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**Paper**
**Статья**

# Pillar[5]arenes with Morpholide and Pyrrolidide Substituents: Synthesis and Complex Formation with Alkali Metal Ions

Dmitry N. Shurpik,[a] Luidmila S. Yakimova,[a] Leysan I. Makhmutova,[a]
Aigul R. Makhmutova,[a] Ildar Kh. Rizvanov,[b] Vitaly V. Plemenkov,[c]
and Ivan I. Stoikov[a@]

[a]Kazan Federal University, A.M. Butlerov Chemical Institute, 420008 Kazan, Russian Federation
[b]A.E. Arbuzov Institute of Organic and Physical Chemistry of KSC RAS, 420088 Kazan, Russian Federation
[c]Immanuel Kant Baltic Federal University, Institute of Biochemistry, 236041 Kaliningrad, Russian Federation
@Corresponding author E-mail: ivan.stoikov@mail.ru

*Novel pillar[5]arenes containing morpholide and pyrrolidide were synthesized by step-by-step functionalization of the perhydroxylated pillar[5]arene. Binding properties of the compounds toward alkali metal cations (Li$^+$, Na$^+$, K$^+$, and Cs$^+$) were investigated. The $10^2$-$10^3$ M$^{-1}$ association constants were determined for the complexes obtained by derivatives of the pillar[5]arenes with alkali metal cations with 1:1 stoichiometry by electron spectroscopy. It was shown, that the Li$^+$ binding was most effective.*

**Keywords**: Pillar[5]arene, synthesis, molecular recognition, heterocycle, macrocycle.

# Пиллар[5]арены с морфолидными и пирролидидными группами: синтез и комплексообразование с ионами щелочных металлов

Д. Н. Шурпик,[a] Л. С. Якимова,[a] Л. И. Махмутова,[a] А. Р. Махмутова,[a]
И. Х. Ризванов,[b] В. В. Племенков,[c] И. И. Стойков[a@]

[a]Казанский (Приволжский) федеральный университет, Химический институт им. А.М. Бутлерова, 420008 Казань, Россия
[b]Институт органической и физической химии им. А.Е. Арбузова КНЦ РАН, 420088 Казань, Россия
[c]Балтийский федеральный университет им. Иммануила Канта, Институт биохимии, 236041 Калининград, Россия
@E-mail: ivan.stoikov@mail.ru

*Синтезированы новые пиллар[5]арены, содержащие морфолидные и пирролидидные группы, пошаговой функционализацией гидроксилированного пиллар[5]арена. Методом электронной спектроскопии изучено взаимодействие полученных соединений с катионами щелочных металлов (Li$^+$, Na$^+$, K$^+$, Cs$^+$) и определены величины констант ассоциации ($10^2$-$10^3$ M$^{-1}$) и стехиометрия (1:1) комплексов. Показано, что наиболее эффективно связывается катион лития.*

**Ключевые слова:** Пиллар[5]арен, синтез, молекулярное распознавание, гетероцикл, макроцикл.

## Introduction

Currently, there is a large number of synthetic macrocyclic platforms for creating supramolecular receptors and each of them has its own particular role in modern supramolecular chemistry. The literature describes a variety of cage-like organic molecules with accessible internal cavities, *e.g.*, crown ethers,[1] cyclodextrins,[2] cucurbiturils,[3] and calixarenes,[4-6] which can serve as hosts. In recent years, a new class of synthetic macrocycles - pillar[n]arenes - attracts the interest of researchers.[7,8]

Pillar[n]arenes belong to a new generation of macrocyclic hosts for supramolecular chemistry. The macrocyclic cavity of pillar[5]arene has the size comparable to a cavity of cyclodextrines and calixarenes well known as effective complexing reagents for organic and inorganic compounds. Their repeating units are connected by methylene bridges at the *para*-positions, forming a special rigid pillar-like architecture.[9] The unique structure and easy functionalization of pillararenes allow the synthesis of novel macrocycles able to bind selectively the different kinds of guests and provide a useful platform for construction of various interesting supramolecular systems.



R = H, Alkyl; n = 1-11
**1**, R = CH₃, n = 1;
**2**, R = H, n = 1
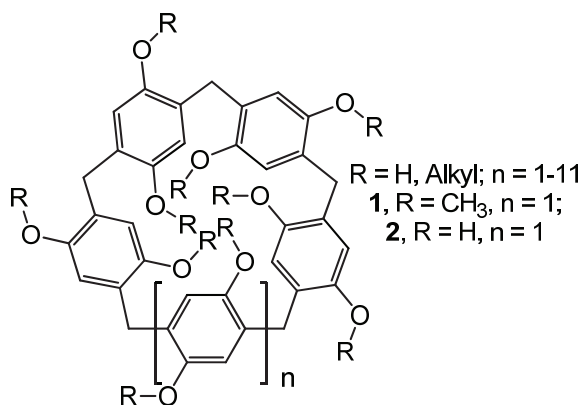
The pillar[5]arene is of the greatest interest among other possible isomers of pillar[n]arenes due to the highest yield of the synthesis.[10,11] In 2008, Tamoko Ogoshi *et al.* published first article about the pillar[5]arene synthesis with 22 % product yield.[9] Later on, the yield was increased up to 71 %[10] by addition of an excess of paraformaldehyde and up to 81 % in the presence of the catalyst, trifluoroacetic acid.[11]

To date, the scope of pillar[5]arenes is very diverse, but no close studies for selective binding of metal cations were published.[12-13] In this work, the synthesis of novel pillar[5]arenes containing morpholide and pyrrolidide units and their receptor properties toward metal ions of *s*-elements (Li$^+$, Na$^+$, K$^+$, Cs$^+$) are described.

## Experimental

### General

$^1$H NMR spectra were recorded on the Bruker Avance-400 (400 MHz) spectrometer and $^{13}$C and 2D NOESY NMR spectra were obtained on the impulse spectrometer Bruker Avance II (with 125 MHz and 500 MHz respectively). Chemical shifts were determined against the signals of residual protons of deuterated

solvent (CDCl$_3$). The concentration of sample solutions was 3-5 %.

Attenuated total internal reflectance IR spectra were recorded with Spectrum 400 (Perkin Elmer) Fourier spectrometer.

Elemental analysis was performed with Perkin Elmer 2400 Series II instrument.

The mass spectra were obtained on Bruker Ultraflex III MALDI-TOF instrument using 4-nitroaniline matrix.

Melting points were determined using the Boetius Block apparatus.

Additional control of the purity of compounds and monitoring of the reaction were carried out by thin-layer chromatography using Silica G, 200 μm plates, UV 254.

Most chemicals were purchased from Aldrich and used as received without additional purification. Organic solvents were purified in accordance with standard procedures.

*General procedure of the synthesis of compounds 1 and 2.* Initial 1,4-dimethoxypillar[5]arene **1** was obtained from commercially available 1,4-dimethoxybenzene by literary method.[11] Further removal of methoxyl protections led to pillar[5]arene **2**.[10] For further purification pillar[5]arene was repeatedly washed with chloroform and water.

*1,4-Dimethoxypillar[5]arene (1).* Product yield: 80 %. Mp: 249 °C, 248.8 °C.[11] $^1$H NMR (CDCl$_3$) δ ppm: 3.74 (s, 30H, -OCH$_3$), 3.76 (s, 10H, -CH$_2$-), 6.80 (s, 10H, ArH). MALDI-TOF MS C$_{45}$H$_{50}$O$_{10}$: calculated [M$^+$] *m/z* = 750.3, found [M+Na]$^+$ *m/z* = 773.4, [M+K]$^+$ *m/z* = 789.5.

*Pillar[5]arene (2).* Product yield: 91 %. The decomposition was observed at 230°C without melting. $^1$H NMR (CD$_3$COCD$_3$) δ ppm: 3.66 (s, 10H, -CH$_2$-), 6.64 (s, 10H, ArH), 7.99 (s, 10H, -OH). MALDI-TOF MS C$_{35}$H$_{30}$O$_{10}$: calculated [M$^+$] *m/z* = 610.2, found [M+Na]$^+$ *m/z* = 633.1, [M+K]$^+$ *m/z* = 649.2.

*General procedure of the synthesis of compound 3.* Pillar[5]arene **2** (1.50 g, 2.4 mmol) was suspended in 70 ml of acetonitrile containing anhydrous K$_2$CO$_3$ (5.00 g, 36 mmol). The reaction mixture was stirred while refluxing for 20 min. An excess of ethyl bromoacetate (6.70 ml, 6.00 mmol) and catalytic amount of KI were added to the suspension formed. The reaction mixture was stirred while refluxing for 24 hrs. After cooling, the residue from the reaction mixture was filtered off and dissolved in minimum amount of chloroform. An excess of methanol was slowly added to the solution obtained. The solvent was removed under reduced pressure. The residue was filtered and dried at r.t. Pillar[5]arene with ester fragments **3** was obtained.

*4,8,14,18,23,26,28,31,32,35-Deca[(ethoxycarbonyl)methoxy]pillar[5]arene (3).* Product yield: 2.81 g (75 %). Mp: 199 °C, 196.7 °C.[13] $^1$H NMR (CDCl$_3$) δ$_H$ ppm (*J*/Hz): 0.96 (m, 30H, -CH$_2$CH$_3$), 3.86 (s, 10H, -CH$_2$-), 4.09 (m, 20H, -CH$_2$CH$_3$), 4.55 (dd, 20H, O-CH$_2$C(O)-), 7.04 (s, 10H, ArH). $^{13}$C NMR (CDCl$_3$) δ$_C$ ppm: 196.3, 148.9, 128.7, 114.4, 65.7, 60.8, 29.2, 13.8. MALDI-TOF MS: calculated [M$^+$] *m/z* = 1471.24, found [M+Na]$^+$ *m/z* = 1494.28. Found: C, 61.30; H, 6.28. Calculated for C$_{75}$H$_{90}$O$_{30}$: C, 61.22; H, 6.16.

*General procedure of the synthesis of compound 4.* In a round-bottom flask equipped with magnetic stirrer, the compound **3** (0.60 g, 0.4 mmol), 60 ml THF and 30 ml NaOH solution (20 %) were refluxed for 15 hrs. After cooling, the solvent was removed under reduced pressure. The residue was dissolved in minimum amount of distilled water. The excess of 2 M aqueous HCl was added to the reaction mixture. The residue from the reaction mixture was filtered off and washed with distilled water for several times.

*4,8,14,18,23,26,28,31,32,35-Deca(carboxymethoxy)pillar[5]arene (4).* Product yield: 0.40 g (83 %). Mp: 243 °C, 293 °C.[14] $^1$H NMR (CDCl$_3$) δ$_H$ ppm (*J*/Hz): 3.74 (s, 10H, -CH$_2$-), 4.41 (d AB-system, 10H, $^2J_{HH}$= 16.0 Hz, O-CH$_2$C(O)-OH), 4.70 (d AB-system, 10H, $^2J_{HH}$= 16.0 Hz, O-CH$_2$C(O)-OH), 7.10 (s, 10H, ArH), 12.94 (br. s, 10H, -C(O)-OH). $^{13}$C NMR (CDCl$_3$) δ$_C$ ppm: 170.47; 148.46; 128.07; 114.24; 65.08; 28.58. IR ν cm$^{-1}$: 3051 (-C(O)-*OH*), 2911

(-CH$_2$-), 1730 (-*C(O)*-OH), 1209 (Ph-O-CH$_2$-). MALDI-TOF MS: calculated [M$^+$] *m/z* = 1190.24, found [M+Na]$^+$ *m/z* = 1213.2. Found: C, 55.63; H, 4.18. Calculated for C$_{55}$H$_{50}$O$_{30}$: C, 55.47; H, 4.23.

*General procedure of the synthesis of compounds 5 and 6.* To decacarboxylic acid **4** (0.30 g, 0.25 mmol) in a round bottom flask, 10 ml (0.08 mmol) of SOCl$_2$ and catalytic amount of DMF were added. The reaction mixture was refluxed for 18 hrs before full dissolution of decacarboxylic acid **4**. The solvent was removed under reduced pressure. The obtained yellow powder was solved in CH$_2$Cl$_2$ (20 ml) and suitable amine (pyrrolidine or morpholine) (7.56 mmol) and triethylamine (5 ml, 0.04 mol) were added. Reaction mixture was stirring at room temperature during 48 hrs under argon, washed with hydrochloric acid solution (2×30 ml) and water (2×30 ml). The organic layer was separated, dried (mol. sieves, 3 Å), the solvent was removed under reduced pressure. The residue was crystallized from ethanol as light-yellow powder.

*4,8,14,18,23,26,28,31,32,35-Decakis[(N-pyrrolidido-carbonyl)methoxy]pillar[5]arene (5).* Light-yellow powder, yield: 0.3 g (70 %). Mp: 267 °C. $^1$H NMR (CDCl$_3$) $\delta_H$ ppm (*J/Hz*): 1.86 (m, 30H, -N(CH$_2$C*H*$_2$)$_2$), 1.98 (m, 10H, -N(CH$_2$C*H*$_2$)$_2$), 3.36 (m, 10H, -N(C*H*$_2$CH$_2$)$_2$), 3.45 (m, 10H, -N(C*H*$_2$CH$_2$)$_2$), 3.58 (m, 10H, -N(C*H*$_2$CH$_2$)$_2$), 3.87 (m, 10H, -N(C*H*$_2$CH$_2$)$_2$), 3.94 (s, 10H, -CH$_2$-), 4.57 (d AB-system, 10H, $^2J_{HH}$ = 14.4 Hz, O-CH$_2$C(O)N-), 4.85 (d AB-system, 10H, $^2J_{HH}$ = 14.4 Hz, O-CH$_2$C(O)N-), 7.48 (s, 10H, ArH). $^{13}$C NMR (CDCl$_3$) $\delta_C$ ppm: 167.66; 149.25; 128.31; 114.81; 66.78; 45.79; 45.37; 29.45; 26.36; 24.26. $^1$H-$^1$H NOESY (NOE) (the major cross-peaks): H$^7$/H$^{10}$, H$^9$/H$^6$, H$^6$/H$^7$, H$^3$/H$^8$, H$^5$/H$^3$. IR ν cm$^{-1}$: 2923 (-CH$_2$-), 2870 (-CH$_2$-), 1651 (C(O)N=), 1210 (Ph-O-CH$_2$-). MALDI-TOF MS: calculated [M$^+$] *m/z* = 1721.9, found [M+Na]$^+$ *m/z* = 1744.8, [M+K]$^+$ *m/z* = 1759.9. Found: C, 66.26; H, 7.02; N, 8.13. Calculated for C$_{95}$H$_{120}$N$_{10}$O$_{20}$: C, 63.01; H, 6.13; N, 6.80 %.

*4,8,14,18,23,26,28,31,32,35-Decakis[(N-morpholido-carbonyl)methoxy]pillar[5]arene (6).* Light-yellow powder, yield: 0.40 g (84 %). Mp: 223 °C. $^1$H NMR (CDCl$_3$) $\delta_H$ ppm (*J/Hz*): 3.49-3.60 (m, 20H, -N(C*H*$_2$CH$_2$)$_2$O), 3.67-3.80 (m, 60H, -C*H*$_2$OC*H*$_2$-, -N(C*H*$_2$CH$_2$)$_2$O), 3.90 (s, 10H, -C*H*$_2$-), 4.65 (d AB-system, 10H, $^2J_{HH}$ = 13.8 Hz, O-CH$_2$C(O)N-), 4.75 (d AB-system, 10H, $^2J_{HH}$ = 13.8 Hz, O-CH$_2$C(O)N-), 7.39 (s, 10H, ArH). $^{13}$C NMR (CDCl$_3$) $\delta_C$ ppm: 167.39; 149.19; 128.41; 114.91; 66.80; 66.25; 45.23; 41.89; 29.31. $^1$H-$^1$H NOESY (NOE) (the major cross-peaks): H$^9$/H$^{10}$, H$^9$/H$^6$, H$^9$/H$^7$, H$^5$/H$^3$, H$^8$/H$^3$. IR ν cm$^{-1}$: 2855 (-CH$_2$-), 1652 (C(O)N=), 1208 (Ph-O-CH$_2$-). MALDI-TOF MS: calculated [M$^+$] *m/z* = 1881.8, found [M+Na]$^+$ *m/z* = 1904.6, [M+K]$^+$ *m/z* = 1919.6. Found: C, 59.63; H, 6.18; N, 7.27. Calculated for C$_{95}$H$_{120}$N$_{10}$O$_{30}$: C, 60.63; H, 6.43; N, 7.44 %.

## Determination of Stability Constant and Stoichiometry of the Complex by UV Titration

The UV measurements were performed with "Shimadzu UV-3600" instrument. The 1·10$^{-3}$ M solution of metal cations of *s*-elements (Li$^+$, Na$^+$, K$^+$, Cs$^+$, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 μL) in methanol was added to 0.5 ml of the solution of receptors **4-6** (3·10$^{-5}$ M) in methanol and diluted to final volume of 3 mL with methanol. The UV spectra of the solutions were then recorded. The stability constant and stoichiometry of complexes were calculated as described elsewhere.[15] Three independent experiments were carried out for each series. Student's *t*-test was applied in statistical data processing.

## Job Plots

Series of the solutions of pillar[5]arene derivatives **4-6** and metal nitrates (LiNO$_3$, NaNO$_3$, KNO$_3$, CsNO$_3$) were prepared in methanol. The volume of the host and guest solutions varied from 0.6:2.4 to 2.4:0.6, respectively, with the total concentration of the host (H) and guest (G) being constant and equal to 1·10$^{-5}$ M.

The solutions were used without further stirring. The absorbance $A_i$ of the complexation systems was measured at the maximum absorbance wavelength of the complex. The absorbance values were used to plot a diagram from which maximum the structures of the complexes were deduced. Three independent experiments were carried out for each system.

## Results and Discussion

### Synthesis of Pillar[5]arenes 5 and 6

The functionalization of pillar[5]arenes with various groups enables tuning their properties *i.e.*, the ability to molecular recognition, catalysis, active and selective transport. Thus, appropriate functionalization procedures are needed to be developed. For the synthesis of new pillar[5]arene derivatives, two synthetic ways are possible: functionalization of pre-formed perhydroxylated pillar[5]arene **2** (Scheme 1) and cyclization/co-cyclization of 1,4-dialkoxybenzene monomers.[16] In this work, we used first way which consists of step-by-step functionalization of the initial perhydroxylated pillar[5]arene **2**. This approach was successfully applied to the synthesis of the thiacalix[4]arene derivatives and made it possible to obtain functionalized macrocycles with high yields.[17-20]

Perhydroxylated pillar[5]arene **2** has ten reactive OH groups and modification of the OH groups can provide various functionalized pillar[5]arene derivatives. Previously, the pillar[5]arene containing ethoxycarbonyl fragments **3** was synthesized by interaction of perhydroxylated pillar[5]arene **2** with ethyl bromoacetate in the presence of potassium carbonate in acetonitrile (Scheme 1). The base and solvent were specified in accordance with their efficiency in alkylation of *p-tert*-butyl thiacalix[4]arene at the lower rim.[4,17] Besides, KI as catalyst was used in alkylation to increase the product yield.[21] The deca-ester **3** was quantitatively hydrolyzed to corresponding deca-acid **4** by NaOH in the THF solution (Scheme 1).

The interaction of the macrocycle **4** with thionyl chloride in the presence of catalytic amounts of DMF led to deca-acid chloride with nearly quantitative yield. The reaction was carried out without adding solvent. The choice of this synthetic strategy was caused by high yields of analogical reactions using tetraacids of *p-tert*-butyl thiacalix[4]arene.[4,17] Then, the reaction of the macrocycle **4** with pyrrolidine and morpholine in methylene chloride was investigated in the presence of triethylamine (Scheme 2). The latter was used for binding HCl released in the reaction and hence for preventing possible acid catalyzed hydrolysis. These base and solvent are effective in acylation.[17] The synthesis was performed during 48 hrs because the macrocycle **4** has many reaction centers. The macrocycles **5** and **6** were synthesized with high yields (70 % and 84 %, correspondingly).

The structure and composition of the pillar[5]arene derivatives **3-6** were characterized by NMR $^1$H, $^{13}$C, 2D NMR NOESY $^1$H-$^1$H, IR spectroscopy, mass spectrometry (MALDI-TOF) and elemental analysis.

As an example, the MALDI-TOF mass spectrum of the pillar[5]arene **5** (M(C$_{95}$H$_{120}$N$_{10}$O$_{20}$)=1722.0) is shown in Fig-
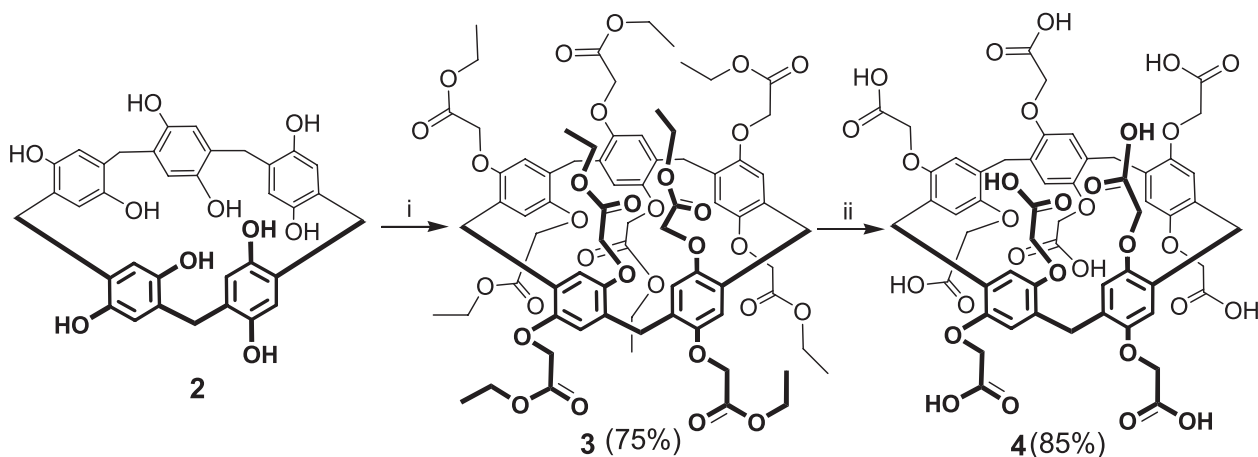
**Scheme 1.** Reagents and conditions: i – ethyl bromoacetate/K$_2$CO$_3$, KI, acetonitrile, reflux; ii - NaOH (20%), THF.
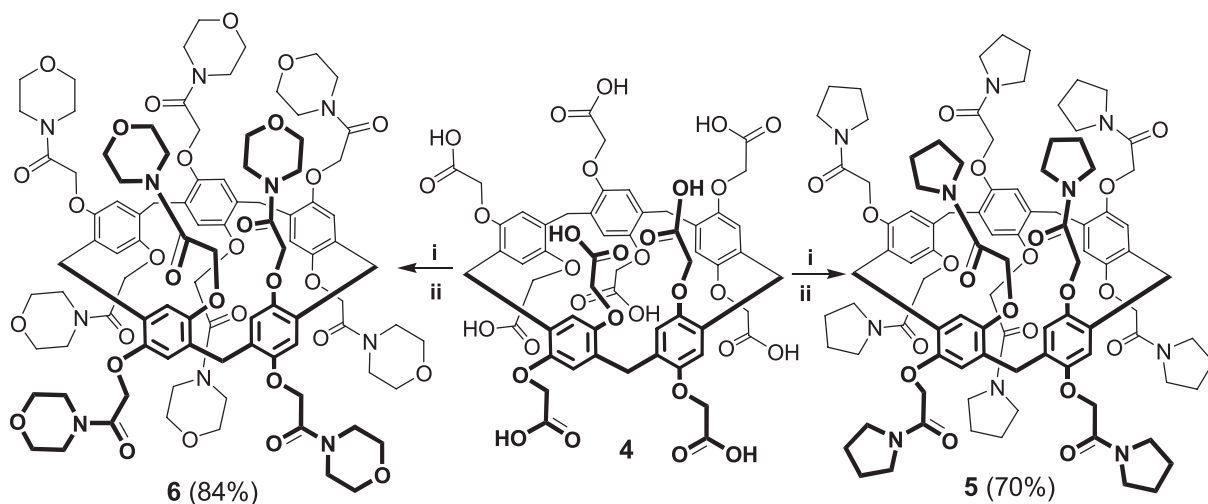


**Scheme 2.** Reagents and conditions: i - SOCl$_2$, reflux; ii - pyrrolidine/morpholine, Et$_3$N/CH$_2$Cl$_2$.

ure 1. In the MALDI-TOF mass spectrum of the compound **5**, the peaks of the molecular ion ($m/z$ (M$^+$) = 1722.8), molecular ion with sodium cation ($m/z$ (M+Na$^+$) = 1744.8) and that with potassium cation ($m/z$ (M+K$^+$) = 1759.9) are presented.
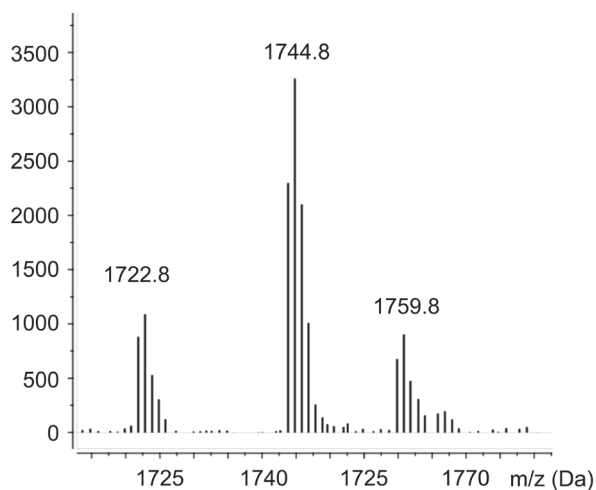


**Figure 1.** MALDI-TOF mass spectrum of compound **5**.

Figure 2 shows the $^1$H NMR spectrum of **5**, in which aromatic proton signals and methylene bridges appear as singlets at 7.49 and 3.90 ppm, correspondingly. It indicates the synthesis of fully acylated product. Interestingly, the chemical shifts and multiplicity of the methylene and aromatic protons are similar to those in calix[n]arene with n≥6.[22] The oxymethylene protons were observed as AB spin system (4.82 and 4.55 ppm) with a spin-spin interaction constant of 14.4 Hz. The pyrrolidine protons appear as multiplets in the field at 3.90 to 1.80 ppm.

The nonequivalence of the protons can result from the macrocycle chirality. The chemical shifts, integrated intensity and multiplicity of all the proton signals in the $^1$H NMR for compound **4** are in good agreement with those proposed for the structure of pillar[5]arene **4**.

The conformational behavior of symmetrical substituted pillar[5]arenes is very important due to rotation ability of the benzene rings, which causes racemization.

When the process is slow (frozen rotation) in terms of the NMR timescale the complication of spin system caused by of the formation of fixed enantiomeric conformer of pillar[5]arenes is observed.[7] A characteristic indicator
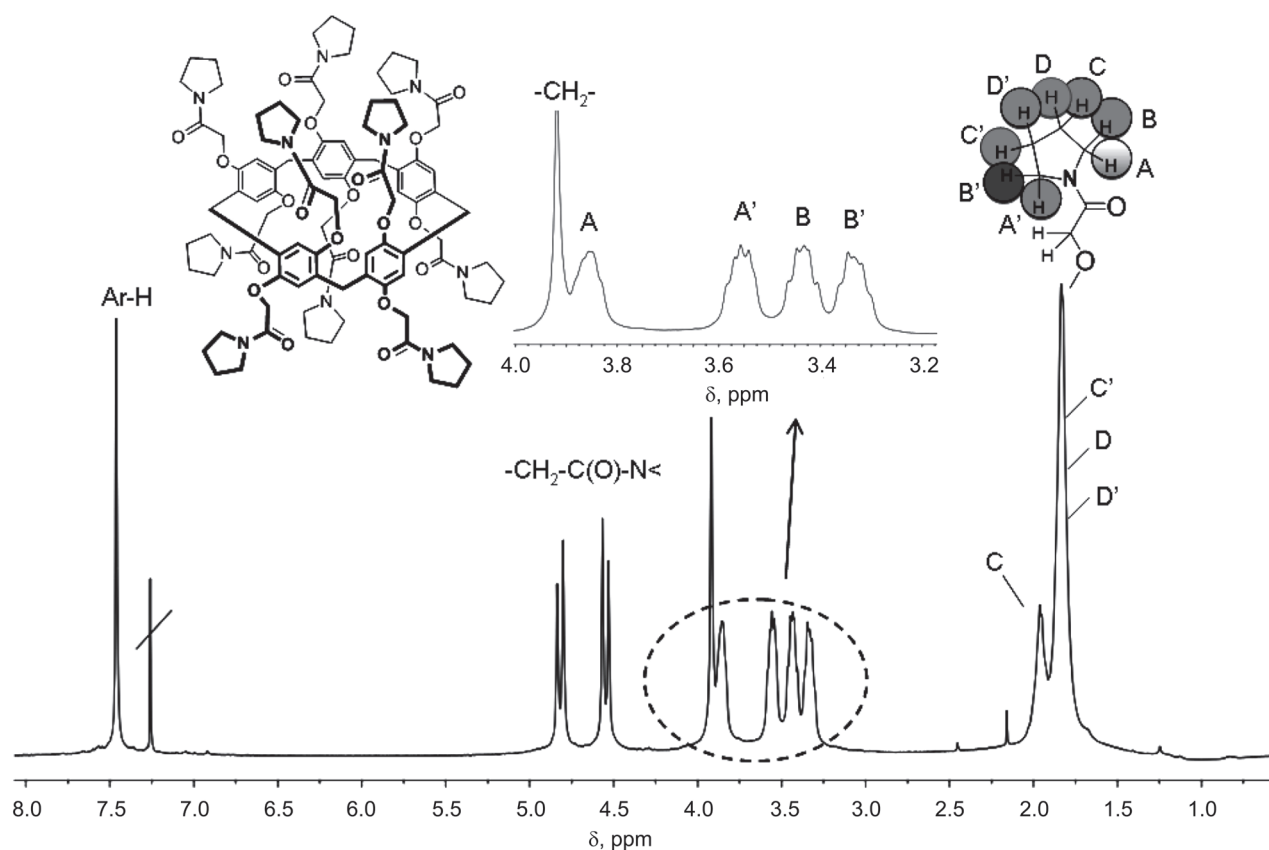
**Figure 2.** ¹H NMR spectrum of compound **5** (CDCl₃, at 25 °C, Bruker Avance-400).

for these molecular dynamics is provided by the signals of the OCH₂ groups in the ¹H NMR spectra. In compounds **3-6** the proton signals of methylene bridge (peak A), both oxymethylene fragments (peak B) were observed as singlet and doublets of AB spin system correspondingly (Figure 3, Table 1).

It indicates that the structure of pillar[5]arenes **3-6** is in frozen Dₙ conformation[7] and mobility of the oxyme-thylene protons was suppressed.[14] Therefore, this fact is in contrast to the review[7] about fast rotation of the benzene rings in compound **3**.
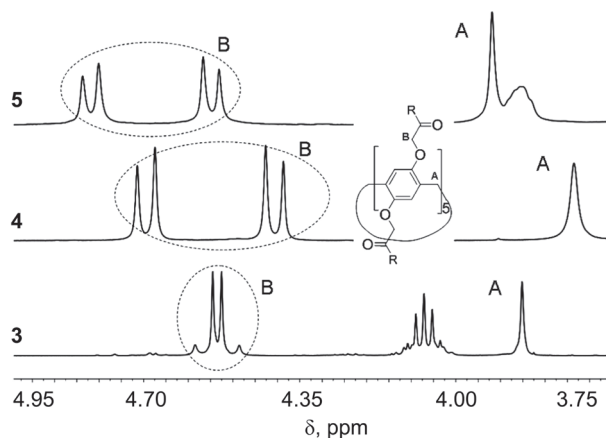


**Figure 3.** Partial ¹H NMR spectra of compounds **3** (R=OH) in DMSO-$d_6$, **4** (R=OC₂H₅) and **5** (R=1-(pyrrolidin-1-yl)) in CDCl₃ at 25 °C.

**Table 1**. Characterization of pillar[n]arenes **3-6** by ¹H NMR spectroscopy in CDCl₃ at room temperature.

| compound | Spin system of the protons | | $^3J_{HH}$/Hz |
|---|---|---|---|
| | CH₂ | OCH₂ | |
| **3** | A₂ (s) | AB | 15.8 |
| **4** | A₂ (s) | AB | 16.0 |
| **5** | A₂ (s) | AB | 14.4 |
| **6** | A₂ (s) | AB | 13.8 |

The IR spectra of the compounds **4-6** contain main characteristic bands of C=O groups. Initial compound **4** with carboxyl groups shows absorption band at 1730 cm⁻¹. It is typical for various carboxylic acids. In the IR spectrum of the macrocycles **5** and **6**, the displacement of this band in short-wave region (1651 cm⁻¹) is observed. Also, an absorption band of morpholide and pyrrolidide fragments (1029-1108 cm⁻¹) absent in the parent macrocycle **4** was recorded. The IR spectrum of the macrocycle **4**, contrary to the pillar[5]arenes **5** and **6** contains valence vibrations of the -OH group (3057 cm⁻¹). This testifies full replacement of hydroxyl protons of the parent macrocycle **4**.

Thus, new pillar[5]arenes containing morpholide and pyrrolidide fragments were synthesized. The structure of the compounds obtained was characterized by ¹H NMR, ¹³C, IR spectroscopy and mass spectrometry (MALDI-TOF). The spatial structure of new functionalized pillar[5]arenes was established by two-dimensional 2D NMR NOESY ¹H-¹H spectroscopy.

## Complexation Study of the Synthesized Pillar[5]arenes 4-6 by UV Spectroscopy

The most popular approach for quantifying host-guest interactions is a UV-titration of the host by the guest solution, fixing the changes in some physical. Changes in the absorbance spectrum of the pillar[5]arenes after addition of nitrates of alkali metals indicated the formation of their complexes with the substrates. The interaction between metal ions and pillar[5]arenes 4-6 in methanol monitored by UV-spectroscopy showed significant changes in the absorbance spectrum of the macrocycles after the addition of the guest molecules. The hyperchromic effect was observed at 200-250 nm. To quantify molecular recognition of the nitrates of alkali metals by pillar[5]arenes 4-6, the stability constants and the stoichiometry of the macrocycle-substrate complex formed in the organic phase were established. To quantify the molecular recognition of the nitrates of alkali metals by pillar[5]arenes 4-6, the stability constants and the stoichiometry of the complex "pillar[5]arene – alkali metal cation" formed in the methanol were established (Table 2). Further information on the metal ions binding stoichiometry of pillar[5]arenes 4-6 was obtained from Job's plot. The Figure 4 shows the results for $5$-Li$^+$ complexation at 220 nm. The maximum point of the mole fractions was found to be about 0.5, suggesting a ligand-metal ratio of 1:1 in the
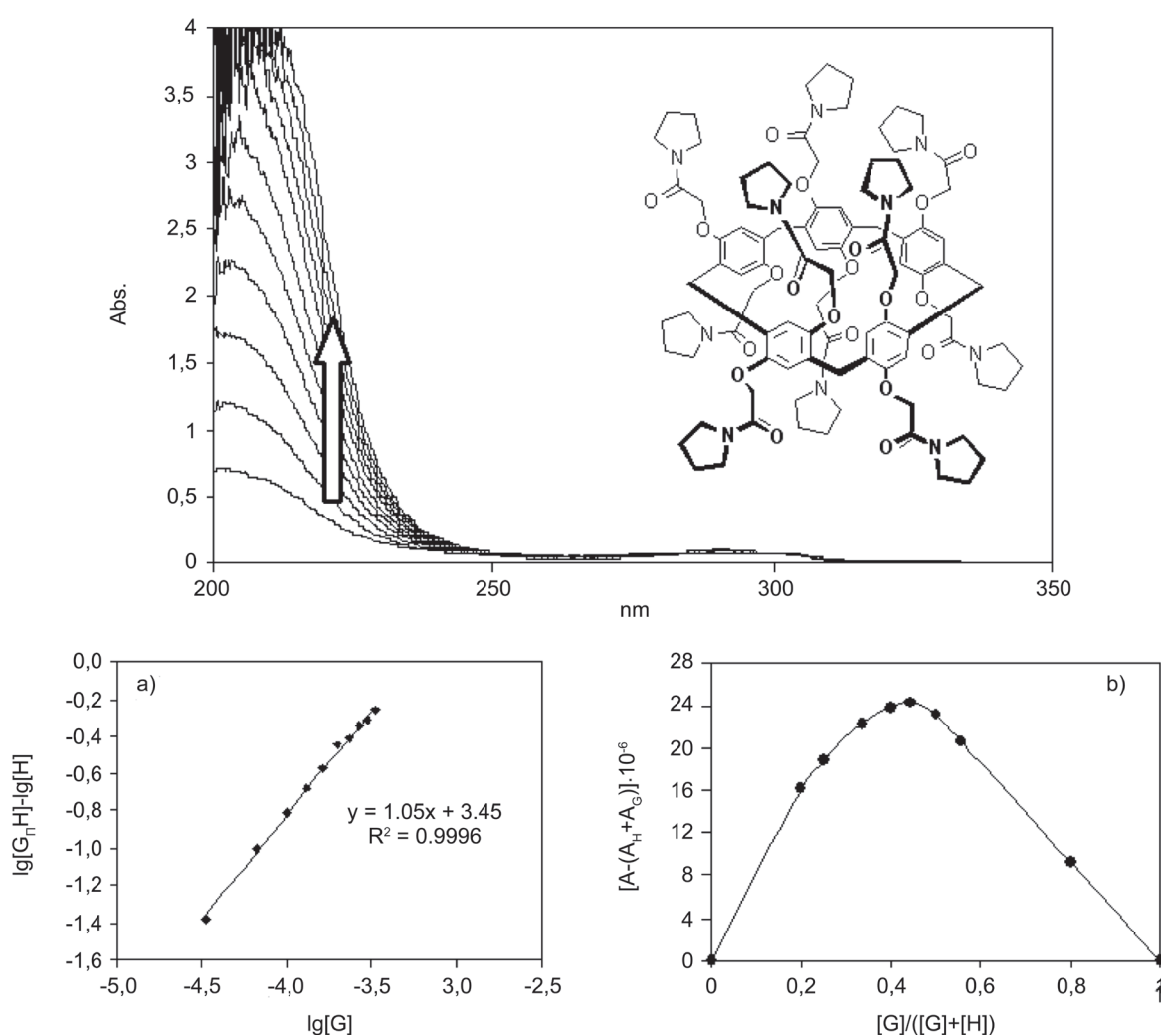


**Figure 4.** Spectrophotometric titration of system pillar[5]arene **5** and Li$^+$ in methanol. The insets show (a) the titration curve and (b) the Job's plot for the determination of the stoichiometry in the complex.

**Table 2.** Association constants ($\lg K_{ass}$) for the complexation of pillar[5]arenes **4-6** with metal ions of $s$- (Li$^+$, Na$^+$, K$^+$, Cs$^+$) elements in methanol at 298 K.

| Host | $\lg K_{ass}$ | | | |
|---|---|---|---|---|
| | Li$^+$ | Na$^+$ | K$^+$ | Cs$^+$ |
| **4** | 3.33±0.11 | 2.67±0.18 | 2.71±0.13 | 2.52±0.16 |
| **5** | 3.53±0.11 | 2.19±0.16 | 2.78±0.12 | 2.31±0.14 |
| **6** | 3.60±0.07 | 2.15±0.02 | 2.46±0.17 | 2.45±0.12 |

complex. Similarly to that, all the systems studied formed the 1:1 complexes. The calibration curve shows a good linearity with the correlation coefficient of 0.9996. Using the same method, the binding stoichiometry coefficients of pillar[5]arene - metal ions were also obtained as a ligand-metal ratio of 1:1 in the complex.

The log$K_{ass}$ values of the complexes obtained varied between 2.15 and 3.60. The pillar[5]arenes **4-6** showed similar binding strength towards Na$^+$, K$^+$, Cs$^+$. In case of Li$^+$ ion the corresponding $K_{ass}$ values were 10-fold higher than those calculated for other ions studied. As a whole, the binding efficiency decayed from Li$^+$ to Cs$^+$. Interestingly, K$^+$ is bonded more strongly than Na$^+$. For the compound **4** containing carboxylic groups, this difference is insignificant while the binding efficiency of K$^+$ *vs* Na$^+$ for the compounds **5** and **6** was higher by four and two times, respectively. The results are in good agreement with those the PM3 (tm) analysis of thermodynamic data.[23] Interestingly, K$^+$ is predicted to be bonded more strongly than Na$^+$ by 25 kJ·mol$^{-1}$. The binding of larger cation can be impeded by rotation of the functional groups of the macrocycle, the energy of the cation desolvation, displacement of encapsulated solvent or other phenomena leading to the selectivity toward Na$^+$ over that to K$^+$.[23]

The results obtained agree with those from molecular simulation[23] of the pillar[5]arene derivatives complexes with metal cations, where a weak non-selective interaction with a series of guests was found. Probably, such an insignificant selectivity among pillar[5]arene derivatives in relation to cations of alkali metals testifies that host-guest binding performed with participation of phenolic oxygen atoms instead of functional groups.

## Conclusion

In summary, symmetric hosts – pillar[5]arenes containing carboxylic, morpholide and pyrrolidide units – were synthesized and its complexation towards the alkali metal cations (Li$^+$, Na$^+$, K$^+$, Cs$^+$) investigated by UV spectroscopy. The values of the association constants (10$^2$-10$^3$ M$^{-1}$) of the complexes obtained by derivatives of the pillar[5]arenes **4-6** with alkali metal cations with 1:1 stoichiometry were determined by electron spectroscopy. It was shown, that the Li$^+$ binding is most effective. However, no significant difference was found in the binding capability toward Na$^+$, K$^+$, and Cs$^+$. Interestingly, K$^+$ cation is bonded more strongly than Na$^+$. For the compound **4** containing carboxylic groups, this difference is insignificant, while binding efficiency of K$^+$ *vs* Na$^+$ for **5** and **6** is four and two times higher, respectively. It was for the first time experimentally confirmed that pillar[5]arene derivatives have coordinated by cations of alkali metals via phenolic oxygen atoms and macrocyclic cavity, with no participation of functional groups.

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