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Unusual functionalization of the lower rim of thiacalix[4]arene: competition of alkylation and transalkylation

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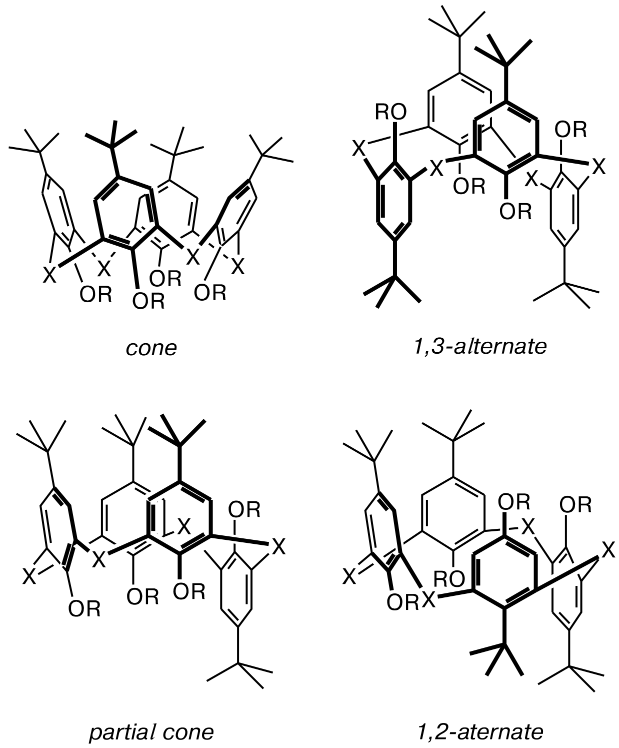
Thiacalix[4]arenes mono-, 1,3-di-, tri-, and tetrasubstituted at the lower rim, including those containing different substituents, were synthesized by the method based on the ability of the phenacyl moiety to serve as the protecting group, as well as to be involved in transalkylation.

Key words: thiacalix[4]arenes, protecting groups, functionalization of the lower rim, transalkylation, X-ray diffraction study.

Thiacalix[4]arenes **1** represent a group of macrocyclic compounds with distinct molecular cavities[1—6] and serve as convenient molecular platforms for the design of preorganized structures and supramolecular ensembles due to a considerable potential for modifications of the upper and lower rims of the macrocycle. The efficiency and selectivity of guest—host interactions can be increased manifold by the selective functionalization with appropriate heteroatomic groups as a result of the formation of receptor systems containing several spatially preorganized binding sites. The existence of several stereoisomers of the thiacalix[4]arene platform, such as *cone, partial cone, 1,3- and 1,2-alternates*,[1] provides additional possibilities for the design of molecular receptors. In addition, the presence of bridging sulfur atoms and an increase in the size of the cavity of the macrocycle in thiacalix[4]arene **1** compared to calix[4]arene **2** results in new features in the chemical behavior, including the complexing ability.[4—6]



1: X = S, R = H
2: X = CH$_2$, R = H

Results and Discussion

It is known that the reactions of calix[4]arene **2** with alkylating agents in the presence of alkali carbonates afford disubstituted derivatives in high yields, whereas tetrasubstituted products are difficult to synthesize even with the use of strong bases, for example, of sodium hydride.[1—3] In the series of thiacalix[4]arenes, tetrasubstituted products are formed even in the presence of alkali carbonates. Hence, the development of approaches to the synthesis of partially substituted derivatives is of great importance.

Such a different behavior of these metacyclophanes is due to changes in the hydrogen bond energy[7] and the acid-base properties of phenol groups[8] at the lower rim of the macrocycles. In our opinion, there are three fundamentally different approaches to the synthesis of partially substituted thiacalix[4]arenes. One approach is based on the optimization of the reaction conditions, including most often the use of stoichiometric amounts of the reagents and a base and the choice of the solvent, in which the intermediates of the reaction are removed from the reaction zone due to their low solubility. This approach was

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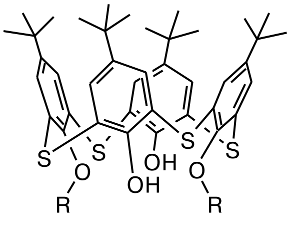
used for the synthesis of 1,3-disubstituted (so-called distally substituted) derivatives **3**—**7** in 50—85% yields.[9—11]



3—**9**

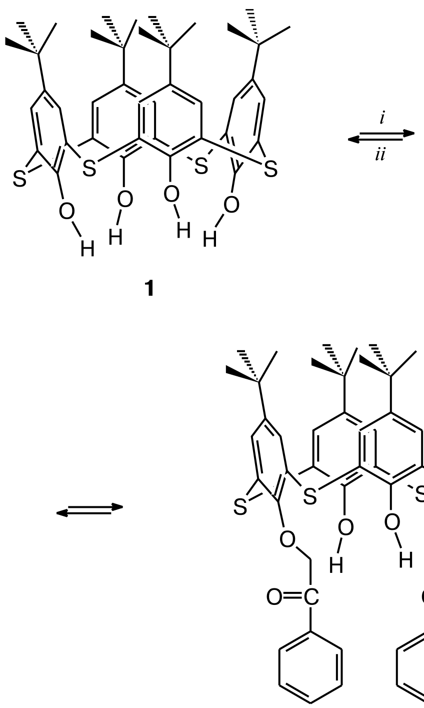
R = Me (**3**), CH_2COOEt (**4**), CH_2COOH (**5**), CH_2Ph (**6**), $CH_2C_6H_4NO_2$ (**7**), $(CH_2)_nY$ (**8**), CH_2COPh (**9**)

Another approach is based on the creation of steric hindrances at the reaction centers by using reagents with bulky substituents. This approach was successfully used for the synthesis of a series of distal thiacalix[4]arenes **8** having the *cone* conformation in yields from 29 to 89% by the Mitsunobu reaction.[12] This approach opens up possibilities for the synthesis of mono- and bis-crown derivatives[13] and some other disubstituted products.[14—17] The third approach to the synthesis of disubstituted thiacalix[4]arene derivatives is described in the present study and is based on the thermodynamic stabilization of the resulting partially substituted products due to the formation of hydrogen bonds between free phenolic hydroxyls and functional groups of the substituents.

α-Bromoacetophenone, whose carbonyl group can form hydrogen bonds with phenolic hydroxyl, is a suitable reagent for the functionalization of the thiacalixarene platform. Earlier, we have described[18] the synthesis of distally substituted product **9** in 15% yield by the reaction of thiacalixarene **1** with α-bromoacetophenone in acetonitrile in the presence of a sixfold excess of cesium carbonate and α-bromoacetophenone.

In the present study, we developed a procedure for the synthesis of compound **9** in high yield (Scheme 1). The reaction of thiacalixarene with α-bromoacetophenone in acetonitrile using the reagent ratio **1** : $BrCH_2C(O)Ph$: CsOH = = 1 : 2 : 2 and cesium hydroxide as the base gave compound **9** in 81% yield. It should be noted that, as opposed to most of the procedures for the preparation of lower-rim functionalized thiacalixarenes, compound **9** can be easily purified by recrystallization from a chloroform—hexane mixture. The structure of compound **9** was confirmed by one- and two-dimensional NMR spectroscopy, IR spectroscopy, MALDI-TOF mass spectrometry, and X-ray diffraction study.

Scheme 1



1

9

i. $PhC(O)CH_2Br$, CsOH, MeCN, 12 h, 82 °C. *ii*. 1) $PhCH_3$ (PhH), heating, $PhNH_2$ ($C_6H_{13}NH_2$); 2) DMF, Na_2CO_3, heating.

The ^1H NMR spectrum of compound **9** shows signals of the phenyl protons of the substituents, two singlets of equal intensity for the aromatic protons of the calixarene platform, a singlet of the methylene protons, and two singlets of the *tert*-butyl protons. This spectral pattern corresponds to the structure of distally substituted thiacalix[4]arene. The signals of the phenyl substituents are observed in the ^1H NMR spectrum (Fig. 1) as a doublet of the *ortho*-phenyl protons (*o*-PhH, δ 8.16) and two triplets of the *para*- (*p*-PhH, δ 7.59) and *meta*-phenyl (*m*-PhH, δ 7.48) protons.

The three-dimensional structure of macrocycle **9** in solution (*cone*) was determined by 2D NOESY spectroscopy. The spectrum shows cross-peaks between the signals for the protons of the hydroxy and methylene groups, the protons of ArH, the substituted and unsubstituted 4-*tert*-butylphenyl fragments, as well as between the signals of the *ortho*-phenyl protons and the protons of the $—OCH_2CO—$ group.

The single-crystal X-ray diffraction data for compound **9**, whose crystals were grown from a chloroform—acetonitrile mixture, confirm the stereoisomeric form *cone* (Fig. 2) of compound **9** and indicate that the stability of this structure is associated with the formation of intramolecular hydrogen bonds.

According to the X-ray diffraction data, compound **9** forms monoclinic crystals containing one independent calixarene molecule and solvent water molecules in a ratio of 1 : 3. One of the *tert*-butyl groups of molecule **9** is disordered over two positions with occupancies of 0.64 and

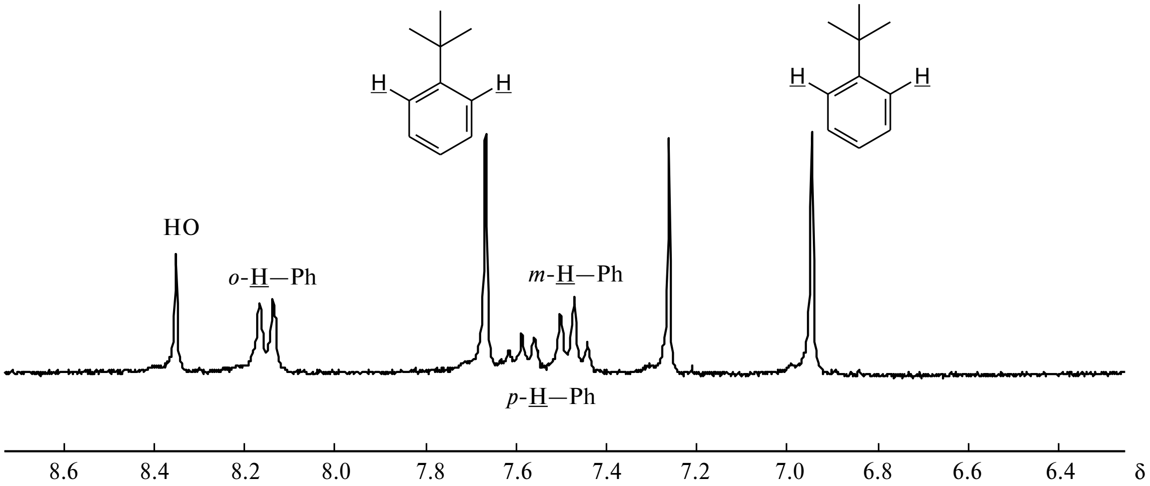


Fig. 1. Fragment of the ^{1}H NMR spectrum of compound **9** in the aromatic proton region (CDCl$_3$, 25 °C).

0.36. Two solvent water molecules are also disordered over two positions with equal occupancy.

In the crystal structure, the calixarene molecule loses the symmetry C_2 and adopts the distorted *cone* conformation (see Fig. 2) because two opposite benzene rings are bent not in the opposite directions, as it is observed in the classical *cone* conformation,[1,3] but in the same direction and are almost parallel to each other (the dihedral angle between the benzene rings is 4.0(1)°, and the dihedral angle between the two other rings is 83.6(2)°).

If the plane passing through four bridging sulfur atoms is taken as the main plane of the molecule, the angles between this plane and the planes of four benzene rings of the molecule are 135.5, 140.7, −68.8, and 107.6°. Apparently, this mutual arrangement is determined by steric hindrance due to the presence of the bulky substituents at the lower rim of the molecule. This is also evidenced by the character of the mutual arrangement of two phenacyl substituents, resulting in the H(52)...O(54) interaction. It should be noted that there are a large number of intramolecular O—H...O, O—H...S, and C—H...O hydrogen bonds in molecule **9**. The parameters of these interactions are given in Table 1.

Only a pair of C—H...O hydrogen bonds (see Table 1) responsible for the formation of centrosymmetric dimers (Fig. 3) belongs to intermolecular interactions. The

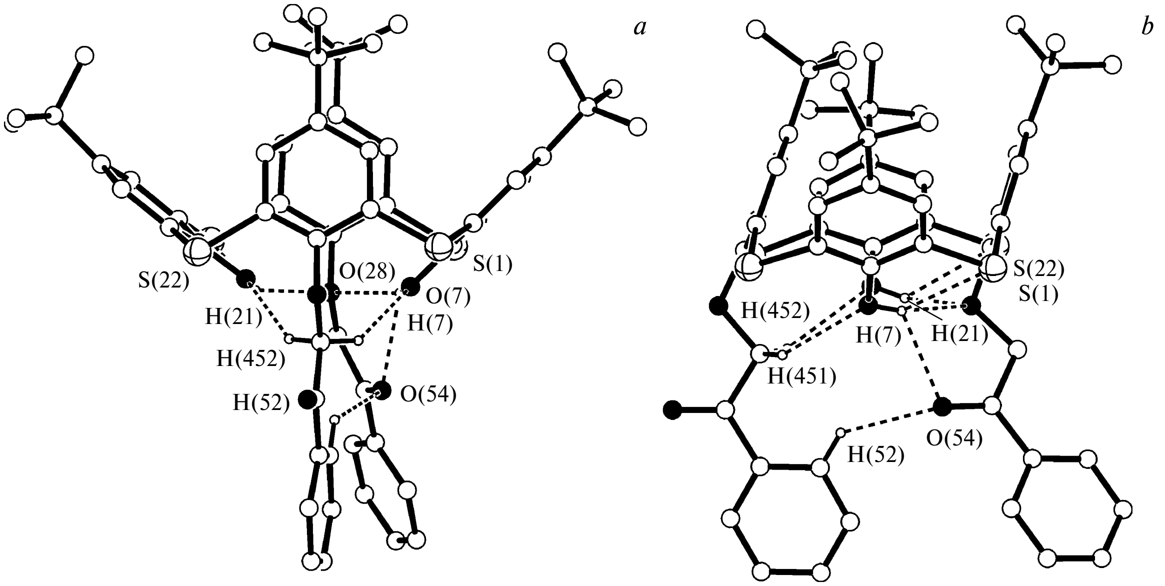


Fig. 2. Two projections of the molecular structure of product **9** in the crystalline state. Only the hydrogen atoms that are involved in the hydrogen bonding (dashed lines) are shown. The solvent water molecules are not shown. The disordered *tert*-butyl groups are presented in positions with the highest occupancy.

Table 1. Hydrogen bond parameters in the crystal structure of compound **9**

D—H...A	d/Å			Angle /deg
	D—H	H...A	D...A	
O(7)—H(7)...S(1)	0.82	2.57	3.072(3)	121
O(7)—H(7)...O(28)	0.82	2.28	3.031(4)	152
O(7)—H(7)...O(54)	0.82	2.43	2.980(5)	125
O(21)—H(21)...S(22)	0.82	2.57	3.072(3)	121
O(21)—H(21)...O(28)	0.82	2.22	2.907(4)	142
C(45)—H(451)...O(7)	0.97	2.53	3.344(5)	141
C(45)—H(452)...O(21)	0.97	2.57	3.413(5)	146
C(52)—H(52)...O(54)	0.93	2.57	3.297(7)	135
C(40)—H(402)...O(21)*	0.96	2.48	3.404(10)	160

* The symmetry operation $-x$, $-y$, $1 - z$.

π—π interaction between the electronic systems of the aromatic rings of two adjacent molecules (the distance between the centers of the rings is 4.186(3) Å, the dihedral angle is 0°, the distance between the planes of the rings is 3.89 Å) also makes a contribution. The closer contact between the benzene rings is hindered by the *tert*-butyl groups. The water molecules that are present in the crystal are apparently weakly bound to a particular functional group of thiacalix[4]arene molecule **9**, which is indirectly evidenced by their disordered arrangement in the crystal structure.

The investigation of the reactivity of compound **9** showed that the phenacyl moiety can be easily and quantitatively removed from the thiacalixarene platform by either heating in DMF in the presence of a base (sodium carbonate) or refluxing in toluene or benzene in the presence of benzylamine or hexylamine (see Scheme 1). Consequently, the phenacyl moiety in compound **9** can act as the efficient protecting group, which opens up new possibilities for the synthesis of mixed and asymmetrically substituted thiacalixarenes.

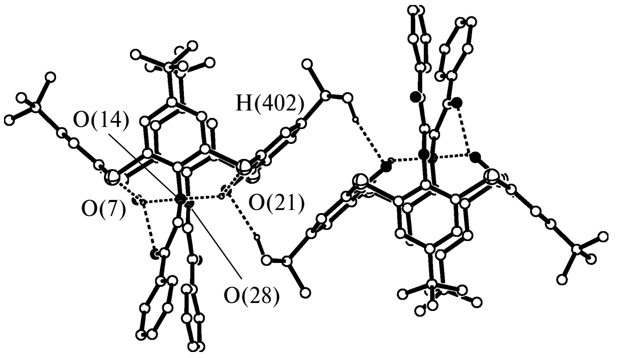


Fig. 3. Formation of a dimer in the crystal structure of compound **9**. Only the hydrogen atoms that are involved in the hydrogen bonding (dashed lines) are shown. The solvent water molecules are not shown.

To realize these possibilities, we made an attempt to perform the functionalization at the remaining free phenol groups of macrocycle **9** with the aim of obtaining tetrasubstituted product **10** containing different substituents (Scheme 2). However, the reaction of compound **9** with 1-iodopropane in acetone in the presence of sodium carbonate afforded unexpected disubstituted product **11**, *viz.*, the dipropoxy derivative, in 89% yield.

The structure of compound **11** was determined by NMR spectroscopy and X-ray diffraction. Compound **11** crystallizes in the individual state and forms monoclinic crystals with one independent calixarene molecule (Fig. 4). In the crystal structure, two *tert*-butyl groups and two propyl groups are disordered over two positions with occupancies of 0.64 and 0.36. The conformation of calixarene molecule **11** in the crystal is analogous to that of compound **9**. Thus, both molecules have a distorted *cone* conformation (the dihedral angle between two opposite benzene rings that are bent in the same direction is 2.9(1)°; the dihedral angle between the other two rings is 62.8(2)°).

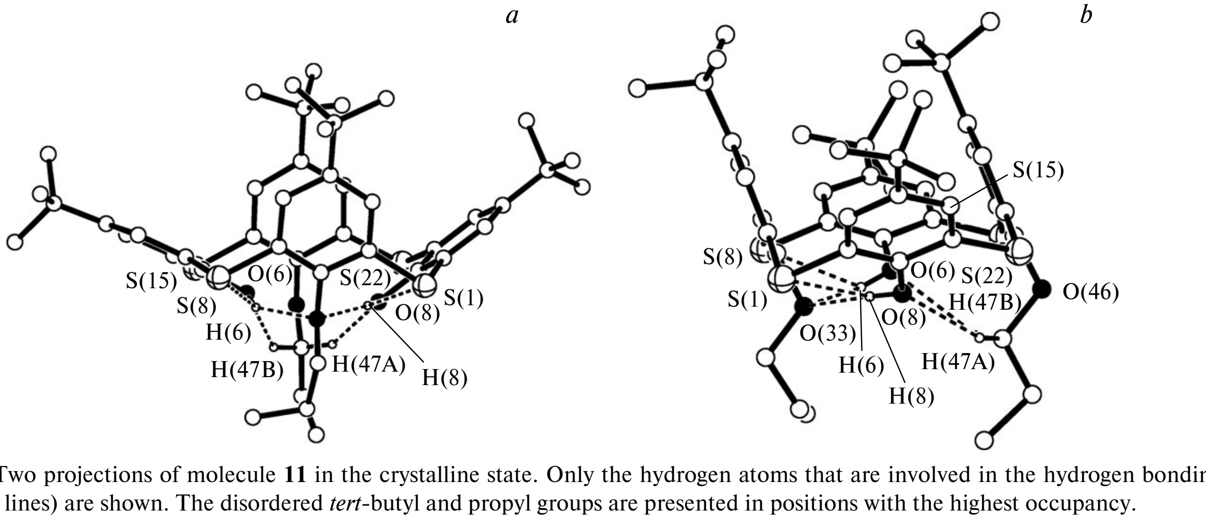
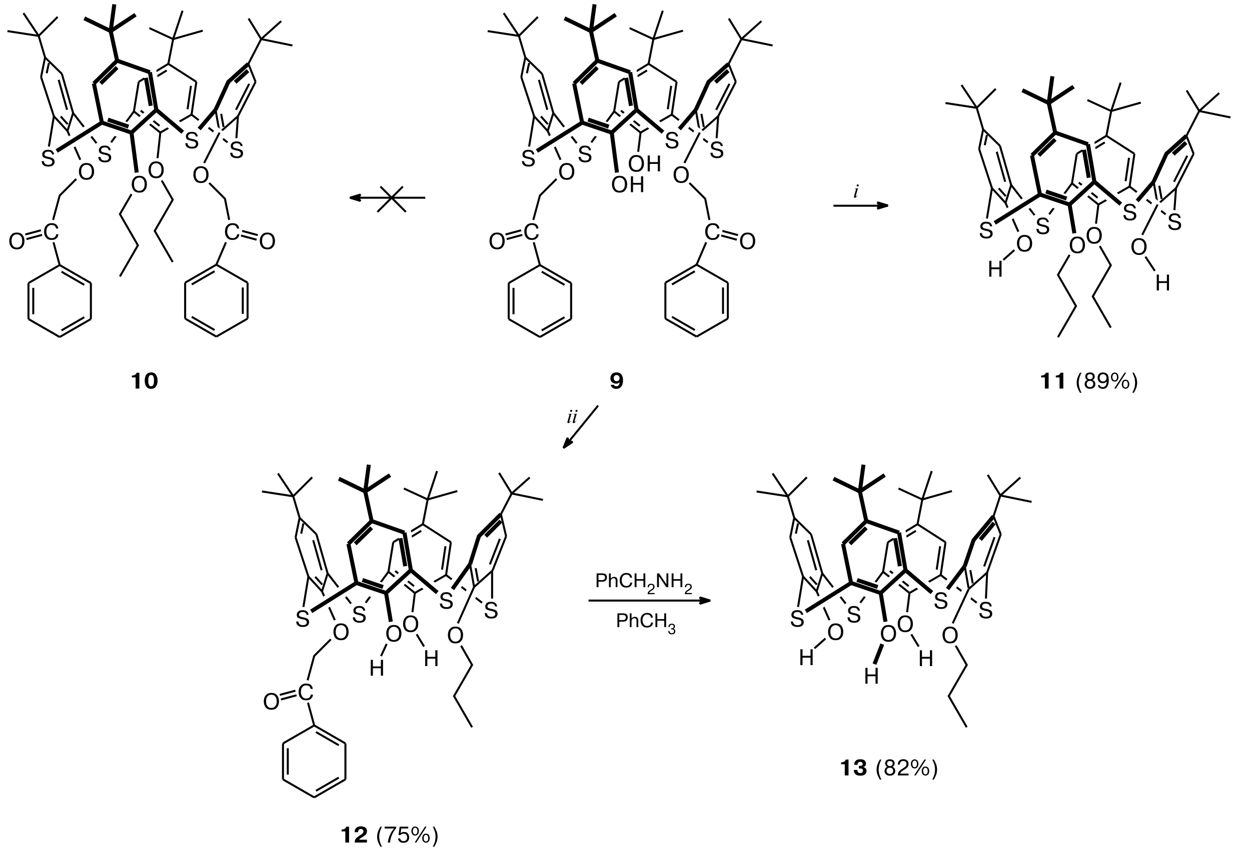


Fig. 4. Two projections of molecule **11** in the crystalline state. Only the hydrogen atoms that are involved in the hydrogen bonding (dashed lines) are shown. The disordered *tert*-butyl and propyl groups are presented in positions with the highest occupancy.

Scheme 2



i. PrI, Na_2CO_3, Me_2CO, 48 h; *ii*. PrBr, Na_2CO_3, Me_2CO, 24 h.

Intermolecular hydrogen bonds were not found in the crystal structure of **11**. The absence of essential interactions is indirectly evidenced also by the disorder of the *tert*-butyl and propyl groups of the molecules. The hydrogen atoms of the hydroxy groups of compound **11** also participate only in intramolecular hydrogen bonds. The involvement of two α-H atoms of the propoxy group in the hydrogen bonding with the oxygen atoms of the hydroxy groups results in the formation of the cyclic hydrogen bond at the lower rim of calixarene. There are also O—H...S bonds. The intramolecular hydrogen bond parameters are given in Table 2.

The formation of product **11** can be attributed to the following several processes: the removal of the phenacyl groups resulting in the formation of the starting thiacalixarene followed by the reaction with 1-iodopropane, the initial alkylation of two free phenol groups followed by the removal of the phenacyl substituents, and the transalkylation through the formation of oxonium cations.

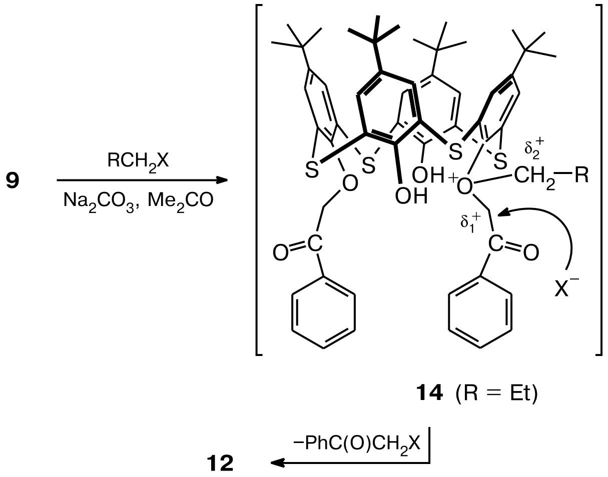
The first pathway can be ruled out because the starting thiacalixarene **1** does not react with iodopropane under these conditions.[19] The reaction by the second pathway is inconsistent with the results of our study of the reaction of macrocycle **9** with less reactive bromopropane (see Scheme 2). In this reaction we obtained asymmetrically substituted thiacalixarene **12** as a result of the replacement of one phenacyl group by the propyl group. Hence, the most possible mechanism of the formation of compound **11** involves the transalkylation. The initially formed oxonium cation **14** is subjected to the nucleophilic attack at the C_α atom of the phenacyl substituent because it is more

Table 2. Intramolecular hydrogen bond parameters in the crystal structure of compound **11**

D—H...A	*d*/Å			Angle /deg
	D—H	H...A	D...A	
O(6)—H(6)...S(8)	0.82	2.60	3.072(4)	118
O(6)—H(6)...O(33)	0.82	2.11	2.797(2)	141
O(8)—H(8)...S(1)	0.82	2.53	3.026(4)	120
O(8)—H(8)...O(33)	0.82	2.10	2.876(3)	159
C(47)—H(47A)...O(8)	0.97	2.46	3.290(4)	144
C(47)—H(47B)...O(6)	0.97	2.52	3.331(5)	142

electrophilic ($\delta_1^+ > \delta_2^+$) compared to the C_α atom of the alkyl group due to the electron-withdrawing character of the adjacent benzoyl substituent (Scheme 3).

Scheme 3



Compound **12** crystallizes in the individual state from a dichlromethane—hexane mixture (1 : 9) and forms orthorhombic crystals with one independent calixarene molecule (Fig. 5). One of the *tert*-butyl groups of the molecule is disordered over two positions with occupancies of 0.64 and 0.36. The conformation of calixarene **12** in the crystal is similar to that of the above-considered two structures. Thus, calixarene **12** has a distorted *cone* conformation; the dihedral angle between two opposite benzene rings that are bent in the same direction is 3.3(3)°; the angle between the two other ring is 67.7(3)°.

Table 3. Intramolecular hydrogen bond parameters in the crystal structure of compound **12**

D—H...A	*d*/Å			Angle /deg
	D—H	H...A	D...A	
O(14)—H(14)...O(21)	0.82	2.28	2.987(6)	145
O(28)—H(28)...O(21)	0.82	2.13	2.913(6)	161
C(45)—H(451)...O(28)	0.97	2.39	3.328(8)	163

The hydrogen atoms of the hydroxy groups of compound **12** participate only in intramolecular hydrogen bonds. As opposed to compound **11**, the cyclic hydrogen bond at the lower rim is not formed in molecule **12** because the propyl substituent in the molecule is twisted in a somewhat different way and only one of two hydrogen atoms of the methylene group is involved in the hydrogen bonding with the oxygen atom of the hydroxy group. The hydrogen bond parameters are given in Table 3. In the crystal structure, there are no essential intermolecular interactions, except for usual van der Waals interactions.

The ^{1}H NMR spectrum shows signals of the aromatic protons of thiacalix[4]arene **12** as two doublets (AB system) and two singlets (Fig. 6). Since different substituents are present at the lower rim of the macrocycle, the spectrum of compound **12** shows signals of the protons of three nonequivalent *tert*-butyl groups with the intensity ratio of 1 : 1 : 2 at δ 0.38, 1.15, and 1.32, signals of the protons of the propoxy group at δ 1.13, 2.17, and 4.22, and a signal of the methylene protons of the benzoylmethyl group at δ 6.47.

The phenacyl group that remains intact in compound **12** can be easily removed by refluxing with benzylamine

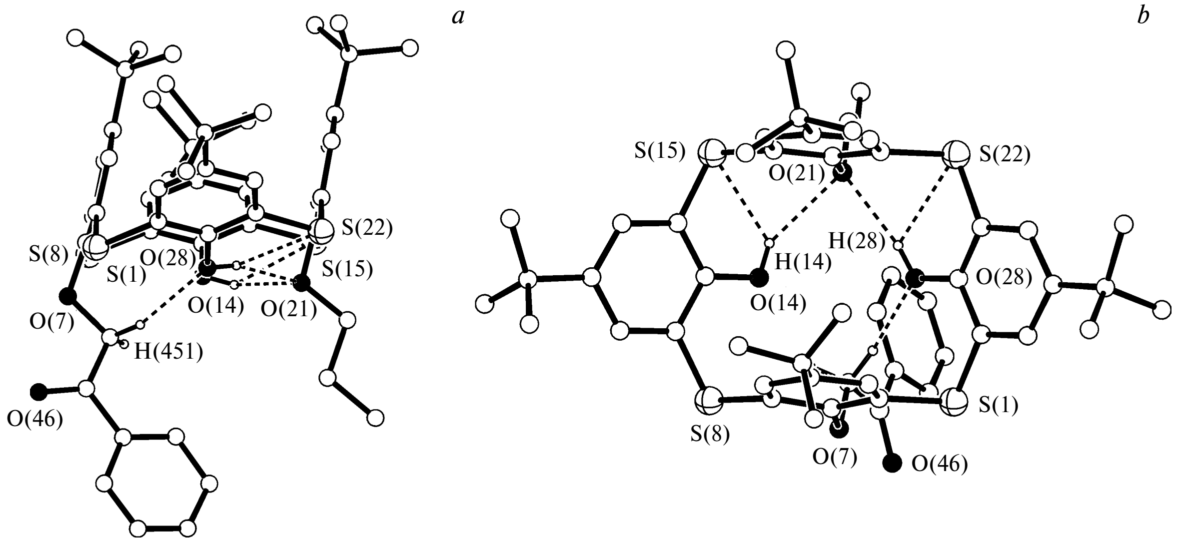


Fig. 5. Two projections of molecule **12** in the crystal structure. Only the hydrogen atoms that are involved in the hydrogen bonding (dashed lines) are shown. The disordered *tert*-butyl group is presented in the position with the highest occupancy.

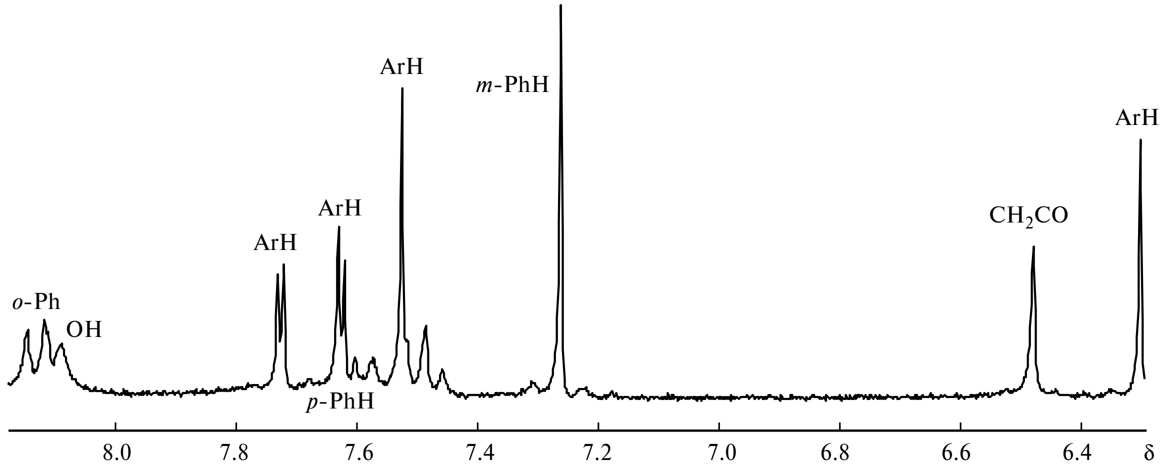


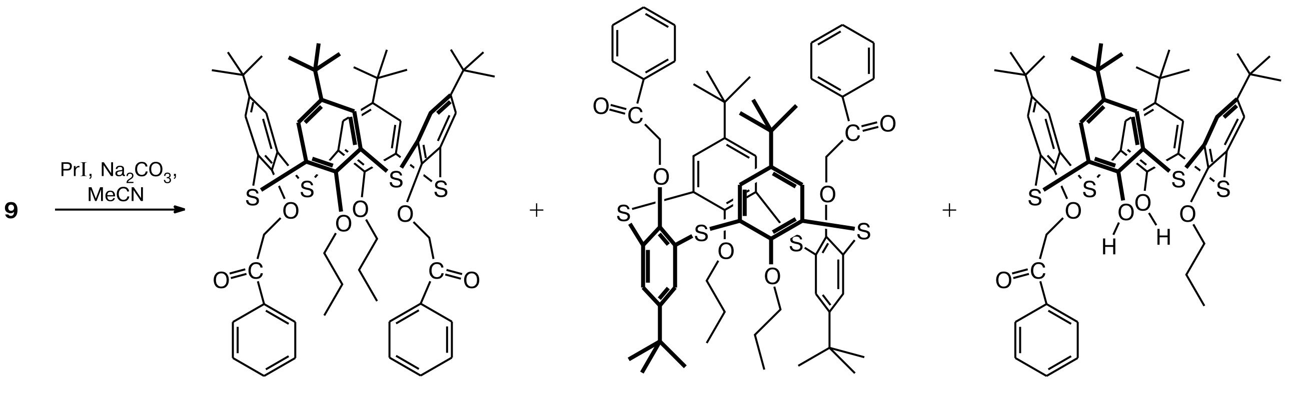
Fig. 6. Fragment of the ^{1}H NMR spectrum of compound **11** ($CDCl_3$, 25 °C).

(see Scheme 2) with the resulting formation of monosubstituted product **13** in high yield (82%). The ^{1}H NMR spectrum of **13** shows signals of the protons of three nonequivalent *tert*-butyl groups with the intensity ratio of 2 : 1 : 1 and signals of the protons of the propyl group. The aromatic protons appear as two singlets and two doublets (AB system). The protons of the hydroxy groups appear as two singlets with the intensity ratio of 1 : 2. The 2D ROESY spectrum of compound **13** shows a cross-peak between the protons of the *tert*-butyl groups and the aromatic protons of calixarene and a cross-peak between the protons of the propyl substituent and the protons of the OH groups. This indicates that macrocycle **13** retains the stereoisomeric *cone* conformation.

The replacement of acetone (see Scheme 2) by more polar and higher-boiling acetonitrile (Scheme 4) led to a sharp decrease (to 10%) in the yield of the transalkylation product, *viz*., compound **12**. The reaction of macrocycle **9** with 1-iodopropane involves the alkylation of free hydroxy groups as the main pathway giving isomeric tetrasubstituted calixarenes **10** and **15**, which differ in the three-dimensional structure of the macrocyclic platform. The MALDI-TOF mass spectra of these compounds have intense molecular ion peaks at *m/z* 1041 $[M + H]^+$, 1064 $[M + Na]^+$, and 1080 $[M + K]^+$.

The ^{1}H NMR spectra of compounds **10** and **15** have the same number of signals with the same multiplicity. The spectra of these compound differ only in the positions of the signals. The spectra show multiplets of the protons of the phenyl rings, two singlets of the aromatic protons with equal intensity, a singlet of the methylene protons of the O—CH_2—C(O)Ph groups, two singlets of the *tert*-butyl protons, and signals of the protons of the propoxy groups. These ^{1}H NMR spectra correspond to the structure of symmetrically tetrasubstituted thiacalix[4]arene containing different substituents. To determine the three-dimensional structures of compounds **10** and **15**, we performed 2D ROESY experiments. The 2D ROESY spec-

Scheme 4



cone-**10** (50%) *1,3-alternate*-**15** (10%) **12** (10%)

trum of compound **10** shows three cross-peaks indicative of the *cone* conformation: a cross-peak between the protons of the *tert*-butyl groups and the aromatic protons of the calixarene platform and cross-peaks between the *ortho*-phenyl protons of the substituent and the protons of the $—OCH_2CO—$ fragment and the propyl group. The predominant formation of the stereoisomeric *cone* conformation (compound **10**) is associated with the template effect of the sodium cation.[5,6,18]

Compound **15** is characterized by the nuclear Overhauser effects (NOE) between the protons of the *tert*-butyl groups and the *ortho*-phenyl protons of the substituent, between the protons of the *tert*-butyl groups and the aromatic protons of calixarene, and between the protons of the propyl substituent and the aromatic protons of calixarene. These interactions can occur only in the *1,3-alternate* conformation.

The structure of compound **15** was confirmed by the X-ray diffraction data. Compound **15** crystallizes in the individual state. In the crystal structure, molecule **15** has a symmetrical structure and occupies a special position on a twofold axis. Hence, there is one-half of molecule **15** per asymmetric unit. The molecular structure of compound **15** is shown in Fig. 7. One of two independent *tert*-butyl groups is disordered over two positions with occupancies of 0.6 : 0.4. There are no essential intermolecular and intramolecular interactions in the crystal.

Therefore, the reaction of bis-phenacyl derivative **9** with haloalkanes occurs *via* two competitive pathways, *viz.*, the alkylation of free phenol groups OH and the transalkylation of the phenacyl moiety (see Schemes 2 and 4), the ratio between these processes being determined by the reaction conditions. We found the following two factors that have a substantial effect on the ratio of the alkylation to transalkylation products: the nature of the cation in alkali carbonate that is used as the base and the solvating ability of the solvent.

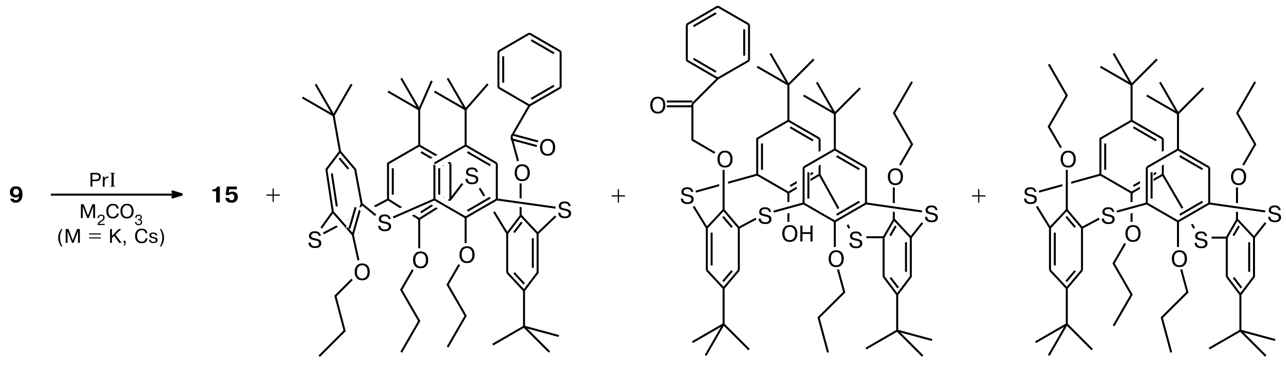
The influence of the alkali metal cation was studied by an example of the reaction of compound **9** with 1-iodopropane. The use of potassium or cesium carbonate instead of sodium carbonate in acetone leads to a sharp change in the reaction pathway. In this case, the alkylation of the free phenol groups OH giving product **15** is the major reaction (Scheme 5). In addition, compounds **16**—**18** were also isolated from the reaction mixture by chromatography. The latter compounds are formed due to the fact that both reactions proceed simultaneously.

The conformation of compound **16**, *viz.*, the *partial cone*, was determined by the 2D ROESY method. Compound **18** was identified based on the results of ^1H NMR spectroscopy and MALDI-TOF mass spectrometry and the data published in the literature.[19]

In the ^1H NMR spectrum of macrocycle **17** (Fig. 8), there are several overlapping multiplets in the aromatic (δ 7—8) and aliphatic (δ 0.5—1.5) regions, as well as a series of signals at δ 3.5—6.5.

The multiplet at δ 5.26 (AB system, J = 28.2 Hz) corresponds to the protons $C(4)H_2$ (δ) (the atomic numbering scheme is shown in Fig. 9), because the HMBC spectrum shows a cross-peak between this proton and the carbonyl C atom (δ 198). The HMBC spectrum also shows a cross-peak between this C atom and the protons H(3) (δ 7.79). The presence of NOE between the protons $C(4)H_2$ (δ) and H(3) (δ) additionally supports the above

Scheme 5



16 **17** **18**

Reagents	Yield (%)			
	15	**16**	**17**	**18**
K_2CO_3, Me_2CO	50	25	<5	<5
Cs_2CO_3, Me_2CO	47	30	<5	<5
K_2CO_3, MeCN	40	<5	43	—
Cs_2CO_3, MeCN	13	70	—	—

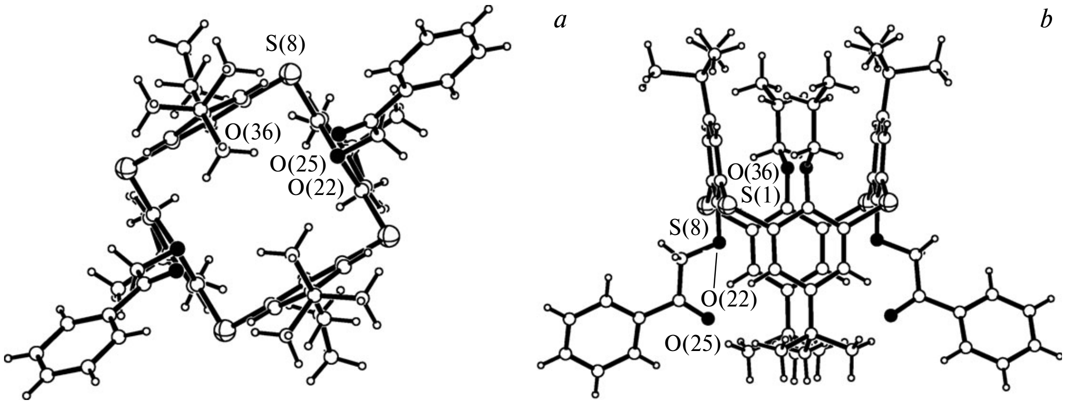


Fig. 7. Two projections of molecule **15** in the crystal structure. The disordered *tert*-butyl group is presented in the position with the highest occupancy.

conclusions (see Fig. 9). In addition, there are overlapping multiplets for the protons $C(3)H_2$ (4 H) of the α and β fragments (see Fig. 9) (δ ~3.84) of compound **17**. Four AB systems (J = 2.7 Hz, the identification based on the 1D TOCSY spectra) in the aromatic region (see Fig. 8) of the protons at the rim of calixarene are indicative of the asymmetric structure.

To determine the conformation of compound **17**, we performed a series of NOE experiments (see Fig. 9). Upon excitation of H(3) (δ fragment, see Fig. 9) (δ 7.79), NOE was observed on $C(4)H_2$ (δ fragment) (δ 5.26) and on two multiplets in the aromatic region corresponding to the protons H(1) and H(2) of the δ fragment (δ 7.20, 7.41) and a signal at δ 1.26 assigned to the protons of one of the *tert*-butyl groups. In turn, the absence of NOE on the signals of the aliphatic protons (H(1), H(2), and H(3)) of the α and β fragments indicates that these fragments are spatially distant from the phenylcarbonyl substituent δ. Upon excitation of the protons $C(3)H_2$ (α and β) (δ 3.84, see Fig. 9), NOE was observed on four doublets of the AB systems belonging to the protons of the rim and the protons $C(2)H_2/C(1)H_3$ (α and β fragments). In addition, there is NOE between $C(4)H_2$ (δ fragment) (δ 5.26) and two doublets of two AB systems (see Fig. 9). Therefore,

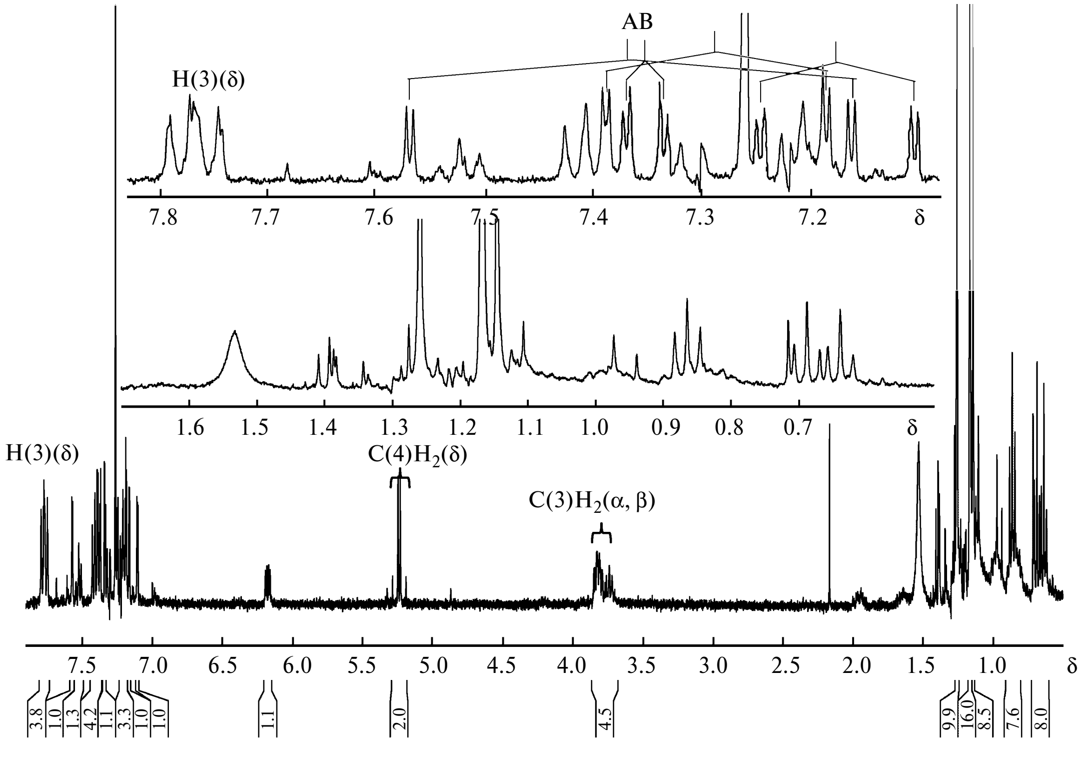


Fig. 8. ^1H NMR spectrum of compound **16** ($CDCl_3$, T = 30 °C); the signals of the AB spin systems of the protons H(5) and H(5´) are labeled (AB).

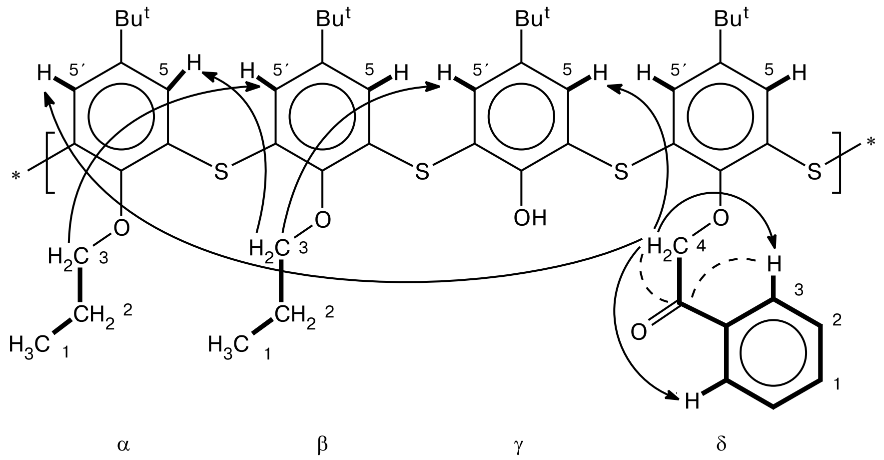


Fig. 9. Main ^{1}H—^{13}C HMBC correlations (dashed lines) and NOE (solid arrows) and main HMBC correlations in fragments α—δ (solid lines).

the observed NOE provide evidence that compound **17** adopts the stereoisomeric *1,3-alternate* conformation (Fig. 10). Compound **17** is a new internal chiral asymmetrically substituted thiacalix[4]arene derivative containing three different achiral fragments.

When acetonitrile is used as the solvent, the nature of the alkali metal cation does not have a substantial effect on the ratio of the alkylation to transalkylation reactions (see Scheme 5) as opposed to the processes in acetone. The total yield of the substitution products changes only slightly. In the presence of Na_2CO_3 (see Scheme 4), the yield is 60% (**10** and **15**); in the presence of K_2CO_3, the yield is 88% (**15—17**); in the presence of Cs_2CO_3, the yield is 83% (**15** and **16**) (see Scheme 5). However, in the presence of potassium or cesium carbonate, as in the case of acetone, the content of the products of both reactions increases. Consequently, the rates of these reactions are comparable, which opens up the possibility of synthesizing asymmetrically substituted thiacalix[4]arene derivatives, in particular, derivatives **16** and **17**, in high yields due to the fine tuning of the experimental conditions.

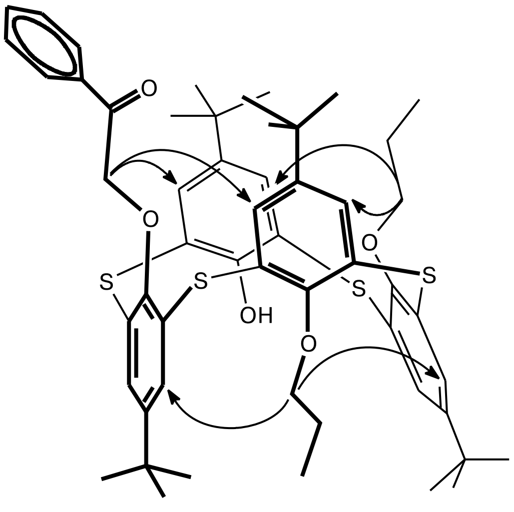


Fig. 10. Conformation of compound **17** in solution, *1,3-alternate*.

Evidently, the alkylation of free phenol groups OH occurs through their deprotonation and the formation of ion pairs, whose structure and reactivity strongly depend on the nature of the cation and the solvating ability of the solvent. Since the smaller alkali metal cation forms stronger ion pairs and leads to a decrease in the reactivity of the anion,[20—22] the transalkylation is the main reaction pathway in acetone in the case of sodium cations. The replacement of the sodium cation by potassium or cesium cations leads to an increase in the reaction rate of alkylation and an increase in the content of the corresponding product in the reaction mixture. The use of the stronger solvating higher-boiling solvent, *viz.*, acetonitrile, has a similar effect, the influence of the nature of the cation being substantially weaker.

To sum up, we showed that the phenacyl substituent has a unique ability to act as the protecting group for phenolic hydroxyls in the chemistry of thiacalixarenes and as the good leaving group in the transalkylation, which opens up wide possibilities for the synthesis of partially and asymmetrically substituted thiacalix[4]arene derivatives.

Experimental

The solvents were purified before use according to known procedures.[23] The ^{1}H and ^{13}C NMR spectra were recorded on Bruker MSL-400 and Bruker DRX-500 spectrometers (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz). The 1D and 2D NMR experiments (DEPT, NOESY, 2D COSY, 2D HSQC, 2D HMBC) were performed in $CDCl_3$ on a Bruker Avance-600 spectrometer (^{1}H, 600.13 MHz; ^{13}C, 150.92 MHz) using signals of the deuterated solvents $CHCl_3$ (δ_H 7.26) and $CDCl_3$ (δ_C 77.16) as the internal standard.[24] The IR spectra were recorded on a Bruker Vector 22 Fourier-transform infrared spectrometer in KBr pellets at 1-cm^{-1} resolution with accumulation of 64 scans in the wavenumber range of 400—4000 cm^{-1} at 20 °C. The molecular mass spectra were obtained on a MALDI-TOF Dynamo

Finnigan mass spectrometer in the concentration range of 10^{-3}—10^{-5} mol L^{-1}. 1,8,9-Trihydroxyanthracene or *p*-nitroaniline was used as the matrix. The purity of the compounds was checked by TLC on Silufol UV-254 plates with the use of a VL-6.LC ultraviolet lamp (6W, 254 nm); in some cases, the spots were visualized with iodine vapor in an iodine chamber. The compositions of the reaction products were confirmed by elemental analysis on a Perkin—Elmer PE 2400 series 2 CHNS/O analyzer. The melting points were measured on a Boetius micro melting-point apparatus equipped with a PHMK 05 visual attachment. Single-crystal X-ray diffraction studies of compounds **9—11** and **15** were carried out at the Department of X-ray Diffraction Studies of the Center of Collaborative Research on the basis of the Laboratory of Diffraction Research Methods of the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Research Center, the Russian Academy of Sciences. The X-ray diffraction data were collected on a CAD-4 Nonius B.V. automated four-circle diffractometer at 20 °C (graphite monochromator, $\omega/2\theta$-scanning technique, variable scan rate, 1—16.4 grad min^{-1}, θ-scan mode). The preliminary data processing was performed with the use of the MolEN program package[25] on an AlphaStation 200. The intensities of three check reflections showed no decrease in the course of X-ray data collection. Empirical absorption corrections were applied. All structures were solved by direct methods with the use of the SIR program[26] and refined first isotropically and then anisotropically using the SHELXL-97[27] and WinGX[28] program packages. The coordinates of the hydrogen atoms of the hydroxy groups in the structures of **9**, **11**, and **12** were located in difference electron density maps (the other hydrogen atoms in all compounds were positioned geometrically) and refined using a riding model. The crystallographic characteristics and the X-ray data collection and structure refinement statistics are given in Table 4. The figures were drawn and the intermolecular interactions were analyzed with the use of the PLATON program.[29] The atomic coordinates and displacement parameters for compounds **11**, **15**, **9**, and **12** were deposited with the Cambridge Structural Database (http://www.ccdc.cam.ac.uk; CCDC 710148, 710149, 710150, and 710151, respectively).

p-tert-Butylthiacalix[4]arene **1** (see Ref. 5) and α-bromoacetophenone[30] were synthesized according to procedures described earlier.

25,27-Bis(benzoylmethoxy)-5,11,17,23-tetra-*tert*-butyl-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (9). α-Bromoacetophenone (0.55 g, 2.76 mmol) and predried cesium hydroxide (0.41 g, 2.73 mmol) were added to a suspension of thiacalixarene **1** (1 g, 1.39 mmol) in anhydrous acetonitrile (60 mL). The reaction mixture was refluxed with stirring for 16 h and then cooled to ~20 °C. The precipitate was filtered off, water (20 mL) was added to the precipitate, and then extraction with chloroform

Table 4. Crystallographic characteristics and the X-ray data collection and structure refinement statistics for compounds **9**, **11**, **12**, and **15**

Parameter	9	11	12	15
Color, habit	Colorless prismatic			
Molecular formula	$C_{56}H_{60}O_6S_4 \cdot 3\ H_2O$	$C_{46}H_{60}O_4S_4$	$C_{51}H_{60}O_5S_4$	$C_{62}H_{72}O_6S_4$
Molecular weight	1011.33	805.18	881.23	1041.48
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*2$_1$/*n*	*C*2/*c*	*Pna*2$_1$	*P*2/*c*
a/Å	13.311(7)	22.893(6)	16.924(4)	11.343(3)
b//Å	22.169(9)	19.559(5)	17.030(5)	13.165(2)
c/Å	20.121(8)	22.630(10)	17.905(5)	19.922(6)
β/deg	105.24(2)	114.34(5)	—	93.59(3)
Volume/Å^3	5729(4)	9232(5)	5160(2)	2969.1(13)
Z	4	8	4	2
d_{calc}/g cm^{-3}	1.173	1.159	1.134	1.165
Absorption coefficient/cm^{-1}	19.34	2.45	2.26	2.08
Absorption correction	psi-scan	psi-scan	psi-scan	psi-scan
Radiation (λ/Å)	Cu-Kα (1.54184)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
F(000)	2152	3456	1880	1112
Number of measured reflections	9943	4884	8028	9345
R_{int}	0.0794	0.0544	0.1819	0.0824
Number of observed independent reflections with $I > 2\sigma(I)$	6667	2559	4229	1639
R factors based on reflections with $I > 2\sigma(I)$				
R	0.0788	0.0618	0.0592	0.0548
R_w	0.2192	0.1545	0.1338	0.1028
Goodness of fit	1.084	0.982	0.999	0.945
Number of refined parameters	627	472	491	334
h, *k*, *l* ranges	$-15 \le h \le 0$, $0 \le k \le 26$, $-22 \le l \le 23$	$0 \le h \le 22$, $-19 \le k \le 0$, $-24 \le l \le 20$	$-21 \le h \le 0$, $-19 \le k \le 0$, $-21 \le l \le 19$	$-13 \le h \le 13$, $-15 \le k \le 11$, $-17 \le l \le 23$
Residual electron density/ e·Å^{-3}, ρ_{max}/ρ_{min}	0.775/−0.542	0.571/−0.294	0.669/−0.346	0.212/−0.170

(2×50 mL) was performed. Chloroform was evaporated until the volume was 3 mL, hexane (10 mL) was added, and the precipitate that formed (0.8 g) was filtered off. An additional amount (0.27 g) of compound **9** was isolated from the filtrate. The total yield was 81%, m.p. 241—242 °C. Trace amounts of tetrasubstituted product **13** in the stereoisomeric *1,3-alternate* conformation[18] were detected in the filtrate. Found (%): C, 70.46; H, 6.13; S, 10.22. $\mathrm{C_{56}H_{60}O_6S_4}$. Calculated (%): C, 70.26; H, 6.32; S, 10.02. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 0.81 (s, 18 H, Bu^t); 1.32 (s, 18 H, Bu^t); 6.17 (s, 4 H, $\mathrm{OCH_2}$); 6.95 (s, 4 H, ArH); 7.48 (t, 4 H, *m*-ArH, *J* = 7.9 Hz); 7.59 (t, 2 H, *p*-ArH, *J* = 7.9 Hz); 7.67 (t, 4 H, ArH); 8.16 (d, 4 H, *o*-ArH, *J* = 7.9 Hz); 8.36 (s, 2 H, OH). IR, ν/cm^{-1}: 3395, 3366 (OH), 1699 (C=O). MALDI TOF MS, *m/z*: 957 [M + H]$^+$, 980 [M + Na]$^+$, 997 [M + K]$^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-dipropoxy-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (11). A mixture of compound **9** (0.2 g, 0.209 mmol), 1-iodopropane (1.8 g, 10.58 mmol), and molten sodium carbonate (0.22 g, 2.09 mmol) in acetone (25 mL) was refluxed with stirring for 48 h. Acetone was removed, chloroform (40 mL) and dilute hydrochloric acid (10 mL) were added to the residue, and the organic phase was separated, washed with water, dried with calcium chloride, and concentrated to 3 mL. Then acetonitrile was added. Compound **11** was obtained in a yield of 150 mg (89%), m.p. 224—226 °C. Found (%): C, 69.00; H, 7.66; S, 15.46. $\mathrm{C_{46}H_{60}O_4S_4}$. Calculated (%): C, 68.62; H, 7.52; S, 15.92. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 0.80 (s, 18 H, Bu^t); 1.15 (t, 3 H, $\mathrm{C\underline{H}_3CH_2}$, *J* = 7.4 Hz); 1.34 (s, 18 H, Bu^t); 2.04 (m, 2 H, $\mathrm{CH_2C\underline{H}_2CH_3}$, *J* = 7.4 Hz); 4.46 (t, 2 H, $\mathrm{OCH_2}$, *J* = 7.4 Hz); 6.96 (s, 4 H, ArH); 7.66 (s, 4 H, ArH); 7.99 (s, 2 H, OH). IR, ν/cm^{-1}: 3381 (OH). MALDI TOF MS, *m/z*: 805 [M + H]$^+$, 828 [M + Na]$^+$, 844 [M + K]$^+$.

25-Benzoylmethoxy-5,11,17,23-tetra-*tert*-butyl-27-propoxy-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (12). A mixture of compound **9** (0.2 g, 0.209 mmol), 1-bromopropane (1.29 g, 10.48 mmol), and molten sodium carbonate (0.22 g, 2.09 mmol) in acetone (25 mL) was refluxed with stirring for 24 h. Acetone was removed, chloroform (25 mL) and water (10 mL) were added to the residue, and the organic phase was washed, separated, and dried with $\mathrm{CaCl_2}$. Then chloroform was removed, and the residue was chromatographed on a column packed with silica gel using dichloromethane as the eluent. Compound **12** was obtained in a yield of 114 mg (74.7%), R_f = 0.55 ($\mathrm{CH_2Cl_2}$), m.p. 223—224 °C. Found (%): C, 69.09; H, 7.22; S, 14.46. $\mathrm{C_{51}H_{60}O_5S_4}$. Calculated (%): C, 69.51; H, 6.86; S, 14.55. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 0.38 (s, 9 H, Bu^t); 1.13 (t, 3 H, $\mathrm{C\underline{H}_3CH_2}$, *J* = 7.3 Hz); 1.15 (s, 9 H, Bu^t); 1.32 (s, 18 H, Bu^t); 2.17 (m, 2 H, $\mathrm{CH_2C\underline{H}_2CH_3}$, *J* = 7.3 Hz); 4.22 (t, 2 H, $\mathrm{OCH_2}$, *J* = 7.3 Hz); 6.30 (s, 2 H, ArH); 6.47 (s, 2 H, $\mathrm{CH_2CO}$); 7.48 (t, 2 H, *m*-PhH, *J* = 7.7 Hz); 7.51 (s, 2 H, ArH); 7.59 (t, 1 H, *p*-PhH, *J* = 7.7 Hz); 7.62 (d, 2 H, ArH, *J* = 2.5 Hz); 7.72 (d, ArH, *J* = 2.5 Hz); 8.07 (s, 2 H, OH); 8.12 (d, 2 H, *o*-PhH, *J* = 7.7 Hz). IR, ν/cm^{-1}: 3378 (OH), 1701 (C=O). MALDI TOF MS, *m/z*: 881 [M + H]$^+$, 903 [M + Na]$^+$, 920 [M + K]$^+$.

5,11,17,23-Tetra-*tert*-butyl-25-propoxy-26,27,28-trihydroxy-2,8,14,20-tetrathiacalix[4]arene (13). A mixture of compound **11** (0.1 g, 0.114 mmol) and benzylamine (0.05 mL, 0.46 mmol) in toluene (15 mL) was stirred at 110 °C for 24 h. Then chloroform (20 mL) and dilute (1 : 3) hydrochloric acid (5 mL) were added. The organic layer was washed with water (2×10 mL) and dried over calcium chloride. The solvent was removed, and the residue was purified by column chromatography using the dichloromethane—hexane mixture (2 : 1) as the eluent, R_f = 0.63 ($\mathrm{CH_2Cl_2}$—hexane (2 : 1)). Compound **13** was obtained in a yield of 68 mg (82%), m.p. 247 °C. Found (%): C, 70.16; H, 6.43; S, 14.40. $\mathrm{C_{51}H_{60}O_5S_4}$. Calculated (%): C, 69.51; H, 6.86; S, 14.55. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 1.19 (s, 9 H, Bu^t); 1.21 (s, 9 H, Bu^t); 1.24 (s, 18 H, Bu^t); 1,25 (t, 3 H, Me, *J* = 7.30 Hz); 2.23 (m, 2 H, $\mathrm{CH_2}$, *J* = 7.30 Hz); 4.36 (t, 2 H, $\mathrm{CH_2O}$, *J* = 7.30 Hz); 7.59 (s, 2 H, ArH); 7.60 (d, 2 H, ArH, *J* = 2.37 Hz); 7.64 (s, 2 H, ArH); 7.64 (d, 2 H, ArH, *J* = 2.37 Hz); 9.21 (s, 2 H, OH); 9.34 (s, 1 H, OH). IR, ν/cm^{-1}: 3397 (OH), 2931, 2870 (*m*-Bu). MALDI TOF MS, *m/z*: 763 [M + H]$^+$.

25,27-Bis(benzoylmethoxy)-5,11,17,23-tetra-*tert*-butyl-26,28-dipropoxy-2,8,14,20-tetrathiacalix[4]arene (10). A mixture of compound **9** (0.2 g, 0.209 mmol), 1-iodopropane (0.642 g, 4.22 mmol), and molten sodium carbonate (0.13 g, 0.125 mmol) in anhydrous acetonitrile (25 mL) was placed in a 100 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser and refluxed with stirring for 24 h. Then the solvent was removed *in vacuo*, water (30 mL) and $\mathrm{CHCl_3}$ (50 mL) were added to the residue, and the organic layer was separated and dried over $\mathrm{CaCl_2}$. The drying agent was filtered off, and chloroform was removed. The residue was chromatographed on a column packed with silica gel using the hexane—dichloromethane mixture (1 : 1) and then the dichloromethane—acetone mixture (30 : 1) as the eluents. Compound **12** was isolated in a yield of 18.5 mg (10%); compound **10**, in a yield of 110 mg (50%); compound **15**, in a yield of 22 mg (10%).

Compound **10**, R_f = 0.45 ($\mathrm{CH_2Cl_2}$), m.p. 115—117 °C. Found (%): C, 70.89; H, 6.62; S, 12.12. $\mathrm{C_{62}H_{72}O_6S_4}$. Calculated (%): C, 70.50; H, 6.97; S, 12.31. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 0.89 (t, 6 H, $\mathrm{—CH_2C\underline{H}_3}$, *J* = 7.7 Hz); 0.96 (s, 18 H, Bu^t); 1.24 (s, 18 H, Bu^t); 1.77 (m, 4 H, $\mathrm{—C\underline{H}_2CH_3}$, *J* = 6.7 Hz); 3.96 (t, 4 H, $\mathrm{—OCH_2}$, *J* = 7.7 Hz); 6.10 (s, 4 H, $\mathrm{OCH_2CO}$); 7.10 (s, 4 H, ArH); 7.39 (t, 2 H, *m*-PhH, *J* = 6.7 Hz); 7.48 (s, 4 H, ArH); 7.53 (t, 4 H, *p*-PhH, *J* = 6.7 Hz); 7.98 (d, 4 H, *o*-PhH, *J* = 6.7 Hz). IR, ν/cm^{-1}: 1706 (C=O). MALDI TOF MS, *m/z*: 1041 [M + H]$^+$, 1064 [M + Na]$^+$, 1080 [M + K]$^+$.

Compound **15**, R_f = 0.31 ($\mathrm{CH_2Cl_2}$), m.p. 256—258 °C. Found (%): C, 70.66; H, 7.13; S, 12.75. $\mathrm{C_{62}H_{72}O_6S_4}$. Calculated (%): C, 70.50; H, 6.97; S, 12.31. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 0.60 (t, 6 H, $\mathrm{—CH_2C\underline{H}_3}$, *J* = 7.8 Hz); 0.96 (s, 18 H, Bu^t); 1.16 (m, 4 H, $\mathrm{—C\underline{H}_2CH_3}$, *J* = 7.8 Hz); 1.27 (s, 18 H, Bu^t); 3.83 (t, 4 H, $\mathrm{—OCH_2}$, *J* = 7.8 Hz); 5.33 (s, 4 H, $\mathrm{OCH_2CO}$); 7.19 (s, 4 H, ArH); 7.36 (s, 4 H, ArH), 7.39 (t, 2 H, *m*-PhH, *J* = 7.8 Hz); 7.51 (t, 4 H, *p*-PhH, *J* = 6.8 Hz); 7.82 (d, 4 H, *o*-PhH, *J* = 7.8 Hz). IR, ν/cm^{-1}: 1699 (C=O). MALDI TOF MS, *m/z*: 1041 [M + H]$^+$, 1064 [M + Na]$^+$, 1080 [M + K]$^+$.

25-Benzoylmethoxy-5,11,17,23-tetra-*tert*-butyl-26,27,28-tripropoxy-2,8,14,20-tetrathiacalix[4]arene (16). A mixture of compound **2** (0.2 g, 0.209 mmol), 1-iodopropane (0.35 g, 2 mmol), and cesium carbonate (0.68 g, 2 mmol) in anhydrous acetonitrile or acetone (25 mL) was placed in a 100 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser and refluxed with stirring for 24 h. The solvent was removed using a water-jet vacuum pump, water (30 mL) and $\mathrm{CHCl_3}$ (50 mL) were added to the residue, the organic layer was separated and dried over $\mathrm{CaCl_2}$, and the drying agent was filtered off. Then chloroform was removed, and the residue was chromatographed on a column packed with silica gel using the hexane—dichloromethane mixture (1 : 1) and then the dichloromethane—acetone mixture (30 : 1) as the eluents. The reaction performed in acetone afforded compound **15** in a yield of 0.1 g (47%) and compound **16** in a yield of 60 mg (30%); the reaction performed in acetonitrile gave compound **15** in a yield of 30 mg (13%) and compound **16** in a yield of 140 mg (70%).

Compound **16**, m.p. 270—272 °C. Found (%): C, 71.22; H, 7.63; S, 13.02. $C_{57}H_{72}O_5S_4$. Calculated (%): C, 70.92; H, 7.52; S, 13.28. ^{1}H NMR ($CDCl_3$), δ: 0.66 (m, 9 H, $-CH_2C\underline{H}_3$); 0.9—1.15 (m, 6 H, $-C\underline{H}_2CH_3$); 1.11 (s, 18 H, Bu^t); 1.26 (s, 9 H, Bu^t); 1.28 (s, 9 H, Bu^t); 3.83 (m, 6 H, $-OC\underline{H}_2$); 5.17 (s, 2 H, $-OC\underline{H}_2C(O)$); 7.12 (d, 2 H, ArH, *J* = 2.3 Hz); 7.32 (s, 2 H, ArH); 7.34 (d, 2 H, ArH, *J* = 2.3 Hz); 7.39 (s, 2 H, ArH); 7.41 (t, 2 H, *m*-PhH, *J* = 7.1 Hz); 7.52 (t, 2 H, *p*-PhH, *J* = 7.1 Hz); 7.77 (d, 2 H, *o*-PhH, *J* = 7.1 Hz). IR, ν/cm^{-1}: 1711 (C=O). MALDI TOF MS, *m/z*: 965 $[M + H]^+$, 988 $[M + Na]^+$, 1005 $[M + K]^+$.

25-Benzoylmethoxy-5,11,17,23-tetra-*tert*-butyl-28-hydroxy-26,27-dipropoxy-2,8,14,20-tetrathiacalix[4]arene (17). A mixture of compound **9** (0.2 g, 0.209 mmol), 1-iodopropane (0.35 g, 2 mmol), and K_2CO_3 (0.28 g, 2 mmol) in anhydrous acetonitrile or acetone (25 mL) was placed in a 100 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser and refluxed with stirring for 24 h. The solvent was removed using a water-jet vacuum pump, water (30 mL) and $CHCl_3$ (50 mL) were added to the residue, the organic layer was separated and dried over $CaCl_2$, and the drying agent was filtered off. Then chloroform was removed, and the residue was chromatographed on a column packed with silica gel using the hexane—dichloromethane mixture (1 : 1) and then the dichloromethane—acetone mixture (30 : 1) as the eluents. The reaction performed in acetone afforded compound **15** in a yield of 108 mg (50%) and compound **17** in a yield of 50 mg (25%); the reaction performed in acetonitrile gave compound **15** in a yield of 80 mg (40%) and compound **17** in a yield of 82 mg (43%).

Compound **17**, m.p. 241 °C. Found (%): C, 70.04; H, 7.15; S, 13.98. $C_{54}H_{66}O_5S_4$. Calculated (%): C, 70.24; H, 7.21; S, 13.89. ^{1}H NMR ($CDCl_3$), δ: 0.64 (t, 3 H, $CH_2C\underline{H}_3$, *J* = 7.5 Hz); 0.69 (t, 3 H, $CH_2C\underline{H}_3$, *J* = 7.5 Hz); 0.86 (m, 2 H, CH_2); 1.1 (m, 2 H, CH_2); 1.14 (s, 9 H, Bu^t); 1.17 (s, 18 H, Bu^t); 1.26 (s, 9 H, Bu^t); 3.84 (m, 4 H, $OCH_2C\underline{H}_2$); 5.26 (m, 2 H, OCH_2CO, *J* = 28.2 Hz); 7.05 (d, 1 H, ArH, *J* = 2.7 Hz); 7.16 (d, 1 H, ArH, *J* = 2.7 Hz); 7.19 (d, 1 H, ArH, *J* = 2.7 Hz); 7.20 (t, 2 H, PhH, *J* = 7.9 Hz); 7.25 (d, 1 H, ArH, *J* = 2.7 Hz); 7.34 (d, 1 H, ArH, *J* = 2.7 Hz); 7.37 (d, 1 H, ArH, *J* = 2.7 Hz); 7.39 (d, 1 H, ArH, *J* = 2.7 Hz); 7.41 (t, 1 H, PhH, *J* = 7.9 Hz); 7.57 (d, 1 H, ArH, *J* = 2.7 Hz); 7.79 (d, 2 H, PhH, *J* = 7.9 Hz); 7.75 (s, 1 H, OH). IR, ν/cm^{-1}: 1711 (C=O). MALDI TOF MS, *m/z*: 923 $[M + H]^+$, 946 $[M + Na]^+$.

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