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Synthesis of Photo–Switchable Derivatives of *p–tert–*Butyl Thiacalix[4]arenes Containing Ethoxycarbonyl and 4–Amidoazobenzene Fragments in the Lower Rim Substituents

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New p-tert-butyl thiacalix[4]arene derivatives containing simultaneously the 4-amidoazobenzene and ethoxycarbonyl fragments at the lower rim in cone and 1,3-alternate conformation of tri- and tetrasubstituted derivatives, correspondingly, were synthesized. It was shown that the replacement of the hydroxyl group by ethoxycarbonyl fragment in a 1,3-disubstituted macrocycle with 4-amidoazobenzene groups leads to the binding of fluoride- and chloride-anions. The substitution of two hydroxyl groups by ethoxycarbonyl fragments dramatically changed the binding properties of tetrasubstituted p-tert-butyl thiacalix[4]arene derivative.

Keywords: Thiacalix[4]arenes, synthesis, photoisomerization, receptor, anions.

Синтез фотопереключаемых производных *п–трет–*бутил тиакаликс[4]арена, содержащих этоксикарбонильные и 4–амидоазобензольные фрагменты по нижнему ободу

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Синтезированы новые три и тетразамещенные по нижнему ободу производные п-трет-бутилтиакаликс[4]-арена, содержащие одновременно 4-амидоазобензольные и этоксикарбонильные фрагменты в конформации конус и 1,3-альтернат, соответственно. Показано, что замещение одной гидроксильной группы на этоксикарбонильный фрагмент в 1,3-дизамещенном макроцикле с 4-амидоазобензольными группами приводит к связыванию фторид- и хлорид-анионов. Замещение же двух гидроксильных групп на этоксикарбонильные фрагменты приводит к драматическому изменению комплексообразующих свойств тетразамещенного производного п-трет-бутилтиакаликс[4]арена.

Ключевые слова: Тиакаликс[4]арены, синтез, фотоизомеризация, рецептор, анионы.

Introduction

The photo-induced structural transformations have found a wide application in material sciences and biology.[1–2] The photo-switchable receptors containing azastilbene,[3–6] spiropyrane[7–9] and chromene[10–12] fragments are described. The azobenzene group is the most known fragment applied in photo-switchable receptors. Now, some examples of photo-switchable synthetic receptors on aza-crown ether[13–14] and aza-calixarene[15–16] platform in relation to some cations have been published. Today, despite of considerable successes in development of photo-switchable receptors of cations, a limited number of publications on photo-switchable synthetic receptors on anions are presented.

Previously, selective synthesis of 1,3-disubstituted thiacalix[4]arene derivative containing 4-amidoazobenzene fragments[17] was successfully performed. Therefore, in an attempt to develop new approaches to the synthesis of heterofunctionalized photoactive derivatives, selective introduction of azobenzene fragments and ester groups to the lower rim of a macrocycle is of interest. It is well known that ester fragments can participate in competitive formation of hydrogen bonds with acid amide protons that significantly change the selectivity of anion binding.[18]

Experimental

General

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

Absorption spectra were recorded on a Lambda 35 (Perkin Elmer) UV-spectrometer. Quartz cuvettes with optical path length of 10 mm were used. Solutions of thiacalix[4]arenes in dichloromethane with concentration of C=10^{-5} M were prepared and the spectra recorded after 10 minutes of incubation. Efficiency of anions binding was estimated by addition of 200-fold excess of a tetrabutylammonium salts in dichloromethane. The experiment was carried out at 25 ºC.

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

Mass spectra were recorded with the MALDI-TOF Dynamo Finnigan (using 1,8,9-trihydroxyanthracene or 4-nitroaniline matrices).

Melting points were determined using the Boetius Block apparatus.

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

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[4'-(2'-oxo-2'-{(*E*)-4''-(phenyldiazenyl)anilino}methoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone*-**2**) and 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-di[(ethoxycarbonyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone*-**3**) were synthesized according to the literature procedure.[17,19]

*5,11,17,23-Tetra-tert-butyl-25,27-dihydroxy-26,28-bis[4'-(2'-oxo-2'-{(E)-4''-(phenyldiazenyl)anilino}methoxy]-27-[(ethoxycarbonyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene (cone-**4**).* *p-tert*-Butyl thiacalix[4]arene **2** (1.00 g, 0.83 mmol) suspended in 30 ml of acetone containing anhydrous Na_2CO_3 (0.36 g, 3.35 mmol). The reaction mixture was stirred while refluxing for 1 hour. To the obtained suspension, ethyl bromoacetate (0.37 ml, 3.35 mmol) in 40 ml of acetone was added. The reaction mixture was stirred while refluxing for 60 hours. After cooling, the residue from the reaction mixture was filtered off, dissolved in chloroform (20 ml) and organic phase was washed with 2M HCl (10 ml). The organic phase was separated, dried over 3 Å molecular sieves. The solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane-ethanol mixture. A light orange powder was obtained. Yield 0.32 g (30 %). Mp: 290 °C. ^{1}H NMR ($CDCl_3$) δ_H ppm (J/Hz): 0.96 (3H, t, $^3J_{HH}$=7.2 Hz, O-CH$_2$-CH_3), 0.99 (18H, s, (CH$_3$)$_3$C), 1.22 (9H, s, (CH$_3$)$_3$C), 1.30 (9H, s, (CH$_3$)$_3$C), 3.87 (2H, q, $^3J_{HH}$=7.2 Hz, O-CH_2-CH$_3$), 4.42 (2H, d AB-system, $^2J_{HH}$= 15.2 Hz, O-CH_2C(O)NH-), 4.80 (2H, s, O-CH_2-), 5.21 (2H, d AB-system, $^2J_{HH}$= 15.2 Hz, O-CH_2C(O)NH-), 7.18 (4H, AB-system, $^4J_{HH}$= 2.4 Hz, ArH), 7.37 (6H, m, Ar^{2}H), 7.55 (2H, s, ArH), 7.64 (2H, s, ArH), 7.76 (4H, m, Ar^{2}H), 7.86 (8H, AA'BB'-system, $^3J_{AB}$ +$^5J_{AB''}$ = 8.8 Hz, Ar^{1}H), 8.52 (1H, s, OH), 10.17 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) δ_C ppm: 14.02; 29.85; 31.08; 31.33; 31.54; 74.79; 119.73; 119.99; 120.16; 122.95; 124.11; 129.06; 129.24; 130.59; 133.27; 133.96; 134.98; 135.06; 140.62; 149.04; 167.54. ^{1}H-^{1}H NOESY spectrum (the most important cross-peaks): H^3/H^{4b}, H$^{3'}$/H$^{4'b}$, H^{3+}/H^{4+b}, H^5/H$^{3''}$, H^9/H^{11}, H^9/H^{12}, H^9/H^7, H^9/H^{7+}, H^9/H$^{9''}$, H^{11}/H$^{9''}$, H^{12}/H$^{9''}$, H^{7a}/H^{7b}. IR ν cm^{-1}: 3341 (OH), 3313 (NH), 1750 (C(O)OEt), 1537 (C(O)NH). MALDI-TOF MS: calculated [M+] m/z = 1280.46, found [M+Na]$^+$ m/z = 1303.4, [M+K]$^+$ m/z = 1319.4. Found (%): C, 67.80; H, 7.24; N, 6.40; S, 10.38. Calculated for $C_{72}H_{76}N_6O_8S_4$: C, 67.47; H, 5.98; N, 6.56; S, 10.01 %.

*5,11,17,23-Tetra-tert-butyl-25,27-bis[4'-(2'-oxo-2'-{(E)-4''(phenyldiazenyl)anilino}methoxy]-26,28-di[(ethoxycarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene(1,3-alternate-**5**).* *p-tert*-Butyl thiacalix[4]arene **3** (0.50 g, 0.56 mmol) suspended in 30 ml of acetone containing anhydrous Cs_2CO_3 (0.73 g, 2.24 mmol) or K_2CO_3 (0.31 g, 2.24 mmol). The reaction mixture was stirred while refluxing for 1 hour. To the obtained suspension, *N*-[(*E*)-4'-(phenyldiazenyl)phenyl]-2-bromoacetamide (0.71 g, 2.24 mmol) in 20 ml of acetone was added. The reaction mixture was stirred while refluxing for 60 hours. After cooling, the residue from the reaction mixture was filtered off, dissolved in chloroform (20 ml) and organic phase was washed with 2M HCl (10 ml). The organic phase was separated, dried over 3 Å molecular sieves. The solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane-ethanol mixture. A light orange powder was obtained. Yield 0.23 g (30 %) and 0.35 g (45%) when Cs_2CO_3 and K_2CO_3 respectively were used. Mp: 258 °C. ^{1}H NMR ($CDCl_3$) δ_H ppm (J/Hz): 0.69 (18H, s, (CH$_3$)$_3$C), 1.25 (6H, t, $^3J_{HH}$=7.2 Hz, O-CH$_2$CH_3), 1.31 (18H, s, (CH$_3$)$_3$C), 4.21 (4H, q, $^3J_{HH}$=7.2 Hz, O-CH_2CH$_3$), 4.64 (4H, s, -OCH_2-), 4.81 (4H, s, -OCH_2-), 7.30 (4H, s, ArH), 7.44–7.55 (4H, m, Ar'H), 7.59 (4H, s, ArH), 7.72 (4H, AB part of the AA'BB'-system, $^3J_{AB}$ +$^5J_{AB'}$= 8.8 Hz), 7.91 (4H, A'B'' part of the AA'BB'-system, $^3J_{AB}$ +$^5J_{AB'}$= 8.8 Hz), 7.94-7.96 (6H, m, Ar'H), 8.95 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) δ_C ppm: 14.25; 30.61; 31.09; 30.70; 60.87; 66.13; 120.45; 123.02; 124.11; 126.18;128.20; 128.36; 128.99; 129.22; 130.92; 133.27; 132.34; 139.99. ^{1}H-^{1}H NOESY spectrum (the most important cross-peaks): H^5/H$^{7''}$, H^7/H$^{4'b}$, H^5/H^{4b}, H^9/H$^{4'b}$, H$^{7'}$/H^{4b}, H^7/H$^{3''}$, H^9/H^{11}, H^9/H^{12}, H^9/H^7, H$^{10'}$/H$^{9''}$. IR ν cm^{-1}: 3385 (NH), 1771 (C(O)OEt), 1531 (C(O)NH).

Results and Discussion

Synthesis of Thiacalix[4]arenes

The *p-tert*-butyl thiacalix[4]arene macrocyclic platform is attractive because it is possible to obtain its stereoisomers

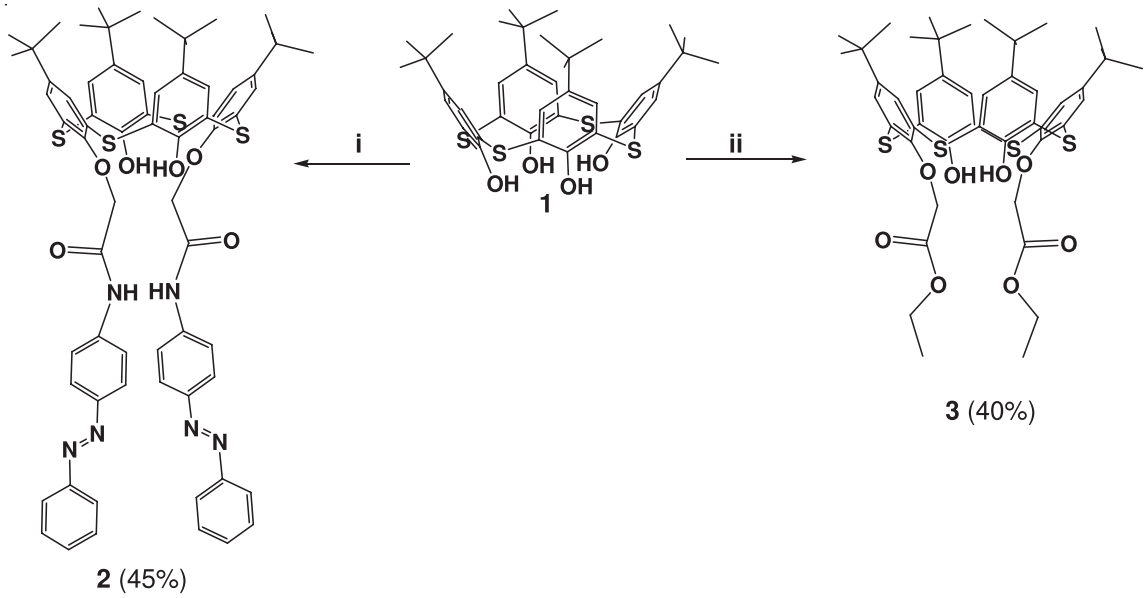
(*cone*, *partial cone*, *1,2-alternate* and *1,3-alternate*) with different spatial arrangement of functional groups.[20–27] The current main objective is the regioselective synthesis of partially substituted *p-tert*-butyl thiacalix[4]arene derivatives, with further functionalization to differently substituted thiacalix[4]arenes with predetermined spatial orientation of binding sites.

The development of the photosensitive systems able to change the structure under the light influence is of main interest. It can be expected that the combination of the advantages of thiacalix[4]arene platform with photo-switchable fragments will provide the control of the selectivity and specificity of the substrate binding. Amidoazobenzene group was chosen as a photoactive fragment. It contains polar NH group required for anion binding and is able to reverse *E*/*Z*-isomerization under light influence.[28-30] Introduction of ester fragment in a macrocycle structure is necessary for realization of the template effect of alkali metal cations at the synthesis of thiacalix[4]arene stereoisomers. Besides, it is known that introduction of an ethoxycarbonyl fragment in the lower rim of a macrocycle significantly influences on the complex formation with anions.[18]

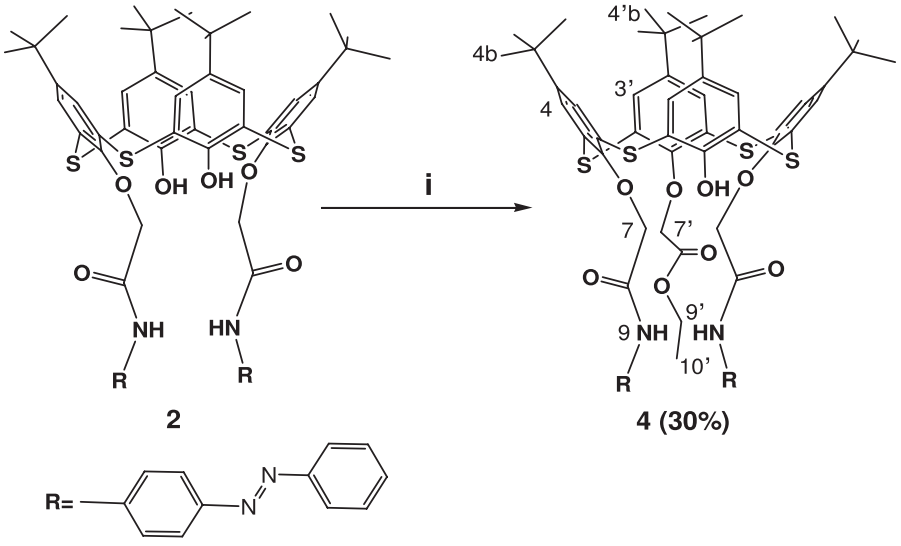
Previously, 1,3-disubstituted at lower rim thiacalix[4]arene derivatives **2** and **3** (Scheme 1) containing the 4-amidoazobenzene[17] and ethoxycarbonyl fragments, respectively, were synthesized.[19]

Then, the interaction of *p-tert*-butyl thiacalix[4]arenes **2** and **3** with ethyl bromoacetate and *N*-[(*E*)-4'-(phenyldiazenyl)phenyl]-2-bromoacetamide, respectively, in acetone, in the presence of alkali metal carbonates has been investigated. The base and solvent were chosen in accordance with their efficiency in the reaction of alkylation of *p-tert*-butyl thiacalix[4]arene at the lower rim.[31]

As a result of the interaction of 1,3-disubstituted thiacalix[4]arene derivative **2** with ethylbromoacetate in the presence of sodium carbonate as a base, macrocycle **4** in



Scheme 1. Reagents and conditions: i, *N*-[(*E*)-4'-(phenyldiazenyl)phenyl]-2-bromoacetamide/Na_2CO_3, acetone, reflux[17]; ii, ethyl bromoacetate/Na_2CO_3, acetone, reflux.[19]



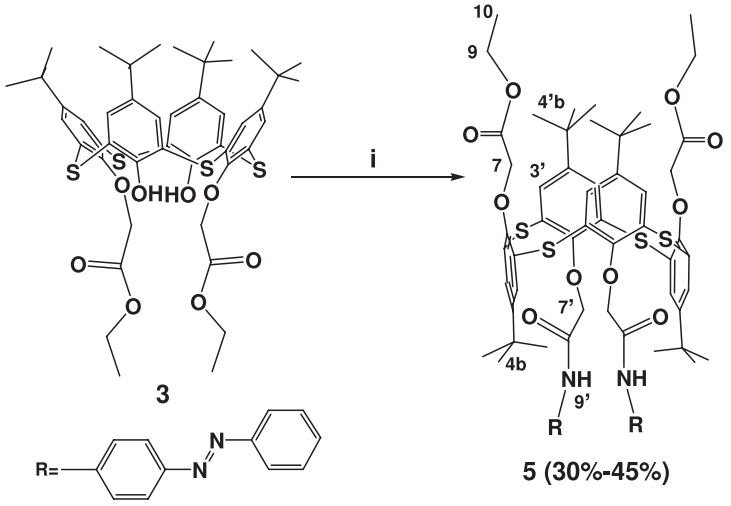
Scheme 2. Reagents and conditions: i, ethyl bromoacetate/Na_2CO_3, acetone, reflux.

cone conformation was isolated with 30 % yield (Scheme 2). It should be noted that the reaction in the presence of potassium and cesium carbonates resulted in a mixture of products which was difficult to separate and characterize. In ^{1}H NMR spectra of the mixtures obtained, a number of signals of *tert*-butyl and oxymethylene fragments were observed. In the field of aromatic fragments the systems of blocked multiplets were found out. It testifies the presence of several products in a sample.

The interaction of thiacalix[4]arene **2** with ethylbromoacetate (Scheme 2) was not succeeded to obtain the tetrasubstituted derivatives. Thus, it was offered to use the return approach with thiacalix[4]arene diester **3** as a parent macrocycle.[19] In the interaction of macrocycle **3** with *N*-[(*E*)-4'-(phenyldiazenyl)phenyl]-2-bromoacetamide in the presence of potassium and cesium carbonates in acetone, the tetrasubstituted at the lower rim macrocycle **5** in the *1,3-alternate* conformation was isolated with 30-45 % yield (Scheme 3).

The reaction in the presence of Na_2CO_3 did not lead to the formation of target products owing to small activity of the base and rather bulky alkylation reagent.

The structure and composition of new thiacalix[4]arene derivatives **4** and **5** were characterized by ^{1}H and ^{13}C NMR, 2D NMR NOESY ^{1}H-^{1}H, IR spectroscopy, mass spectrometry (MALDI-TOF) and elemental analysis.



Scheme 3. Reagents and conditions: i, *N*-[(*E*)-4'-(phenyldiazenyl)phenyl]-2-bromoacetamide/K_2CO_3 or Cs_2CO_3, acetone, reflux.

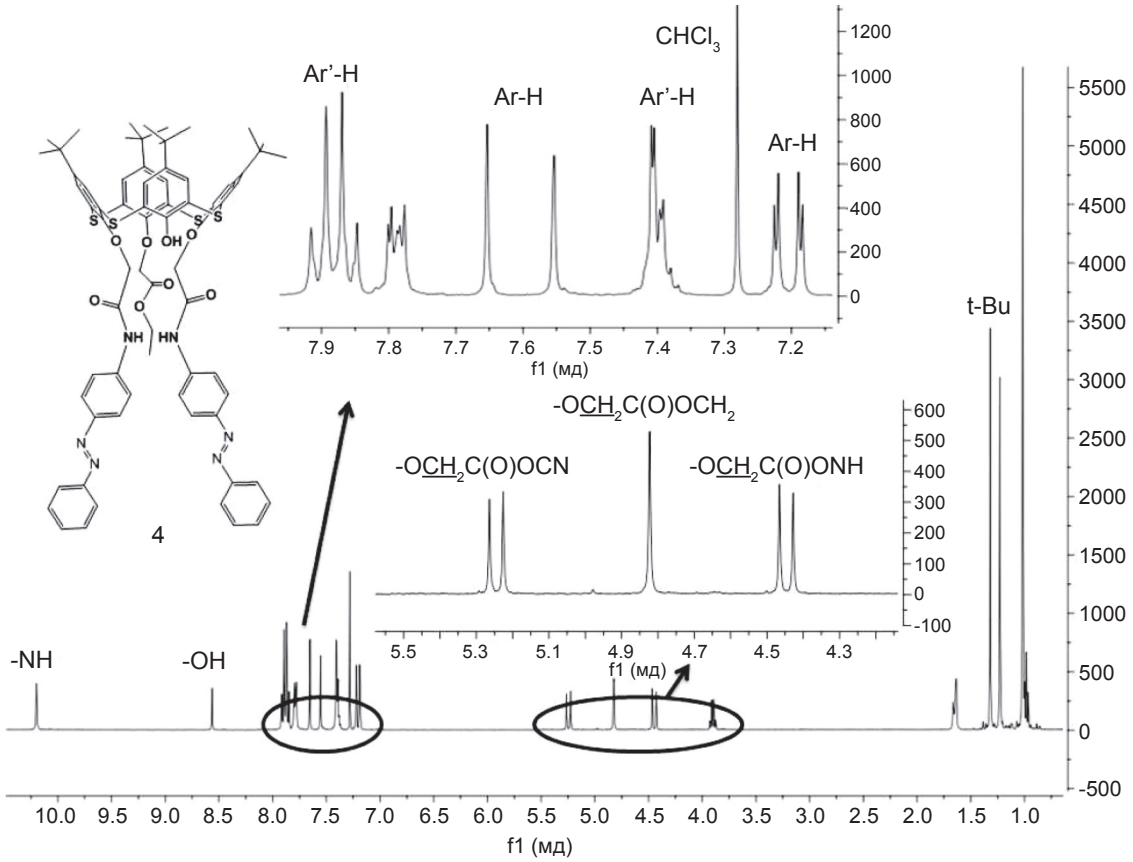


Figure 1. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, at 25 °C, Bruker Avance-400).

In the ^{1}H NMR spectrum of the compound **4** (Figure 1), the signals of *tert*-butyl protons were observed as three singlets with intensity ratio of 2:1:1 (0.99, 1.22 and 1.30 ppm). This confirms the formation of the trisubstituted product. The oxymethylene protons of the ethoxycarbonyl group were observed as singlets while the oxymethylene protons of 4-amidoazobenzene fragments as AX-spin system (4.22 and 5.22 ppm) with a spin-spin interaction constant of 15.1 Hz. The signals of the aromatic protons of the macrocycle were observed as two singlets (7.55 and 7.64 ppm) and two doublets of AB-spin system (7.16 and 7.20 ppm) with a spin-spin interaction constant of 2.4 Hz, and the signals of the azobenzene fragments as multiplets in the field of 7.37-7.90 ppm. The signals of the hydroxyl and amide protons gave singlets in a weak field at 8.52 and 10.17 ppm, respectively. The chemical shifts, multiplicity and the integral intensity of the proton signals in ^{1}H NMR spectrum of the compound **4** are in good agreement with the proposed structure of *p-tert*-butyl thiacalix[4]arene **4**.

As an example, the MALDI-TOF mass spectrum of the trisubstituted at the lower rim *p-tert*-butyl thiacalix[4]arene **4** (M($C_{72}H_{76}N_6O_8S_4$)=1281.67) is shown in Figure 2. In the MALDI-TOF mass spectrum of the compound **4** the peaks of the molecular ion with sodium cation (*m/z* ($M+Na^+$)= 1303.4) and with potassium cation (*m/z* ($M+K^+$)=1319.4) are presented.

Thus, the obtained thiacalix[4]arenes **4** and **5** are in the *cone* and in the *1,3-alternate* conformation, respectively. The structure has been confirmed by 2D NMR NOESY ^{1}H-^{1}H spectroscopy. The presence of two proton singlets for the *tert*-butyl groups, two singlets for the oxymethylene protons and two singlets for the aromatic protons of the macrocycle in the ^{1}H NMR spectrum of the lower rim tetrasubstituted *p-tert*-butyl thiacalix[4]arenes **5** shows the symmetry in the structure. However, in the ^{1}H NMR spectrum of the thiacalix[4]arenes **4**, the signals of the oxymethylene protons were observed as singlet and an AX system due to the diastereotopy of the -O-CH_2- protons of the 4-amidoazobenzene substituent. Also, the presence of hydroxyl proton signals at 8.54 ppm in the ^{1}H NMR spectrum of compounds **4** indicates an incomplete alkylation of the lower rim of initial thiacalix[4] arene **2**.

In the IR spectrum of the macrocycle **4** (Table 1), an absorption band for the valence vibrations of the ester fragment appeared (ν, 1694-1701 cm^{-1}), which was absent in the parent thiacalix[4]arene **2**. Also, in the IR spectrum of thiacalix[4]arene **4** an absorption band for the valence vibrations of the hydroxyl and amide groups (ν, 3341 and 3313 cm^{-1}, respectively) was observed indicating incomplete substitution of the lower rim of the initial macrocycle **2**. In the IR spectrum of the macrocycle **5** in contrast to the thiacalix[4]arene **4**, only valence vibrations of the amide group (3385 cm^{-1}) are presented. This testifies full replacement of hydroxyl protons of the parent macrocycle **3**.

Table 1. The values of the valence vibrations of the macrocycle **2**, **4** and **5** in the IR spectra.

compound	ν (-OH), cm^{-1}	ν (-NH), cm^{-1}	ν (-C(O)OEt), cm^{-1}
2	3389	3334	–
4	3341	3313	1750
5	–	3385	1771

Thus, new tri- and tetrasubstituted derivatives of thiacalix[4]arene containing 4-amidoazobenzene and ethoxycarbonyl fragments have been synthesized. The structure of the obtained compounds was characterized by ^{1}H and ^{13}C NMR, IR spectroscopy and mass spectrometry

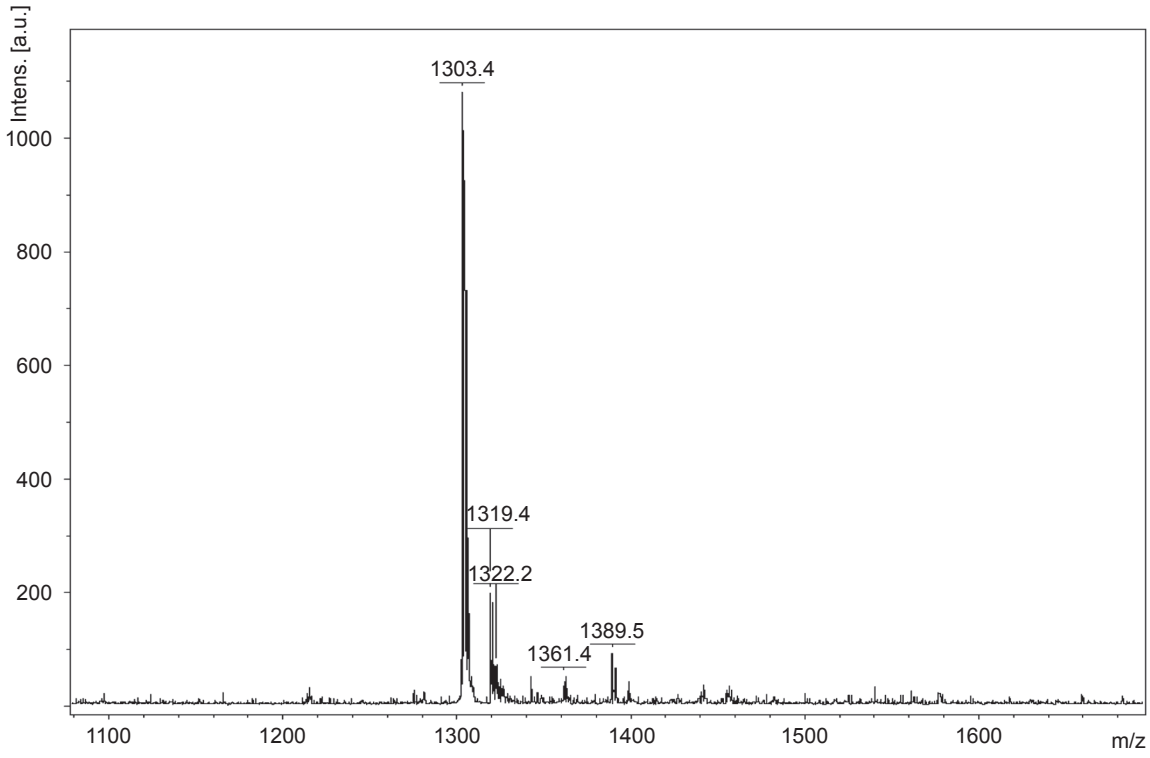


Figure 2. MALDI-TOF mass spectrum of compound **4.**

(MALDI-TOF). The spatial structure of the new heterofunctionalized thiacalix[4]arenes was established by two-dimensional 2D NMR NOESY ^{1}H-^{1}H spectroscopy.

Photoisomerization and Complexation Study

It is well known that azobenzene fragments belong to photochrome groups. Configuration transition from *E*-form to *Z*-form appears under irradiation by UV light of wavelength 360-370 nm. The reverse process from *Z*-form to *E*-form appears under visible light irradiation with wavelength of 420 nm or in a darkness under heating.[32]

The ability of the synthesized *p-tert*-butyl thiacalix[4] arenes **4** and **5** and parent 1,3-disubstituted macrocycle **2** to change configuration under UV irradiation at 365 nm as a result of the *E*/*Z*-isomerization of the photo-switchable fragment was investigated by electron spectroscopy. It was found that for *E*-configuration of the compound **2** several absorption band maxima at 300 nm, characteristic for the macrocyclic ring of the *p-tert*-butyl thiacalix[4]arene, and those at 350 nm and 450 nm, corresponding to π-π* and n-π* electron transition of the azobenzene fragments were observed (Figure 3). By irradiating the sample with UV light at 365 nm for two minutes, the *E*-configuration

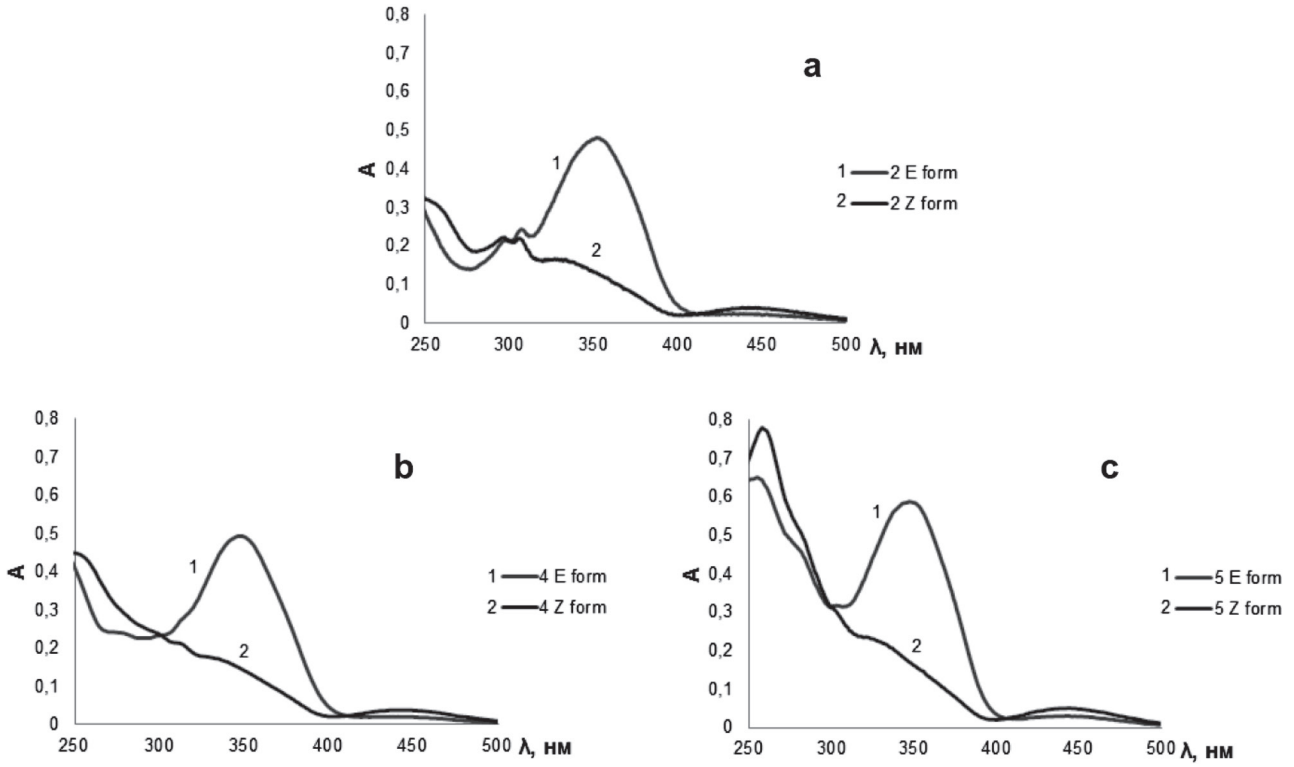


Figure 3. Absorption spectra (a-d) of the macrocycles **2, 4** and **5** before UV irradiation (*E*-configuration) and after UV irradiation (*Z*-configuration) (λ=365 nm, CH_2Cl_2).

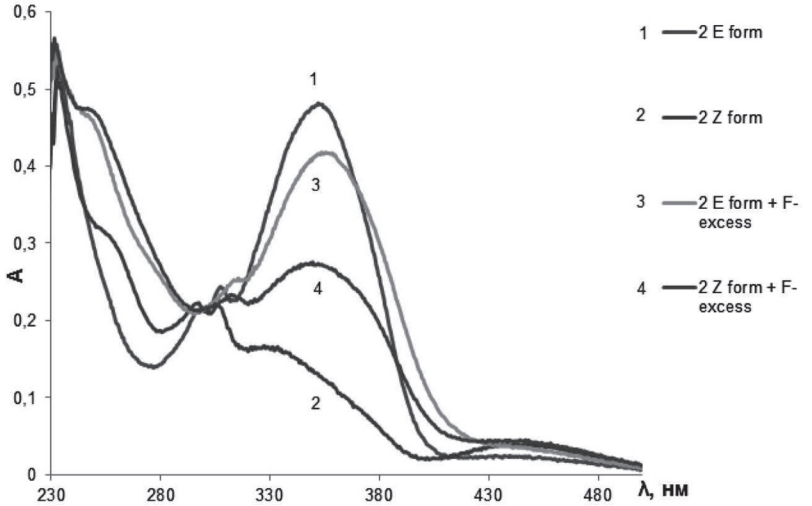


Figure 4. The UV spectra of macrocycle **2** (*E*- and *Z*-forms) at addition of 200-fold excess of fluoride anions (CH_2Cl_2).

of *p-tert*-butyl thiacalix[4]arene **2** transformed to the *Z*-configuration. The observed absorption band at 350 nm disappeared and that at 450 nm increased. Changes were also observed in the 300 nm region. Specifically, the band transfer intensity at 310 nm decreased (Figure 3). This process is reversible, and in 6 minutes the macrocycle **2** fully returned to its initial state with the *E*-configuration. The UV spectrum recorded after an hour remained the same.

In the case of the macrocycles **4** and **5**, the similar changes were observed. In the case of tri- and tetra-substituted derivatives **4** and **5**, the only difference between the absorption spectra of parent compound **2** and new synthesized macrocyles **4**, **5** was in the 260-320 nm region (Figure 3). Also, nature of change in absorption spectra under UV irradiation (λ=365 nm) differs at an *E*/*Z*-isomerization. The intensity of an absorption band enhanced at 270 nm and at 260 nm for compounds **4** and **5**, respectively. The *E/Z*-isomerization of the macrocycles **4** and **5** was achieved during 1 minute and the reverse process took about 10 minutes for the macrocycle **4** and 30 minutes for the compound **5**. Increasing time of the reversed process to the initial *E*-configuration of the compound **5** is possibly due to the steric barrier of the thiacalix[4]arene macrocyclic platform following the introduction of the ethoxycarbonyl groups.

To establish the dependence of the efficiency of a complex formation for *E*- and *Z*-configuration of thiacalix[4] arenes containing a photo-switchable fragment, we studied the receptor properties of the parent 1,3-disubstituted macrocycle **2** and synthesized thiacalix[4]arenes **4-5** in relation to some anions: F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, $CH_3CO_2^-$, NO_3^-. It was shown that the macrocycle **2** selectively binds fluoride ion. Thiacalix[4]arene **4** exerted analytical response toward fluoride- and chloride anions. The macrocycle **5** did not bind the anions studied because of negative allosteric effect of the *1,3-alternate* conformation.

In the Figure 4, the absorption spectra of 1,3-di-substituted thiacalix[4]arene **2** in the presence and absence of the excess of fluoride anion are presented. The addition of the excess of fluoride ions to the receptor **2** in *E*-configuration resulted in hypochromic effect of the maximum of absorption band at 350 nm with simultaneous hyperchromic effect of the maximum absorption band at 260 nm. In the case of *Z*-form of the compound **2**, excess of fluoride anion with the subsequent radiation for 2 minutes produced hyperchromic effect of the maximum absorption bands at 250 nm and 350 nm.

The change of absorption spectra at interaction of macrocycle **4** with excess of fluoride anion is similar in case of the macrocycle **2**. The addition of excess of chloride anion to the receptor **4** led to hypochromic effect of the maximum absorption bands at 350 and 270 nm. Introduction of one etoxycarbonyl group in the structure of the 1,3-disubstituted thiacalix[4]arene **2** led to binding of chloride anions together with fluorides by the macrocycle **4**. Probably, the carbonyl group of the ester fragment as the proton-acceptor changed a macrocycle conformation through hydrogen binding with hydroxyl and amide protons. As a result, it influenced the cavity size of the receptor and selectivity of binding.

The interaction of the macrocycle **5** with an excess of the studied anions did not follow considerable changes in the adsorption spectra. Compound **5** has *1,3-alternate* conformation and probably the volume of *tert*-butyl groups prevents the foramotion of the complex with anions. It is also known that the realization of negative allosteric effect interfering with a complex formation can take place at the substrate binding by derivatives of calix- and thiacalix[4] arene in *1,3-alternate* conformation.[33, 34]

Thus, the existence of the hydroxyl groups in structure of the receptors **2** and **4** and also their *cone* conformation are necessary criterion for anion binding.

For the quantitative characterization of complexation ability of the compounds **2** and **4** toward anions (X = F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, $H_2PO_4^-$, NO_3^-), the association constants (Table 2) and stoichiometry of the complexes formed were determined. By isomolar series method, it was established that the thiacalix[4]arenes studied form 1:1 complexes with the tetrabutylammonium salts in CH_2Cl_2. The association constants for the complexes studied were determined in CH_2Cl_2 by dilution method. Calculation of the association constants (Table 2) was carried out by the Benesi-Hildebrand method.[35]

Table 2. The logarithms of the association constant (log K_{ass}) for the receptors **2** and **4** with anions, the stoichiometry of the host:guest complexes is 1:1.

Receptor	Anion	
	F^-	Cl^-
2 *E* form	3.34±0.21	–
2 *Z* form	2.54±0.17	–
4 *E* form	3.26±0.25	3.53±0.18
4 *Z* form	2.84±0.30	3.24±0.23

From Table 2, the biggest difference in the binding constants between *E*- and *Z*- configurations was found for parent 1,3-disubstituted macrocycle **2**. Introduction of one ethoxycarbonyl group in the receptor structure decreased distinction of binding between *E*- and *Z*- configurations, meanwhile the receptor **4** has an advantage toward chloride anion.

Conclusion

New photo-switchable substituted at the lower rim *p-tert*-butyl thiacalix[4]arenes containing 4-amidoazo-benzene and ethoxycarbonyl groups were synthesized. It is shown that replacement of one hydroxyl group by ethoxycarbonyl fragment in the 1,3-disubstituted macrocycle containing 4-amidoazobenzene groups resulted in binding fluoride and chloride anions. Replacement of two hydroxyl groups with ethoxycarbonyl fragments significantly changed the binding properties of the tetrasubsituted *p-tert*-butyl thiacalix[4]arene derivative.

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