Journal of Inclusion Phenomena and Macrocyclic Chemistry (2007) 58:55–61
DOI 10.1007/s10847-006-9117-y

Synthesis of New Calix[4]arenes Functionalizated by Acetylhydrazide Groups

SERGEY N. PODYACHEV[1,*], VIKTOR V. SYAKAEV[1], SVETLANA N. SUDAKOVA[1], ROALD R. SHAGIDULLIN[1], DARYA V. OSYANINA[1], LUDMILA V. AVVAKUMOVA[1], BORIS I. BUZYKIN[1], SHAMIL K. LATYPOV[1], INGMAR BAUER[2], WOLF D. HABICHER[2] and ALEXANDER I. KONOVALOV[1]

[1]*A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of Russian Academy of Sciences, Arbuzov str., 8, 420088, Kazan, Russia;* [2]*Dresden University of Technology, Institute of Organic Chemistry, Mommsenstrasse 13, D-01062, Dresden, Germany*

(Received: 27 February 2006; in final form: 18 April 2006)

Key words: calix[4]arene, calix[4]resorcinarene, calix[4]pyrogallolarene, hydrazide, hydrogen bond, extraction

Abstract

A series of new calix[4]phenols, calix[4]resorcinols and calix[4]pyrogallols with acetylhydrazide substitutes has been synthesized with high yields by hydrazinolysis of ester group containing calix[4]arenes. The synthesized calix[4]phenols adopt the cone conformation while the calix[4]resorcinol and calix[4]pyrogallol derivatives prefer the boat conformation. The amide fragment of the hydrazide groups predominantly exists in the *trans*-conformation. The binding ability of synthesized calix[4]arenes toward transition and alkali metals by solvent extraction has been investigated.

Introduction

The calix[n]arene platform is of great interest for the building of various binding sites to recognize cations, anions and neutral molecules [1, 2]. The application of reactants with good leaving groups, such as Br or Cl is a well-known procedure for the functionalization of the hydroxyl groups of these macrocycles. Such approach is successful for the introduction of ester fragments into the calixarene matrix with quantitative yields. However this technique is less efficient for the introduction of certain functional groups, such as amide, amine, hydrazine and others. To overcome this difficulty it was suggested to include such functional groups into the side chains of calixarenes, using calixarenyloxyacetic acid esters.

Hydrazides of carboxylic acids also show unique complexation properties [3]. Their biological activity often can be considerably enhanced when complexed with transition metal ions. These complexes in turn are very promising candidates for anticancer, germicidal, antiviral and antimicrobial agents [4]. At the same time hydrazides of carboxylic acids are key reagents for the synthesis of other nitrogen containing derivatives including acylhydrazones, acylsemicarbazones and heterocycles.

In this context, it is interesting to combine the unique properties of calix[4]arenes and acylhydrazides. For this purpose a simple hydrazinolysis of ester containing compounds was the matter of choice. We also propose that this approach may be universal for calix[4]arenes, calix[4]resorcinols, calix[4]pyrogallols and their acyclic analogues.

To verify this assumption, in this paper, we present details of the synthesis and characterization of a new family of hydrazides – derivatives of calix[4]arene. The hydrogen bonds are one of the most important interactions which determine the conformational properties, intramolecular interactions and the self-assembly of supramolecular structures. From this point of view we have paid a particular attention on the study of structural peculiarities specified by the hydrogen bonds. To investigate the ion-binding properties of new hydrazides, the solvent extraction of transition and alkali metals with some of them has been also carried out.

Experimental

Instrumentation and materials

All reagents were used as commercially received without further purification. $CHCl_3$ and CCl_4 were distilled over P_2O_5. $CDCl_3$ (99.8% isotopic purity) and DMSO-d_6 (99.5% isotopic purity) from Aldrich were used for NMR spectroscopy.

Microanalyses of C, H, N were carried out with a CHN-S analyzer (Carlo Erba). NMR experiments were

* Author for Correspondence. E-mail: spodyachev@iopc.knc.ru

performed on a Bruker AVANCE-600 spectrometer at 303 K equipped of a 5 mm diameter broadband probe head working at 600.000 MHz in ^{1}H and 150.864 MHz in ^{13}C experiments. Chemical shifts were reported relative to TMS as an internal standard. Assignment was accomplished by means of 2D ^{1}H–^{13}C HSQC and 2D ^{1}H–^{13}C HMBC methods. Values of NOE were determined by DPFGNOE pulse sequence [5]. IR absorption spectra of Nujol emulsions and CCl_4 solutions (10^{-2}–10^{-4} M) of compounds were recorded on a Vector-22 Bruker FT-IR spectrophotometer with a resolution of 4 cm^{-1}. Molecular structure was optimized by semi-empirical geometry optimization (AM1) incorporated in the HyperChem7.03 program package [6].

Syntheses and characterization

The synthetic route and the structural formulae of the investigated compounds are described in Scheme 1. Parent calix[4]arene (**4**–**6**) [7–10], the phenoxyacetic- (**7**–**9**) [11–13] and calix[4]arenyloxyacetic acid ethyl ester with cone conformation (**10**–**12**) [7, 8, 10, 14] were prepared according to the literature methods.

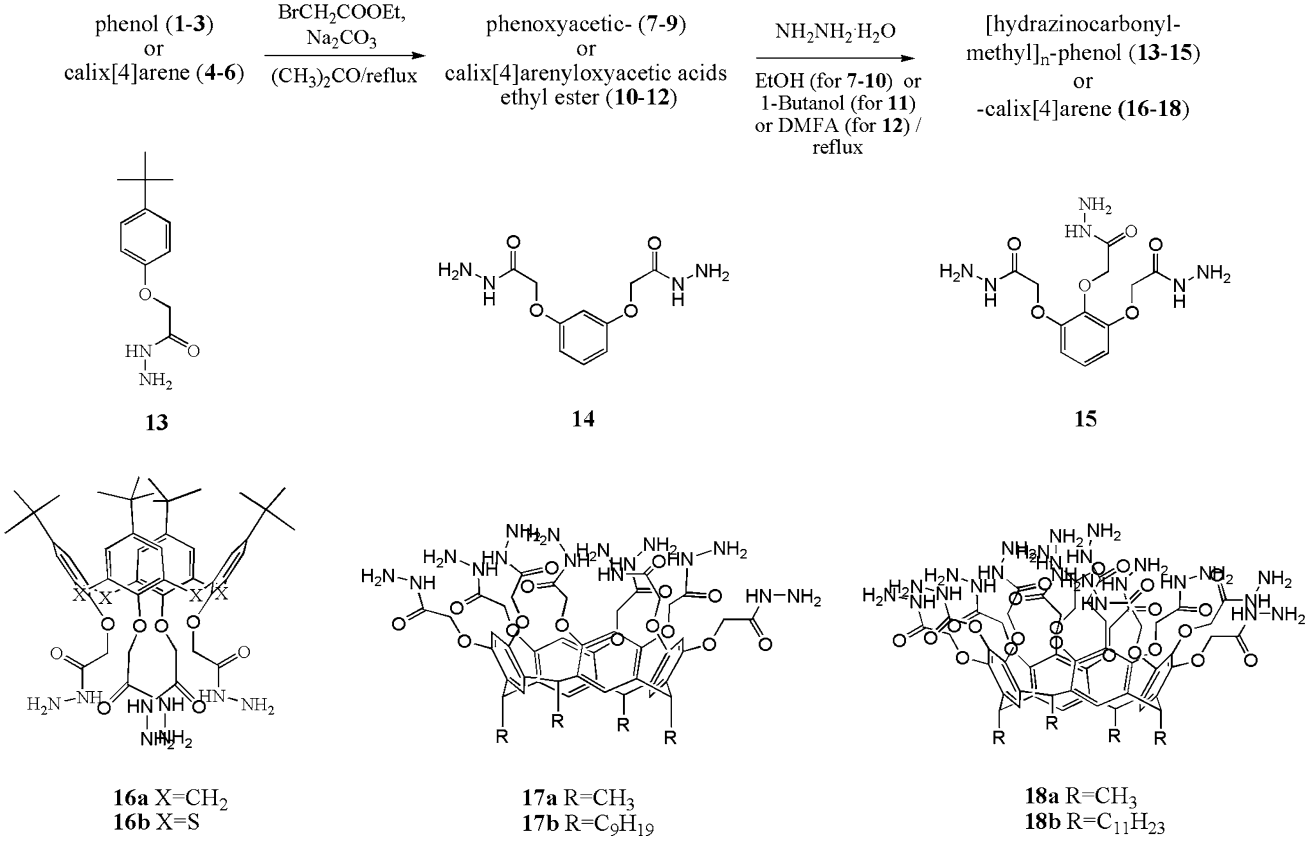
The general procedure for synthesis of acetylhydrazides **13**–**18** is as follows:

To a solution of (1 mmol) corresponding phenoxyacetic acid ethyl ester **7**–**9** (or calix[4]arenyloxyacetic acid ethyl ester **10**–**12**) in 40 ml EtOH (1-butanol for **11** and DMF for **12**) under stirring a 4-fold excess of NH_2–$NH_2{\cdot}H_2O$ with respect to each ester group of these compounds was added. The reaction mixture was refluxed for 3 h (36 h). The precipitate was filtered off, washed several times with a mixture of water/EtOH (1:1). The solvent was removed for **18** from the reaction mixture by distillation and the solid remainder was also washed several times with a mixture of water/EtOH (1:1). The products **16**–**18** were obtained as a white powder with yield 80–95%.

The IR (Table 1) and 1H NMR spectroscopic data (Table 2 and Scheme 2), elemental analysis and mass spectra (MALDI-TOF) confirm the composition and the structure of all synthesized compounds.

Method for extraction

Aqueous picrate solution (5 ml, 2.5×10^{-4} M) which was buffered to pH = 6.0 with tris(hydroxymethyl)aminomethane–HCl (0.05 M) and 5 ml of a solution of extractant (1×10^{-3} M for **16** or 4×10^{-3} M for **13**) in $CDCl_3$ were magnetically stirred in a flask. The extraction equilibrium was reached after vigorous stirring for 1.5 h at 20 °C. After that the two phases were allowed to settle for 1 h. The absorbances A_1 of the aqueous phase after extraction, and, A_0 of the aqueous phase before extraction, were measured at 355 nm (the wavelength of maximum absorption of the picrate ion, λ_{max} = 355 nm). The percentage of cation extracted was calculated as the ratio $100\times(A_0-A_1)/A_0$. All data were obtained from two independent experiments. Aqueous solutions of transition metal picrates (5 ml,



Scheme 1. Synthesis of the hydrazides **13--18**.

Table 1. The frequencies of characteristic vibrations (ν, cm^{-1}) in the IR spectra of acetylhydrazides **13**–**18** in Nujol or CCl_4[a]

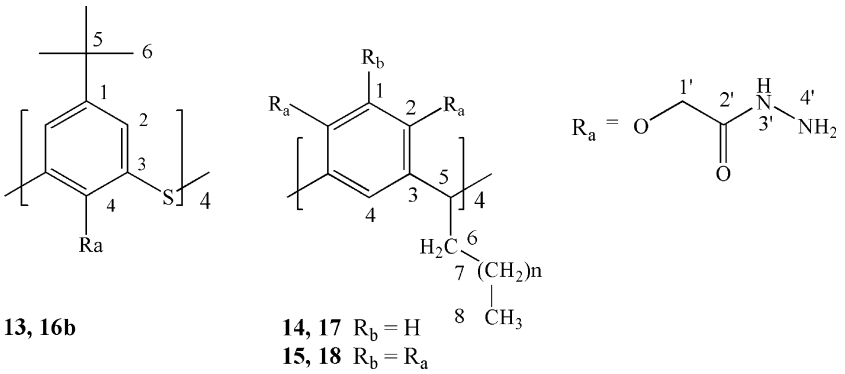
Vibration, assignment	Compound											
	13		**14**	**15**	**16a**		**16b**		**17a**	**17b**	**18a**	**18b**
	Nujol	CCl_4	Nujol	Nujol	Nujol	CCl_4	Nujol	CCl_4	Nujol	Nujol	Nujol	Nujol
$\nu_{as}NH_2NH$ free or week H-bonded	[b]	3452s	[b]	[b]	[b]	[b]	[b]	[b]	3440 3428 3407	3452 3433 3408	3443	3435sh
$\nu_{as}NH_2NH$ H-bonded or ν_sNH_2 free–week H-bonded	3340sh 3322	3367 3338	3314 3254br	3340 3314 3260br	[c] 3316vbr	[c] 3322vbr	[c] 3324vbr	[c] 3340vbr	3325sh 3315sh 3309br 3260sh	3323 3301 3280 3258	3310sh 3298s 3270sh	[c] 3305s 3270
ν_sNH_2 H-bonded	3205	–	3203 [c]	3200	3215	3217	3210	3208	3193	3193	3199	3199
δNH_2	1644	1627	1632	1630sh	[c]	[c]	1622	1623	1619	1620 1613	[c]	1619br
δNH	[c]	1545	1529	1526	1536	[d]	1526	[d]	[c]	[c]	1530 1518	[c] 1523br
νC=O	1660	1693	1680	1680	1679vbr	1686	1674	1678	1696 1675	1694 1675	1668br	1673br
νPh	1611 [c] 1518	1600 1585 1514	1598 1501	1605 1589 1501	1613 [c]	[d]	1600sh [c] 1500sh	[d]	1586 1509m 1496 m	1590 1505 [c]	1604 [c]	[c] [c]

[a]Concentration is 0.1 mM.
[b]No absorption bands.
[c]Characteristic vibrations are not assigned due to band overlapping.
[d]Characteristic vibrations are not assigned due to overlapping solvent absorption.
Additional characteristics of absorption bands: sh – shoulder; br – broad; vbr – very broad. The maxima of rather intensive bands within a given group of signals are solid underlined. The bands comparable to them on intensity are dashed underlined.

Table 2. ^1H and ^{13}C chemical shifts[a] (ppm) of compound **13**–**18** in DMSO

Atom	Compound															
	13		**14**		**15**		**16b**		**17a**		**17b**		**18a**		**18b**	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1		143.45	6.56	101.91		136.97		148.29	6.45	[b]	6.48	99.73		143.38		143.91
2	7.28	126.12		158.93		151.37	7.35	135.21		[b]		153.84		147.09		147.22
3	6.89	114.19	6.52	107.48	6.65	107.49		128.55		[b]		126.98		136.55 133.28		143.03 133.54
4		155.62	7.17	129.93	6.98	124.05		158.40	7.48 6.21	[b]	7.38 6.10	121.11 120.81	7.08 5.69	120.56 120.34	7.38 6.10	121.11 120.81
5		33.84						34.52	4.61	[b]	4.57	35.60	4.72	31.32	4.55	37.13
6	1.23	31.37					1.10	31.26		[b]	1.79	36.23		20.81	1.77	36.01
7											1.21	29.43–31.31			1.22	29.86–31.96
8									1.37		0.82	13.81	1.41		0.84	13.77
1′	4.44	66.32	4.44	66.32	4.53[c] 4.47[d]	67.19[c] 71.38[d]	4.86	75.37	4.39	[b]	4.39	67.54	4.45[c] 4.20[d]	71.16	4.45	71.39
2′		166.55		166.55		166.64[c] 167.43[d]		169.14		[b]		166.97		166.73		166.84
3′	9.30		9.30		9.29[b] 9.26[d]		9.87		8.30		8.25		9.20		9.42	
4′	4.32		4.32		3.40		3.5		3.44		3.38		3.65		3.85	

[a]Numbering according to Scheme 2.
[b]Signal not assigned as it was covered by other signals or due to low concentration of the compound.
[c]For substitution in 2-position.
[d]For substitution in 1-position.



Scheme 2. Atom numbering of compounds **13--18**.

[metal nitrate] = 1×10^{-2} M; [picric acid] = 2.5×10^{-4} M) were prepared by stepwise addition to the calculated amount of metal nitrate of a 2.5×10^{-4} M aqueous picric acid solution which was buffered to pH = 6.0 with tris(hydroxymethyl)aminomethane–HCl (0.05 M) and stirred for 1 h. In a similar manner aqueous solutions of alkali metal picrates (5 ml, [metal chloride] = 1×10^{-2} M; [picric acid] = 2.5×10^{-4} M) were prepared using metal chlorides.

Results and discussion

The new family of calix[4]arenes functionalizated by acetylhydrazide groups (**16**–**18**) and their acyclic analogues (**13**–**15**) have been obtained with high yields by refluxing a solution of the corresponding phenoxyacetic or calixarenyloxyacetic acid esters with an excess of NH_2–NH_2·H_2O (Scheme 1). The synthesis of *O*,*O*,*O*,*O*-tetrakis[hydrazinocarbonylmethyl]-4-*tert*-butylcalix[4]arenas **16a** by a hydrazinolysis procedure also has been described earlier [15]. However following this method, we were not able to isolate a pure product. Therefore we have modified the conditions for the synthesis using large excess of NH_2–NH_2·H_2O, higher boiling EtOH instead of MeOH as a solvent and extended the reaction time from 1 to 36 h. We also have synthesized the entirely substituted product **17** and the sterically more hindered compound **18** by application of high-boiling 1-butanol for **17** and DMF for **18** as solvents.

IR spectra of **16a** and **16b** in solid state show a noticeable similarity with spectrum of their acyclic analogue **13**. As a result, the frequencies of the characteristic vibrations (*v*NH, *v*C=O, *v*Ph, Table 1) have the same maxima. Differences in the spectral behavior of **16a** and **16b** arise in the region of the C–X–C bridge vibrations and in some peculiarities below 1300 cm^{-1}. At the same time IR spectra of **16a** and **16b** in comparison with **13** have broader absorption bands. It can be explained by the presence of four fragments in **16a** and **16b**, which are similar to **13**. It leads to a variety of conformational states and the appearance of additional intra- and intermolecular interactions.

According to literature data [16], the absorption peaks in solid phase at 3316 cm^{-1} (3324 cm^{-1}) for **16a** (**16b**) can be interpreted as $\nu_{as}NH_2NH$ (overlap or mixed vibrations), 3215 cm^{-1} (3210 cm^{-1})–as ν_sNH_2 (Table 1). The presence of amide-II absorption bands (δNH) with a maximum at ~1520 cm^{-1} indicates the presence of the *trans*-conformation of the amide group [17] for **13** and **16**.

When going to a CCl_4 solution, these parameters for the tetrahydrazides of calix[4]arenes **16** differ dramatically from their acyclic analogue **13**. Thus, for **13** the frequencies $\nu_{as}NH_2NH$ and ν_sNH_2 significantly increase (from 3330 to 3452 cm^{-1} and from 3205 to 3338 cm^{-1}, respectively), indicating the disruption of intermolecular hydrogen bonds and the presence of free monomers in solution [18]. The frequencies mentioned for **13** in CCl_4 correspond to the *trans*-amide form of the hydrazide fragment [17].

At the same time the absorption parameters *v*NH for **16a** (**16b**) practically are not changing to a concentration of ~10^{-4} M ($\nu_{as}NH_2NH$: 3316 cm^{-1} (3324 cm^{-1}) → 3322 cm^{-1} (3348 cm^{-1}) and ν_sNH_2 3215 cm^{-1} (3210 cm^{-1}) → 3217 cm^{-1} (3220 cm^{-1})) and have almost the same values as for compound **13** in solid phase. This fact could indicate the participation of hydrazide fragments in intramolecular hydrogen bonds both in solution and in solid phase. Some increase of the $\nu_{as}NH_2NH$ frequencies in solution could be an evidence for the participation of NH_2NH groups in intermolecular hydrogen bonding.

The absence of free *v*NH vibrations in the IR spectra of **16a** and **16b** in contrast to **13** suggests a uniform ordering of four *tert*-butylphenoxyacetylhydrazide fragments fixed by intramolecular hydrogen bonds both in crystal phase and in CCl_4 solution. In fact the ^{1}H NMR spectrum (DMSO, 303 K) of **16b** corresponds to a highly symmetrical structure. The spectrum contains only one signal for each group of protons (Table 2 and Scheme 2). There are eight signals in the ^{13}C NMR spectrum. Thus from ^{1}H and ^{13}C NMR one can conclude that tetrahydrazide **16b** in solution adopts either a 1,3-alternate or a cone conformation.

However in the case of 1,3-alternate and partial cone conformations the disruption of intramolecular hydrogen bonds and the appearance of free $\nu_{as}NH_2NH$ vibrations in the IR spectrum in the region of ~3450 cm^{-1} as for **13** should be observed. The NOE

enhancement [5] in NMR experiment measured to distinguish between these two conformers also supported that **16b** prefers the cone conformation. Namely, there are strong NOE couplings between the *tert*-butyl and aromatic protons, weak interaction between protons of amide and O–CH_2 groups and no effects between protons of O–CH_2 groups with aromatic or *tert*-butyls protons [19, 20].

The molecular structure of cone conformer **16b**, as obtained by semi-empirical geometry optimization (AM1), highlights the possibility of circular intramolecular hydrogen bonding –C(O) ···HN (2.13–2.18Å) and –HNH ··NH_2 (2.52–2.54Å) (Figure 1). This possibility is supported by NMR data. The peak of the amide protons is quite sharp and its chemical shift does not depend on the solvent ($\delta(CDCl_3)$ = 9.88 ppm *versus* δ(DMSO) = 9.87 ppm). However, a similar proton in model compound **13** resonates a different way: in $CDCl_3$ at 7.9 ppm and in DMSO at 8.9 ppm. Thus we can conclude that there are strong circular intramolecular hydrogen bonds between all NH ···O=C groups of tetrathiacalix[4]arene **16b**. The absence of free *v*NH vibrations in the IR spectrum and the presence of only single $\nu_{as}NH_2NH$ absorption peak indicating equal hydrogen bonds also support this conclusion.

The increase of the number of acetylhydrazide groups in compound **14** as compared with **13** is accompanied by the appearance of a new peak (3254 cm^{-1}) in its IR spectrum in solid phase. This frequency value is lower than $\nu_{as}NH_2NH$ (3322 cm^{-1}) for **13**, but their intensity values are comparable with each other. At the same time the carbonyl absorption is shifted to higher frequencies and the δNH_2 vibration frequency for **14** is lower than for **13** (Table 1). However, all other absorption frequencies observed for **14** are similar to those of **13**. All the above indicates that one of the hydrazide groups in **14** forms strong hydrogen bonds as in **13**, but another group obviously is involved in stronger hydrogen interactions.

The presence of a third hydrazide fragment in 15 leads to the appearance of an additional absorption peak $\nu_{as}NH_2NH$ (3340 cm^{-1}) with a higher frequency value compared with **14** and **13**. The increase of the absorption frequency of that peak indicates the participation of the third hydrazide group in weaker hydrogen bonds.

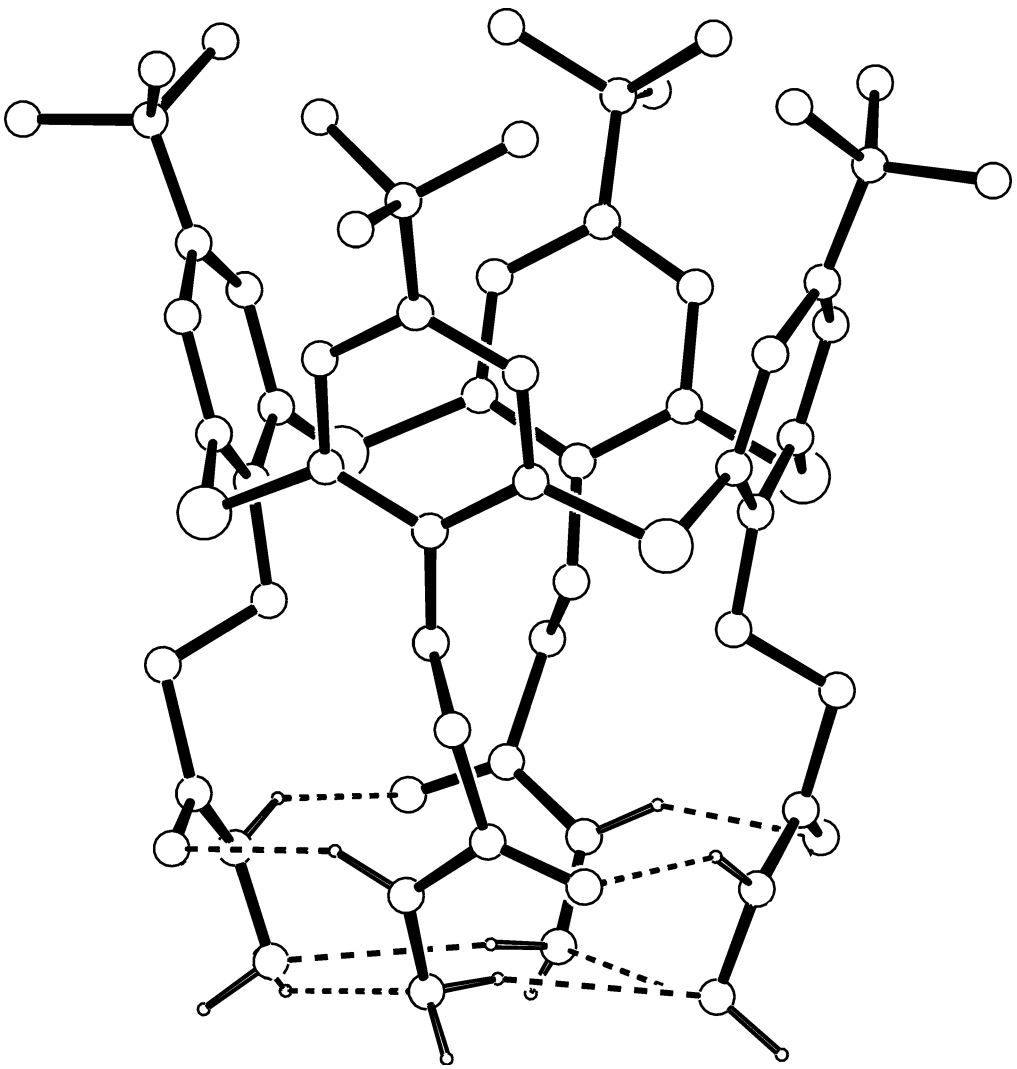


Figure 1. Molecular structure of tetrahydrazide **16b**, obtained by semi-empirical geometry optimization (AM1).

IR spectra of calix[4]arenes **17**, **18** in solid phase differ essentially from the spectra of their acyclic analogues by the appearance of high frequency absorption peaks in the *v*NH region. The maxima of these peaks are nearly equal to those of the free NH vibrations of acetylhydrazide **13**, which are observed in CCl_4 solutions. They have not been detected in the IR spectra of **16a** and **16b**. Thus, the increase of the number of hydrazide fragments on the aromatic rings in contrast to monosubstituted phenol fragments leads to a steric hindrance in the molecules. As a result it prevents all hydrazide groups from binding by strong hydrogen bonds.

Unfortunately detailed investigations of the structure of these molecules by IR spectroscopy in solution are feasible only with difficulty because resorcinol and pyrogallol derivatives are insoluble in nonpolar solvents. However, they are more soluble in polar solvents, for example in DMSO, whereas compounds **15** and **18a** are soluble even in water.

^{1}H NMR spectra of hydrazides **17**, **18** in DMSO at 303 K show broad signals. In all cases there are two signals for each proton of aromatic group. With increasing temperature to 373 K coalescence of these peaks is observed. Compounds **17**, **18** were synthesized from calixarenes having cone conformation. Taking this fact and the obtained results into consideration, it may be concluded that at ambient temperature compounds **17**, **18** adopt a less symmetrical ''boat'' conformation [21], where two opposite phenyl rings face to each other in the cavity and two flattened rings are oriented outside the cavity. In some usual cases fast interconversion between boat – cone – boat conformations is observed. In our situation this phenomenon does not occur. The hydrazide groups of adjacent aromatic rings are probably connected by intramolecular hydrogen bonds.

The chemical shift values of the compounds presented in Table 2 correspond only to the *trans*-amide form of the hydrazide fragment. In all cases we found a prevalence of the *trans*-conformers with a percentage of 98–100%, which is in accordance with IR data. Only for compound **18b** this value decreases to 90%. The assignments of *cis*/*trans*-rotamers were done from the NMR spectroscopic data as described in our previous work [22]. It is interesting to note that spectra of solutions of hydrazides **16** in contrast to those of **17** and **18** considerably change upon heating. Bearing in mind the complexity of the problem, a more detailed study is in progress.

In order to evaluate the ability of calix[4]arenes **16a** and **16b** to recognize metal ions, a liquid–liquid extraction experiment of these ions has been carried out (Figure 2). To understand the chelating effect of four acetylhydrazide fragments in the metal binding, the behavior of the acyclic monomeric analogue **13** was studied. It was observed that the metals presented in Figure 2 are not extracted by compound **13**. At the same time hydrazidocalix[4]arene **16a** and hydrazidothiacalix[4]arene **16b** show a significant complexation with d- and f-elements and a lack of binding with alkali metals. The extraction yield for the alkali ions ($E < 1\%$) was very low. Also a poor extraction was observed for the alkali-earth metal ion Ca^{2+} (16.4% for **16a** and $E = 5.5\%$ for **16b**), which is however still apparently higher than for alkali metal ions. It's known that the Ca^{2+} ion is more hydrated than alkali ions [23]. The strong ability of the ligand to desolvate the metal ion can be attributed to the four hydrazide groups preorganized on the lower rim and the hydrophobicity of the molecular cavity. So, the extraction selectivity for transitions metals over alkali and alkali-earth metal ions could be efficiently used in practice.

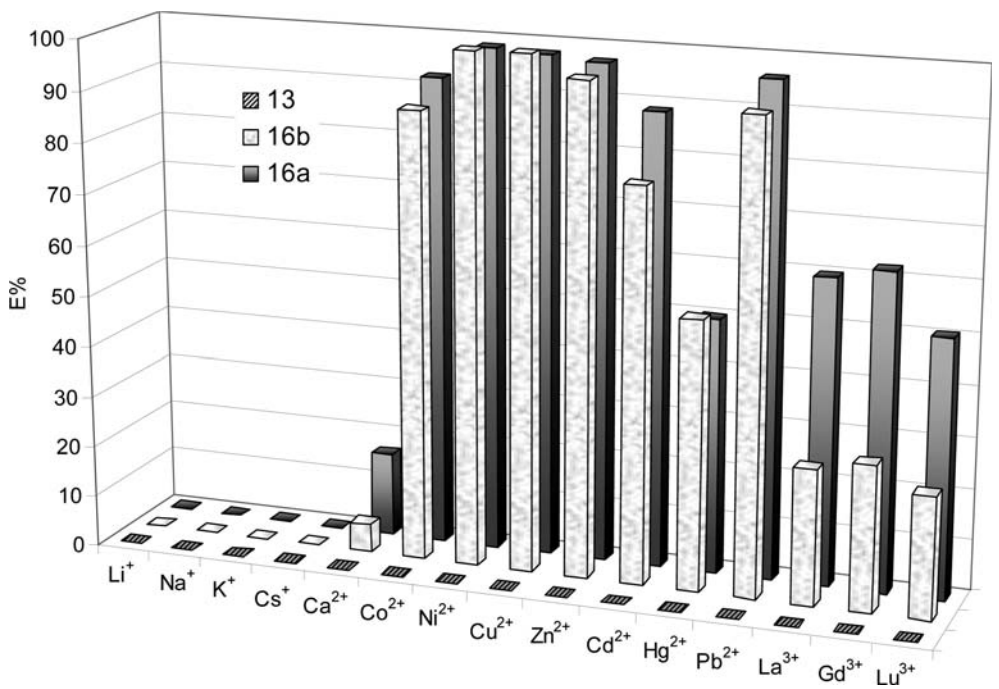


Figure 2. Extraction percentage of cations as a function of the nature of the ligands.

The presence of soft binding sites in **16**, which are usually provided by nitrogen atoms, yields the most effective extraction of d-elements. The extraction selectivity of **16a** and **16b** is similar. However the extraction efficiency for **16b** is lower. This fact is probably due to the S atom not being involved in the metal coordination. But the increased size of the lower rim in thiacalix[4]arenes as compared with calix[4]arenes leads to an increase of conformational flexibility of **16b** which results in a decreasing efficiency of its interaction with metal ions.

Conclusions

Our experimental results have confirmed that the acetylhydrazide derivatives can be effectively obtained for family of calix[4]arenes. The synthesized calix[4]phenoles adopt the cone conformation while the calix[4]resorcinol and calix[4]pyrogallol derivatives prefer the boat conformation. The amide fragment of the hydrazide groups predominantly exists in the *trans*-conformation. The strong circular intramolecular hydrogen bonds between all NH· O=C groups for tetrathiacalix[4]arene **16b** are realized. The hydrazide groups of adjacent aromatic rings in calix[4]resorcinols **17** and calix[4]pyrogallols **18** are connected by intramolecular hydrogen bonds. Based on extraction data it has been concluded that differences in the binding ability can be attributed to the preorganization of acetylhydrazide groups on the calix[4]arene platform.

These results open the way for obtaining of new nitrogen-containing calixarenes on the basis of their acetylhydrazide derivatives. Further deeper investigations of the complexability with various ions, biological and catalytic activity of new family of hydrazides require more experiments, which we are presently involved in.

Acknowledgements

This work was supported by the Russian Fund for Basic Research (grants 04-03-32992a, 05-03-08086ofi_a, 05-03-32558a) and a grant of the Academy of Science of the Republic of Tatarstan (07-7.1-264).

References

1. C.D. Gutsche: Calixarenes Revisited. In: J.F. Stoddart (ed.), *Monograph in Supramolecular Chemistry*, The Royal Society of Chemistry, Cambridge (1998).
2. Z. Asfary, V. Böhmer, J. Harrowfield, and J. Vicens (eds.) *Calixarenes 2001*, Kluwer Academic Publishers, Dordrecht (2001).
3. R.I. Machkhoshvili and R.N Shchelokov: *Russ. J. Coord. Chem* **26**, 677 (2000).
4. V. Kogan, V. Zelentsov, G. Larin, and V. Lhukov: *Complexes of transitional metals with hydrazones*. In: A.Y. Tsivadze (ed.), Nauka, Moscow, (1990).
5. K. Stott, J. Stonehouse, J. Keeler, T.L. Hwang, and A.J Shaka: *J. Am. Chem. Soc*. **117**, 4199 (1995).
6. HyperChem 7.03 Molecular Mechanics and Quantum Chemical Calculations Package, HyperCub Inc., Canada (2002).
7. K. Iwamoto and S Shinkai: *J. Org. Chem*. **57**, 7066 (1992).
8. N. Iki, F. Narumi, T. Fujimoto, and S Miyano: *J. Chem. Soc. Perkin Trans*. **2**, 2745 (1998).
9. W. Iwanek: *Tetrahedron Asymmetry* **9**, 3171 (1998).
10. A.N. Koppehele, Ph.D. Thesis, Dresden University of Technology, (2005).
11. A. Yamada, T. Murase, K. Kikukawa, T. Arimura, and S Shinkai: *J. Chem. Soc. Perkin Trans. 2* **5**, 793 (1991).
12. A.W. Archer and P.A Claret: *J. Chem. Soc. Sect. C*. **9**, 1296 (1970).
13. A. Giacosa: *J. Praktisch. Chemie*. **2**, 396 (1879).
14. G.R. Davletshina, I. Stibor, E.Kh. Kazakova, E.M. Pinkhasik, F.Kh. Karataeva, and A.I Konovalov: *Russ. J. Gen. Chem*. **67**, 1909 (1997).
15. E.A. Alekseeva, V.A. Bacherikov, A.I. Gren, A.V. Mazepa, V.Y. Gorbatyuk, and S.P Krasnoshchekaya: *Russ. J. Org. Chem* **36**, 1321 (2000).
16. A.P. Grekov and V.Ya. Veselov: *Physical chemistry of hydrazine*. In: U.L. Spirin (ed.), Naukova Dumka, Kiev (1979).
17. L.J. Bellamy: *The IR Spectra of Complex Organic Molecules*, 2nd ed.,, Wiley, New York, Methuen, London (1958).
18. E. Titov, A. Grekov, I. Rybachenkov, and V Shevchenko: *Teor. Eksp. Khim*. **4**, 742 (1968).
19. A.G.S Hogberg: *J. Am. Chem. Soc*. **102**, 6046 (1980).
20. L. Abis, E. Dalcanale, A. DuVosel, and S. Spera: *J. Org. Chem* **53**, 5475 (1988).
21. P. Lhotak, V. Stastny, P. Zlatuskova, I. Stibor, V. Michlova, M. Tradlecova, M. Havlicek, and J. Sykora: *Collect. Czech. Chem. Commun*. **65**, 757 (2000).
22. V.V. Syakaev, S.N. Podyachev, B.I. Buzykin, Sh.K. Latypov, W.D. Habicher, and A.I. Konovalov: *J. Mol. Struct*. (in press).
23. M.A. Burgess: *Metal Ions in Solution*, Ellis Horwood, England (1978).