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New materials based on tubular nanodimensional structures

1. Synthesis, structural studies and determination of interproton distances in solutions of functionalized thiacalix[4]arenes according to NMR spectroscopic data (NOESY)

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New derivatives of *p-tert*-butylthiacalix[4]arene were synthesized. The conformation of the macrocycles and interproton distances in the synthesized thiacalix[4]arenes in solutions were determined by NMR spectroscopy. *p-tert*-Butylthiacalix[4]arene distally disubstituted at the lower rim adopts the *cone* conformation, and the tetrasubstituted products are formed in the *1,3-alternate* conformation.

Key words: thiacalix[4]arene, alkylation, NOESY NMR spectroscopy, nanostructures, stereoisomers.

Model biomimetic transport systems based on synthetic or artificial ion channels are used in the creation of new sensors, pharmaceuticals, and systems for drug delivery.[1,2] One of the directions for obtaining non-peptide ion channels is based on the use of supramolecular and molecular structures derived from various macrocycles.[3] The authors of several works[3—7] develop approaches towards tubular nanodimensional structures based on self-organization of functionalized calix[4]arenes (*m*-cyclophanes) to form channel-like supramolecular assemblies due to specific interactions between groups properly oriented in space or to coordination around an appropriate substrate. We propose an alternative approach (Fig. 1, *a*), namely, a design of rigidly organized macrocyclic molecular tubes from tris-, tetrakis-, and pentakiscalix[4]arenes and thiacalix[4]arenes, *i.e.*, synthesis of covalently bound cylindrical stacks of macrocycles (*m*-cyclophanes). A stack of macrocyclic rings is a molecular tube through which a substrate flux can pass. A uniaxial stack of calixarenes forms an empty column, *i.e.*, a molecular tube for pumping substrates from one aqueous phase into another through a lipophilic membrane.[3]

Calix[4]arenes in the *cone*[8] and *1,3-alternate*[9—12] conformations are synthetically convenient macrocyclic scaffolds (see Fig. 1, *b*) for constructing tubular nanodimensional structures, whose internal diameter (1 nm) allows Na^+ and K^+ cations to pass through the macrocycle.[9,10] We propose that thiacalix[4]arenes di- and tetrasubstituted at the lower rim in the *cone* and *1,3-alternate* conformations, respectively, were used as precursors of tris- and oligocalix[4]arenes. The use of thiacalixarene derivatives as "building" blocks in the synthesis of nanotubes seems attractive, because thiacalix[4]arenes tetrasubstituted at the lower rim in the *1,3-alternate* conformation[13] can be synthesized rather easily, unlike the "classical" calix[4]arenes.

The directed synthesis of macropolycyclic compounds capable of forming supramolecular structures demands, as a rule, the use of either a template or pre-organized conformationally rigid precursors.[14] Therefore, both the theoretical estimation and experimental determination of the spatial structure of, and interatomic distances, in the starting functionalized macrocycles in solutions are needed.[15]

Studies on the spatial structures of relatively small organic compounds in solutions are based on both data from 1D NMR spectroscopy and the use of dynamic NMR [16—18] and 2D NMR spectroscopy,[19,20] in particular, NOESY procedure.[21,22]

In the present study, 1D ^{1}H and 2D NMR spectroscopy (COSY, NOESY, FastNOESY)[23,24] was used to establish conformations of thiacalix[4]arene derivatives **1—3**, interproton distances,[25,26] and the character of intermolecular interaction of protons and analyze the influence of solvents on the geometry of these compounds.

Experimental

^{1}H NMR spectra for 5—10% solutions of substances in $CDCl_3$ were recorded on a Varian XL-300 instrument (300 MHz) with a VTC-4 temperature device in a regime of internal stabilization of the ^{2}H resonance line. ^{1}H NMR spectra were recorded

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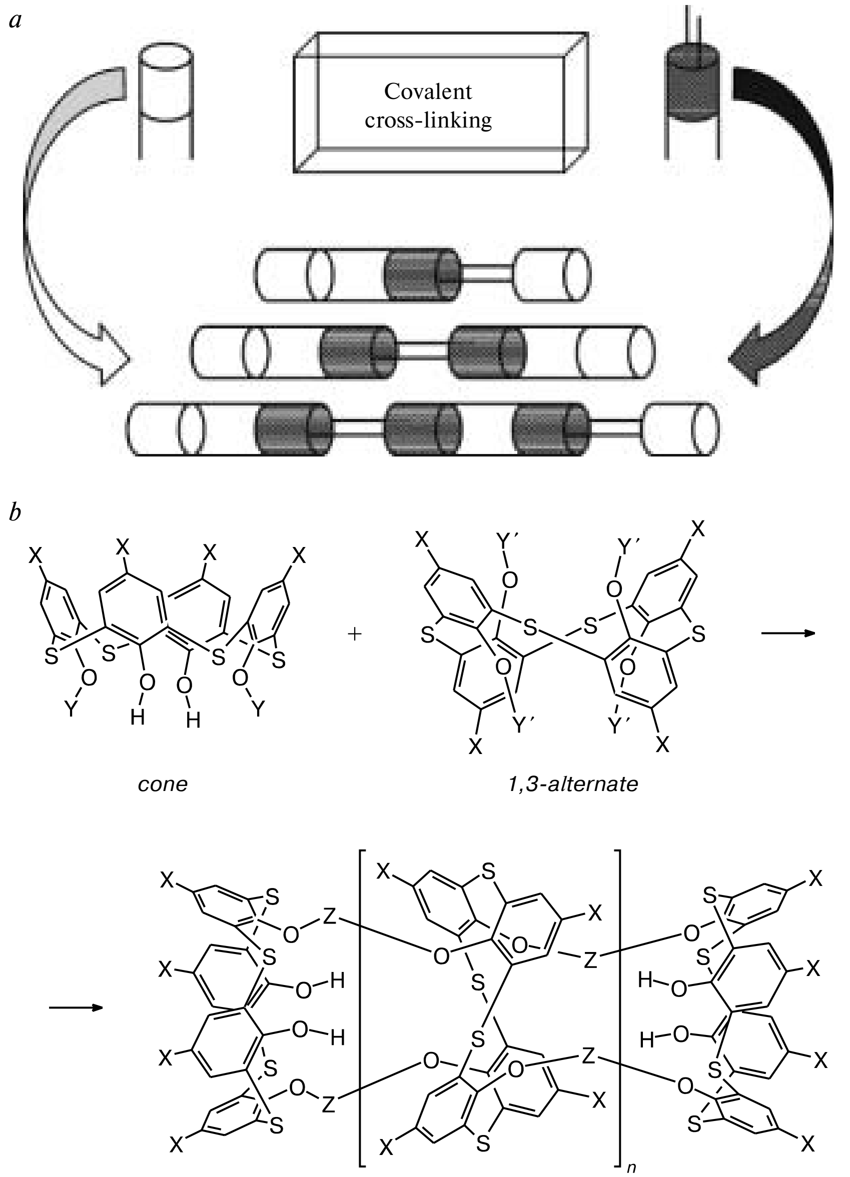

Fig. 1. Blockwise or modular approach to the synthesis of organic nanotubes (*a*) based on thiacalix[4]arenes (*b*).

with pulses of 10°—15° and delays between pulses DL = 1—5 s, the number of scans being 1—256. Chemical shifts were determined relatively to the resonance line of reference liquids. The accuracy of determination of chemical shifts was 0.01 ppm, and that of spin-spin coupling constants was 0.5 Hz. For 2D NMR experiments (NOESY), the following condition was fulfilled: $AT + DL + \tau_{mix} = 1.26T_l$, where T_l is the longitudinal relaxation time for protons of calix[4]arene, AT is the selection time, and τ_{mix} is the mixing time. When a 2D spectrum was processed, the Gaussian line shape and a digital resolution of 2K×2K were used for digital filtration; the number of scans being 16, and the selection time, AT = 0.5 s. The mixing time τ_{mix} ranged from 0.1 to 0.8 s. Spectra were recorded using a phase-sensitive procedure for 256 points of the F1 and F2 coordinates. The error of determination of the interproton distances was ≤8%.

Mass spectra were obtained on MX-1310 (EI) and Dynamo Finnigan (MALDI-TOF) mass spectrometers using 1,8,9-trihydroxyanthracene or 4-nitroaniline as matrices. IR spectra were recorded on a Bruker Vector 2-2 Fourier spectrometer in KBr pellets in an interval of 400—4000 cm^{-1} with resolution of 1 cm^{-1} for 64 scans. The reaction course was monitored by ^{1}H NMR spectroscopy and TLC on Silufol UV-254 plates (detection with I_2 vapor).

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[*N*-(4-nitrophenylcarbamoylmethoxy)]-2,8,14,20-tetrathiacalix[4]arene (1). A mixture of *p-tert*-butylthiacalix[4]arene[27] (1.00 g, 1.39 mmol), *N*-(4-nitrophenyl)bromoacetamide (0.81 g, 3.10 mmol), and anhydrous CsOH (0.84 g, 5.60 mmol) was refluxed in MeCN (60 mL) under argon for 20 h. The solvent was removed *in vacuo*, the residue was dissolved in chloroform, washed with 3 *M* HCl, and dried with $MgSO_4$. The solvent was removed *in vacuo* and the residue was recrystallized from a $CHCl_3$—EtOH mixture. Compound **1** was obtained in 77% yield (1.15 g), m.p. 315 °C. Found (%): C, 62.58; H, 5.73; S, 11.71;

N, 5.38. $C_{56}H_{60}N_4O_{10}S_4$. Calculated (%): C, 62.43; H, 5.61; S, 11.90; N, 5.20. ^{1}H NMR, δ: 1.17 (s, 18 H, H(4a), Me_3C); 1.30 (s, 18 H, H(4b), Me_3C); 4.74 (s, 4 H, OCH_2); 7.63 (s, 4 H, H(2)); 7.64 (d, 4 H, H(6), J = 9.3 Hz); 7.76 (s, 4 H, H(3)); 8.17 (d, 4 H, H(7), J = 9.3 Hz); 8.93 (s, 2 H, NH); 10.69 (s, 2 H, OH). IR, ν/cm^{-1}: 3648 (OH); 3341 (NH); 1709 (C=O); 1599 (C(O)—NH); 1546, 1512 (NO_2). MS, m/z: 1076.32 $[M]^+$ (EI); 1078.03 $[M + H]^+$, 1102.49 $[M + Na]^+$, 1116.13 $[M + K]^+$ (MALDI-TOF).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(4-bromomethylbenzyloxy)-2,8,14,20-tetrathiacalix[4]arene (2). A mixture of *p-tert*-butylthiacalix[4]arene[27] (1.00 g, 1.38 mmol), *p*-xylylenedibromide (2.20 g, 8.33 mmol), and anhydrous potassium carbonate (3.83 g, 27.78 mmol) in acetone (70 mL) was refluxed with stirring for 25 h. The solvent was removed, and a residue was treated with 3 *M* HCl and extracted with $CHCl_3$ (50 mL). The organic phase was dried with $MgSO_4$. After the solvent was removed, the residue was washed with light petroleum. Compound **2** was obtained in 49% yield (0.98 g), m.p. 236—238 °C (decomp.). Found (%): C, 59.40; H, 5.21; S, 9.10; Br, 21.17. $C_{72}H_{76}Br_4O_4S_4$. Calculated (%): C, 59.51; H, 5.27; S, 8.82; Br, 21.99. ^{1}H NMR, δ: 0.81 (s, 36 H, CMe_3); 4.46 (s, 8 H, $BrCH_2$); 5.08 (s, 8 H, OCH_2); 6.96 (d, 8 H, H(7), J = 8.0 Hz); 7.11 (d, 8 H, H(8), J = 8.0 Hz); 7.12 (s, 8 H, H(3)). IR, ν/cm^{-1}: 606 (C—Br). MS (MALDI-TOF), m/z 1449.78 $[M + H]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[4-(4-nitrophenoxy)benzyloxy]-2,8,14,20-tetrathiacalix[4]arene (3). 4-Bromomethyl-4′-nitrodiphenyl ether (2.57 g, 8.33 mmol) was added to a suspension of *p-tert*-butylthiacalix[4]arene[27] (1.00 g, 1.38 mmol), and anhydrous potassium carbonate (1.15 g, 8.33 mmol) in anhydrous acetone (70 mL). The reaction mixture was refluxed for 40 h with stirring. After the solvent was removed, the residue was dissolved in $CHCl_3$ (60 mL) and washed with water. The organic phase was dried with $MgSO_4$. After the solvent was removed, the residue was recrystallized from an acetone—dichloromethane (1 : 1) mixture to yield compound **3** (1.92 g, 85%), m.p. 255—256 °C. Found (%): C, 67.78; H, 5.17; S, 7.83; N, 3.47. $C_{92}H_{84}N_4O_{16}S_4$. Calculated (%): C, 67.79; H, 5.19; S, 7.87; N, 3.44. ^{1}H NMR, δ: 0.96 (s, 36 H, CMe_3); 5.10 (s, 8 H, OCH_2); 6.79 (d, 8 H, H(8), J = 8.5 Hz); 7.00 (dt, 8 H, H(11), J = 9.3 Hz, J = 2.3 Hz); 7.03 (d, 8 H, H(7), J = 8.5 Hz); 7.18 (s, 8 H, H(3)); 8.19 (dt, 8 H, H(12), J = 9.3 Hz, J = 2.3 Hz). IR, ν/cm^{-1}: 1513 (NO_2). MS (MALDI-TOF), m/z 1627.21 $[M + H]^+$.

Results and Discussion

The modular or blockwise approach to the synthesis of nanodimensional structures based on *m*-cyclophanes assumes the covalent assembling of pre-organized conformationally rigid macrocyclic scaffolds. To estimate the structural pre-organization in the synthesis of nanodimensional organic tubes derived from *p-tert*butylthiacalix[4]arene derivatives in the *cone* and *1,3-alternate* conformations, it was necessary to determine intramolecular distances between reaction centers of the macrocycles in solution. Therefore, we synthesized new thiacalix[4]arenes **1—3** as model compounds for studying the spatial structures of precursors of organic nanotubes. The conformational behavior of calix[4]arenes is usually discussed in terms of four ideal conformations: *cone*, *partial cone*, *1,2-alternate*, and *1,3-alternate*.[8] The conformation of the synthesized derivatives was established by 2D NMR spectroscopy. The compositions and structures of the compounds were elucidated using ^{1}H, ^{13}C, 2D COSY and NOESY NMR spectroscopic procedures, IR spectroscopy, and mass spectrometry. Assignment of signals in the ^{1}H and ^{13}C NMR spectra of newly synthesized thiacalix[4]arene derivatives is a difficult problem, which could be solved by homonuclear 2D ^{1}H—^{1}H COSY and NOESY NMR procedures.

To synthesize a precursor of a terminal fragment of the organic nanotube, we proposed a one-step alkylation of *p-tert*-butylthiacalix[4]arene with *N*-(4-nitrophenyl)bromoacetamide affording macrocycle **1** in the *cone* conformation. It is well known that the *p*-nitroacetanilide fragment is convenient for the formation of both the amino function following reduction of the nitro group and the carboxy group upon hydrolysis of the amido group.

The replacement of methylene bridges by sulfur atoms in the molecule of "classical" *p-tert*-butylcalix[4]arene[8] changes the chemical behavior of the thia analog.[13] The distinctive feature of the alkylation of thiacalix[4]arene in the lower rim is its low regio- and stereoselectivity, since it is difficult to stop the substitution in a certain step.[13] As a rule, a mixture of poorly separable partial substitution products is formed.

Scheme 1

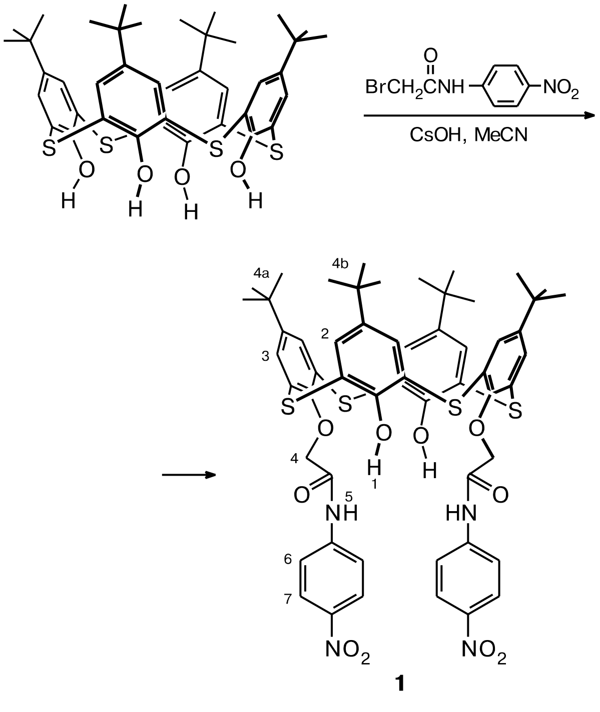

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Table 1. ^{1}H NMR spectra of compound **1** in different solvents

Proton	δ_H		
	CD_2Cl_2	$CDCl_3$	C_6D_6
H(1)	10.62	10.69	10.65
H(2)	7.65	7.63	7.42
H(3)	7.72	7.76	7.89
H(4)	4.67	4.74	7.60
H(4a)	1.11	1.17	0.92
H(4b)	1.21	1.30	1.22
H(5)	8.96	8.93	9.52
H(6)	7.55	7.64	7.70
H(7)	8.05	8.17	8.00

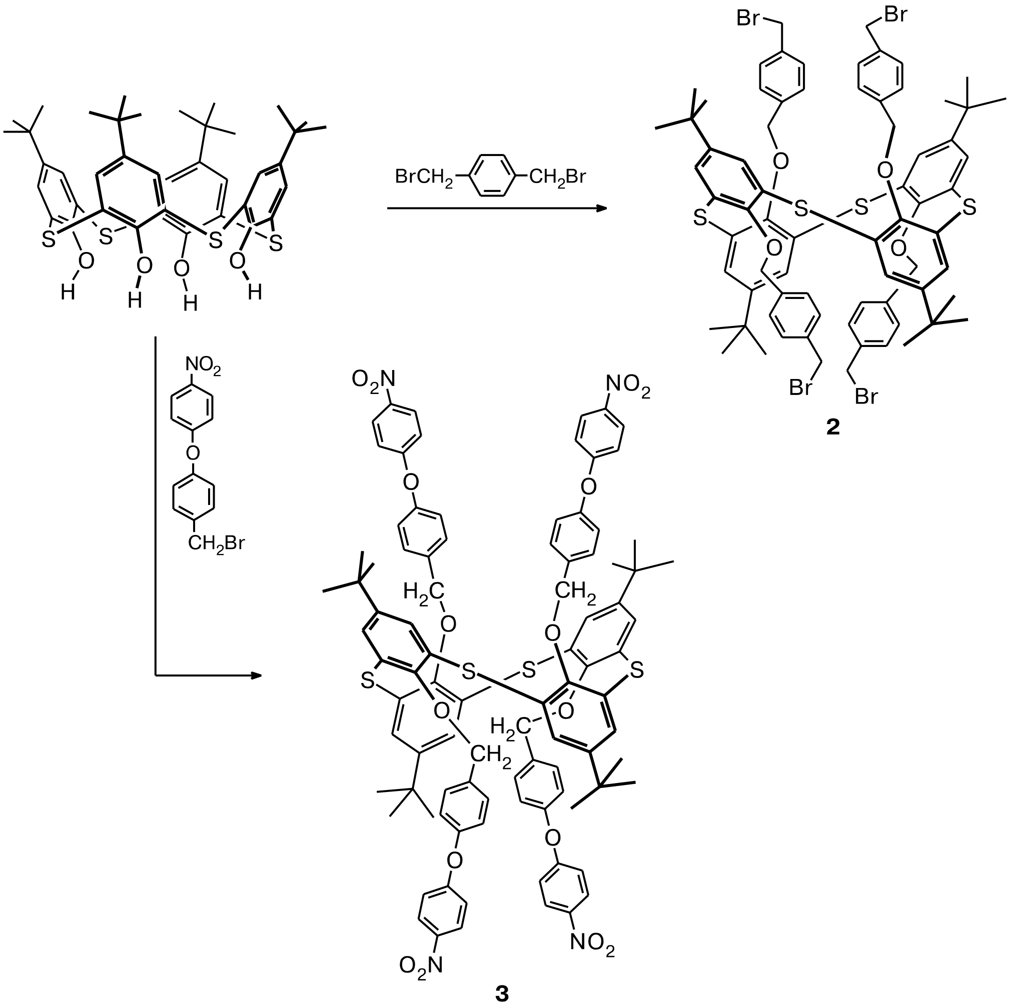
The regioselective alkylation of *p*-*tert*-butylthiacalix[4]arene with *N*-(4-nitrophenyl)bromoacetamide was performed in MeCN in the presence of cesium hydroxide. Thiacalix[4]arene **1** 1,3-disubstituted at the lower rim was obtained in high yield (77%) (Scheme 1).

The reaction stops in the step of formation of disubstituted thiacalix[4]arene **1** because of low solubility of product **1** in MeCN. The structure of compound **1** and, in particular, the spatial structure of the macrocycle, was established by NMR spectroscopy (^{1}H, COSY, and NOESY) (Table 1). The influence of the solvent nature on chemical shifts and multiplicity of signals is insignificant (see Table 1), indicating that macrocycle **1** retains its conformation under the conditions studied.[14]

The singlet shape of the resonance lines of aromatic protons, the δ_H values in the ^{1}H NMR spectrum, and the absence of cross-peaks due to the interactions of the aromatic protons with protons of the lateral substituents suggest the *cone* conformation.

The next stage was the synthesis of tetrasubstituted thiacalix[4]arenes in the *1,3-alternate* conformation. It is well known that the starting *p*-*tert*-butylthiacalix[4]arene adopts the *cone* conformation in both crystal and solution because of cooperative bonding due to a cyclic system of hydrogen bonds.[13] Nevertheless, its alkylation, regardless

Scheme 2



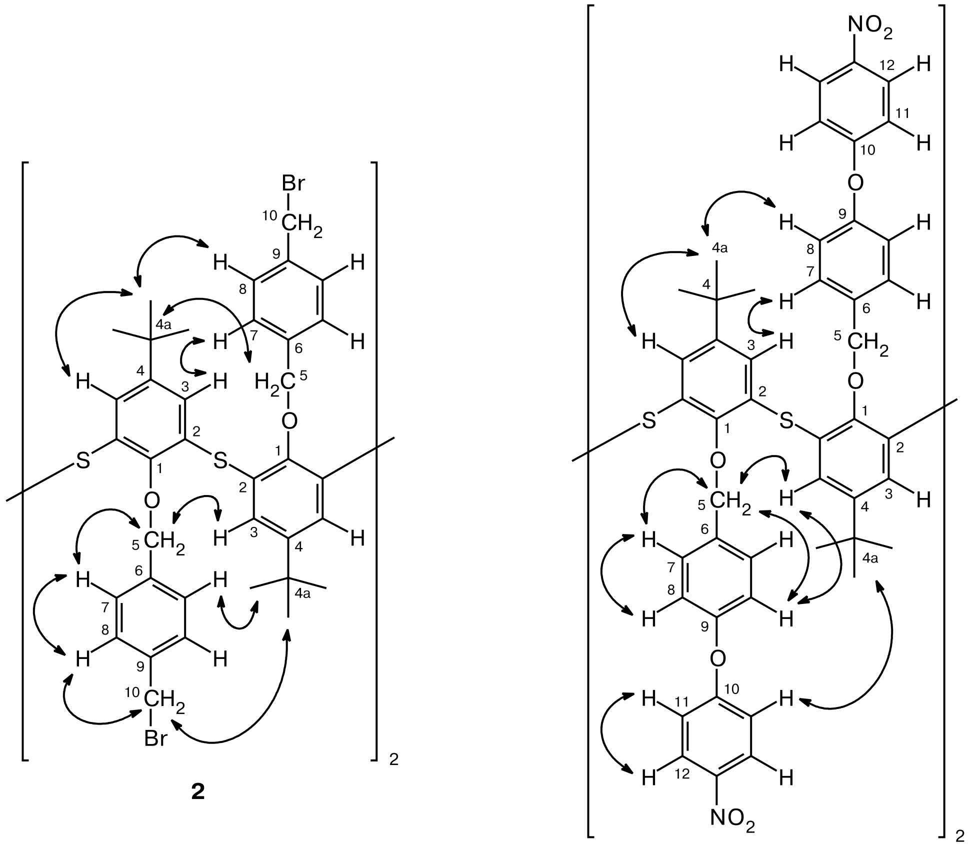
of the nature of the base used,[28] affords tetrasubstituted products in the *1,3-alternate* conformation. Macrocycles **2** and **3** were obtained by the alkylation of *p-tert*-butylcalix[4]arene with the corresponding alkyl bromides in acetone in the presence of potassium carbonate (Scheme 2).

The use of ^{1}H, COSY, and NOESY NMR spectroscopic procedures made it possible to completely assign the signals and establish that tetrasubstituted thiacalixarene **2** and **3** exist in the *1,3-alternate* conformation (Fig. 2). The NOESY spectrum of macrocycle **2** recorded at a mixing time of 0.5 s is presented in Fig. 3.

Compound **3** has a similar structure. The NOESY spectrum indicates unambiguously the *1,3-alternate* conformation. This follows, in particular, from cross-peaks H(3)/H(5) and cross-peaks of the aromatic protons H(7) and H(8) with the H(3) protons and the H(4a) protons of the *tert*-butyl group.

The NOESY NMR spectroscopic procedure makes it possible to measure distances between protons in solutions.[19,21,29] Integrated intensities and their relationship to interproton distances were examined by the complete analysis of the cross relaxation matrix.[21,22,30] Note that the method of obtaining the cross relaxation rate constant from the ratio of integrated intensities of the cross to diagonal peak is more efficient when integrated intensities of diagonal and cross-peaks can be measured.[25]

A series of 2D NOESY NMR experiments with different mixing times was performed in a regime of fast spectrum recording to determine the interproton distances in calix[4]arenes under study. In this recording regime, a delay between the pulse sequence of an order of one longitudinal relaxation time T_l is used, which is much shorter than the recommended 3—5 T_l times. On going from one NOESY experiment to another, a condition T_{rel} = DL + AT + τ_{mix} = const is fulfilled. To optimize the sensitivity (best signal/noise ratio at a minimum time of spectrum recording), one can choose T_{rel} equal to $1.26T_l$, where the maximum longitudinal relaxation time of all protons present in the spectrum is taken. The integrated intensity of the cross-peak is normed to the integrated intensity of the diagonal peak, which allows one to avoid a contribution of longitudinal relaxation and gives a linear dependence of this ratio on the mixing time for an easy calculation of the cross relaxation rate constant. The effective distances between particular protons were calcu-



2

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Fig. 2. Structural fragments of compounds **2** and **3** and the scheme of arrangement of protons between which the NOE is observed in the 2D NOESY NMR spectrum.

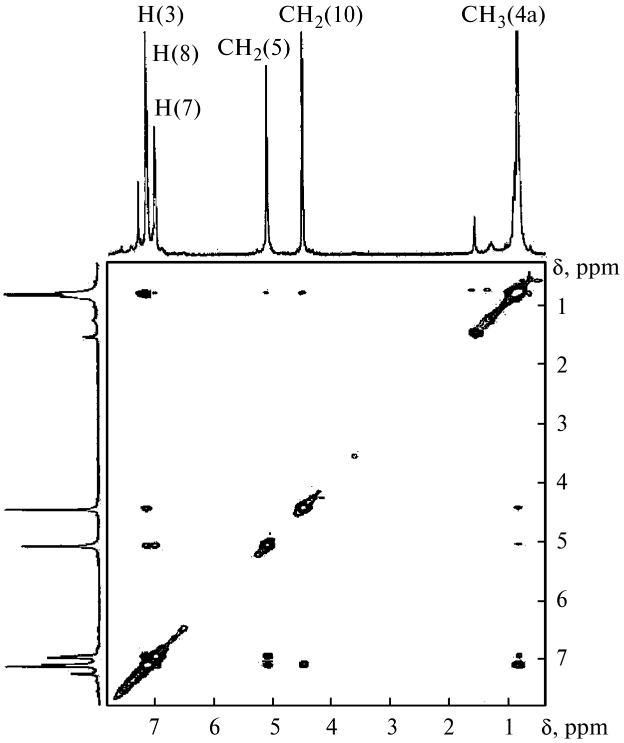

Fig. 3. 2D NOESY NMR spectrum recorded at a mixing time of 0.5 s and one-dimensional projections of the ^{1}H NMR spectra of compound **2** in CDCl$_3$.

lated from the dependence of the ratios of integrated intensities. For compounds **2** and **3**, the distance between the aromatic protons H(7) and H(8) equal to 2.45 Å was used as reference.[30]

The results of studies of compound **1** are presented in Table 2, and those for tetrasubstituted products **2** and **3** are given in Table 3. In the case of macrocycle **1**, we may conclude that the thiacalix[4]arene scaffold was fixed in solution in the *cone* conformation by a system of hydrogen bonds between the amido groups (NH(5)) and phenolic hydroxy groups (OH(1)). This suggests conformational pre-organization of *m*-cyclophane **1** in organic solvents (see Table 1) suitable for subsequent covalent cross-linking to form organic nanotubes (see Fig. 1). A comparison of the interproton distances in tetrasubstituted thiacalix[4]arenes **2** and **3** (see Table 3) showed that the *tert*-butyl groups of the macrocycles conformationally organize the lateral substituents: they are remote from each other due to repulsion. At the same time, steric hindrance of the methylene group (C(10)H$_2$), which can be unfavorable for its reactivity, is observed in the case of compound **2**.

Table 2. Experimental values of interproton distances in macrocycle **1**

Proton pair	*r*/Å	
	CD$_2$Cl$_2$	CDCl$_3$
H(1)/H(4)	2.91	2.76
H(1)/H(5)	2.47	2.38
H(1)/H(6)	2.31	2.33
H(2)/H(4b)	2.65	2.78
H(3)/H(4a)	2.65	2.59
H(5)/H(4)	2.73	2.79
H(6)/H(4)	3.22	3.17
H(6)/H(7)	2.45	2.45

Table 3. Experimental values of interproton distances (*d*) in macrocycles **2** and **3**

2		**3**	
Proton pair	*d*/Å	Proton pair	*d*/Å
H(3)/H(4a)	—	H(3)/H(4a)	2.63
H(3)/H(5)	—	H(3)/H(5)	2.63
H(4a)/H(5)	3.75	H(4a)/H(11)	—
H(4a)/H(7)	3.28	H(5)/H(7)	2.40
H(4a)/H(10)	3.49	H(5)/H(8)	3.28
H(5)/H(7)	2.74	H(7)/H(3)	2.97
H(7)/H(8)	2.45	H(7)/H(8)	2.45
H(8)/H(10)	2.68	H(11)/H(12)	2.58

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