J Incl Phenom Macrocycl Chem (2010) 66:349–355
DOI 10.1007/s10847-009-9652-4

ORIGINAL ARTICLE

Syntheses, reactions and crystal structures of 1,3-alternate *p-tert*-butylthiacalix[4]arene esters and amides

Li Liu · Kun Huang · Chao Guo Yan

Received: 28 March 2009 / Accepted: 18 July 2009 / Published online: 2 August 2009

Abstract *p-tert*-Butylthiacalix[4]arene was efficiently alkylated in the system of K_2CO_3/KI/acetone to give several thiacalixarene derivatives in *1,3-alternate* conformation with functional ester, chloro, cyano and amide groups. Thiacalixarene tetraacateate can be converted to bicyclic amides by ammonolysis with alkylenediamine, and to sulfonylcalixarene by oxidation with hydrogen peroxide in acetic acid. Single crystal X-ray diffraction analysis reveals that thiacalixarene and sulfonylcalixarene exist mainly in *1,3-alternate* conformation.

Keywords Calixarene · Thiacalixarene · Alkylation · Conformation · Crystal structure

Introduction

During the past decades, thiacalixarenes, in which sulfur atoms instead of methylene bridge of calixarenes, have attracted much attention as examples of simple or novel receptors in supramolecular chemistry [1, 2]. As with the calix[4]arenes, thiacalix[4]arenes have larger cavity, can be easily functionalized at the upper and lower rim of the macrocycle as well as on the sulfur atoms, show stronger affinity towards transition metal ions. These stimulated a lot of chemist to design versatile supramolecular receptors and other chemical engineering using thiacalix[4]arenes as platform [3–5]. A variety of thiacalixarene derivatives having functional groups on lower and upper rim have been prepared for versatile potential uses [6–11]. During our on-going research on thiacalix[4]arene derivatisation we noted that the presence of four sulphur atoms implicates many novel features of the conformational behavior and the solid-state preferences. In this paper we wish to report syntheses, reactions and crystal structures of a series of *p-tert*-butylthiacalix[4]arene functional esters and amides.

L. Liu · K. Huang · C. G. Yan (✉)
College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China
e-mail: cgyan@yzu.edu.cn

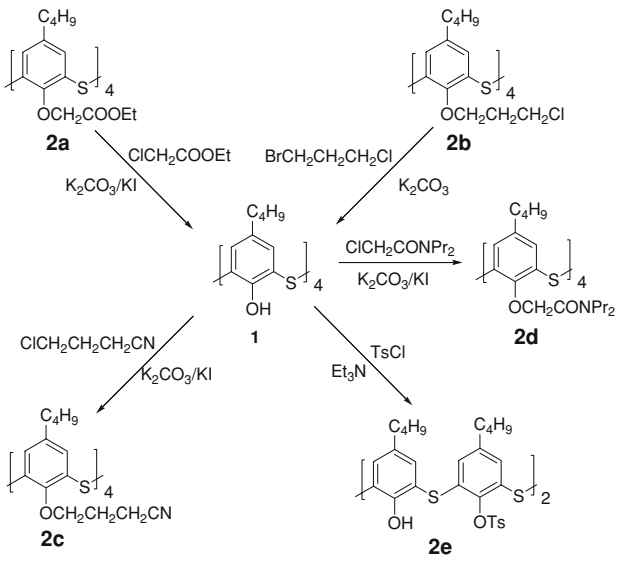
Results and discussion

Tetrtraalkylation of the phenolic hydroxyl groups in lower rim of thiacalixarene is a standard method by which to modify the calix[4]arene skeleton [12, 13]. Accordingly, several groups have studied the alkylation of thiacalixarenes with ethyl α-bromoacetate using the M_2CO_3/acetone/reaction system (M = Li, Na, K, and Cs) [14–16]. This reaction exhibits a surprisingly pronounced template effect, and leads to high yields of the corresponding tetraacetates in various con-formations (cone, partial cone, 1,3-alternate) [17]. By using ethyl α-chloroacetate as alkylating reagent, we carried out the alkylation reaction of thiacalixarene **1** in the system of K_2CO_3/KI/acetone. The desired ethyl thiacalixarylacetate **2a** was prepared in satisfied yield (62%), which is pure enough for analysis without chromatographic purification. The ^{1}H NMR spectrum is extremely simple and shows the presence of one conformer. The singlet at 7.66 ppm observed for the aromatic hydrogen atoms, one singlet at 4.92 ppm for OCH_2CO groups and singlet at 1.32 ppm for the *t*-butyl groups together with the singlet set of signals OCH_2CH_3 groups indicate the high symmetry of the product. According to the different deshielding zone of the adjacent phenyl units and *tert*-butyl groups, Nobuhiko Iki [14] has indicated that the isomer which exhibited butyl and OCH_2CO protons at 1.09 and 5.18 ppm, respectively,

was assigned to *cone* **2a**, while that which exhibited protons at 1.25 and 4.60 ppm was assigned to *1,3-alternate* **2a**. Thus we could conclude that our product **2a** exists mainly in *1,3-alternate* configuration (Scheme 1).

Under the similar reaction condition *p-tert*-thiacalix[4]arene **1** was alkylated in the system of K_2CO_3/acetone with 1-bromo-3-chloropropane to give *O*-(3-chloropropyl)thiacalixarene **2b** in 86% yield. In such reaction condition 3-chloro group remained unreactive and very higher yield of thiacalixarene with functional chloroalkyl group can be conveniently prepared. When 4-chlorobutyronitrile and *N,N*-dipropyl α-chloroacetamide were used as alkylating reagents, *p-tert*-thiacalix[4]arene **1** was alkylated in K_2CO_3/KI/acetone system for five days. After workup the tetrasubstituted thiacalix[4]arenes having functional cyano groups **2c** and amido groups **2d** were prepared in 70% and 54% yields, respectively. In such case pure products could be gotten by merely crystallization from ethanol and no need further purification with LC. IR spectra of products **2c** and **2d** clearly displays a stronger absorption at 2,230 cm^{-1} for cyano groups and 1,644 cm^{-1} for amide carbonyl group. ^{1}H NMR spectra shows that thiacalixarene **2b–2d** all exist in *1,3-alternate* configuration. As for an example the ^{1}H NMR spectrum of **2c** showed one singlet at 7.38 ppm for phenolic protons and one singlet at 1.32 ppm for *tert*-butyl groups.

Single crystal of **2c** was determined by X-ray diffraction analysis. The perspective view with the some atomic numbering scheme is shown in Fig. 1. The crystal data and refinement details are given in Table 1. It is clearly seen that thiacalix[4]arene **2c** adopted an *1,3-alternate* conformation. The four cyanopropyl groups are divided into two groups



Scheme 1 Synthesis of thiacalix[4]arenes **2a–2e**

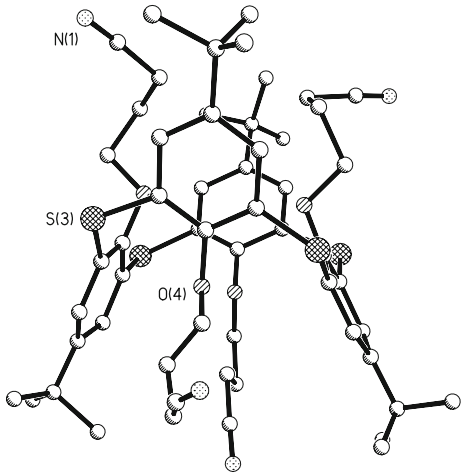


Fig. 1 Molecular structure of compound **2c**

with the two standing upside and other two pointing downside. Intramolecular hydrogen bond C(53)-H(53A)…N(4) were formed between cyano groups and *tert*-butyl groups with the distance of 3.33 (Table 2). The intermolecular hydrogen bonds are also formed between cyano groups and *tert*-butyl groups C(27)-H(27A)…$N(1)^A$, C(57)-H(57A)…N(3), and another hydrogen bond between sulfur atom and *tert*-butyl group C(24)-H(24C)…$S(3)^B$ is also formed. Through the intermolecular hydrogen bonds the molecule **2c** form a 2D networks in solid state.

The sulfonylation reaction of *p-tert*-butylthiacalixarene is very interesting. The mixture of thiacalixarene **1** and excess *p*-toluenesulfonyl chloride with triethylamine as acid-capture reagent in chloroform was heated at 50–60 °C for 12 h. After workup we are surprised to find that 1,3-ditosylthiacarlixarene **2e** was produced in 92% yield. Prolonging the reaction time or adding more *p*-toluenesulfonyl chloride in the reaction still gave 1,3-ditosylthiacarlixarene **2e** as main compound. ^{1}H NMR spectra shows that thiacalixarene **2e** displays sign of two phenolic hydroxyl groups at 7.24 ppm, two singlets at 7.37, 6.99 ppm for protons at phenolic ring and two singlets at 1.27 and 0.82 ppm for *tert*-butyl groups, which indicates there two kinds of phenolic ring in the molecule. The molecular structure is shown in Fig. 2. It is clearly seen that the 1,3-phenolic hydroxyl groups were *O*-tolylated. The two phenolic ring bearing toluenesulfonyl groups stand more perpendicularly than the other two phenolic rings. The remained two pheolic hydroxyl groups provided good chance for further chemical modification of thiacalixarene (Scheme 2).

Thiacalixarene tetraacetate **2a**, which have precisely defined three-dimensional structures, is valuable building block for the construction of more sophisticated thiacalixarene systems. The reactions of tetraacetate **2** with an excess of ethylenediamine, or propylenediamine were

Table 1 Crystal data and structure refinement details of thiacalixarene

Phase	2c	2e	3a	4a (partial cone)	4a (1,3-alternate)
Empirical formula	$C_{56}H_{68}N_4O_4S_4.CHCl_3$	$C_{54}H_{60}O_8S_6.2CHCl_3$	$C_{55}H_{66}Cl_2N_4O_9S_4$	$C_{56}H_{72}O_{20}S_4.CHCl_3$	$C_{56}H_{72}O_{20}S_4$
Formula weight	1108.75	1268.12	1126.26	1312.74	1193.38
Temperature (K)	293(2)	296(2)	193(2)	273(2)	273(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, P2(1)/c	Monoclinic,C2/c	Monoclinic, P2(1)/c	Triclinic	Monoclinic, *C 2/c*
a (Å)	12.7934(17	27.747(6)	15.5068(19)	11.683(3)	24.18(1)
α	90	90.00	90	76.051(4)	90
b (Å)	15.078(2)	12.513(2)	13.7553(17)	15.575(4)	13.712(6)
β	99.044(2)	103.025(5)	91.538(3)	82.672(4)	123.35
c (Å)	30.941(2)	18.047(3)	28.088(4)	19.961(5)	21.990(9)
γ	90	90.00	90	69.836(4)	90
Volume ($Å^3$)	5928.1(14)	6105(2)	5989.0(13)	3304.8(15)	6090(4)
Z, Calculated density ($g·cm^{-3}$)	4, 1.242	4, 1.380	4, 1.249	2, 1.319	4, 1.302
Absorption coefficient (mm^{-1})	0.342	0.537	0.302	0.334	0.228
F(000)	2,344	2,640	1,636	1,380	2,456
θ range for data collection	0.993–25.01	1.52–28.35	0.993–25.35	0.981–25.00	2.20–25.00
h, *k*, *l* ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-35 \le l \le 36$	$-36 \le h \le 35$, $-16 \le k \le 16$, $-23 \le l \le 23$	$-17 \le h \le 18$, $-16 \le k \le 16$, $-33 \le l \le 30$	$-13 \le h \le 12$, $-18 \le k \le 10$, $-23 \le 20$	$-28 \le h \le 24$, $-16 \le k \le 11$, $-26 \le l \le 25$
Reflections collected/ unique	41868/10373 [R(int) = 0.1902]	28011/7548 [R(int) = 0.1766]	56287/ 10886[R(int) = 0.1533]	17091/11411 [R(int) = 0.0628]	11345/4202 [*R*(int) = 0.057]
Completeness to theta = 27.50	99.3%	98.8	99.3%	98.1%	78.2%
Data/restraints/ parameters	10373/0/649	7548/0/343	10886/0/795	11411/8/774	4202/4/339
Goodness-of-fit on F^2	0.925	0.938	0.979	1.045	0.99
Final *R* indices [$I > 2\sigma$ (I)]	R1 = 0.0850, wR2 = 0.1950	R1 = 0.0795, wR2 = 0.1831	R1 = 0.0986, wR2 = 0.2622	R1 = 0.1161, wR2 = 0.2912	$R_1 = 0.1004$, $wR_2 = 0.2926$
R indices (all data)	R1 = 0.2329, wR2 = 0.2383	R1 = 0.2024, wR2 = 0.2184	R1 = 0.1422, wR2 = 0.3006	R1 = 0.2256, wR2 = 0.3484	$R_1 = 0.1607$, $wR_2 = 0.3219$
Largest diff. peak and hole($e·Å^{-3}$)	0.401 and –0.510	2.065 and −0.962	0.989 and −0.892	0.928 and −0.615	0.91and −0.55

Table 2 Hydrogen bonding parameters in crystal structure of 2c

D–H…*A*	*D*–H	H…*A*	*D*…*A*	*D*–H…*A*
C(53)-H(53A)…N(4)	0.97	2.61	3.33	131
C(27)-H(27A)…N(1)[a]	0.97	2.32	3.21	154
C(24)-H(24C)…S(3)[b]	0.96	2.83	3.68	147
C(57)-H(57A)…N(3)	0.98	2.04	2.95	154

[a] $-1+x, y, z$

[b] $1-x, 1/2+y, 1/2-z$

carried out by refluxing the reactants in ethanol for about 24 h. We wish to let only one amino group of ethylenediamine to attack the ester group to give the thiacalixarene

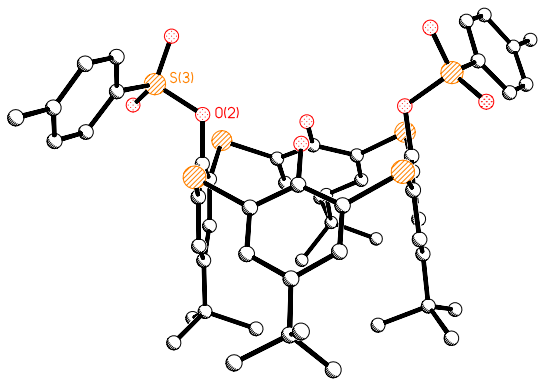
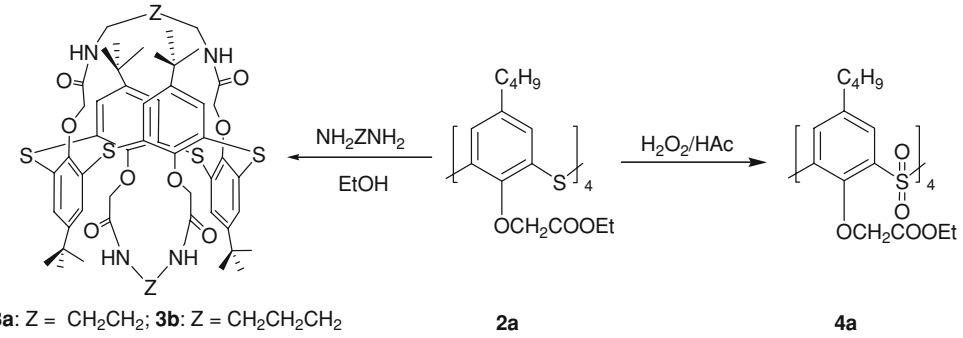


Fig. 2 Molecular structure of compound **2e**

Scheme 2 Synthesis of thiacalixarene bicyclic amides **3a–3b**



amide derivative with four free terminal amino groups. But the ^{1}H NMR and single crystal analysis show that the prepared product is thiacalixarene bicyclic amide **3a–3b**. Similarly to that of tetraacetate **2a**, ^{1}H NMR spectrum of **3a** show one singlet at 7.66 ppm for the aromatic hydrogen atoms and one singlet at 1.32 ppm for the *t*-butyl groups. The one singlet at 4.40 ppm for OCH_2CO groups and another singlet at 3.05 ppm for the four NCH_2 units clearly show that the product has high symmetry and the two amino groups of ethylenediamine all reacted with ester groups.

The single crystal of **3a** suitable for X-ray diffraction was obtained by slow evaporation of compound **3a** in mixed solution of chloroform and methanol. The molecular structure of thiacalixarene **3a** is shown in Fig. 3. There are three chloroform molecules and two methanol molecules in the crystal. There are some disorders of *t*-butyl groups including C30(C30′), C31(C31′), C32(C32′), C51(C51′), C52(C52′) atoms and bridging ethylenediamine unit including O8(O8′), N3(N3′), N4(N4′), C11(C11′), C12(C12′) atoms. From Fig. 3 it can be seen that the thiacalix[4]arene adopts *1,3-alternate* configuration, which also indicated that precursor **2a** is also in *1,3-alternate* configuration because the configuration of **2a** could not be changed in the ammonolysis process. Ethylenediamine reacted with two ester groups respectively on upper rim and lower rim to form two diamide cycles. Due to this cyclic diamide bridge the opposing pairs of phenyl rings significantly inclined to each other. The whole molecule looks like as a carcerand compound. It is pity no solvent molecule was found trapped in its cavity. As shown by the packing diagram intramolecular hydrogen bonds between N2-H3A…O2 exist in the molecule. But no intermolecular hydrogen bonds exist among the molecules to form interesting supramolecular structures. It should be pointed that the similar types of (lower rim) proximally bridged *p-tert*-butylthiacalix[4]arenes bicyclic diamides have been prepared by direct aminolysis of the starting cone tetraacetates with aliphatic α,ω-diamines. The structures of the corresponding products were also proved by X-ray analysis [18].

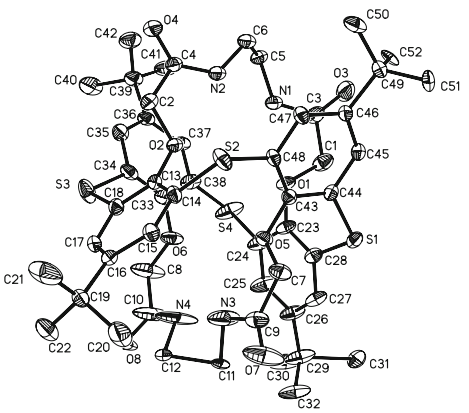


Fig. 3 Molecular structure of compound **3a**

The presence of sulfur atoms in the thiacalixarene skeleton offers another pathway for derivatization of the molecule: reactions on the bridging moieties [19, 20]. Oxidation of the prepared thiacalixarene tetraacetate **2a** and tetraamide **2d** were carried out by using aqueous H_2O_2 as oxidant in refluxing chloroform/acetic acid for two days. After work up the sulfone bridging calixarenes **4a** and **4b** were obtained in high yields (85%). IR spectrum of products **4a** clearly displays a stronger absorption at 1,767 cm^{-1} for carbonyl groups and another absorption at 1,025 cm^{-1} for S=O bonds. ^{1}H NMR spectra of **4a** showed a mixed peak at 8.57–7.74 ppm for phenolic protons, one singlet at 4.84 ppm for OCH_2CO group and one singlet at 1.44 ppm for *tert*-butyl groups.

The single crystal structure of **4a** was determined by X-ray diffraction analysis, which was obtained from $CHCl_3$/ethanol (Fig. 4). Form the molecular picture it was clearly found to be in the 1,3-alternate configuration with oxygen atoms of the sulfones pointing outward. The S=O bond distances were in the range of 1.421(5)–1.441(5). The four phenolic ring stands more parallel comparing with thiacalixarene such as **2c**, which might attribute to the push of S=O bonds. In another attempt of crystallization we also obtained the single crystal of sulfone bridging calixarene **4a** in *partial cone* configuration, which was drawn in

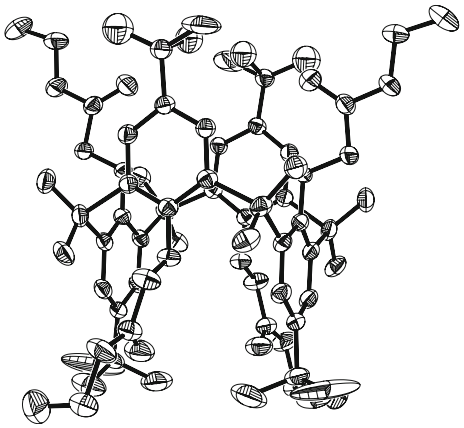


Fig. 4 Molecular structure of *p1,3-alternate* isomer of **4a**

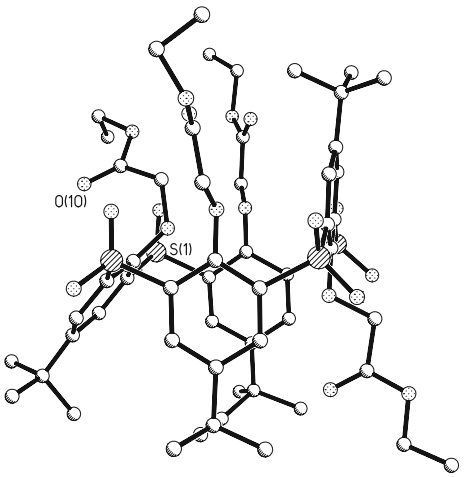


Fig. 5 Molecular structure of *partial cone* isomer of **4a**

Fig. 5. We could not detect its presence in the product sample by ^{1}H NMR spectrum. From the Fig. 5 it is clearly seen that on phenolic ring stands opposite to the other three phenolic rings with the oxyacetate group pointing to downside.

In conclusion a series of thiacalixarene derivatives in *1,3-alternate* conformation with functional ester, chloro, cyano, amide and toluenesulfonyl groups were efficiently prepared by the peralkylation of in *p-tert*-butylthiacalix[4]arene in K_2CO_3/KI/acetone system. Thiacalixarene bicyclic amides and sulfonylcalixarenes were also synthesized by convenient procedure. Single crystal X-ray diffraction analysis confirmed that these kinds of functional thiacalixarene and sulfonylcalixarenes exist mainly in *1,3-alternate* conformation. The reaction procedure is convenient, involving simple experimental procedure and product isolation. Thus our present protocol provides practical methods for the regioselective synthesis of functional thiacalixrene compounds.

Experimental

Reaction of *p*-tert-butylthiacalix[4]arene with ethyl α-chloroacetate

A suspension of *p*-tert-butylthiacalix[4]arene **1** (6.94 mmol, 5.0 g) and anhydrous potassium carbonate (43.4 mmol, 6.0 g), potassium iodide (3.0 mmol, 0.45 g) in dry acetone (100 mL) was heated to refluxing under nitrogen for at least 0.5 h. Then ethyl α-chloroacetate (5.3 mL, 50 mmol) was added. The reaction mixture was refluxed 5 days. After removal of acetone, the residue was dissolved in water and acidified with hydrochloride acid, then extracted with $CHCl_3$. The yellow organic layers were separated and dried with $MgSO_4$. Evaporation of the solvent yields red oil, which was titrated with alcohol to give yellow crude products, recrystallized from absolute ethanol to give the white solid of **2a**: Yield: 62%, mp: $>$ 250 °C. IR (KBr) υ: 1,759 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.66 (s, 8H, ArH), 4.92 (s, 8H, $COCH_2O$), 4.40 (q, $J = 7.1$ Hz, 8H, OCH_2), 1.37 (t, $J = 7.1$ Hz, 12H, CH_3), 1.32 (s, 36H, CH_3) ppm; Anal Calcd for $C_{56}H_{72}O_{12}S_4$: C 63.31, H 6.81; Found: C 63.58, H 7.03.

Reaction of *p-tert*-butylthiacalix[4]arene with 1-bromo-3-chloropropane

A suspension of *p-tert*-butylthiacalix[4]arene **1** (4.17 mmol, 3.0 g) and anhydrous potassium carbonate (21.7 mmol, 3.0 g) in dry acetone (100 mL) was heated to refluxing under nitrogen for at least 0.5 h. Then 1-bromo-3-chloropropane (4.0 mL) was added. The reaction mixture was refluxed 5 days. After removal of acetone, the residue was dissolved in water and acidified with hydrochloride acid, then extracted with $CHCl_3$. The yellow organic layers were separated and dried with $MgSO_4$. Evaporation of the solvent yields red oil, which was titrated with alcohol to give yellow crude products, recrystallized from absolute ethanol to give the white solid of **2b**: Yield: 86%, mp: $>$250 °C. IR (KBr) υ: 2985(w), 2936(w), 1548(m), 1379(m), 1309(m), 1203(vs), 1161(m), 1112(m), 1076(m), 1027(m), 929(m), 858(m), 823(m), 731(m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.36 (s, 8H, ArH), 3.99 (t, $J = 6.6$ Hz, 8H, OCH_2), 3.73 (t, $J = 7.2$ Hz, 8H, CH_2Cl), 3.20 (br, 8H, CH_2), 1.30 (s, 36H, CH_3) ppm; Anal Calcd for $C_{52}H_{68}Cl_4O_4S_4$: C 60.08, H 6.67; Found: C 59.76, H 6.43.

Reaction of *p-tert*-butylthiacalix[4]arene with 4-chlorobutyronitrile

A suspension of *p-tert*-butylthiacalix[4]arene (2.0 g, 2.8 mmol) and anhydrous potassium carbonate (3.0 g, 21.7 mmol), potassium iodide (0.45 g,3.0 mmol) in dry acetone (50 mL) was heated to refluxing under nitrogen for 2 h. Then 4-chlorobutyronitrile (1.4 g, 13.5 mmol) was

added. The reaction mixture was refluxed for five days. The solid was filtrated off. The solution was concentrated to nearly dry and ethanol was added to give crude product. Then recrystallization from chloroform and ethanol gives pure white solid of **2c**: Yield: 70%; mp: 235–237 °C, IR(KBr) υ: 2,230 (C≡N) cm^{-1}; ^1H NMR($CDCl_3$, 600 MHz) δ: 7.38 (s, 8H, ArH), 3.96 (t, $J = 7.2$ Hz, 8H, OCH_2), 1.98–1.94 (m, 8H, CH_2CN), 1.32 (s, 36H, $C(CH_3)_3$), 1.25–1.23 (m, 8H, CH_2CH_2); Anal Calcd for $C_{56}H_{68}N_4O_4S_4$: C 67.98, H 6.93, N 5.66; Found: C 68.31, H 7.28, N 5.42.

Reaction of *p-tert*-butylthiacalix[4]arene with N, N-dialkyl α-chloroacetamide

p-tert-Buthylthiacalix[4]arene (2.0 g, 2.8 mmol), K_2CO_3 (3.0 g, 21.7 mmol) in dry acetone (100 mL) were stirred at room temperature for 2 h. Then $ClCH_2CON(i\text{-}Pr)_2$ (4.0 g, 22.4 mmol) and KI (0.45 g, 3.0 mmol) were added and the resulting mixture was refluxing for 3 days. The solid was filtrated off. The solution was concentrated to nearly dry and ethanol was added to give crude product. Then recrystallization from ethanol gives pure white solid of **2d**: Yield: 54%; mp: 206–208 °C; IR(KBr) υ: 1,644 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.64 (s, 8H, ArH), 5.07 (s, 8H, OCH_2CO), 3.38–3.24 (m, 16H, $N(CH_2CH_2CH_3)_2$), 1.68–1.77 (m, 16H, $NCH_2CH_2CH_3$), 1.36 (s, 36H, $C(CH_3)_3$), 0.99–1.06 (m, 24H, $NCH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 164.8, 152.0, 147.5, 131.6, 129.2, 67.9, 46.7, 45.3, 33.1, 29.0, 19.8, 19.0, 9.8, 9.3; Anal Calcd for $C_{72}H_{108}N_4O_8S_4$: C 67.25, H 8.46, N 4.36; Found: C 67.18, H 8.25, N 4.11.

Reaction of *p-tert*-butylthiacalix[4]arene with *p*-toluenesulfonyl chloride

p-tert-Buthylthiacalix[4]arene (2.0 g, 2.8 mmol), *p*-toluenesulfonyl chloride and triethylamine (1.0 mL) in dry chloroform (10 mL) were heated to 50–60 °C for 12 h. Then the mixture was washed with water. The chloroform was concentrated to nearly dry and ethanol was added to give crude product. Then recrystallization from ethanol and chloroform gave pure white solid of **2e**: Yield: 92%. Mp: >250 °C ^1H NMR($CDCl_3$, 600 MHz) δ: 7.85 (s, 4H, ArH), 7.58 (s, 4H, ArH), 7.37 (s, 4H, ArH), 7.24 (s, 2H, ArOH), 6.99 (s, 4H, ArH), 2.48 (s, 6H, CH_3), 1.27 (s, 18H, $C(CH_3)_3$), 0.82 (s, 18H, $C(CH_3)_3$); Anal Calcd for $C_{54}H_{60}O_8S_6$: C 63.00, H 5.87; Found: C 62.65, H 6.13.

Reaction of *p*-tert-butylthiacalix[4]arene with diamine

A solution of ethyl *p*-butylthiacalix[4]arylacetate **2a** (1.1 g, 1.0 mmol) and ethylenediamine (10 mL) in ethanol (20 mL) was refluxed for 24 h. The volatile material was removed by evaporation. The residue was washed with larger quantity of water and recrystallizated from methanol and chloroform to give grey solid **3a**: Yield: 80%; mp: >250 °C; IR(KBr) υ: 3,416 (NH), 1,682 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.41 (s, 8H, ArH), 5.45 (s, 4H, CONH), 4.40 (s, 8H, OCH_2), 3.05 (s, 8H, $NHCH_2CH_2NH$), 1.28 (s, 36H, $C(CH_3)_3$); Anal Calcd for $C_{52}H_{64}N_4O_8S_4$: C 62.37, H 6.44, N 5.59; Found: C 62.69, H 6.71, N 5.33.

The same procedure was used by using propylene diamine to substitute ethylene dimine to give the product **3b**: grey solid, 72%; mp: >250 °C; IR(KBr) υ: 3,415 (NH), 1,668 (C=O) cm^{-1}; ^1H NMR($CDCl_3$, 600 MHz) δ: 7.40 (s, 8H, ArH), 5.47 (s, 4H, CONH), 4.32 (s, 8H, OCH_2), 3.12 (br, 8H, $NHCH_2CH_2NH$), 1.67 (br, 4H, CH_2), 1.28 (s, 36H, $C(CH_3)_3$); Anal Calcd for $C_{54}H_{68}N_4O_8S_4$: C 63.01, H 6.66, N 5.44; Found: C 63.29, H 6.75, N 5.17.

Reaction of *p*-tert-butylthiacalix[4]arene with hydrogen peroxide

To a solution of **2a** (1.000 g, 0.94 mmol) in chloroform (10 mL) were added acetic acid (20 mL) and hydrogen peroxide (30%, 10 mL). The mixture had been stirred at 60 °C for 2 days. 100 mL of water was added. The organic layer was separated and the water layer was extracted with chloroform (15 mL). Then the organic layer washed with a solution of $NaHSO_3$. After evaporation of the solvent, a white powder was obtained and washed with petroleum ether to give **4a**: Yield: 85%; mp: > 250 °C. IR (KBr) υ: 1,767 (C=O), 1,025 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ: 8.57–7.74 (m, 8H, ArH), 4.83 (s, 8H, OCH_2CO), 4.25 (s, 8H, OCH_2,) 1.44 (s, 36H, $C(CH_3)_3$), 1.11 (12H, CH_3); Anal Calcd for $C_{56}H_{72}O_{20}S_4$: C 56.36, H 6.08; Found: C 56.51, H 6.37.

The same procedure was used by using **2d** to substitute **2a** to give the product **4b**: white solid, 85%; mp: 238–340 °C; IR (KBr) υ: 1,677 (C=O), 1,026 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ: 8.18 (s, 8H, ArH), 4.90 (s, 8H, OCH_2), 3.26–2.92 (m, 16H, NCH_2), 1.53–1.50 (m, 16H, CH_2), 1.29 (s, 36H, $C(CH_3)_3$), 0.82–0.80 (m, 24H, CH_3); ^{13}C NMR ($CDCl_3$, 600 MHz) δ: 163.1, 151.0, 146.6, 134.0, 132.5, 72.6, 46.1, 45.1, 33.3, 28.7, 20.2, 19.4, 9.7, 9.3; Anal Calcd for $C_{72}H_{108}N_4O_{16}S_4$: C 61.16, H 7.70, N 3.96; Found: C 60.87, H 7.54, N 3.62.

Supplementary material

Crystallographic data can be obtained from the Cambridge Crystallographic Data Center, by quoting the reference number CCDC-714942 for **2c**, CCDC-714943 for **2e**, CCDC 715766 for **3a**, CCDC 724339 for *1,3-alternate*

isomer of **4a**, and CCDC 724056 for *partial cone* isomer of **4a**.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (Grant No. 20672091)

References

1. Lhoták, P.: Chemistry of thiacalixarenes. Eur. J. Org. Chem. 1671–1692 (2004)
2. Morohashi, N., Narumi Iki, N., Hattori, T., Miyano, S.: Thiacalixarenes. Chem. Rev. **106**, 5291–5316 (2006)
3. Liu, L., Han, J., Yan, C.G.: Progress in study of novel supramolecular host-thiacalixarene. Chin. J. Org. Chem. **27**, 907–917 (2007)
4. Iki, N., Miyano, S.: Can thiacalixarene surpass calixarene. J. Incl. Phenom. Macrocycl. Chem. **41**, 99–105 (2001)
5. Dhir, A., Bhalla, V., Kumar, M.: Ratiometry of monomer/excimer emissions of dipyrenyl thiacalix[4]arene for Cu^{2+} detection: a potential Cu^{2+} and K^{+} switched INHIBIT logic gate with NOT and YES logic functions. Tetrahedron Lett. **49**, 4227–4230 (2008)
6. Stoikov, I.I., Yushkova, E.A., Zhukov, A.Y., Zharov, H., Antipin, I.S., Konovalov, A.I.: The synthesis of *p-tert*-butyl thiacalix[4]arenes functionalized with secondary amide groups at the lower rim and their extraction properties and self-assembly into nanoscale aggregates. Tetrahedron **64**, 7112–7121 (2008)
7. Li, X., Gong, S.L., Yang, W.P., Chen, Y.Y., Meng, X.G.: The influence of isomerism on the self-assembly behavior and complexation property of 1,3-alternate tetraaminopyridyl-thiacalix[4]arene derivatives. Tetrahedron **64**, 6230–6237 (2008)
8. Šimánová, M., Dvořáková, H., Stibor, I., Pojarová, M., Lhoták, P.: Synthesis and conformational behaviour of lower-rim tetraacetylated thiacalix[4]arenes. Tetrahedron Lett. **49**, 1026–1029 (2008)
9. Štastný, V., Stibor, I., Dvořáková, H., Lhoták, P.: Synthesis of (thia)calix[4]arene oligomers: towards calixarene-based dendrimers. Tetrahedron **60**, 3383–3391 (2004)
10. Lhoták, P., Himl, M., Stibor, I., Petříčková, H.: Alkylation of thiacalix[4]arenes. Tetrahedron Lett. **43**, 9621–9624 (2002)
11. Desroches, C., Kessler, V., Parola, S.: The formylation of the upper-rims of thiacalixarenes: synthesis of the first tetra-formylated and the first *meta*-substituted thiacalix[4]arenes. Tetrahedron Lett. **45**, 6329–6331 (2004)
12. Duta, M., Asfri, Z., Kruchinina, N., Thurey, P., Hagege, A., Leroy, M.: Thiacrowncalix[4]arene derivatives: synthesis and complexing properties. Supramol. Chem. **17**, 221–226 (2005)
13. Bhalla, V., Kumar, M., Hattori, M.S.: Stereoselective synthesis of all stereoisomers of vicinal and distal bis(*O*-2-aminoethyl)-*p-tert*-butylthiacalix[4]arene. Tetrahedron **60**, 5881–5887 (2004)
14. van Leeuwen, F.W.B., Beijleveld, H., Kooijman, H., Spek, A.L., Verboom, W., Reihoudt, D.N.: Synthesis and conformational evuation of p-tert-butylthiacalix[4]arene-crowns. J. Org. Chem. **69**, 3928–3936 (2004)
15. Iki, N., Narumi, F., Fujimoto, T., Morohashi, N., Miyano, S.: Selective synthesis of three conformational isomers of tetrakis[(ethoxycarbonyl)methoxy]thiacalix[4]arene and their complexation properties towards alkali metal ions. J. Chem. Soc. Perkin Trans. **2**, 2745–2750 (1998)
16. Singh, S.P., Chakrabarti, A., Chawla, H.M., Pant, N.: Aminolysis of p-tert-butyltetrathiacalix[4]arene tetraethylacetates in cone, partial cone and 1, 3-alternate conformation: synthesis of amide based receptors for oxyanions. Tetrahedron **64**, 1983–1987 (2008)
17. Akdas, H., Mislin, G., Graf, E., Hosseini, M.W., Cian, A.D., Fischer, J.: Synthesis and solid state structural analysis of conformers of tetrakis((ethoxycarbonyl)methoxy)tetrathiacalix[4]arene. Tetrahedron Lett. **40**, 2113–2116 (1999)
18. Šťastný, V., Stibor, I., Petrickova, H., Sýkora, J., Lhoták, P.H.: Thiacalix[4]arene derivatives with proximally bridged lower rim. Tetrahedron **61**, 9990–9995 (2005)
19. Lhoták, P.: Regioselective and stereoselective oxidation of thiacalix[4]arene tetraacetate: synthesis of all possible sulfinylcalix[4]arenes. Tetrahedron **57**, 4775–4779 (2001)
20. Mislin, G., Graf, E., Hosseini, M.W., Cian, A.D., Fischer, J.: Sulfone-calixarenes: a new class of molecular building block, Chem. Commun. **134**, 5–1346 (1998)