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Asymmetric Calix[4]-thiacalix[4]arene Tubes: Synthesis and Ionophore Properties

E. V. Khomich, M. N. Kashapov, I. M. Vatsuro, E. A. Shokova, and B. B. Kovalev

Lomonosov Moscow State University, Moscow, 119992 Russia
e-mail: kovalev@petrol.chem.msu.ru

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Abstract—Asymmetric *p-tert*-butylcalix[4]-*p*-R-thiacalix[4]arene tubes (R = *tert*-Bu, H, 1-adamantyl) were prepared for the first time by reaction of tosyloxyethoxy derivative of *p-tert*-butylcalix-[4]arene and the corresponding *p*-R-thiacalix[4]arenas in acetonitrile in the presence of K_2CO_3. Complex formation of compounds obtained with sodium, potassium, and rubidium iodides in $CDCl_3$–CD_3OD, 4:1, was studied by means of ^1H NMR. The ionophore properties of the molecule were governed by the character of substituents on the upper rim of the thiacalixarene fragment, and only the molecular tube containing a fragment of the *p*-(1-adamantyl)-thiacalix[4]arene quantitatively bound potassium ions (quickly) and rubidium ions (slowly).

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The necessity of selective recognition and isolation of alkali metal salts is of significant interest [1]. In this connection the discovery of the potassium channels of prokaryotic microbes *Streptomyces lividans* [2] provided a possibility to investigate the structural requirements to the channels by building up their synthetic analogs, in particular, based on calixarenes [3]. Recently calix[4]arene tubes **I** and **II** (Fig. 1), biscalix[4]arenes linked on the lower rim by four ethylene bridges, attracted much interest by their exclusive selectivity in binding potassium ions in the presence of other ions of metals from IA and IIA groups [4–8]. Calixarene fragments in these compounds control the entering of cations into the cryptand-like cavity similarly to the action of filteres of the cell potassium channels formed by tyrosine fragments [9]. The rate of complexing proved to depend strongly on the character of substituents at the upper rim of the calix[4]arene macroring [5, 7].

This class of ionophores was extended by obtaining a symmetric molecular tube **III** based on two *p-tert*-butylthiacalixarenes [10]. Due to replacement of methylene bridging groups by sulfide ones the entrance filteres and the molecular cavity in this molecule are somewhat larger than in tubes **I** and **II**, and the conformational flexibility of the macroring also increases. Therefore thiacalixarene **III** exhibited low activity in binding cations of IA group metals compared to compounds **I** and **II** and no selectivity to any ion. It was also found that compounds **I** and **II** bound Ag^+ [6, 11] and Tl^+ [12] localizing the cation between ether oxygen atoms or within the aromatic calixarene cavity.

In this study we obtained for the first time new type ionophores: asymmetric heterotubes **IV** built up from fragments of calix[4]arene and thiacalix[4]arene. In contrast to the previously synthesized tubes **I–III** heterotubes **IV** possess entrance calixarene filteres of different size. Besides the replacement of one thiacalix-[4]arene fragment of tube **III** by a classic calix[4]arene should lead to the formation of a molecule with a slightly smaller molecular cavity and a higher rigidity that presumably would affect the confomational and ionophore properties. Ionophore characteristics of heterotubes **IV** with various substituents in the thiacalixaren moiety (R = *tert*-Bu, H, 1-Ad) with respect to the IA group metals were estimated by ^1H NMR spectroscopy.

Asymmetric calix[4]-thiacalix[4]arene tubes **IVa–IVc** were prepared by reaction of previously described tosyloxyethoxy derivative of *p-tert*-butyl-calix[4]arene (**V**) [13] with various *p*-R-thiacalix[4]arenes **VIa–VIc** (R = *tert*-Bu [14], H [15], 1-adamantyl [16]) in acetonitrile in the presence of K_2CO_3 (see the scheme) similarly to the synthesis of calixarene tubes **I–III** [4, 5]. The possibility to oxidize the epithiabridges [17] alongside the modification of the upper and/or lower rim of the macroring was used in modification of obtained tubes **IV**. To this end the recently developed method of stereoselective oxidation

by sodium nitrate in the trifluoroacetic acid of thiacalix-[4]arenas in the *cone* conformation into sulfoxides [18] was applied leading to tetrasulfoxide **VIII**.

To elucidate the effect of adamantane substituents in calixarene tubes on the cations binding and to compare the properties of heterotubes and "classic" tubes from the corresponding *p*-(3-R-adamantyl)-calix[4]arenes **VIIa** and **VIIb** [19] we prepared adamantyl-substituted "classic" molecular tubes **IXa** and **IXb**. The known biscalix[4]arene (**Ia**) [4, 5] was also synthesized as a reference.

The structure of compounds obtained was confirmed by ^{1}H, ^{13}C NMR, and mass spectra (ESI). The ^{1}H NMR spectra of heterotubes **IV** and asymmetric classic tubes **IX** in $CDCl_3$ at 303 K are well resolved and contain each four singlets of equal intensity in the aromatic region, two pairs of multiplets of ethylene protons, one (for heterotubes **IV**) or two(for asymmetric tubes **IX**) pairs of doublets from fragments $ArCH_2Ar$ (partially overlapped), and also a double set of signals from adamantyl and/or *tert*-butyl groups [unambiguous assignment of signals has been performed using a series of 1D (NOE) experiments]. ^{13}C NMR spectra contain each sixteen aromatic signals, four signals of OCH_2 groups, and from four (compound **IVa**) to sixteen (compound **IXb**) signals from substituents of the upper rim. The doubld set of all resonance signals indicates that both calix[4]arene and thiacalix[4]arene fragments of molecular tubes **IV** and **IX** contain two kinds of aromatic rings in conformity to C_{2v} symmetry.

The fact that calixarene tubes which formally should belong to C_{4v} symmetry appear in the NMR spectra as less symmetric is well understood and is due to conformational properties of calixarene fragments forming the tube [5]. It was established that the macrorings are subjected to slow in the NMR time scale interconversions between two conformers *flattened cone* (Fig. 2). The rate of this exchange was measured in $CDCl_3$: k_{exch} ~1–3 s^{-1} (depending on the character of substituent on the upper rim) for classic tubes **I** and **II** at 328 K and close to 9 s^{-1} for thiatube **III** at 273 K [10]. This difference in rates indicates the significant increase in the conformational flexibility of calixarene tubes in going from methylene bridges to sulfide ones.

The conformational flexibility of new calixarene tubes that we have synthesized was investigated by means of dynamic and two-dimensional EXSY (2D, EXchange Spectroscopy) NMR experiments. Heating to 328 K in $CDCl_3$ resulted in broadening of signals of heterotubes

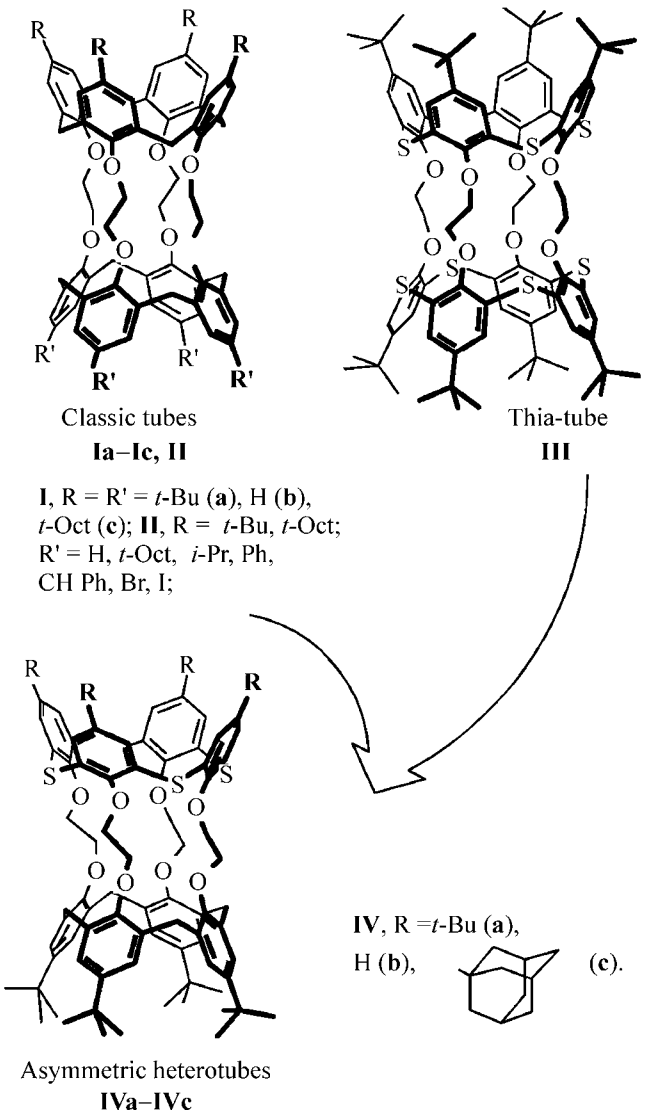
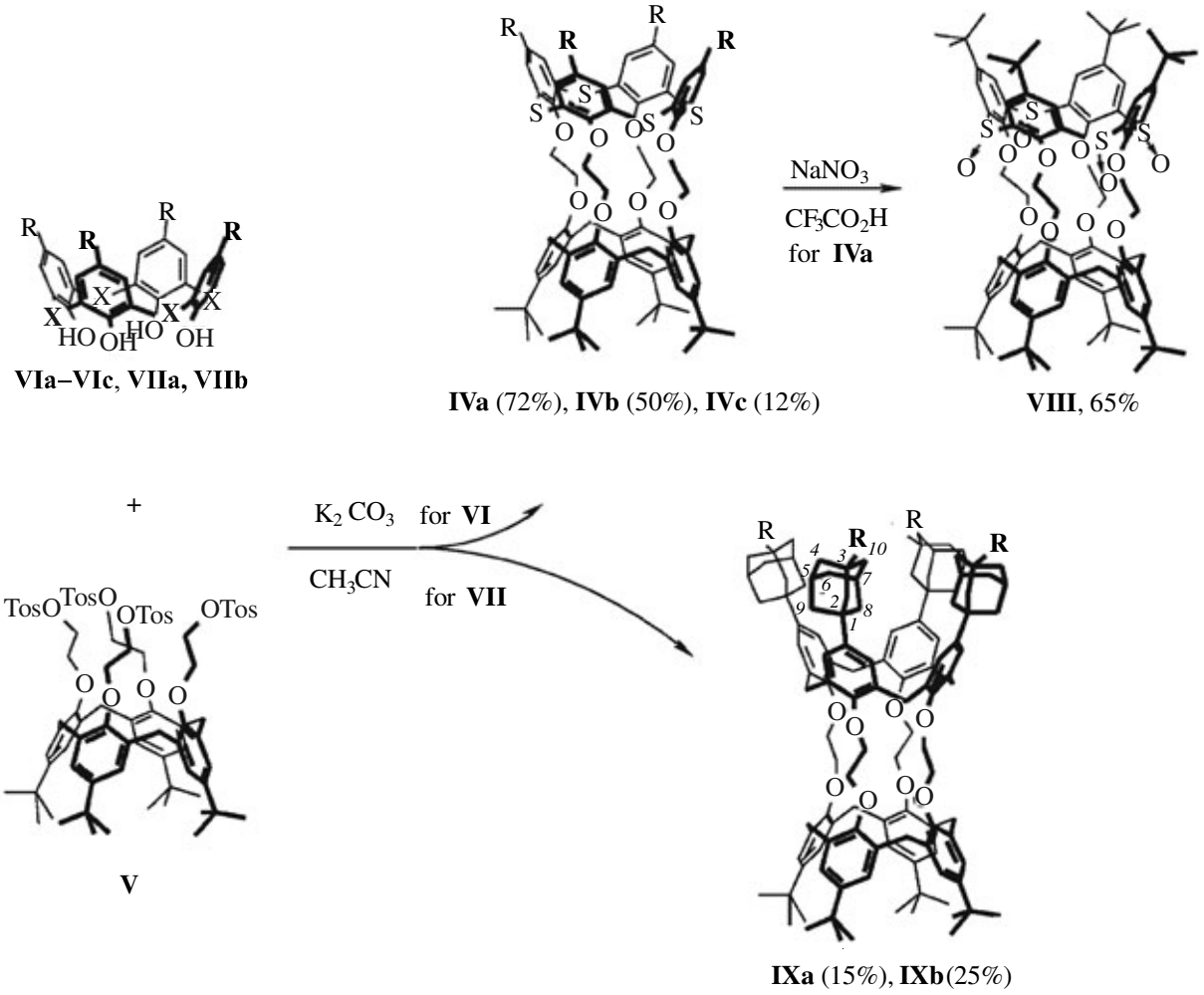


Fig. 1. Calix[4]arene tubes.

IV in the ^{1}H NMR spectra, the most prominent for compound **IVc** with the adamantyl substituents on the upper rim of the thiacalixarene fragment (Fig. 3). At the same time the spectra of classic tubes **IX** remain without visible changes in agreement with the data for tubes **I** and **II** [5]. The 2D EXSY experiments make it possible to give an approximate quantitative estimation of the conformational flexibility of the molecule [20]. The exchange NMR experiments on aromatic protons have been carried out at 328 K for tubes **IVa**, **IVb**, and **IX** and at 303 K for compound **IVc** (since the measurements should be performed under conditions where the signals are not yet significantly broadened). In all cases intensive exchange cross-peaks were observed proving the

Scheme.



VI, X = S, R = *t*-Bu (**a**), H (**b**), 1-Ad (**c**); **VII, X** = CH_2, R = 1-Ad (**a**), 3-*i*-Pr-1-Ad (**b**); **IX**, R = H (**a**), *i*-Pr (**b**).

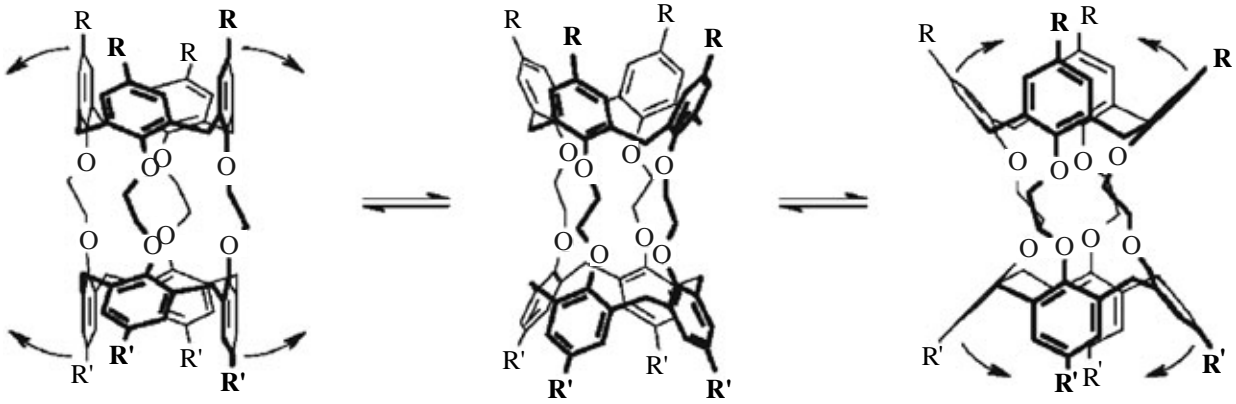


Fig. 2. Interconversions of conformers *flattened cone* in calixarene tubes.

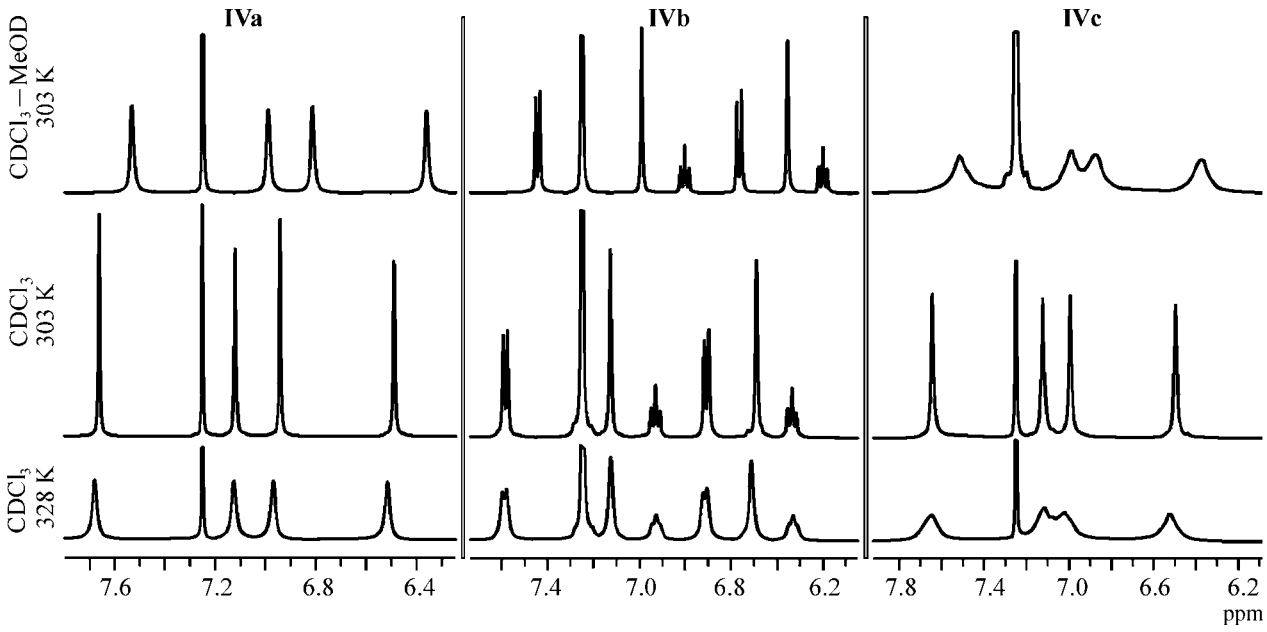


Fig. 3. Aromatic regions of ^{1}H NMR spectra of heterotubes **IVa–IVc** under various conditions.

occurrence of the conformational interconversions. The quantitative data obtained from the spectral measurements permitted estimation of the flexibility of the tubes synthesized. The same experiment carried out with classic tube **Ia** gave the k_{exch} value well consistent with the previously reported [5].

It turned out that the flexibility of classic tubes **IX** is very similar to that of tube tube **Ia**, k_{exch} ~1s^{-1} at 328 K. The same value of k_{exch} was observed for heterotubes **IV** at lower temperature (303 K). For compounds **IVa** and **IVb** at 328 K k_{exch} ~2.5s^{-1}. The flexibility of heterotubes grows in the series (**IVb**)<(**IVa**)<(**IVc**). This result is well consistent with the known data for classic tubes **I** and **II** where the flexibility of compounds grows with the growing size of substituents at the upper rim [5]. Thus the obtained heterotubes **IV** proved to be somewhat more flexible than classic tubes **I** or **IX** but more rigid compared to thiatube **III**.

The ^{1}H NMR spectra of compounds synthesized were also registered in a mixture $CDCl_3$–MeOD, 4:1, for just this solvent was used in the study of heterotubes complexing with alkali metal cations. Unexpectedly we observed here a considerable broadening of signals in the spectrum of adamantyl-containing heterotube **IVc** (Fig.3). This unusual behavior of compound **IVc** is likely to originate from the higher hydrophobism of adamantane structure compared to that of *tert*-butyl groups and hydrogen atoms in compounds **IVa** and **IVb**, and this is manifested in the dynamic properties of the molecules in the given mixed solvent. On the other hand in the spectra of adamantyl-substituted classic tubes **IX** no notable broadening of signals occurred at increased polarity of the solvent.

Thus our data show that the dynamic properties of calixarene tubes are significantly affected both by the macroring type (classic or thiacalixarene) and the character of substituents on the upper rim.

Complex formation with alkali metals cations. One of the most striking properties of calix[4]arene tubes **I** and **II** is their very high affinity and selectivity with respect to potassium ions compared to their behavior toward the other alkali metal and barium ions [4]. We investigated complexing of heterotubes **IV** with ions of Na^+, K^+, and Rb^+ by means of quantitative NMR measurements. To elucidate the role of the thiacalixarene fragment and the substituents on the upper rim we also studied the ionophore characteristics of classic tubes **Ia** and **IX.**

A solution of 1 μmol of calixarene tube in 0.54 ml of deuterochloroform was charged into an NMR tube containing 50 μmol of metal iodide in 0.135 ml of deuteromethanol. The samples were dispersed by ultrasonic irradiation for 1 min, and then the ^{1}H NMR spectra were registered after required time intervals (starting with 5 min after mixing). Inasmuch as the binding of ions in the calixarene tubes is accompanied by considerable changes in the ligand structure in going from C_{2v} symmetry to C_{4v} symmetry, the complex formation rate is easily estimated by simple integrating of signals from the free

Binding (%) of alkali metal ions by calixarene tubes **Ia, IV, VIII**, and **IX**

Tube no.	Na^+	K^+			Rb^+					
	144 h	10 min	1 h	2 h	10 min	1 h	12 h	48 h	144 h	312 h
Ia	0	100			1.6	2.9	6.8	10.8	15.7	
IVa	0	22.1	31.9	32.6	1.0	1.8	5.2	9.4	15.0	
IVb	0	0	0	0	0	0	0	0	0	
IVc	0	100			13.3	21.6	42.4	61.7	83.1	96.3
VIII	0	0	0	0	0	0	0	0	0	
IXa	0	100			4.9	6.3	8.9	10.8	12.6	
IXb	0	100			3.9	4.5	6.3	8.3	9.6	

ligand and from the complex in the ^{1}H NMR spectra. Some of the data obtained are compiled in the table.

Firstly we studied complexing with potassium ions. It turned out that in the case of heterotubes **IV** the character of the substituent at the upper rim of the thiacalixarene frqagment crucially affected the binding of potassium ions. Whereas the heterotube **IVc** with the 1-adamantyl substituent formed the complex quickly and quantitatively (Fig. 4), compound **IVb** with unsubstituted *para*-positions in the thiacalix[4]arene fragment did not at all take part in the complexing. Heterotube **IVa** obtained from *p-tert*-butylthiacalix[4]arene has intermediate characteristics: The equilibrium (~35% of the complex) is attained in 1–2 h after mixing the ligand with the metal salt. Adamantyl-substituted classic tubes **IX** same as the known receptor **Ia** quantitatively form complexes with potassium ions faster than within 5 min. Obviously in the latter case the substitution of *tert*-butyl groups by 1-adamantyl or 3-isopropyl-1-adamantyl does not affect the ionophore properties of the biscalixarene.

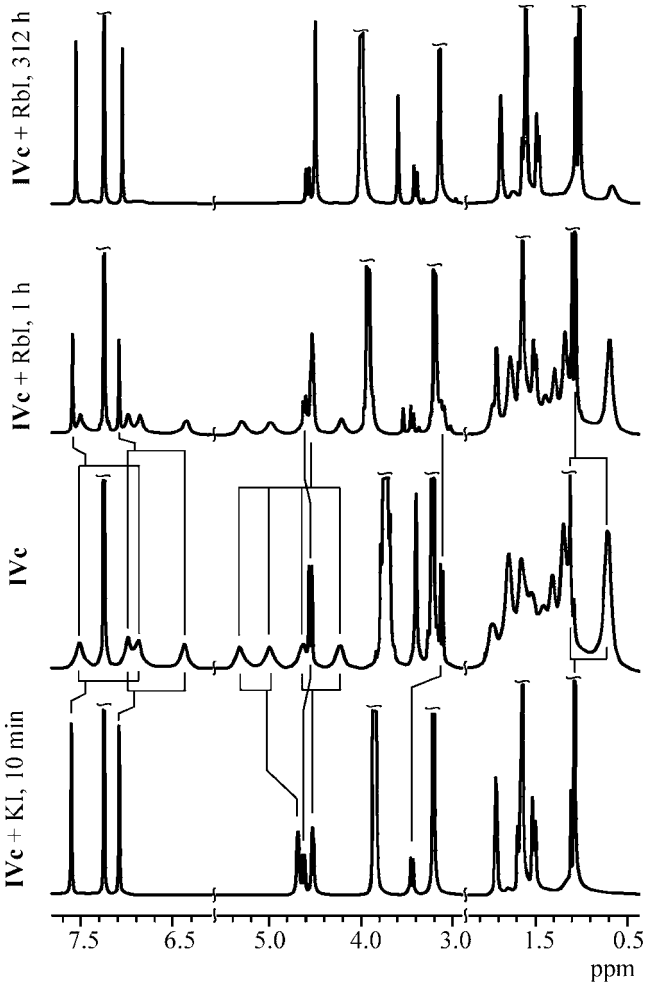


Fig.4. ^{1}H NMR spectra of ligand **IVc** and its mixtures with KI and RbI.

Next we studied the behavior of the calixarene tubes synthesized toward sodium and rubidium ions. As seen from the table, none of the ligands obtained in this study formed complexes with sodium ions. Unexpected and worth attention result was obtained in the study of complexing with rubidium ions. It is known [4, 5, 7] that if classic tubes **I** and **II** form any complexes with rubidium ions, the process is slow and far from quantitative disregarding what substituents are present at the upper rim of the calixarene. Classic tubes **IX** also were inefficient in binding the rubidium ions, and as seen from the table, they were comparable with ligand **Ia**. However heterotube **IVc** with the adamantane substituents in the thiacalixarene fragment binds rubidium to the same extent as classic tubes **Ia** and **IX** whereas compound **IVb** with thiacalixarene fragment of the molecule is capable of slow (within several days) but practically quantitative binding of rubidium ions forming a complex of C_{4v} symmetry (Fig.4). Compound **IVa** with *tert*-butyl groups in the no

substituents totally lacks ionophore properties with respect to alkali metal ions (see the table).

The oxidation of sulfide bridges results in the loss of the ionophore activity of the molecule, apparently due to the electron-withdrawing action of the sulfoxide groups. Compound **VIII** does not form complexes with any of the cations studied (see the table).

The data obtained manifest unique ionophore qualities of ligand **IVc** containing the thiacalix[4]arene fragment with adamantine substituents at the upper rim. The reason of this fact is understandable in the framework of the complexing mechanism suggested in [4–8]. In keeping with the mechanism in the course of complex formation the cation axially enters through the calixarene filter and localizes among eight oxygen atoms (Fig. 5). The binding efficiency is governed by a combination of two factors: by the filters size (i.e., by the diameter of the aromatic cavity of the calix-arene macrorings), and by the capability of the receptor to conserve the cation within the molecular tube. The increased filter size in going from the derivatives of classic calix[4]arenas to the molecular tubes containing the thiacalix[4]arene fragment facilitate the entrance of rubidium cations into the cryptand-like cavity of ligands **IV**. The increase in the binding efficiency with respect to potassium and rubidium cations with the growing lipophilism of substituents in the thiacalixarene fragments of heterotubes **IV** occurs apparently because the more hydrophobic and bulky groups protect better the metal cation from the polar methanol molecules, and this fact in its turn favors the greater stability of the complex. The comparison of the so-called "lipophilic layer thickness" (the distance from the first atom of the substituent and the plane through the carbons most remote from the first one) shows that this parameter is greater by a factor of 5 in 1-adamantyl groups than in *tert*-butyl groups (Fig. 5).

The changes in the chemical shifts in the ^{1}H NMR spectra on complex formation were measured for the complexes of heterotubes **IVa** and **IVc** with potassium and rubidium ions, and also for the complexes of classic tubes **IX** with potassium ions. In all cases a downfield shift was observed for the signals of aromatic, methylene protons, and the signals from substituents at the upper rim; at the same time the signals of OCH_2 groups in the complexes suffered mostly an upfield shift. Similar trends were formerly observed in the spectra of calixarene tubes as a result of redistribution of the electron density in the ligand molecule at binding the cation [4, 12]. The changes in the chemical shifts of the signals from aromatic ring protons, from $ArCH_2Ar$ groups, and from substituents attached to the upper rim in general are consistent with the data reported for compound **Ia** [4]; however, the behavior of signals from OCH_2 groups is quite different for classic tubes **IX** and heterotubes **IV**. The signals belonging to these groups on binding the potassium ions with ligands **IX** shift downfield by 0.24 ppm in agreement with the behavior of ligand **Ia**. At the same time in the spectra of heterotubes at binding the potassium and rubidium ions a weak deshielding is observed of protons close to the classic calixarene fragment (on the average by +0.09 ppm), and relatively strong shielding of protons more close to the thiacalixarene fragment (on the average by –0.59 ppm). These data in all likelihood evidence that the metal cation at the complex formation is localized within the cryptand-like cavity, and the difference in the chemical shifts of the ethylene protons is due to the significant asymmetry of ligands **IV** originating from the presence of bridging sulfur in the thiacalixarene fragment.

Hence we synthesized for the first time asymmetric heterocalixarene tubes **IV** composed of *p*-R-thiacalix-[4]arene and *p-tert*-butylcalix[4]-arene fragments, and their binding properties were investigated with respect

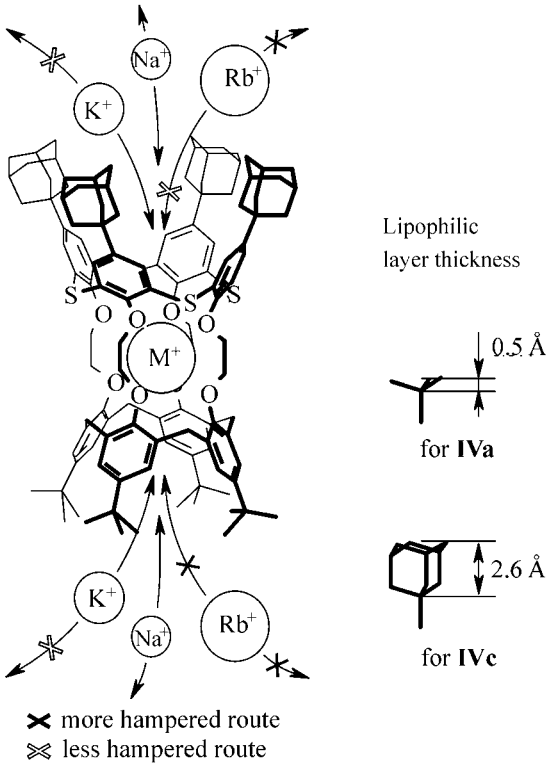


Fig. 5. Schematic representation of possible routes of complex formation and decomposition between alkali metal cations with ligand **IVc**. Lipophilic layer thickness in compounds **IVa** and **IVc**.

to the metals of IA group. The character of the substituent in the thiacalixarene fragment of ligands **IVa–IVc** (R = H, *tert*-Bu, 1-adamantyl) crucially affects the capture of the metal cation. Therewith only for *p*-(1-adamantyl)-thiacalix[4]arene-*p*-*tert*-butylcalix[4]arene heterotube **IVc** a fast and efficient complexing was observed with potassium ions. Derivative **IVc** is the first in this ligand family capable of complete binding of rubidium ions, yet far slower than the capture of potassium ions. Inasmuch as such characteristics were not observed in first synthesized adamantly-substituted classic tubes **IX**, the heterotube **IVc** should apparently be regarded as possessing a unique combination of the properties of calixarene filters and high lipophilism of adamantyl substituents protecting the bound metal cation from the solvent molecules.

EXPERIMENTAL

^{1}H, ^{13}C, 1D, 2D EXSY NMR spectra were registered on a spectrometer Bruker Avance 400 (400 MHz) in $CDCl_3$ or in a mixture $CDCl_3$–CD_3OD, 4:1, solvent signals served as internal reference. The following notations were used in description of ^{1}H NMR spectra of calixarene tubes synthesized: *class* ArH, signals of aromatic protons from phenol fragments connected by methylene groups; *thia*-ArH, signals of aromatic protons from phenol fragments connected by sulfide bridges; *class t*-Bu, proton signals of *tert*-butyl substituents in the classic calixarene fragment; *thia-t*-Bu, proton signals of *tert*-butyl substituents in the thiacalixarene fragment. The numbering of carbon atoms of the adamantine skeleton used in the ^{13}C NMR spectra of calixarene tubes **IVc**, **IXa**, and **IXb** is given on the scheme. ESI mass spectra were measured on Agilent 1100 LC/MS instrument. The preparative column chromatography was performed using silica gel Kieselgel 40/60 (Merck). TLC was carried out on DC Alufolien Kieselgel 60 F_{254} (Merck) plates, spots visualized under UV irradiation.

Bis-*p*-*tert*-butyl-calix[4]arene (**Ia**) [4], tetra[(4-methylphenyl)sulfonyloxyethoxy]-*p*-*tert*-butylcalix-[4]arene (**V**) [13], *p*-*tert*-butylthiacalix-[4]arene (**VIa**) [14], thiacalix[4]-arene (**VIb**) [15], *p*-(1-adamantyl)thia-calix[4]arene (**VIc**) [16], *p*-(1-adamantyl)calix-[4]arene (**VIIa**) [19], and *p*-(3-isopropyl-1-adamantyl)calix[4]-arene (**VIIb**) [19] were prepared by known procedures.

General procedure of preparation of calixarene tubes IVa–IVc, IXa, and IXb. A dispersion of 0.15 mmol of tetra[(4-methylphenyl)sulfonyloxyethoxy]-*p*-*tert*-butylcalix[4]arene (**V**), 0.162 mmol of *p*-substituted thiacalix[4]arene **VIa–VIc**, or adamantylcalix[4]arene **VIIa** or **VIIb**, and 0.1 g (0.75 mmol) of potassium carbonate in 25 ml of acetonitrile was heated at reflux with stirring for 120 h. The reaction mixture was cooled, the solvent was distilled off at a reduced pressure, the residue was treated with a hot mixture ethanol–water, 4:1, the precipitate was filtered off, dried, and subjected to chromatography (eluent hexane–chloroform, 2:1).

***p*-*tert*-Butylcalix[4]-*p*-*tert*-butylthiacalix[4]arene tube (IVa)**. Yield 72%, mp > 350°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.66 s (4H, *thia*-ArH), 7.12 s (4H, *class* ArH), 6.94 s (4H, *thia*-ArH), 6.49 s (4H, *class* ArH), 5.43 m (4H, OCH_2), 5.07 m (4H, OCH_2), 4.79 m (4H, OCH_2), 4.66 d (4H, $ArCH_2Ar$, *J* 12.76Hz), 4.35 m (4H, OCH_2), 3.25 d (4H, $ArCH_2Ar$, *J*12.76Hz), 1.33 s (36H, *t*-Bu), 0.85 s (18H, *thia-t*-Bu), 0.82 s (18H, *class t*-Bu). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 160.93, 158.32, 156.12, 152.92, 145.86, 145.67, 144.53, 144.30 (ArC), 135.42, 134.10 (ArCH), 133.42, 131.92, 131.04, 127.88 (ArC), 125.47, 124.66 (ArCH), 73.96, 73.45, 73.17, 72.56 (OCH_2), 34.32, 34.07, 33.83, 33.58 [$\underline{C}(CH_3)_3$], 32.01 ($ArCH_2Ar$), 31.75, 31.44, 31.10, 30.85 [$C(\underline{C}H_3)_3$]. Mass spectrum, *m*/*z* (I_{rel}, %): 1496.6 [*M* + Na]$^+$ (100), 1495.7 (99), 1497.7 (55). $C_{92}H_{112}NaO_8S_4$. Calculated *M* 1495.7.

***p*-*tert*-Butylcalix[4]-*p*-*H*-thiacalix[4]arene tube (IVb)**. Yield 50%, mp > 350°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.58 d (4H, *thia*-ArH, *J* 7.83Hz), 7.13 s (4H, *class* ArH), 6.93 t (2H, *thia*-ArH, *J* 7.83Hz), 6.71 d (4H, *thia*-ArH, *J* 7.83Hz), 6.49 s (4H, *class* ArH), 6.33 t (2H, *thia*-ArH, *J* 7.83Hz), 5.36 m (4H, OCH_2), 4.97 m (4H, OCH_2), 4.59 d (4H, $ArCH_2Ar$, *J* 12.63Hz), 4.33 m (4H, OCH_2), 3.25 d (4H, $ArCH_2Ar$, *J* 12.63Hz), 1.32 s (18H, *t*-Bu), 0.82 s (18H, *t*-Bu). Mass spectrum, *m*/*z* (I_{rel}, %): 1271.8 [*M* + Na]$^+$ (100), 1272.6 (83), 1273.4 (39). $C_{78}H_{80}NaO_8S_4$. Calculated *M* 1271.5.

***p*-*tert*-Butylcalix[4]-*p*-(1-adamantyl)thiacalix-[4]arene tube (IVc)**. Yield 12%, mp > 350°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.64 s (4H, *thia*-ArH), 7.13 s (4H, *class* ArH), 6.99 s (4H, *thia*-ArH), 6.49 s (4H, *class* ArH), 5.45 m (4H, OCH_2), 5.11 m (4H, OCH_2), 4.75 m (4H, OCH_2), 4.67 d (4H, $ArCH_2Ar$, *J*12.63Hz), 4.35 m (4H, OCH_2), 3.25 d (4H, $ArCH_2Ar$, *J*12.63Hz), 2.20–1.35 m (60H, AdH), 1.33 s (18H, *t*-Bu), 0.83 s (18H, *t*-Bu). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 161.25, 158.65, 156.06, 153.01, 146.05, 145.83, 144.44, 144.28 (ArC), 135.43, 134.15 (ArCH), 133.33, 131.98, 130.73, 127.72 (ArC), 125.42, 124.64 (ArCH), 74.14, 73.51, 73.12, 72.66 (OCH_2), 43.46, 42.68

(AdC^{2,8,9}), 36.81, 36.57 (AdC^{4,6,10}), 35.88, 35.44 (AdC^{1}), 34.06, 33.58 [$\underline{C}(CH_3)_3$], 32.08 ($ArCH_2Ar$), 31.75, 31.10 [$C(\underline{C}H_3)_3$], 29.04, 28.79 (AdC^{3,5,7}). Mass spectrum, *m/z* (I_{rel}, %): 1808.9 [*M* + Na]$^+$ (100), 1808.1 (78), 1809.9 (64). $C_{116}H_{136}NaO_8S_4$. Calculated *M* 1807.9.

***p-tert*-Butylcalix[4]-*p*-(1-adamantyl)calix[4]arene tube (IXa)**. Yield 15%, mp> 350°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.10 s (4H, *t*-Bu-ArH), 7.07 s (4H, Ad-ArH), 6.54 s (4H, Ad-ArH), 6.49 s (4H, *t*-Bu-ArH), 5.17 m (8H, OCH_2), 4.60 d (4H, $ArCH_2Ar$, *J* 12.63Hz), 4.58 d (4H, $ArCH_2Ar$, *J* 12.63Hz), 4.39 C (8H, OCH_2), 3.26 br.s (8H, $ArCH_2Ar$, *J* 12.63Hz), 2.12–1.35 m (60H, AdH), 1.32 C (18H, *t*-Bu), 0.82 C (18H, *t*-Bu). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 157.08, 157.03, 155.88, 155.78, 144.87, 144.73, 144.46, 144.33, 135.17, 135.12, 131.95, 131.80 (ArC), 125.47, 125.01, 124.77, 124.41 (ArCH), 72.92, 72.52 (OCH_2), 43.87, 42.99 (AdC^{2,8,9}), 37.07, 36.85 (AdC^{4,6,10}), 35.68, 35.16 (AdC^{1}), 32.53, 32.26 [$\underline{C}(CH_3)_3$], 31.74, 31.05 [$C(\underline{C}H_3)_3$], 29.30 ($ArCH_2Ar$), 29.25, 28.99 (AdC^{3,5,7}). Mass spectrum, *m/z* (I_{rel}, %): 1753.0 [*M* + K]$^+$ (100), 1752.0 (77), 1754.0 (66). $C_{120}H_{144}KO_8$. Calculated *M* 1752.1.

***p-tert*-Butylcalix[4]-*p*-(3-isopropyl-1-adamantyl)calix[4]arene tube (IXb)**. Yield 25%, mp > 350°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.09 s (4H, *t*-Bu-ArH), 7.08 s (4H, Ad-ArH), 6.51 s (4H, Ad-ArH), 6.50 s (4H, *t*-Bu-ArH), 5.18 m (8H, OCH_2), 4.59 br.s (8H, $ArCH_2Ar$, *J* 12.38Hz), 4.40 s (8H, OCH_2), 3.28 d (4H, Ad-$ArCH_2Ar$, *J* 12.38Hz), 3.26 d (4H, *t*-Bu-$ArCH_2Ar$, *J* 12.38Hz), 2.20–1.10 m [60H, AdH + $C\underline{H}(CH_3)_2$], 1.32 s (18H, *t*-Bu), 0.85 d (12H, $CH(C\underline{H}_3)_2$, *J* 6.82Hz), 0.82 s (18H, *t*-Bu), 0.78 d [12H, $CH(C\underline{H}_3)_2$, *J* 6.82Hz]. ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 156.03, 155.94, 152.94, 152.89, 144.84, 144.48, 144.43, 144.30, 135.14, 135.07, 131.93, 131.82 (ArC), 125.45, 125.01, 124.71, 124.34 (ArCH), 72.98, 72.63, 72.56 (OCH_2), 45.94, 44.23 (AdC^{2}), 43.42, 42.97 (AdC^{8,9}), 38.57, 38.26 (AdC^{4,10}), 37.73, 37.70 [$\underline{C}H(CH_3)_2$], 36.72, 36.51 (AdC^{6}), 36.33, 35.87 (AdC^{1}), 35.53, 35.14 (AdC^{3}), 34.05, 33.54 [$\underline{C}(CH_3)_3$], 32.48, 32.36 ($ArCH_2Ar$), 31.72, 31.03 [$C(\underline{C}H_3)_3$], 29.56, 29.31 (AdC^{5,7}), 16.45 [$CH(\underline{C}H_3)_2$]. Mass spectrum, *m/z* (I_{rel}, %): 1921.5 [*M* + K]$^+$ (100), 1922.3 (76). $C_{132}H_{168}KO_8$. Calculated *M* 1920.2.

***p-tert*-Butylcalix[4]-*p-tert*-butylsulfinylcalix[4]arene tube (VIII).** A mixture of 20 mg (0.02mmol) of heterotube **IVa**, 60 mg (0.7mmol) of $NaNO_3$, and 2 ml of CF_3COOH was stirred for 7 h under an inert atmosphere. On completion of the reaction the mixture was poured into water, the reaction product was extracted into dichloromethane (3×10 ml). The combined organic solutions were washed with water, dried with $MgSO_4$, and evaporated; the residue was subjected to chromatography (eluent hexane–chloroform, 2:1).

Yield 15 mg (65%), mp > 350°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.26 s (4H, ArH), 8.17 s (4H, ArH), 7.43 s (4H, ArH), 7.34 s (4H, ArH), 5.12 m (12H, $OC\underline{H}_2$ + $ArCH_2Ar$), 4.59 m (8H, $OC\underline{H}_2CH_2O$), 3.65 d (4H, $ArCH_2Ar$, *J* 13.39Hz), 1.42 s (18H, *t*-Bu), 1.25 s (36H, *t*-Bu), 0.90 s (18H, *t*-Bu). Found, %: C 71.21%; H 7.67%; S 8.17%. $C_{92}H_{120}O_{12}S_4$. Calculated, %: C 71.47%; H 7.82%; S 8.29%.

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REFERENCES

1. Ikeda, A. and Shinkai, S. *Chem. Rev*., 1997, vol. 97, p. 1713; Beer, P.D., Gale, P.A., and Chen, Z., *Adv. Phys. Org. Chem.,* 1998, vol. 31, p. 1; Zhang, X.X., Izatt, R.M., Bradshaw, J.S., and Krakowiak, K.E., *Coord. Chem. Rev.,* 1998, vol. 174, p. 179.
2. Doyle, D.A., Cabral, J.M., Pfuetzner, R.A., Kuo, A., Gulbis, J.M., Cohen, S.L., Chait, B.T., and MacKinnon, R., *Science,* 1998, vol. 280, p. 69.
3. Gokel, G.W., *Chem. Commun.,* 2000, p. 1; De Mendoza, J., Cuevas, F., Prados, P., Meadows, E.S., and Gokel, G.W., *Angew. Chem. Int. Ed.,* 1998, vol. 37, p. 1534; Tanake, Y., Kobuke, Y., and Sokabe, M., *Angew. Chem. Int. Ed.,* 1995, vol. 34, p. 693.
4. Schmitt, P., Beer, P., Michael, G., and Sheen, P., *Angew. Chem., Int. Ed.,* 1997, 36, p. 1840.
5. Matthews, S.E., Schmitt, P., Felix, V., Drew, M.G.B., and Beer, P.D., *J. Am. Chem. Soc.,* 2002, vol. 124, p. 1341.
6. Budka, J., Lhotak, P., Stibor, I., Michlova, V., Sykova, J., and Cisarova, I., *Tetrahedron Lett.,* 2002, vol. 43, p. 2857.
7. Matthews, S.E., Felix, V., Drew, M.G.B., and Beer, P.D., *Org. Biomol. Chem.,* 2003, vol. 1, p. 1232.
8. Makha, M., Nichols, P.J., Hardie, M.J., and Raston, C.L. *J. Chem. Soc., Perkin Trans. 1,* 2002, p. 354; Notti, A., Occhipinti, S., Pappalardo, S., Parisi, M.F., Pisagatti, I., White, A.J.P., and Williams, D.J., *J. Org. Chem.,* 2002, vol. 67, p. 7569.
9. Dougherty, D.A., *Science,* 1996, vol. 271, p. 163.
10. Matthews, S.E., Felix, V., Drew, M.G.B., and Beer, P.D., *New J. Chem.,* 2001, vol. 25, p. 1355.

11. Felix, V., Matthews, S.E., Beer, P.D., and Drew, M.G.B., *Phys. Chem. Chem. Phys.,* 2002, vol. 4, p. 3849.
12. Matthews, S.E., Rees, N., Felix, V., Drew, M.G.B., and Beer, P.D., *Inorg. Chem.,* 2003, vol. 42, p. 729.
13. Cobben, P.L.H.M., Egberink, R.J.M., Bomer, J.G., Bergveld, P., Verboom, W., and Reinhoudt, D.N., *J. Am. Chem. Soc.,* 1992, vol. 114, p. 10573.
14. Kumagai, H., Hasegawa, M., Miyanari, S., Sugawa, Y., Sato, Y., Hori, T., Ueda, S., Kamiyama, H., and Miyano, S., *Tetrahedron Lett.,* 1997, vol. 38, p. 3971.
15. Higuchi, Y., Narita, M., Niimi, T., Ogawa, N., Hamada, F., Kumagai, H., Iki, N., Miyano, S., and Kabuto, C., *Tetrahedron,* 2000, vol. 56, p. 4659.
16. Shokova, E., Tafeenko, V., and Kovalev, V., *Tetrahedron Lett.,* 2002, vol. 43, p. 5153.
17. Shokova, E.A. and Kovalev, V.V., *Zh. Org. Khim.,* 2003, vol. 39, p. 13; Lhotak, P., *Eur. J. Org. Chem.,* 2004, p. 1675.
18. Lhotak, P., Moravek, J., Smejkal, T., Stibor, I., and Sykora, J., *Tetrahedron Lett.,* 2003, vol. 44, p. 7333.
19. Khomich, A.N., Shokova, E.A., and Kovalev, V.V., *Synlett.,* 1994, p. 1027.
20. Perrin, C.L. and Dwyer, T.J., *Chem. Rev.,* 1990, vol. 90, p. 935.