Reactions of resorcinarene with $N,N$-dimethylcarbamoyl and $N,N$-dimethylthiocarbamoyl chlorides: factors affecting the process performance

Anastasia V. Burikhina, Olga S. Serkova, Dmitrii V. Tarasenko, Irina I. Levina, Anastasia V. Gorlova, and Vera I. Maslennikova*

Moscow State Pedagogical University, Nesvizhskii Lane 3, Moscow, 119021 Russia
E-mail: him-vim@mail.ru

DOI: http://dx.doi.org/10.3998/ark.5550190.p009.492

Abstract
Carbamoylation and thiocarbamoylation of resorcinarenes in the presence of alkali metal carbonates were studied. The effects of the pre-organization of the resorcinarene molecule, the base used, and the nature of the acylating reagent on the reaction outcome were demonstrated. It was shown that octacarbamoylated resorcinarenes in the boat conformation show high absorption properties and selectivity towards cesium cations.

Keywords: Resorcinarenes, pre-organization, carbamoylation, thiocarbamoylation, alkali metal cations, complexation

Introduction
Resorcinarenes, polyhydroxyaromatic compounds having a molecular cavity, form a convenient basis for the design of receptor systems, because of the ease of modification of these compounds and the possibility of immobilization of the macrocycle in a definite conformation.\textsuperscript{1-4} O-Acylation\textsuperscript{5-9} and O-alkylation of resorcinarenes\textsuperscript{10-15} are used most often to introduce ionophoric groups. Using these reactions, a broad range of polyfunctionalized derivatives of resorcinarenes have been synthesized; many of these compounds exhibit acceptor properties towards metal cations.\textsuperscript{16-21} It is noteworthy that the receptor properties of the synthesized compounds and their selectivity are determined by pre-organization of the macrocyclic core of resorcinarene and the nature of the immobilized ionophoric groups.

In order to create new receptor systems with functional groups containing various sets of electron-donating atoms and located in space in a definite way, we studied carbamoylation and thiocarbamoylation of resorcinarenes with a specific pre-organization of the macrocyclic core.
In agreement with this goal, as macrocyclic substrates, we chose resorcinarenes 1 with $recc$ configuration of alkyl (a-d), alkyaryl (e) and phenyl (f) substituents in the methyldiene bridges, for which crown is the major conformation, and tetranaphthylresorcinarene 2, which occurs in the chair conformation with the $rcct$ configuration of the naphthyl moieties (Fig. 1). $NN$-Dimethylcarbamoyl and $NN$-dimethylthiocarbamoyl chlorides served as the acylating reagents.

![Figure 1. Structure of resorcinarenes 1,2.](image)

**Results and Discussion**

Carbamoylation of resorcinarenes 1 and 2 with $NN$-dimethylcarbamoyl chloride was carried out in acetone at 55-60 °C. Alkali metal carbonates (Na$_2$CO$_3$, K$_2$CO$_3$, Cs$_2$CO$_3$) were used as bases. The resorcinarene : carbamoyl chloride : carbonate reactant ratio was 1:12:12.

In the presence of Na$_2$CO$_3$, the reaction was in all cases slow and non-selective. Even long-term heating (for more than 40 h) of the reaction mixtures did not result in the formation of percarmamoylated resorcinares, as indicated by MALDI data for the obtained products.

The results of carbamoylation of resorcinarenes 1 and 2 in the presence of potassium and cesium carbonate depended on the pre-organization of the macrocyclic substrate and the nature of the carbonate. When $recc$ resorcinarenes 1a,b,e reacted with carbamoyl chloride in the presence of K$_2$CO$_3$, the reaction was complete in 10-12 h to give octacarbamoylated products 3a,b,e (Scheme 1, Table 1).
Scheme 1. N,N-Dimethylcarbamoylation of resorcinarenes 1.

Table 1. Yields, melting points and MALDI data of carbamoylation products 3-5

<table>
<thead>
<tr>
<th>No</th>
<th>R</th>
<th>Yield, %</th>
<th>Mp, °C</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>CH₃</td>
<td>42</td>
<td>260-261*</td>
<td>1113.5 [M⁺]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1151.1 [M⁺+K⁺]</td>
</tr>
<tr>
<td>3b</td>
<td>C₃H₇</td>
<td>68</td>
<td>210-212</td>
<td>1226 [M⁺]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1263.9 [M⁺+K⁺]</td>
</tr>
<tr>
<td>3e</td>
<td>CH₂CH₂C₆H₅</td>
<td>40</td>
<td>212-214</td>
<td>1473 [M⁺]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1511.8 [M⁺+K⁺]</td>
</tr>
<tr>
<td>4a</td>
<td>CH₃</td>
<td>54</td>
<td>230-232*</td>
<td>1245.8 [M⁺+Cs⁺]</td>
</tr>
<tr>
<td>4b</td>
<td>C₃H₇</td>
<td>72</td>
<td>238-240*</td>
<td>1357.7 [M⁺+Cs⁺]</td>
</tr>
<tr>
<td>4c</td>
<td>C₆H₁₃</td>
<td>60</td>
<td>198-200</td>
<td>1525 [M⁺+Cs⁺]</td>
</tr>
<tr>
<td>4d</td>
<td>C₉H₁₉</td>
<td>57</td>
<td>223-224</td>
<td>1594 [M⁺+Cs⁺]</td>
</tr>
<tr>
<td>4e</td>
<td>CH₂CH₂C₆H₅</td>
<td>70</td>
<td>245-247*</td>
<td>1606 [M⁺+Cs⁺]</td>
</tr>
<tr>
<td>5</td>
<td>C₁₀H₇</td>
<td>77(a); 83(b)ᵃ</td>
<td>290-305*</td>
<td>1561 [M⁺]</td>
</tr>
</tbody>
</table>

*melting with decomposition; ᵃthe synthesis was carried out in the presence of K₂CO₃ (a) or Cs₂CO₃ (b)

The mass spectra (Table 1) of 3a,b,e exhibited peaks corresponding to the octacarbamoylated resorcinarenes 3a,b,e and their complexes with the potassium cation. The ¹H and ¹³C NMR spectra of 3a,b,e were found to exhibit broadened proton and carbon signals of the resorcinarene core and carbamate groups. This spectral pattern is possible in the case of coexistence of both potassium-coordinated and uncoordinated resorcinarene molecules,
occurring in various conformations owing to retarded boat-crown-boat interconversion (Scheme 1). According to elemental analysis and NMR spectroscopy data, the isolated products 3a,b,e were complexes of the following composition: 3a•2C₆H₁₄, 3b•C₆H₁₄, 3e•C₆H₁₄.

In the presence of Cs₂CO₃, percarbamoylation of resorcinarenes 1a-e with N,N-dimethylcarbamoyl chloride was complete in 8 h, and the yields of products 4 were higher than those of 3 (Table 1). The difference between the melting/decomposition points of compounds 3a,b,e and 4a,b,e is 20-30 °C (Table 1). The mass spectra of 4a-e exhibited only intense peaks, the spectral parameters corresponding to a 1:1 resorcinarene complex with the cesium cation (Table 1). According to elemental analysis and NMR spectroscopy data, as in the previous case, solvent molecules were incorporated in octacarbamates 4a-e, apart from CsCl, to form complexes 4a•CHCl₃•C₆H₁₄, 4b•2C₆H₁₄, 4c•C₆H₁₄, 4d•C₆H₁₄, and 4e•C₆H₁₄. The ¹H NMR spectra exhibited two singlets for the ortho- and meta-protons of the benzene rings, one signal for protons of the methylidene bridge, and four singlets corresponding to the methylamide protons. This spectral pattern is characteristic of rccc resorcinarenes existing in the flattened boat conformation. With this spatial arrangement of the octacarbamoylated resorcinarene molecule, the carbamate groups located on the vertically arranged benzene rings are spatially proximate and provide stable ion–dipole interaction with the cesium cation (Scheme 1).

As shown by additional experiments, octacarbamoylated resorcinarenes exhibit selectivity towards cesium cations. The addition of cesium carbonate or hydroxide to a solution of the potassium complex of tetra(phenethyl)resorcinarene 3e (m/z 1511.8 [M⁺+K⁺]) induces displacement of the potassium cation to give complex 4e with a cesium cation (Scheme 1). The mass spectrum of the isolated product exhibited a peak with a mass number of 1606 corresponding to the complex of octacarbamoylated resorcinarene with cesium. The melting point and spectral data of the isolated product fully coincided with the data obtained previously for complex 4e.

A similar result was obtained when resorcinarene 1e was carbamoylated with N,N-dimethylcarbamoyl chloride in the presence of a mixture of equal amounts of potassium and cesium carbonate (Scheme 1). The reactant ratio was as follows: resorcinarene : carbamoyl chloride : K₂CO₃: Cs₂CO₃ = 1:12:6:6. The physicochemical and spectral characteristics of the isolated product fully corresponded to complex 4e.

In the carbamoylation of rett tetrnapthylresorcinarene 2, unlike that of rccc resorcinarene 1, the reaction outcome did not depend substantially on the base chosen (either K₂CO₃ or Cs₂CO₃). In both cases, the reaction ended in the formation of an individual compound: octacarbamoylated derivative 5, as indicated by elemental analysis and mass spectrometry data (Scheme 2, Table 1).
Scheme 2. N,N-Dimethylcarbamoylation of tetrathylresorcinarene 2.

Doubling of the proton and carbon signals of the benzene ring and carbamate groups in the \( ^1H \) and \( ^{13}C \) NMR spectra of compound 5 and the upfield shift (\( \delta_H \) 5.25 ppm) of the H\(^3h\) protons of the benzene rings in the \( ^1H \) NMR spectrum attested to retention of the initial chair conformation with \( C_{2h} \) symmetry.\(^{23,24}\)

The thiocarbamoxylation of resorcinarenes 1 and 2 with \( N,N \)-dimethylthiocarbamoyl chloride was carried out, like carbamoylation, upon refluxing in acetone in the presence of potassium and cesium carbonate. Replacement of the acylating reagent resulted in a sharp increase in the process duration. Completion of the reaction required 48–57 h.

With rccc resorcinarenes 1a,b,e as substrates in the presence of Cs\(_2\)CO\(_3\), the reaction was selective giving only the fully acylated resorcinarenes 6a-c (Scheme 3). The elemental analysis and mass spectrometry data for 6a-c correspond to single octathiocarbamoxylated derivatives containing no species in the cavity (Table 2). The \( ^1H \) and \( ^{13}C \) NMR spectra of compounds 6a-c exhibited proton and carbon signals for the resorcinarene core and the carbamate groups, the integrated intensities of the signals being in line with calculated values, and the IR spectra showed strong C=S absorption bands (1170 cm\(^{-1}\)).

Scheme 3. N,N-Dimethylthiocarbamoxylation of resorcinarenes 1a,b,e.
Table 2. Yields, melting points, and MALDI data of compounds 6-9

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Yield, %</th>
<th>M.p., °C</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>CH$_3$</td>
<td>45</td>
<td>312-314*</td>
<td>1241 [M$^+$]</td>
</tr>
<tr>
<td>6b</td>
<td>C$_3$H$_7$</td>
<td>31</td>
<td>308-310*</td>
<td>1352 [M$^+$]</td>
</tr>
<tr>
<td>6c</td>
<td>CH$_2$CH$_2$C$_6$H$_5$</td>
<td>66</td>
<td>196-198</td>
<td>1601 [M$^+$]</td>
</tr>
<tr>
<td>7</td>
<td>C$_6$H$_5$</td>
<td>58</td>
<td>309-310*</td>
<td>1140 [M$^+$]</td>
</tr>
<tr>
<td>8</td>
<td>C$_6$H$_5$</td>
<td>54</td>
<td>178-180*</td>
<td>1432 [M$^+$-4CH$_3$]</td>
</tr>
<tr>
<td>9</td>
<td>C$_{10}$H$_7$</td>
<td>54</td>
<td>248-250*</td>
<td>1690 [M$^+$]</td>
</tr>
</tbody>
</table>

* melting with decomposition

Resorcinarenes 1f, 2 with aryl substituents R in the lower rim of the macrocycle behaved in a different way. In the case of tetraphenylresorcinarene 1f, the use of Cs$_2$CO$_3$ as the base resulted in tetracarbamoylated product 7 isolated in a 58% yield (Scheme 4). The formation of the tetraacylated derivative was indicated by elemental analysis and mass spectrometry data (Table 2). In the IR spectrum of 7, C=S absorption band at 1170 cm$^{-1}$ and OH band at 3228 cm$^{-1}$ were detected.

Scheme 4. Reaction of tetraphenylresorcinarene 1f with $N,N$-dimethylthiocarbamoyl chloride.

The NMR data for resorcinarene 7 correspond to a C$_{4v}$-symmetric molecular structure, which is possible only in the case of a uniform order of immobilization of hydroxyl and thiocarbamoyl groups on all four benzene rings of the macrocycle. The $^1$H NMR spectrum of 7 exhibited a singlet for hydrogen atoms of four hydroxyl groups, degenerate proton signals of the benzene rings of the macrocyclic core, and the methyamide proton signals with a 24-proton total integrated intensity. The $^{13}$C NMR spectrum exhibited a singlet for the thione carbon, two singlets of the carbon atoms of aminomethyl groups, and four singlets for the resorcinol-ring carbon atoms.

By replacing Cs$_2$CO$_3$ and K$_2$CO$_3$ and increasing the thiocarbamoylation time to 57 h, we obtained perflunctionalized product 8 in the boat conformation in 54% yield (Scheme 4). The elemental analysis and mass spectrometry data (Table 2) confirmed the formation of totally acylated resorcinarene 8. The IR spectrum of 8 exhibited an intense C=S absorption band at 1170
cm\(^{-1}\), and the \(^1\)H NMR spectrum showed no signals for hydroxyl protons. The \(^1\)H and \(^13\)C NMR spectra had a more complicated pattern with signal broadening owing to retardation of the boat-crown-boat interconversion (Scheme 1) as a result of steric crowding of molecule 8 created by eight bulky functional groups.

The thiocarbamoylation of tetraneptylresorcinarene 2 in the presence of Cs\(_2\)CO\(_3\) afforded a mixture of compounds with different degrees of functionalization, which proved to be inseparable. A success was achieved when K\(_2\)CO\(_3\) was used, octa(thiocarbamate) 9 was isolated from the reaction mixture in 54\% yield (Scheme 5).

**Scheme 5.** N,N-Dimethylthiocarbamoylation of resorcinarene 2.

The introduction of eight functional groups into rctt-resorcinarene 2 with remote benzene rings did no affect the conformation of the macrocyclic core. The elemental analysis, mass spectrometry (Table 2), and IR and NMR spectroscopy fully corresponded to the octa(thiocarbamoyl)resorcinarene 9.

Thus, we synthesized a new family of oligofunctionalized resorcinarenes with a specific orientation of the carbamate and thiocarbamate groups immobilized on a macrocyclic matrix. It was found that octacarbamoylated recc resorcinarenes in the boat conformation exhibit a high capacity for recognition, binding, and recovery of cesium cations. In addition, resorcinarenes containing carbamate and thiocarbamate groups are of interest as potential receptors for organic amines and alcohols.

**Experimental Section**

**General.** \(^1\)H and \(^13\)C NMR spectra (TMS as an internal standard) were recorded on a Jeol ECX-400 spectrometer operating at 400 MHz for \(^1\)H, 100.5 MHz for \(^13\)C. The signals of 3-9 were assigned using H-H homonuclear double resonance (proton spin decoupling). The full assignment of the signals of compounds 3-9 was based on \(^1\)H/\(^13\)C 2D correlation. Elemental analysis was performed on Thermo Flash EA1112 CHN Elemental analyzer. IR spectra were measured on a NICOLETE 380 Thermo spectrometer in reflection mode in the 4000–500 cm\(^{-1}\) range for samples as Nujol mulls. Resorcinarenes 1 and 2 were synthesized by procedures
reported in 25 and 7, respectively.

**General procedure of N,N-Dimethylcarbamoylation of resorcinarenes 1 and 2.** N,N-Dimethylcarbamoyl chloride (2.65 mmol) was added to a suspension of resorcinarene (0.221 mmol) and metal carbonate (2.65 mmol) in acetone (10 mL). The reaction mixture was stirred at reflux for 40 h (Na₂CO₃), 10-12 h (K₂CO₃), or 8 h (Cs₂CO₃). After that, acetone was fully evaporated, and 10 mL of 5% sulfuric acid was added. The insoluble precipitate was filtered off and washed with 60 mL of water and 20 mL of hexane. The product was kept for 5 h at 80 °C/1 mmHg.

**Complex 3a 2C₈H₁₄.** Beige powder; yield 0.125 g (42%). decomp. p 260-261 °C. ¹H NMR (CDCl₃): δ 0.87 (t, J 7.0 Hz, 12H, CH₃-hexane), 1.29 (m, 16H, CH₂-hexane), 1.46 (d, J 6.9 Hz, 12H, CH₃), 2.52 (s, 12H, NCH₃), 2.82 (s, 12H, NCH₃), 3.01 (s, 12H, NCH₃), 3.13 (s, 12H, NCH₃); 4.37 (q, J 6.8 Hz, 4H, H¹), 6.01 (s, 2H, H₃⁰), 6.95 (s, 2H, H₅⁰), 7.32 (s, 2H, H³⁰). ¹³C NMR (CDCl₃): δ 14.13 (CH₃-hexane), 20.31 (CH₃), 22.72 (CH₂-hexane), 31.60 (CH₂-hexane), 32.26 (C¹), 35.99 (NCH₃), 36.48 (NCH₃), 36.83 (NCH₃), 115.87 (C⁵⁰), 116.90 (C³⁰), 125.26 (C²⁰), 125.68 (C⁶⁰), 131.94 (C²⁰); 135.68 (C²⁰), 146.22 (C⁴⁰), 153.89 (C⁰), 154.43 (C=O). IR, λ, cm⁻¹: 1701.3 (C=O). MS, m/z: 1113.5 [M⁺], 1151.1 [M⁺+K⁺]. Calculated for C₈₆H₇₂N₉O₁₆ KCl 2C₈H₁₄(%): C 60.05, H 7.41, N 8.24. Found (%): C 60.37, H 7.71, N 8.13.

**Complex 3b C₆H₁₄.** Beige powder; yield 0.208 g (68%); mp 220-212 °C. ¹H NMR (d₆-DMSO, 25°C): δ 0.83 (t, J 7.3 Hz, 12H, CH₂CH₂CH₃), 1.14 (m, J 7.4 Hz, 8H, CH₂CH₂CH₃), 1.28 (m, 8H, CH₂-hexane), 2.03 (m, 8H, CH₂CH₂CH₃), 2.46 (s, 24H, NCH₃), 2.64 (s, 24H, NCH₃), 4.16 (t, J 7.4 Hz, 4H, H¹), 6.10 (s, 4H, H₃⁰), 7.19 (s, 4H, H₅⁰). ¹³C NMR (d₆-DMSO, 25 °C): δ 14.14 (CH₃-hexane), 14.39 (CH₃), 20.90 (CH₂), 21.19 (CH₂), 22.70 (CH₂-hexane), 31.63 (CH₂-hexane), 33.09 (C¹), 36.10 (NCH₃), 36.75 (NCH₃), 38.77 (NCH₃), 40.01 (NCH₃), 102.92 (C⁰), 123.78 (C¹), 125.48 (C⁰), 152.11 (C²⁰); 154.15 (C⁰); MS, m/z: 1226 [M⁺], 1263.9 [M⁺+K⁺]. Calculated for C₆₄H₆₈N₈O₁₆ KCl C₆H₁₄(%): C 60.65, H 7.42, N 8.08. Found (%): C 60.91, H 7.26, N 8.27.

**Complex 3c C₆H₁₄.** Beige powder; yield 0.143 g (40%). decomp.p 212-214 °C. ¹H NMR (d₆-DMSO, 25 °C): δ 0.85 (t, J 6.9 Hz, 12H, CH₃-hexane), 1.27 (m, 16H, CH₂-hexane), 2.23 (m, 8H, CH₂CH₂Ph), 2.55 (br.m, 8H, CH₂CH₂Ph), 2.78 (s, 24H, NCH₃), 2.85 (s, 24H, NCH₃), 4.33 (t, J 7.3Hz, 4H, H¹), 7.04 (m, 12H, H₃⁰, o-Ph), 7.16 (m, 16H, H₅⁰, p, m-Ph). ¹³C NMR (d₆-DMSO, 25°C): δ 14.13 (CH₃-hexane), 22.70 (CH₂-hexane), 31.67 (CH₂-hexane), 33.92 (CH₂CH₂Ph), 35.47 (CH₂CH₂Ph), 35.88 (NCH₃), 36.03 (C¹), 36.19 (NCH₃), 116.41 (C⁰), 125.66 (C²⁰), 126.08 (C⁰), 128.10 (Ph), 128.14 (Ph), 141.39 (C⁴⁰), 153.35 (C=O). IR, λ, cm⁻¹: 1703.6 (C=O). MS, m/z: 1473 [M⁺], 1511.8 [M⁺+K⁺]. Calculated for C₆₈H₉₆N₈O₁₆ KCl C₆H₁₄(%): C 66.14, H 6.78, N 6.86. Found (%): C 66.52, H 6.39, N 6.48.

**Complex 4a CHCl₃ C₆H₁₄.** Beige powder; yield 0.177 g (54%). decomp.p 230-323 °C. ¹H NMR (CDCl₃): δ 0.86 (t, J 7.3 Hz, 12H, CH₃-hexane), 1.26 (m, 16H, CH₂-hexane), 1.46 (d, J 6.9 Hz,
12H, CH₃); 2.61 (s, 12H, NCH₃), 2.82 (s, 12H, NCH₃), 3.01 (s, 12H, NCH₃), 3.09 (s, 12H, NCH₃). 4.40 (q, J 6.8 Hz, 4H, H¹), 6.01 (s, 2H, H³b), 6.77 (s, 2H, H⁵b), 7.16 (s, 2H, H⁵v), 7.37 (s, 2H, H³v). ¹³C NMR (CDCl₃): δ 14.14 (CH₃-hexane), 20.31 (CH₃), 22.72 (CH₂-hexane), 31.61 (CH₂-hexane), 32.26 (C¹); 35.99(NCH₃). 36.48 (NCH₃); 36.83 (NCH₃); 115.87 (C⁵b), 116.90 (C⁵v), 125.26 (C³b), 125.68 (C³v), 131.97 (C²v); 135.68 (C²b), 146.22 (C⁴b), 148.22 (C⁴v), 153.89 (C=O), 154.43 (C=O). IR, λ, cm⁻¹: 1705.3 (C=O). MS, m/z: 1245.8 [M⁺+Cs⁺]. Calculated for C₅₀H₂₂N₅O₁₆ CsCl CHCl₃ C₆H₁₄(%): C 50.88, H 5.90, N 7.53. Found(%): C 50.86, H 6.02, N 7.18.

**Complex 4b 2C₆H₁₄.** Beige powder; yield 0.249 g (72%); decomp.p 238-240 °C. ¹H NMR (d₆-DMSO, 25 °C): δ 0.83 (t, J 7.3 Hz, 12H, CH₂(CH₂)₅CH₃, 12H, CH₃-hexane), 1.14 (m, J 7.4 Hz, 8H, CH₂(CH₂)CH₃), 1.28 (m, 16H, CH₂-hexane), 2.03 (m, 8H, CH₃CH₂CH₃), 2.46 (s, 24H, NCH₃), 2.64 (s, 24H, NCH₃), 4.16 (t, J 7.4 Hz, 4H, H¹), 6.10 (s, 4H, H³), 7.19 (s, 4H, H⁵). ¹³C NMR (d₆-DMSO, 25 °C): δ 14.16 (CH₃-hexane), 14.39 (CH₃), 20.90 (CH₂), 21.19 (CH₂), 22.70 (CH₂-hexane), 31.64 (CH₂-hexane), 33.09 (C¹), 36.10 (NCH₃), 36.75 (NCH₃), 38.77 (NCH₃), 40.01 (NCH₃), 102.92 (C⁵), 123.78 (C³), 125.48 (C²); 152.11 (C⁴); 154.02 (C=O). MS, m/z: 1357.7 [M⁺+Cs⁺]. Calculated for C₆₄H₈₈N₈O₁₆ CsCl 2C₆H₁₄(%): C 58.28, H 7.47, N 7.15. Found(%): C 58.61, H 7.16, N 6.76.

**Complex 4c C₆H₁₄.** Beige powder; yield 0.219 g (60%); mp. 198-200 °C. ¹H NMR (CDCl₃, 25 °C): δ 0.83 (t, J 6.4 Hz, 12H, CH₂(CH₂)₅CH₃, 6H, CH₃-hexane), 1.22 (m, 32H, CH₂(CH₂)₅CH₃, 8H, CH₂-hexane), 1.75 (m, 8H, CH₂(CH₂)₅CH₃), 2.62 (s, 12H, NCH₃), 2.80 (s, 12H, NCH₃), 3.00 (s, 12H, NCH₃), 3.08 (s, 12H, NCH₃), 4.26 (t, J 6.8 Hz, 4H, H¹), 6.06 (s, 2H, H³b), 6.69 (s, 2H, H⁵b), 7.19 (s, 2H, H⁵v), 7.32 (s, 2H, H³v). ¹³C NMR (CDCl₃, 25 °C): δ 14.11 (CH₃, CH₃-hexane), 22.80 (CH₂, CH₂-hexane), 23.05 (CH₂), 28.20 (CH₂), 29.71 (CH₂), 31.64 (CH₂-hexane), 31.84 (CH₂), 33.09 (C¹), 36.47 (NCH₃), 36.60 (NCH₃), 36.74 (NCH₃), 36.78 (NCH₃), 115.88 (C⁵), 117.08 (C³), 125.94 (C²), 126.03 (C³), 130.03 (C⁵), 134.62 (C²), 146.04 (C⁴), 148.75 (C⁴), 153.93 (C=O), 154.28 (C=O). MS, m/z: 1525 [M⁺+Cs⁺]. Calculated for C₇₆H₁₁₂N₈O₁₆ CsCl C₆H₁₄(%): C 59.75, H 7.71, N 6.80. Found(%): C 59.84, H 7.37, N 6.68.

**Complex 4d C₆H₁₄.** Beige powder; yield 0.228 g (57%); mp. 223-224 °C. ¹H NMR (d₆-DMSO, 25 °C), δ, ppm: 0.84 (t, J 6.9 Hz, 12H, CH₂(CH₂)₅CH₃, 6H, CH₃-hexane), 1.22 (m, 56H, CH₂(CH₂)₅CH₃, 8H, CH₂-hexane), 2.00 (m, 8H, CH₂(CH₂)₅CH₃), 2.88 (br.s, 48H, NCH₃), 4.17 (t, J 7.7 Hz, 2H, H¹), 4.22 (t, J 7.6 Hz, 2H, H¹), 6.15 (s, 4H, H³), 7.12 (s, 4H, H⁵). ¹³C NMR (d₆-DMSO, 25 °C): δ 14.14 (CH₃-hexane), 14.40 (CH₃), 21.18 (CH₂), 22.90 (CH₂, CH₂-hexane), 31.64 (CH₂-hexane), 33.09 (C¹), 36.10 (NCH₃), 36.75 (NCH₃), 102.92 (C⁵), 123.72 (C³), 125.48 (C²), 152.11 (C⁴), 154.28 (C=O). MS, m/z: 1594 [M⁺+Cs⁺]. Calculated for C₈₈H₁₃₆N₈O₁₆ CsCl C₆H₁₄(%): C 62.15, H 8.32, N 6.17. Found(%): C 62.55, H 8.27, N 6.57.

**Complex 4e C₆H₁₄. Method 1.** The general procedure of carbamoylation of 1e was used. Method 2. Cesium carbonate (0.06 mmol) was added to a solution of complex 3a (0.06 mmol) in 5 mL of acetone. The suspension was stirred for 3 h at 20 °C. Then acetone was distilled off and the residue was washed with water (10 mL) and hexane (5 mL) and dried for 5 h at 80 °C/1 mmHg. Method 3. Cesium hydroxide (0.06 mmol) was added to a solution of complex 3a (0.06 mmol) in
5 mL of acetone. The resulting suspension was stirred for 3 h at 20 °C. The precipitate formed was filtered off, washed with water (10 mL) and hexane (5 mL), and dried for 5 h at 80 °C/1 mmHg. Method 4. Carbamoyl chloride (2.65 mmol) was added to a suspension of resorcinarene 1e (0.221 mmol), potassium carbonate (1.3 mmol), and cesium carbonate (1.3 mmol) in 10 mL of acetone. The reaction mixture was stirred at reflux for 8 h. After that, acetone was completely distilled off, and 10 mL of 5% sulfuric acid was added to the reaction mixture. The insoluble precipitate was filtered off and washed with 60 mL of water and 20 mL of hexane. The product was dried for 5 h at 80 °C/1 mmHg. Beige powder; yield 0.267 g (70%) (method 1), 0.08 g (79%, method 2), 0.084 g (83%, method 3), 0.317 g (85%, method 4); decomp.p 245-247 °C. Octa(N,N-dimethylcarbamoyl)tetrannaphyl-resorcinarene (5). Beige powder; yield 0.265 g (77%, in the presence of K2CO3); 0.286 g (83%, in the presence of Cs2CO3); mp 290-305 °C. General procedure of N,N-dimethylthiocarbamoylation of resorcinarenes 1a,b,e,f. N,N-Dimethylthiocarbamoyl chloride (3.25 mmol) and cesium carbonate (3.25 mmol) was added to a solution of the specified resorcinarene (0.27 mmol) in 10 mL of acetone. The reaction mixture was stirred for 48 h at 50-55 °C. Then acetone was completely distilled off, and 20 mL of 5% sulfuric acid was added to the residue. The precipitate was filtered off and washed with water (50 mL) and hexane (10 mL). The product was dried for 6 h at 75-80 °C in vacuo (1 mmHg). Octa(N,N-dimethylthiocarbamoyl)-tetramethyl-resorcinarene (6a). Beige powder; yield 0.165 g (45%); decomp.p 312-314 °C. 1H NMR (CDCl3, 25 °C): δ 2.24 (s, 12H, NCH3), 2.35 (s, 12H, NCH3), 2.68 (s, 12H, NCH3), 2.92 (s, 12H, NCH3), 5.25 (s, 2H, H3b), 6.20 (s, 2H, H5v) 6.21 (s, 4H, H1), 6.50 (d, J 6.8 Hz, 4H, H2-Naph), 6.93 (dd, J 6.8 Hz, J 8.0 Hz,4H, H1-Naph), 6.95 (dd, J 7.3 Hz, J 6.8 Hz, 4H, H2-Naph), 7.03 (dd, J 7.1 Hz, J 6.8 Hz, 4H, H6-Naph), 7.14 (s, 2H, H5h), 7.17 (s, 2H, H5v), 7.39 (d, J 8.0 Hz, 4H, H4-Naph), 7.41 (d, J 7.8 Hz, 4H, H5-Naph), 7.44 (d, J 8.2 Hz, 4H, H4-Naph). 13C NMR (CDCl3, 25 °C): δ 34.72 (C1), 35.25 (NCH3), 36.13 (NCH3), 36.14 (NCH3), 36.21 (NCH3), 116.70 (C5b), 117.50 (C5v), 124.10 (C-Naph), 124.42 (C-Naph), 124.53 (C-Naph), 124.79 (C-Naph), 126.23 (C-Naph), 126.34 (C-Naph), 127.82 (C-Naph), 128.01 (C-Naph), 128.57 (C2v); 128.55 (C2h); 130.62 (C3h), 130.84 (C3v), 147.74 (C8h), 148.50 (C4v), 152.82 (C=O), 153.77 (C=O). IR, λ, cm−1: 1719.4 (C=O). MS, m/z: 1561 [M++Cs+]. Calculated for C84H96N8O16 CsCl C6H14(%): C 62.55, H 6.42, N 6.48. Found(%): C 62.84, H 6.27, N 6.68. General procedure of N,N-dimethylthiocarbamoylation of resorcinarenes 1a,b,e,f. N,N-Dimethylthiocarbamoyl chloride (3.25 mmol) and cesium carbonate (3.25 mmol) was added to a solution of the specified resorcinarene (0.27 mmol) in 10 mL of acetone. The reaction mixture was stirred for 48 h at 50-55 °C. Then acetone was completely distilled off, and 20 mL of 5% sulfuric acid was added to the residue. The precipitate was filtered off and washed with water (50 mL) and hexane (10 mL). The product was dried for 6 h at 75-80 °C in vacuo (1 mmHg).
DMSO): δ 21.13 (CH$_3$), 31.99 (C1), 38.73 (NCH$_3$), 39.04 (NCH$_3$), 43.15 (NCH$_3$), 43.54 (NCH$_3$), 118.65 (C$^{5b}$), 119.64 (C$^{5v}$), 125.81 (C$^{3b}$), 132.35 (C$^{2v}$), 136.54 (C$^{2h}$); 148.47 (C$^{4h}$); 150.78 (C$^{4v}$), 185.70 (C=S), 186.48 (C=S). IR, λ, cm$^{-1}$: 1125.7 (C=S). MS, m/z: 1241 [M$^+$].

Calculated for C$_{56}$H$_{72}$N$_8$O$_8$S$_8$ (%): C, 71.34; H, 5.30; N, 4.91. Found (%): C, 71.43; H, 5.35; N, 4.64.

Octa(N,N-dimethylthiocarbamoyl)-tetrapropyl-resorcinarene (6b). Light yellow powder; yield 0.285 g (66%). mp 196-198 °C. 1H NMR (d$_6$-DMSO, 25 °C): δ 0.80 (br.s, 12H, CH$_2$CH$_2$Ph), 2.57 (m, J 7.8 Hz, 4H, CH$_2$CH$_2$Ph), 2.75 (m, J 6.4 Hz, 4H, CH$_2$CH$_2$Ph), 2.92 (s, 12H, NCH$_3$), 3.05 (s, 12H, NCH$_3$), 3.18 (s, 12H, NCH$_3$), 3.31 (s, 12H, NCH$_3$), 4.24 (t, J 6.4 Hz, 4H, H$^1$), 6.61 (s, 2H, H$^{3b}$), 6.65 (s, 2H, H$^{5v}$), 6.80 (s, 2H, H$^{3h}$), 7.06-7.15 (m, 20H, Ph) 7.59 (s, 2H, H$^{3v}$). 13C NMR (CDCl$_3$, 25 °C): δ 34.19 (CH$_2$CH$_2$Ph), 36.27 (CH$_2$CH$_2$Ph), 36.54 (C1), 38.61 (N-CH$_3$), 39.36 (NCH$_3$), 43.42 (NCH$_3$), 119.47 (C$^{5b}$), 120.63 (C$^{5v}$), 125.61 (Ph), 127.32 (C$^{3b}$), 128.68 (Ph), 129.10 (Ph), 129.52 (C$^{2v}$), 141.59 (C$^{2h}$); 148.63 (C$^{4b}$), 151.77 (C$^{4v}$), 186.29 (C=S), 186.67 (C=S). IR, λ, cm$^{-1}$: 1161.9 (C=S), 1100.0 (C=S). MS, m/z: 1601 [M$^+$]. Calculated for C$_{84}$H$_{96}$N$_8$O$_8$S$_8$ (%): C 62.97, H 6.04, N 6.99. Found (%): C 62.61, H 6.02, N 6.63.

Tetrahydroxy-tetra(N,N-dimethylthiocarbamoyl)-tetraphenyl-resorcinarene (7). Beige powder; yield 0.1774 g (58%); decom.p 309-310 °C. 1H NMR (DMSO, 25 °C): δ 2.93 (s, 12H, NCH$_3$), 3.24 (s, 12H, NCH$_3$), 5.58 (s, 4H, H$^1$), 6.10 (s, 4H, H$^5$), 6.10 (s, 4H, H$^5$), 6.69 (m, 8H, Ph), 6.93 (m, 12H, Ph), 8.56 (s, 4H, OH). 13C NMR (DMSO, 25 °C): δ 41.90 (C1), 44.33 (NCH$_3$), 45.03 (NCH$_3$), 102.71 (C$^5$), 120.89 (C$^{3h}$), 125.01 (C$^{3v}$), 127.66 (C$^{3h}$), 127.84 (C$^3$), 129.09 (C$^{2h}$), 146.25 (C$^2$), 153.06 (C$^4$), 186.63 (C=S). IR, ν, cm$^{-1}$: 3402 (OH), 1145 (C=S). MS m/z: 1136 [M$^+$]. Calculated for C$_{64}$H$_{60}$N$_8$O$_8$S$_8$ (%): C, 67.34; H, 5.30; N, 4.91. Found (%): C, 67.43; H, 5.35; N, 4.64.

Octa(N,N-dimethylthiocarbamoyl)-tetraphenyl-resorcinarene (8). The synthesis was conducted similarly to the synthesis of 6 by stirring resorcinarene 1f (1.6448 g, 0.207 mmol), N,N-dimethylthiocarbamoyl chloride (3.077 g, 24.9 mmol), and potassium carbonate (2.4651 g, 24.9 mmol) in 10 mL of acetone for 57 h at 50-55 °C. Then acetone was completely distilled off, and 20 mL of 5% sulfuric acid was added to the residue. The product was extracted with CH$_2$Cl$_2$ (10 mL), the organic layer was separated, CH$_2$Cl$_2$ was distilled off, the residue was dissolved at reflux in a minimum amount of methanol, and the solution was refluxed for 5 min. The methanol-insoluble precipitate was filtered off, washed with hot methanol, and dried for 6 h at
75-80 °C in vacuo (1 mmHg). Beige powder; yield 0.3138 g (54%); decom.p 248-250 °C. $^1$H NMR (CDCl$_3$, 25 °C):δ 2.74 (s, 12H, NCH$_3$), 2.94 (s, 12H, NCH$_3$), 3.29 (s, 12H, NCH$_3$), 3.36 (s, 12H, NCH$_3$), 5.61 (s, 4H, H$^1$), 6.31-6.83 (m, 2H, H$^{3h}$; 2H, H$^{5v}$; 2H, H$^{5h}$; 2H, H$^{3v}$), 6.90-7.10 (br.s, 20H, Ph). $^{13}$C NMR (CDCl$_3$, 25 °C):δ 36.72 (NCH$_3$), 39.05 (NCH$_3$), 43.28 (NCH$_3$), 45.09 (NCH$_3$), 46.82 (C$^1$), 119.01 (C$^{3v}$), 126.31 (C$^{2}$), 128.05 (C$^{5v}$,5h), 129.53 (C$^{3}$), 140.61 (C$^{3h}$), 147.56 (C$^{2}$), 150.07 (C$^{4}$), 154.53 (C$^{4h}$), 185.46 (C=S). IR, ν, cm$^{-1}$: 1163 (C=S).

Octa(N,N-dimethylthiocarbamoyl)-tetranaphthyl-resorcinarene (9).

$N,N$-Dimethylthiocarbamoyl chloride (0.932 g, 7.55 mmol) and potassium carbonate (1.057 g, 7.55 mmol) were added to a solution of tetranaphthylresorcinarene 2 (0.3406 g, 0.343 mmol) in acetone (10 mL). The reaction mixture was stirred for 12 h at room temperature and for 48 h at 50-55°С. Acetone was distilled off, and 20 mL of 5% sulfuric acid was added to the residue. The product was extracted with CH$_2$Cl$_2$ (10 mL), and the organic layer was separated and washed with 50 mL of distilled water. Then CHCl$_3$ was distilled off, 50 mL of hexane was added to the amorphous residue, and the formed powdered precipitate was filtered off and washed with 15 mL of hexane. The product was dried for 6 h at 75-80°С in vacuo (1 mmHg). Beige powder; yield 0.3138 g (54%). decom.p 248-250 °C. $^1$H NMR (CDCl$_3$, 25 °C):δ 2.02 (s, 12H, NCH$_3$), 2.75 (s, 12H, NCH$_3$), 3.28 (s, 12H, NCH$_3$), 3.58 (s, 6H, NCH$_3$), 3.62 (s, 6H, NCH$_3$), 6.22 (s, 4H, H$^1$), 6.32 (s, 2H, H$^{3h}$), 6.52 (d, $J$ 7.3 Hz, 4H, H$^2$-Naph), 6.75 (s, 2H, H$^{5v}$), 6.79 (s, 2H, H$^{5h}$), 6.93 (dd, $J$ 7.8 Hz; $J$ 6.9 Hz, 4H, H$^3$-Naph), 6.96 (s, 2H, H$^{5h}$), 7.01 (dd, $J$ 7.8 Hz; $J$ 7.3 Hz, 4H, H$^3$-Naph), 7.19 (dd, $J$ 7.8 Hz; $J$ 6.9 Hz, 4H, H$^7$-Naph), 7.44 (d, $J$ 8.3 Hz, 4H, H$^4$-Naph), 7.61 (d, $J$ 8.2 Hz, 4H, H$^8$-Naph), 7.8 (d, $J$ 8.8 Hz, 4H, H$^5$-Naph). $^{13}$C NMR (CDCl$_3$, 25 °C):δ 37.48 (NCH$_3$), 42.17 (NCH$_3$), 44.11 (NCH$_3$), 119.53 (C$^{3h}$), 120.15 (C$^5$), 123.7 (C$^1$-Naph), 124.02 (C$^{2}$-Naph), 124.99 (C$^{3}$-Naph), 125.21 (C$^6$-Naph), 125.82 (C$^{10}$-Naph), 126.6 (C$^2$-Naph), 127.2 (C$^4$-Naph), 128.03 (C$^8$-Naph), 130.34 (C$^9$-Naph), 131.36 (C$^3$), 132.89 (C$^{2}$), 133.37 (C$^{3h}$), 138.45 (C$^{2h}$), 149.82 (C$^{4h}$), 150.48 (C$^4$), 187.39 (C=S). IR, ν, cm$^{-1}$: 1160 (C=S), 1125 (C=S). MS m/z: 1689 [M$^+$]. Calculated for C$_92$H$_{88}$N$_8$O$_8$S$_8$(%): C, 65.37; H, 5.25; N, 6.63. Found (%): C, 65.54; H, 5.29; N, 6.59.

**Acknowledgements**

The work was supported in part by the Russian Foundation for Basic Research (project no. 15-03-03345a).

**References**


doi:10.1016/j.ccr.2012.10.006

doi:10.1080/10610270902980663

doi:10.1021/jo01310a046

doi:10.1021/ja00539a012

doi:10.1002/(SICI)1521-3749(200005)626:5<1246::AID-ZAAC1246>3.0.CO;2-F

doi:10.1021/jo981386n

doi:10.1021/jo981386n

doi:10.1139/v95-275


doi:10.1039/P29960002561

doi:10.1016/S0927-7757(01)00979-7

doi:10.1007/s10847-005-1252-3

doi:10.1002/ejoc.20121509


doi:10.1016/j.talanta.2004.06.033

doi:10.1016/j.colsurfa.2015.06.002


