. Strelenko, and J. A. K. Howard, *Eur. J. Org. Chem.*, 2003, 3189.
44. S. N. Dmitrieva, Ph. D. (Chem.) Thesis, N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Moscow, 2003, 170 pp. (in Russian).
45. S. P. Gromov, S. N. Dmitrieva, and V. E. Krasnovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 540 [*Russ. Chem. Bull.*, 1997, **46**, 519 (Engl. Transl.)].
46. S. P. Gromov and S. N. Dmitrieva, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 542 [*Russ. Chem. Bull.*, 1999, **48**, 537 (Engl. Transl.)].
47. RF Patent 2215738, 2003; *Byul. Izobr.* [*Invention Bulletin*], 2003, No. 31 (in Russian).
48. S. P. Gromov, S. N. Dmitrieva, and M. V. Churakova, *Synthesis*, 2003, 593.
49. S. P. Gromov, S. N. Dmitrieva, M. V. Churakova, A. I. Vedernikov, N. A. Kurchavov, A. V. Churakov, L. G. Kuz´mina, and J. A. K. Howard, *Zh. Org. Khim.*, 2004, **40**, 1247 [*Russ. J. Org. Chem.*, 2004, **40** (Engl. Transl.)].
50. V. G. Avakyan, S. P. Gromov, S. N. Dmitrieva, A. I. Vedernikov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 25 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 24].
51. M. C. Etter, R. B. Kress, J. Bernstein, and D. J. Cash, *J. Am. Chem. Soc.*, 1984, **106**, 6921.

Received December 10, 2003;
in revised form March 24, 2004