J Incl Phenom Macrocycl Chem (2012) 74:265–275
DOI 10.1007/s10847-012-0109-9

ORIGINAL ARTICLE

Monosodium salt of *p-tert*-butylcalix[4]arene in the reactions with electrophilic reagents. Synthesis and structure of monofunctionalized calix[4]arenes

Olexander A. Yesypenko · Vyacheslav I. Boyko · Mariia A. Klyachina · Svitlana V. Shishkina · Oleg V. Shishkin · Volodymyr V. Pyrozhenko · Ivan F. Tsymbal · Vitaly I. Kalchenko

Received: 25 July 2011 / Accepted: 4 January 2012 / Published online: 11 February 2012

Abstract Monosodium salt of *p-tert*-butylcalix[4]arene reacts with alkyl halides or aroyl chlorides in DMF formed the *cone*-shaped monoalkyloxycalix[4]arenes or 1,3-diacyloxycalix[4]arenes, respectively. Diacyloxycalix[4]arenes are easily transformed into monoacyloxycalix[4]arenes in the *partial cone* conformation by interaction with NaOMe. The influence of intramolecular hydrogen bonding on course of alkylation and acylation reactions as well as the structure of the synthesized compounds in solution and crystalline state are discussed.

Keywords Alkylation · Acylation · Conformers · Monoalkyloxy-*p-tert*-butylcalix[4]arenes · Monoacyloxy-*p-tert*-butylcalix[4]arenes · 1,3-diacyloxy-*p-tert*-butylcalix[4]arenes

Introduction

Calixarenes [1], which have the unique cape-shaped structure, are widely used as building blocks for the synthesis of host molecules with different supramolecular functions. Due to their capability to recognize, they can bind and separate similar in properties cations, anions, or neutral organic molecules. Applications of calixarenes as chemical sensors, extractants for radioactive waste processing, materials for non-linear optics, and bio-active compounds were reported [2–4].

To increase efficiency and selectivity of calixarene complexation the functionalization at the wide and/or narrow rims of the macrocycle is carried out. The alkylation and acylation of phenolic hydroxyl groups is the most important method for modification. Monoethers of calixarenes are used as starting materials for the synthesis of di-, three- and tetraheterofunctional host-molecules. The special attention to the monoalkylation processes associated with design and synthesis of inherently chiral calix[4]arenes, which are based on the unsymmetrical array of different substituents on the calix[4]arene skeleton. Over the past decade, many inherently chiral calixarenes have been prepared, and some of them have been applied to chiral recognition and asymmetric catalysis [5–9]. Monoacylcalixarenes considered as convenient model for studying of the mechanism of acylation/deacylation proteolytic enzymes [10].

Tert-butyl depleted monoalkoxycalix[4]arenes are obtained in 75% yield by the reaction of tetrahydroxycalix[4]arene with excess of alkyl halides in presence of one equivalent of NaOMe [11]. But in the case of *p-tert*-butylcalix[4]arene **1**, due to its bad solubility both in polar and nonpolar solvents, the products of the further (deeper) alkylation are formed alongside with monoalkylated derivatives [12, 13], and the significant part of the starting tetrahydroxycalixarene remains unreacted. Therefore, several indirect methods are proposed for the synthesis of monoalkyloxy-*p-tert*-butylcalix[4]arenes. These methods involve preliminary protection of three hydroxyl groups of

O. A. Yesypenko · V. I. Boyko (✉) · M. A. Klyachina · V. V. Pyrozhenko · I. F. Tsymbal · V. I. Kalchenko
Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska Str 5, Kyiv 02660, Ukraine
e-mail: v_boyko@ioch.kiev.ua

S. V. Shishkina (✉) · O. V. Shishkin
STC "Institute for Single Crystal", National Academy of Sciences of Ukraine, Lenin Ave 60, Kharkhiv 61001, Ukraine
e-mail: sveta@xray.isc.kharkov.com

O. V. Shishkin
V.N.Karazin Kharkiv National University, 4 Svobody Sq, Kharkiv 61077, Ukraine

tetrahydroxycalixarene [14, 15] or dealkylation of its di- or tetraalkylated derivatives with iodotrimethylsilane [16] or aluminum chloride [17]. However, these methods are preparatively inconvenient. Monobenzoyloxycalix[4]arene was prepared also with high yield by the interaction of *p-tert*-butylcalix[4]arene with chlorine anhydrides of benzoic acids at the presence of 15-fold butyl-imidazole excess [10, 18]. Unfortunately, the configuration of these compounds is not determined unambiguously. Only triflate and mesylate derivatives are known for monosulfo-*p-tert*-butylcalix[4]arenes [19, 20].

It is assumed that the intermediates in the reaction of hydroxycalixarenes with electrophile (alkyl and acyl halides, sulfochloride) in the presence of inorganic base are salts of calix[4]arenes [21]. The salts of tetrahydroxycalix[4]arene with alkaline metals were received earlier [22–24], but their chemical properties were not investigated.

In this article we investigate behavior of monosodium salt of *p-tert*-butylcalix[4]arene in the reactions of alkylation and acylation.

Materials and methods

Melting points were determined on a Boëtius apparatus and were uncorrected. The ^{1}H NMR spectra were recorded on Varian VXR-300 spectrometer (299.943 MHz), ^{13}C NMR— on Varian GEMINI 2000 (100.607 MHz), the internal standard— TMS. IR spectra were recorded on UR-20 spectrometer. Reactions were carried out in anhydrous solvents and in atmosphere of argon.

Synthesis of *p-tert*-butylcalix[4]arene monosodium salt **2**

A suspension of *p-tert*-butylcalix[4]arene **1** (1.00 g, a complex with toluene, 1.35 mmol) and MeONa (0.08 g, 1.48 mmol) in dry DMF (40 mL) was stirred at 60–70 °C until full dissolution of reagents and then for 1 h. The solvent was removed *in vacuo* (0.02-mm Hg, 55–65 °C in a bath). The solid was washed twice by diethyl ether and dried *in vacuo*. The salt **2** was obtained as a solvate with two molecules of DMF (white solid) in 96% yield (1.21 g). Mp > 300 °C (Mp 338–340 °C [23]). IR (KBr), ν, cm^{-1}: 3185 (OH, broad, ass.), 1670 (C = O, DMF); IR (CH_2Cl_2), ν, cm^{-1}: 3190 (OH, broad, ass), 1675 (C = O, DMF). ^{1}H NMR (benzene-D_6), δ: 1.27 (s, 36H, t-Bu), 1.91 and 2.43 (s + s, 2 × 3H + 2 × 3H, Me groups of DMF), 3.52 (d, 4H, Ar–CH_{2eq}, $^{2}J_{HH}$ = 12.3 Hz), 4.83 (d, 4H, Ar–CH_{2ax}, $^{2}J_{HH}$ = 12.3 Hz), 7.19 (s, 8H, Ar–*H*), 7.66 (s, 2 × 1H, C*H* = O of DMF), 13.81 (br s, 3H, O*H*).

Alkylation of *p-tert*-butylcalix[4]arene monosodium salt **2**

The solution of alkyl iodide or alkyl bromide (6.5–8.0 mmol) in DMF (5 mL) was added to the solution of the salt **2** obtained in situ from calix[4]arene **1** (1.00 g, a complex with toluene, 1.35 mmol) in dry DMF (40 mL). In the case of alkyl bromide the KI (0.03 g) was added. The reaction mixture was stirred at 60–70 °C for 15–20 h. The solution was concentrated under reduced pressure to the volume of 25 mL and treated with 3% HCl (100 mL). After stirring for 2–3 h the precipitate was filtered off, washed with water and dried in the air. The product was refluxed in diethyl ether (20–25 mL) for 1–2 h (in the case of **3d** 10 mL of ethyl acetate were used) and left for 15–20 h at 5–10 °C. The precipitate of tetrahydroxycalixarene **1** was filtered off, the solvent was evaporated, residue was refluxed in methanol (7–10 mL) and cooled at 5 °C for 10–15 h. The precipitate was filtered off and dried in the air.

5,11,17,23-Tetra-tert-butyl-25-methyloxy-26,27,28-trihydroxycalix[4]arene ***3a***. Yield 0.69 g (77%), Mp 205–206 °C (203–204 °C [16]).

5,11,17,23-Tetra-tert-butyl-25-propyloxy-26,27,28-trihydroxycalix[4]arene ***3b***. Yield 0.66 g (72%), Mp 238–240 °C (239–240 °C [25]).

5,11,17,23-Tetra-tert-butyl-25-octyloxy-26,27,28-trihydroxycalix[4]arene ***3c***. Yield 0.63 g (65%), Mp 164–165 °C (164–166 °C [17]).

5,11,17,23-Tetra-tert-butyl-25-ethyloxycarbonylmethyloxy-26,27,28-trihydroxycalix[4]arene ***3d***. Yield 0.70 g (71%), Mp 273–274 °C (275–276 °C [12]).

Acylation of *p-tert*-butylcalix[4]arene monosodium salt **2**

The solution of the benzoyl chloride or sulfochloride (1.50 mmol) in DMF (5 mL) at 30–40 °C was added to the solution of the salt **2** obtained in situ from calix[4]arene **1** (1.00 g, a complex with toluene, 1.35 mmol) in dry DMF (40 mL). The reaction mixture was stirred at 30–40 °C for 15–20 h and cooled to 5–10 °C. The precipitate was filtered off, washed with DMF and dried in the air. The product was purified from tetrahydroxycalix[4]arene **1** by refluxing in 5 mL of chloroform for 1 h. After cooling for 2–3 h at 5–10 °C calixarene **1** was filtered off, washed with small amount of the cooled solvent and dried in the air. The yield of compound **1** was 44–49%. Calix[4]arenes **4b**, **c** were obtained after removal of the solvent from the filtrate. Compound **4a** was obtained by crystallization of the residue from acetonitrile.

5,11,17,23-Tetra-tert-butyl-25,27-bis(4′-methylphenyl sulfonyloxy)-26,28-dihydroxycalix[4]arene ***4a***. White

solid. Yield 0.340 g (26%), Mp 301–302 °C (acetonitrile). IR (KBr), ν, cm^{-1}: 3560 (OH, broad), 1365 and 1380 (SO_2 ass), 1165 (SO_2 sim); IR (CH_2Cl_2), ν, cm^{-1}: 3560 (OH, broad), 1380 (SO_2 ass), 1165 (SO_2 sim). ^{1}H NMR ($CDCl_3$), δ: 0.85 (s, 18H, t-Bu), 1.28 (s, 18H, t-Bu), 2.49 (s, 6H, Ar–CH_3), 3.06 (d, 4H, Ar–CH_{2eq}, $^2J_{HH}$ = 14.1 Hz), 3.94 (d, 4H, Ar–CH_{2ax}, $^2J_{HH}$ = 14.1 Hz), 4.55 (s, 2H, OH), 6.64 (s, 4H, Ar–H), 7.01 (s, 4H, Ar–H), 7.37 (d, 4H, SO_2–O–Ar–H, $^3J_{HH}$ = 8.2 Hz), 7.83 (d, 4H, SO_2–O–Ar–H, $^3J_{HH}$ = 8.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.89 (SO_2PhCH_3), 30.91, 31.73 (CCH_3), 32.30 (Ar–CH_2–Ar), 33.99, 34.06 (Ar–CMe_3), 125.22, 125.91 (C^{Ar}–H), 127.88 (C^{Ph}–Me), 128.38, 129.78 (C^{Ph}–H), 133.08, 133.20 (C^{Ar}–H), 141.84, 142.30 (C^{Ar}–t-Bu), 145.10 (C^{Ph}–SO_2), 149.10 (C^{Ar}–OSO_2), 149.78 (C^{Ar}–OH). Anal. Found, %: C 72.77; H 7.16; S 6.70. Calc. for $C_{58}H_{68}O_8S_2$, %: C 71.88; H 7.04; S 6.69.

5,11,17,23-Tetra-tert-butyl-25,27-bis(4′-chlorophenylcarboxy)-26,28-dihydroxycalix[4]arene ***4b***. White solid. Yield 0.314 g (25%), Mp > 340 °C (ethyl acetate). IR (KBr), ν, cm^{-1}: 3565 (OH, monomeric), 1736 (C = O); IR (CH_2Cl_2), ν, cm^{-1}: 3565 (OH, monomeric), 1735 (C = O). ^{1}H NMR ($CDCl_3$), δ: 0.99 (s, 18H, t-Bu), 1.18 (s, 18H, t-Bu), 3.49 (d, 4H, Ar–CH_{2eq}, $^2J_{HH}$ = 14.2 Hz), 3.92 (d, 4H, Ar–CH_{2ax}, $^2J_{HH}$ = 14.2 Hz), 5.06 (s, 2H, OH), 6.90 (s, 4H, Ar–H), 7.01 (s, 4H, Ar–H), 7.47 (d, 4H, C(O)–Ar–H, $^3J_{HH}$ = 8.4 Hz), 8.24 (d, 4H, C(O)–Ar–H, $^3J_{HH}$ = 8.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 31.12, 31.59 (CCH_3), 33.43 (Ar–CH_2–Ar), 33.95, 34.19 (Ar–CMe_3), 125.48, 126.04 (C^{Ph}H), 127.64, 127.73 (C^{Ph}–CH_2), 129.26, 131.58 (C^{Ac}H), 131.65 (C^{Ac}–C(O)O), 140.31 (C^{Ac}–Cl), 142.66, 142.89 (C^{Ph}–t-Bu), 148.90 (C^{Ph}–OC(O)), 150.11 (C^{Ph}–OH), 163.84 (C(O)O). Anal. Found, %: C 74.88; H 6.86; Cl 7.50. Calc. for $C_{58}H_{62}Cl_2O_6$, %: C 75.23; H 6.75; Cl 7.66.

5,11,17,23-Tetra-tert-butyl-25,27-bis(4′-methylphenylcarboxy)-26,28-dihydroxycalix[4]arene ***4c***. White solid. Yield 0.360 g (30%), Mp > 340 °C (benzene). IR (KBr), ν, cm^{-1}: 3560 (OH), 1730 (C = O); IR (CH_2Cl_2), ν, cm^{-1}: 3560 (OH), 1730 (C = O). ^{1}H NMR ($CDCl_3$), δ: 0.98 (s, 18H, t-Bu), 1.18 (s, 18H, t-Bu), 2.50 (s, 6H, Ar–CH_3), 3.46 (d, 4H, Ar–CH_{2eq}, $^2J_{HH}$ = 14.3 Hz), 3.97 (d, 4H, Ar–CH_{2ax}, $^2J_{HH}$ = 14.3 Hz), 5.26 (s, 2H, OH), 6.87 (s, 4H, Ar–H), 7.21 (s, 4H, Ar–H), 7.31 (d, 4H, C(O)–O–Ar–H, $^3J_{HH}$ = 7.6 Hz), 8.24 (d, 4H, C(O)–O–Ar–H, $^3J_{HH}$ = 7.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.89 ($C^{Ac}CH_3$), 31.15, 31.63 (CCH_3), 33.29 (Ar–CH_2–Ar), 33.95, 34.17 (Ar–CMe_3), 125.44, 125.87 (C^{Ph}H), 126.74, 127.80 (C^{Ph}–CH_2), 129.57, 130.42 (C^{Ac}H), 131.79 (C^{Ac}–C(O)O), 142.44, 143.10 (C^{Ph}–t-Bu), 143.99 (C^{Ac}–Me), 148.56 (C^{Ph}–OC(O)), 150.27 (C^{Ph}–OH), 164.77 (C(O)O). Anal. Found, %: C 79.60; H 8.02. Calc. for $C_{60}H_{68}O_6$, %: C 81.41; H 7.74.

Reaction of 25-(4′-methylphenylcarboxy) calix[4]arene **5c** with 4-chlorobenzoyl chloride

To the solution of salt **2** obtained in situ from calix[4]arene **1** (0.483 g, 0.652 mmol) in dry DMF (20 mL) monoaroylcalixarene **5c** (0.500 g, 0.652 mmol) was added. The reaction mixture was stirred for 4–5 h at 60–70 °C and then the solution of 4-chlorobenzoyl chloride (0.170 g, 1.98 mmol) in DMF (5 mL) was added. The reaction mixture was stirred for 4–5 h at 60–70 °C and cooled. The precipitate was filtered off, washed with DMF and dried in the air. Product was separated from tetrahydroxycalix[4]arene **1** by refluxing in 5 mL of chloroform for 1 h. After cooling for 2–3 h at 5–10 °C, calixarene **1** was filtered off, washed with small amount of the cooled solvent and dried in the air. Yield of compound **1** was 0.384 g. Chloroform was evaporated, the crude product (containing 8–9% of **4c** accordingly ^{1}H NMR spectrum) was crystallized from ethyl acetate. Calix[4]arene **4d** was filtered off and dried. The filtrate (solution in DMF) was poured to 3% HCl (50 ml). After stirring for 1–2 h, the precipitate was filtered off, washed with water and dried in the air. The precipitate was refluxed in chloroform (5 mL) for 1–2 h and left for 15–20 h at 5–10 °C. The rest of 4-chlorobenzoic acid was filtered off, the filtrate was evaporated. The residue was unreacted **5c** (0.083 g).

5,11,17,23-Tetra-tert-butyl-25-(4′-methylphenylcarboxy)-27-(4′-chlorophenylcarboxy)-26,28-dihydroxycalix[4]arene ***4d***. White solid. Yield 0.325 g (55%), Mp > 350 °C (ethyl acetate). ^{1}H NMR ($CDCl_3$), δ: 0.98 (s, 18H, t-Bu), 1.17 (s, 18H, t-Bu), 2.53 (s, 3H, CH_3), 3.47 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 14.0 Hz), 3.48 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 14.2 Hz), 3.93 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 14.0 Hz), 3.95 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 14.2 Hz), 5.18 (s, 2H, OH), 6.89 (s, 4H, Ar–H), 7.02 (s, 4H, Ar–H), 7.30 (d, 2H, Me–Ar–H, $^3J_{HH}$ = 8.0 Hz), 7.47 (d, 2H, Cl–Ar–H, $^3J_{HH}$ = 8.6 Hz), 8.19 (d, 2H, Me–Ar–H, $^3J_{HH}$ = 8.0 Hz), 8.28 (d, 2H, Cl–Ar–H, $^3J_{HH}$ = 8.6 Hz). Anal. Found, %: C 78.19; H 7.56; Cl 3.70. Calc. for $C_{59}H_{65}ClO_6$, %: C 78.25; H 7.23; Cl 3.91.

Reaction of bis(4′-methylphenylsulfonyloxy) calix[4]arene **4a** with sodium methoxide

The suspension of **4a** (0.10 g, 0.10 mmol) and powdered MeONa (0.01 g, 0.18 mmol) in 5 mL of DMF was stirred at 30–40 °C to full dissolution of reagents. The reaction mixture was stirred 30 min and then was poured to 3% HCl (10 mL). The mixture of compounds **5a** and **6** were extracted by chloroform (3 × 5 mL), the organic layer was washed with water and dried over Na_2SO_4. Chloroform was evaporated, the residue was stirred in boiling methanol

(5 mL), precipitate (calixarene **5a**) filtered off, washed with methanol and dried in the air. The filtrate was concentrated under reduced pressure to the 1/2 of volume. After 48 h at −10 °C the precipitate was filtered off. After removal of methanol from filtrate, calixarene **6** was obtained as colorless substance.

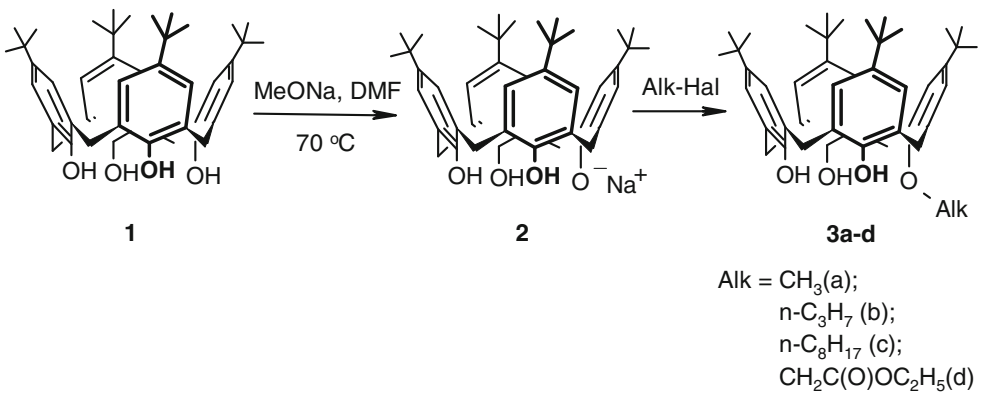
5,11,17,23-Tetra-tert-butyl-25-(4′-methylphenylsulfonyloxy)-26,27,28-trihydroxycalix[4]arene ***5a***. White solid. Yield 0.026 g (44%), Mp 292–294 °C. IR (KBr), ν, cm^{-1}: 3520 (OH), 3340 and 3282 (OH···O, broad), 1365 (SO_2 ass), 1165 (SO_2 sim); IR (CH_2Cl_2), ν, cm^{-1}: 3500 (OH), 3350 (OH···O, broad), 1365 (SO_2 ass), 1165 (SO_2 sim). ^{1}H NMR ($CDCl_3$), δ: 1.09 (s, 9H, t-Bu), 1.17 (s, 9H, t-Bu), 1.19 (s, 18H, t-Bu), 2.47 (s, 3H, Ar–CH_3), 3.24 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 13.9 Hz), 3.42 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 13.9 Hz), 4.08 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 13.9 Hz), 4.17 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 13.9 Hz), 6.99 (s, 8H, Ar–*H*), 7.39 (d, 2H, SO_2–O–Ar–*H*, $^3J_{HH}$ = 8.2 Hz), 7.73 (s, 2H, O*H*), 7.95 (d, 2H, SO_2–O–Ar–*H*, $^3J_{HH}$ = 8.2 Hz), 9.22 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$), δ: 21.75 (Ph–*C*H_3), 31.00, 31.40, 31.57 (C*C*H_3), 32.59, 32.63 (Ar–*C*H_2–Ar), 33.97, 34.01, 34.31 (Ar–*C*Me_3), 125.93, 125.98, 126.14, 127.33 (C^{Ar}–H), 127.49, 127.96, 128.15, 128.22 (*C*–CH_2), 129.10, 130.38 (C^{Ph}–H), 134.57 (C^{Ph}–CH_3), 141.98, 143.72, 144.41 (C^{Ar}–t-Bu), 146.10 (C^{Ph}–S), 147.34 (C^{Ar}–OS), 149.26, 150.60 (C^{Ar}–OH). Anal. Found, %: C 77.30; H 6.93; S 3.81. Calc. for $C_{51}H_{62}O_6S$, %: C 76.27; H 7.78; S 3.99.

5,11,17,23-Tetra-tert-butyl-25,26,27-tri(4′-methylphenylsulfonyloxy)-28-hydroxycalix[4]arene ***6***. White solid. Yield 0.043 g (44%), Mp 133–135 °C. IR (KBr), ν, cm^{-1}: 3590 (OH), 1380 (SO_2 ass), 1165 (SO_2 sim); IR (CH_2Cl_2), ν, cm^{-1}: 3590 (OH), 1380 (SO_2 ass), 1165 (SO_2 sim). ^{1}H NMR ($CDCl_3$), δ: 0.79 (s, 18H, t-Bu), 1.28, 1.29 (s + s, 9H + 9H, t-Bu), 2.44 (s, 6H, Ar–CH_3), 2.50 (s, 3H, Ar–CH_3), 2.60 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 14.1 Hz), 3.05 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 14.5 Hz), 4.01 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 14.5 Hz), 4.02 (s, 1H, O*H*), 4.18 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 14.1 Hz), 6.45 (d, 2H, SO_2Ar–*H*, $^3J_{HH}$ = 8.2 Hz), 6.98 (s, 2H, Ar–*H*), 7.06 (c, 2H, Ar–*H*), 7.24 (s, 2H, Ar–*H*), 7.26 (s, 2H, Ar–*H*), 7.42 (d, 2H, SO_2Ar–*H*, $^3J_{HH}$ = 8.2 Hz), 7.62 (d, 4H, SO_2Ar–*H*, $^3J_{HH}$ = 8.2 Hz), 8.19 (d, 2H, SO_2Ar–*H*, $^3J_{HH}$ = 8.2 Hz).

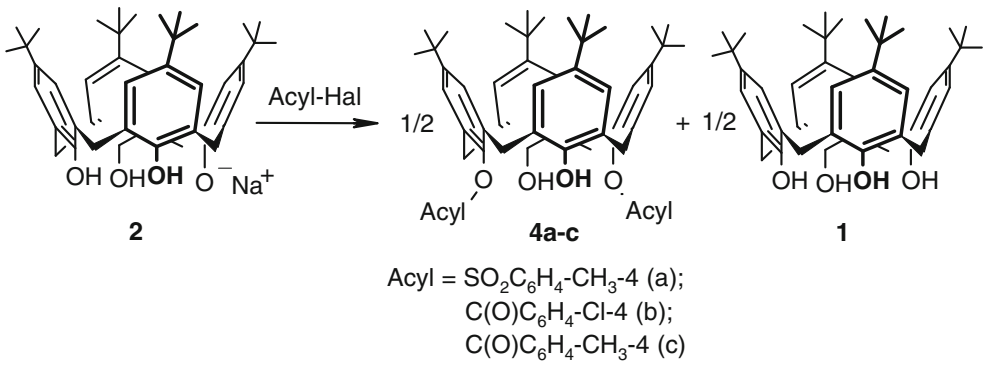
Reaction of diacyloxycalic[4]arenes **4b**, **c** with sodium methoxide

The suspension of **4b**, **c** (0.1 g, 0.10 mmol) and powdered MeONa (0.01 g, 0.18 mmol) in 5 mL of dry DMF was stirred at 40–50 °C to full dissolution of reagents (10–15 min). The reaction mixture was poured to 3% HCl (10 mL). After stirring for 30 min product was filtered off, washed with water and dried in the air.

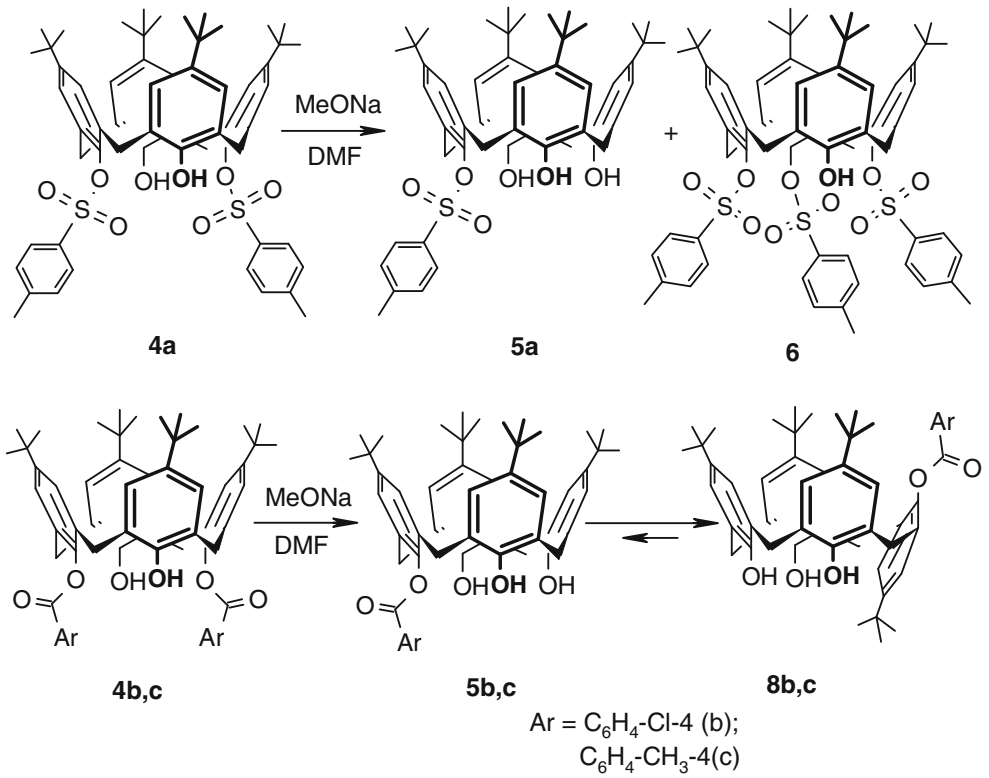
5,11,17,23-Tetra-tert-butyl-25-(4′-chlorophenylcarboxy)-26,27,28-trihydroxycalix[4]arene ***5b***. White solid. Yield 0.081 g (95%), Mp 316–317 °C with decomp. (acetone) (> 200 °C [10]). IR (KBr), ν, cm^{-1}: 3510 (OH), 3365 and 3320 (OH···O,broad), 1725 (C = O); IR (CH_2Cl_2), ν, cm^{-1}: 3490 (OH), 3330 (OH···O, broad), 1725 (C = O). ^{1}H NMR ($CDCl_3$, 50 °C), δ: 0.74 (s, 18H, t-Bu), 1.40, 1.41 (s + s, 9H + 9H, t-Bu), 3.54 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 13.8 Hz), 3.86 (d, 2H, Ar–CH_2–Ar-anti, $^2J_{HH}$ = 16.8 Hz), 4.03 (d, 2H, Ar–CH_2–Ar-anti, $^2J_{HH}$ = 16.8 Hz), 4.16 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 13.8 Hz), 6.34 (d, 2H, Cl–Ar–*H*, $^3J_{HH}$ = 8.1 Hz), 6.41 (d, 2H, Cl–Ar–*H*, $^3J_{HH}$ = 8.1 Hz), 6.49 (d, 2H, Ar–*H*, $^4J_{HH}$ = 2.2 Hz), 6.70 (s, 2H, O*H*), 6.84 (d, 2H, Ar–*H*, $^4J_{HH}$ = 2.2 Hz), 7.21 (s, 2H, Ar–*H*), 7.37 (s, 2H, Ar–*H*), 8.63 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$), δ: 31.23, 31.91, 32.08 (C*C*H_3), 32.32 (Ar–*C*H_2–Ar), 33.74, 34.59, 34.97 (Ar–*C*Me_3), 38.59 (Ar–*C*H_2–Ar, anti), 125.13, 125.35, 125.73 (C^{Ph}H), 126.63, 127.48 (C^{Ph}–CH_2), 127.62 (C^{Ph}H), 127.90 (C^{Ac}H), 128.63 (C^{Ph}–CH_2), 130.83 (C^{Ac}H), 131.40 (C^{Ph}H), 139.03 (C^{Ac}–Cl), 143.72, 144.41 (C^{Ph}–t-Bu), 146.42 (C^{Ac}–C(O)O), 147.56 (C^{Ph}–OC(O)), 149.34, 150.19 (C^{Ph}–OH), 162.00 (*C*(O)O). Anal.



Scheme 1 Synthesis of calix[4]arene monosodium salt **2** and monoalkyloxycalix[4]arenes **3a–d**



Scheme 2 Sulfonylation and acylation of monosodium salt **2**



Scheme 3 Reaction of calix[4]arenes **4a, b, c** with sodium methoxide

Found, %: C 77.90; H 7.73; Cl 4.46. M 787.49. Calc. for $C_{51}H_{59}ClO_5$, %: C 77.79; H 7.55; Cl 4.50. M^+ 787.3.

5,11,17,23-Tetra-tert-butyl-25-(4′-methylphenylcarboxy)-26,27,28-trihydroxycalix[4]arene ***4c***. White solid. Yield 0.080 g (92%), Mp 310–311 °C (acetonitrile) (> 200 °C [10]). IR (KBr), ν, cm^{-1}: 3510 (OH), 3380 (OH···O, broad), 1718 (C = O); IR (CH_2Cl_2), ν, cm^{-1}: 3480 (OH), 3325 (OH···O, broad), 1720 (C = O). ^{1}H NMR ($CDCl_3$, 50 °C), δ: 0.76 (s, 18H, t-Bu), 1.37 and 1.38 (s + s, 9H + 9H, t-Bu), 2.10 (s, 3H, Ar–CH_3), 3.51 (d, 2H, Ar–CH_{2eq}, $^2J_{HH}$ = 13.7 Hz), 3.88 (d, 2H, Ar–CH_2–Ar-anti, $^2J_{HH}$ = 16.3 Hz), 3.98 (d, 2H, Ar–CH_2–Ar-anti, $^2J_{HH}$ = 16.3 Hz), 4.10 (d, 2H, Ar–CH_{2ax}, $^2J_{HH}$ = 13.7 Hz), 6.39 (d, 2H, Me–Ar–*H*, $^3J_{HH}$ = 8.0 Hz), 6.52 (d, 2H, Me–Ar–*H*, $^3J_{HH}$ = 8.0 Hz), 6.54 (d, 2H, Ar–*H*, $^4J_{HH}$ = 2.2 Hz), 6.78 (s, 2H, O*H*), 6.86 (d, 2H, ArH, $^4J_{HH}$ = 2.2 Hz), 7.17 (s, 2H, Ar–*H*), 7.34 (s, 2H, Ar–*H*), 8.63 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$), δ: 21.50 (Ar–*C*H_3), 31.26, 31.90, 32.09 (C*C*H_3), 32.39 (Ar–*C*H_2–Ar), 33.79, 34.53, 34.94 (Ar–*C*Me_3), 38.03 (Ar–*C*H_2–Ar, anti), 125.29, 125.31, 125.70, 127.55 (C^{Ph}H), 128.59 (C^{Ac}H), 128.62 (C^{Ph}–CH_2), 129.80 (C^{Ac}H), 131.89 (C^{Ph}–CH_2), 143.06 (C^{Ac}–Me), 143.63, 144.17 (C^{Ph}–t-Bu), 146.31 (C^{Ac}–C(O)O), 147.61 (C^{Ph}–OC(O)), 148.40, 149.94 (C^{Ph}–OH), 163.34 (*C*(O)O). Anal. Found, %: C 80.93; H 8.10. Calc. for $C_{52}H_{62}O_5$, %: C 81.42; H 8.15.

The X-ray diffraction study

The colorless crystals of **5a** $C_{51}H_{62}O_6S \cdot C_2H_3N$ are monoclinic. At 100 K a = 12.7285 (5), b = 12.5200 (3), c = 30.661 (1) Å, β = 99.617 (3)°, V = 4817.4 (3) Å^3, Mr = 844.12, Z = 4, space group $P2_1/n$, d_{calc} = 1.164 g/cm^3, μ(MoKα) = 0.116 mm^{-1}, F (000) = 1816. Intensities of 20071 reflections (8152 independent, R_{int} = 0.060) were measured on the "Xcalibur-3" diffractometer (graphite monochromated MoKα radiation, CCD detector, ω-scanning, 2Θmax = 50°).

Table 1 Absorption bands in IR spectra for OH-groups of calix[4]arenes **3** and **5** (KBr,ν,cm^{-1})

Comp.	R	OH associated	OH monomeric
3a	CH_3	3175, 3280	–
3b	*n*-C_3H_7	3260, 3330	–
3c	*n*-C_8H_{17}	3200, 3365	–
3d	$CH_2C(O)OC_2H_5$	3220, 3365	–
5a	4-$MeC_6H_4S(O)_2$ (mono)	3285, 3340	3520
5b	4-$ClC_6H_4C(O)$ (mono)	3320, 3365	3510
5c	4-$CH_3C_6H_4C(O)$ (mono)	3380	3510

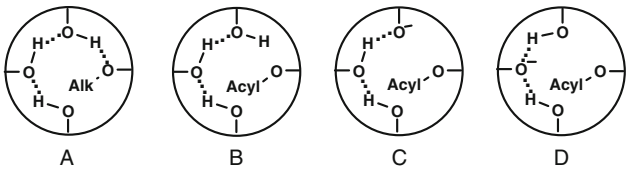
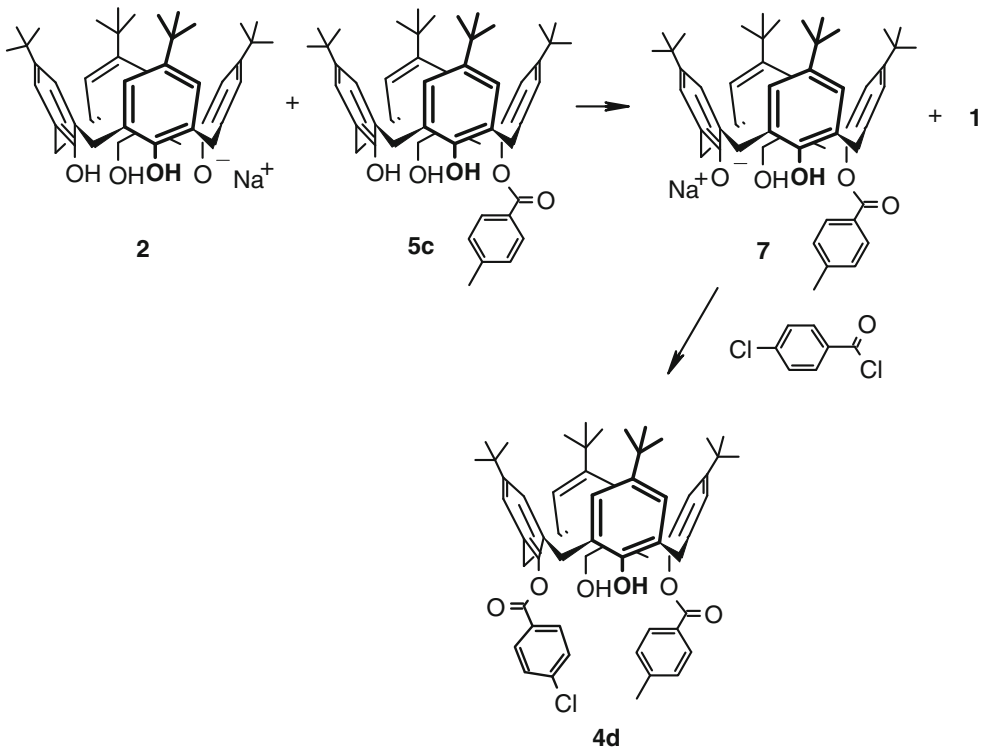


Fig. 1 The hydrogen bonds in monoalkyloxycalix[4]arene (**A**) and monoacyloxycalix[4]arenes (**B**, **C**, **D**)

The colorless crystals of **5b** $C_{51}H_{59}O_5Cl \cdot C_3H_6O$ are monoclinic. At 100 K a = 25.0535 (5), b = 9.8937 (2), c = 18.5773 (3) Å, β = 93.726 (2)°, V = 4595.1 (2) Å^3, Mr = 845.51, Z = 4, space group $P2_1/c$, d_{calc} = 1.222 g/cm^3, μ(MoKα) = 0.134 mm^{-1}, F (000) = 1816. Intensities of 22931 reflections (8004 independent, R_{int} = 0.030) were measured on the "Xcalibur-3" diffractometer (graphite monochromated MoKα radiation, CCD detector, ω-scanning, 2Θmax = 50°).

The structures were solved by direct method using SHELXTL package [26]. Positions of the hydrogen atoms were located from electron density difference maps and refined by "riding" model with Uiso = nUeq of the carrier atom (n = 1.5 for methyl and hydroxyl group and for water molecule and n = 1.2 for other hydrogen atoms). The hydrogen atoms of hydroxyl group which take part in the formation of the hydrogen bonds are refined in isotropic approximation. The restrains for the bond lengths (Csp^3–Csp^3 1.54 Å) in the disordered fragments were applied during the refinement of the structures. Full-matrix least-squares refinement of the structures against F^2 in



Scheme 4 Synthesis of heteroacylated calix[4]arene **4d**

anisotropic approximation for non-hydrogen atoms using 8095 (**5a**), 7980 (**5b**) reflections was converged to: $wR_2 = 0.083$ ($R_1 = 0.046$ for 4218 reflections with $F > 4\sigma$ (F), $S = 0.810$) for structure **5a** and $wR_2 = 0.124$ ($R_1 = 0.046$ for 5194 reflections with $F > 4\sigma$ (F), $S = 0.926$) for structure **5b**. The final atomic coordinates, and crystallographic data for molecules **5a** and **5b** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 816614 for **5a** and CCDC 816615 for **5b**.

Results and discussion

Calixarene monosodium salt **2** was formed by stirring of the suspension of calix[4]arene **1** and sodium methoxide (in an equimolar ratio) in DMF at 60–70 °C (Scheme 1). Unlike the starting reagents (tetrahydroxycalix[4]arene **1** and sodium methoxide), salt **2** is well soluble in DMF. After evaporation of solvent the salt was obtained as a solvate with two molecules of DMF. It should be noted, that monosodium salt **2** is also well soluble in acetone, acetonitrile, chloroform and while heating in benzene and toluene. It isn't dissolved in diethyl ether and THF. The solution of calix[4]arene monosodium salt **2** was used for chemical transformations in situ. Due to the good solubility of salt **2** and alkylating or acylating reagents in DMF the processes were carried out in the homogeneous environment, which raised the selectivity of the reactions.

For alkylation of calix[4]arene monosodium salt **2** the 5–6-fold excesses of the corresponding alkylating reagents were used. In the case of less reactive alkyl bromides the catalytic quantity of dry KI was added for their conversion to more active alkyl iodides. The reaction was performed at 60–70 °C for 15–20 h to give the *cone*-shaped monoalkyloxycalix[4]arenes **3a–d** in 65–77% yields (Scheme 1).

The sulfonylation and acylation of monosodium salt **2** by the equimolar quantity of sulfonyl or benzoyl chloride led to the formation of trace amounts of monoacylated calixarenes while the basic products of the reaction were distal diacylated calix[4]arenes **4a–c** and tetrahydroxycalix[4]arene **1** (Scheme 2).

Calixarenes **4a–c** reacts with sodium methoxide, but the ways of its transformations are different. In the solution of DMF there is a disproportionating of disulfonyloxycalixarene **4a** with the formation of mono- **5a** and trisulfonylated calixarenes **6**. The same disproportionation of 1,3-bistriflate calyx[4]arene under the influence of palladium catalysts was previously observed, but the product yield was significantly lower [19]. In the case of diacyloxycalixarenes **4b**, **c** occurs elimination of one of the acyl group (Scheme 3).

The various result of alkylation and acylation of monosodium salt of *p-tert*-butylcalix[4]arene **2** can be explained by different acidity of the hydroxyl groups of monofunctionalized derivatives, which is caused by the change of hydrogen bonding system. All the hydrogen atoms of the hydroxyl groups of compounds **3** take part in the formation of hydrogen bonds: two OH…OH and one OH…OAlk. This is confirmed by their IR spectra, which contain the only broad absorption bands of the associated hydroxyl groups at 3190–3365 cm^{-1} (Table 1). Therefore transformation into anion requires the additional energy for cleavage of the hydrogen bonds.

In the case of monoacyloxycalixarenes **5** oxygen atoms bearing electron acceptor carbonyl or sulfonyl groups, consequently, aren't hydrogen bonded. As a result, only two hydrogen atoms form the hydrogen bonds and the third one remain free and it is observed broad absorption bands

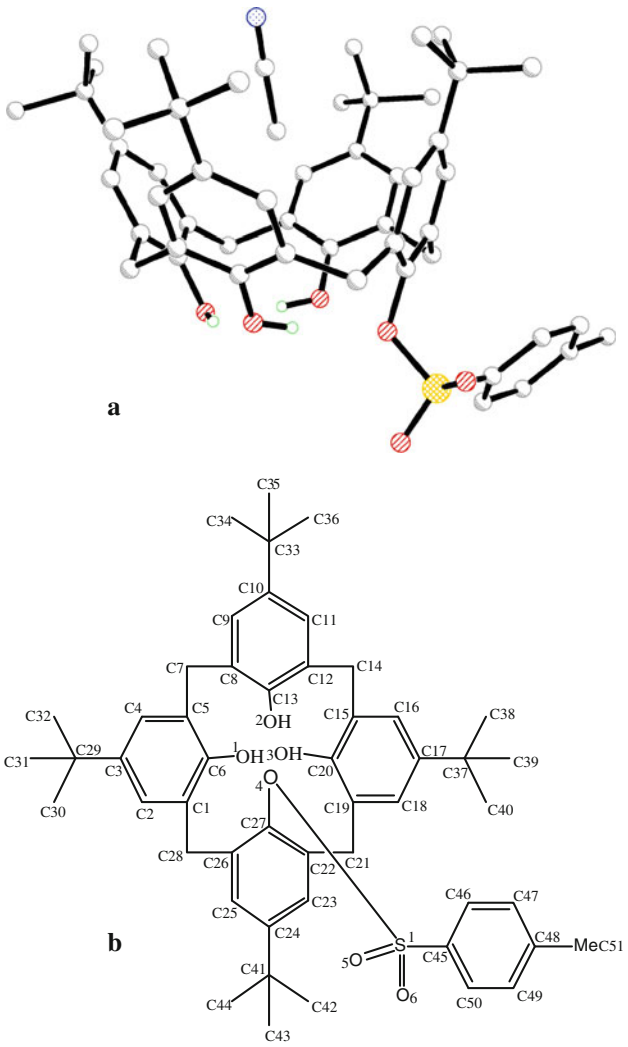


Fig. 2 The molecular structure of **5a** (**a**) and numbering scheme of atoms (**b**) according to X-ray diffraction data

of the associated hydroxyl groups at 3285–3380 cm^{-1} and narrow band of the monomeric OH group at 3510 cm^{-1} in the IR spectra. The lower energy is required for the remove of proton, which isn't hydrogen bonded, therefore these compounds easily form anion C even by the interaction with such a weak base as salt **2** (Fig. 1). Anion C formed in this case can be stabilized by the hydrogen bonding with the only one neighboring hydroxyl group. Therefore C undergoes the fast transformation into anion D, which is more favorable because it can be stabilized by two hydrogen bonds.

The following reaction of the salt D with acyl chloride gives 1,3-disubstituted products **4**. The reaction of **5c** with *p-Cl*-benzoyl chloride in the presence of calixarene sodium salt confirms the stronger acidity of monoacylated derivative in comparison to monoalkylated one. After stirring of the equimolar quantities of monoacylated derivative **5c** and sodium salt **2** in DMF within 9 h acyl chloride was added (Scheme 4).

Compound **4d** is a major product of the reaction and can be formed only from *p-Cl*-benzoyl chloride and anion **7**. According to the ^{1}H NMR spectrum the mixture of products contains 37% of **4d** (64% based on conversion of monoacylated calixarene **5c**). When **5c** was replaced by monoalkylated calixarene **3b** the mixture with the major unreacted monopropyloxycalixarene **3b** was obtained.

According to the ^{1}H NMR spectrum at the room temperature in $CDCl_3$ solution diacyloxycalixarenes **4b**, **c** are present in the *flattened cone* conformations as proved by the small distances between the resonance signals of the axial and equatorial protons of methylene bridges ($\Delta\delta \sim 0.5$ ppm). This value is nearly 1 ppm for sulfonyloxycalixarenes **4a**, **5a**, and **6** that conforms to a regular *cone* conformation.

The X-ray diffraction study of the compound **5a** demonstrates that these molecules in the crystalline phase have a *cone* conformation of macrocycle (Fig. 2).

Moreover, the molecule **5a** and solvent acetonitrile molecule form the "host–guest" complex (Fig. 2a). It is

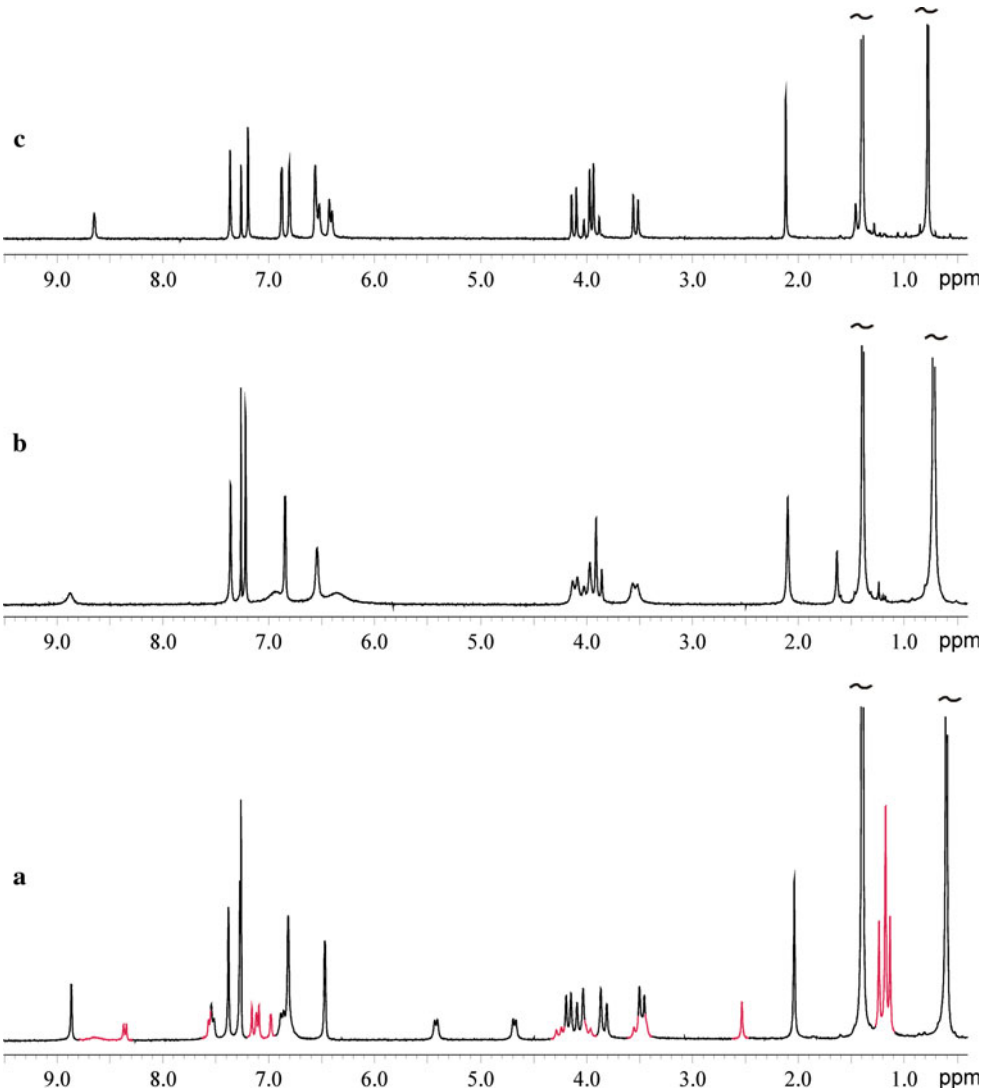


Fig. 3 The ^{1}H NMR spectrum of **5c–8c** (300 MHz, $CDCl_3$) at −60 °C (**a**), 25 °C (**b**) and 50 °C (**c**)

possible to assume that the formation of this complex provides additional promotion of the *cone* conformation of macrocycle which is stabilized by relatively strong intramolecular hydrogen bond at lower rim. The *p*-toluenesulfonyl substituent has exo-orientation relatively the macrocycle cavity and it is orthogonal with respect to the C22…C27 aromatic ring (the C26–C27–O4–S1 torsion angle is −88.1 (2)°). The tolyl group is located in *–sc*-conformation relatively the C27–O4 bond and is turned in such way that the plane of the C45…C50 aromatic ring is orthogonal to the O4–S1 bond (the C45–S1–O4–C27, and the O4–S1–C45–C46 torsion angles are −70.8 (2)°, and 87.2 (2)°, respectively).

Completely different situation is observed for monoacyloxycalixarenes **5b**, **c**. The ^{1}H NMR spectrum at room temperature in the $CDCl_3$ solution are typical for *partial cone* conformation **8b**, **c** (Fig. 3b), although previously a *cone* conformation was given for this type of compounds [18]. They have the pair of doublets from the equatorial and axial protons of methylene groups between *syn*-oriented phenyl rings (AX-spin system, δ 3.53 ppm and 4.12 ppm, $^{2}J_{HH} = 13.7$ Hz) and pair of doublets from the protons of methylene groups between *anty*-oriented phenyl rings (AB-spin system, δ 3.90 ppm and 4.00 ppm, $^{2}J_{HH} = 16.2$ Hz). In the ^{13}C NMR spectrum the signals of carbonic atoms of methylene bridges are at 38.03 ppm (between *anty*-oriented phenyl rings) and 32.39 ppm (between *syn*-oriented phenyl rings) that confirmed the *partial cone* conformation [27]. At the same time the broadened signals in this spectrum indicate the occurrence of some dynamic processes in solution of monoacyloxycalixarenes which are probably associated with conformation conversions of macrocycle. For a more detailed study of these processes we carried out investigation of compounds **5b**, **c** using dynamic NMR methods. We found that at −60 °C monoacyloxycalixarenes exists in solution as mixture of two interconvertible conformers: *cone* (red line) **5b**, **c** and *partial cone* (black line) **8b**, **c** in the ratio 1: 4 for **5c–8c** (Fig. 3a) and 1: 10 for **5b–8b**. In consideration of large volume of acyl substitute such conversion is only possible sequential inversion of unsubstituted phenolic rings.

It should be noted that in the low temperature we observe one more dynamic process for *partial cone* conformer. It is shown by change in the form of signals for aromatic protons of acyl substituent. With decreasing temperature these signals first broadened and then divided into four doublets with nearly equal intensity ($^{3}J_{HH} = 7.7$ Hz) in the range of 7.5, 6.9, 5.4, and 4.7 ppm (Fig. 3a). The location of aromatic protons in the range of 4.5–5.5 ppm is unusual and indicates their effective magnetic shielding of other benzene rings of macromolecule. This is only possible if the acyl fragment is located inside the cavity of the macrocycle.

For further studies of the spatial structure of the acylated calixarene we performed X-ray diffraction study. In the crystalline phase the molecule **5b** is observed as monosolvate with acetone where the macrocycle has a *partial cone* conformation (Fig. 4a). The chlorophenylcarboxylic substituent at the inverted aromatic ring is turned in such way that the chlorophenyl fragment is located inside the cavity of the macrocycle and it has almost orthogonal orientation with respect to the opposite aromatic ring. However, conjugation between chlorophenyl ring and carbonyl group is not disturbed (the O4–C45–C46–C47 torsion angle is 4.8 (3)°).

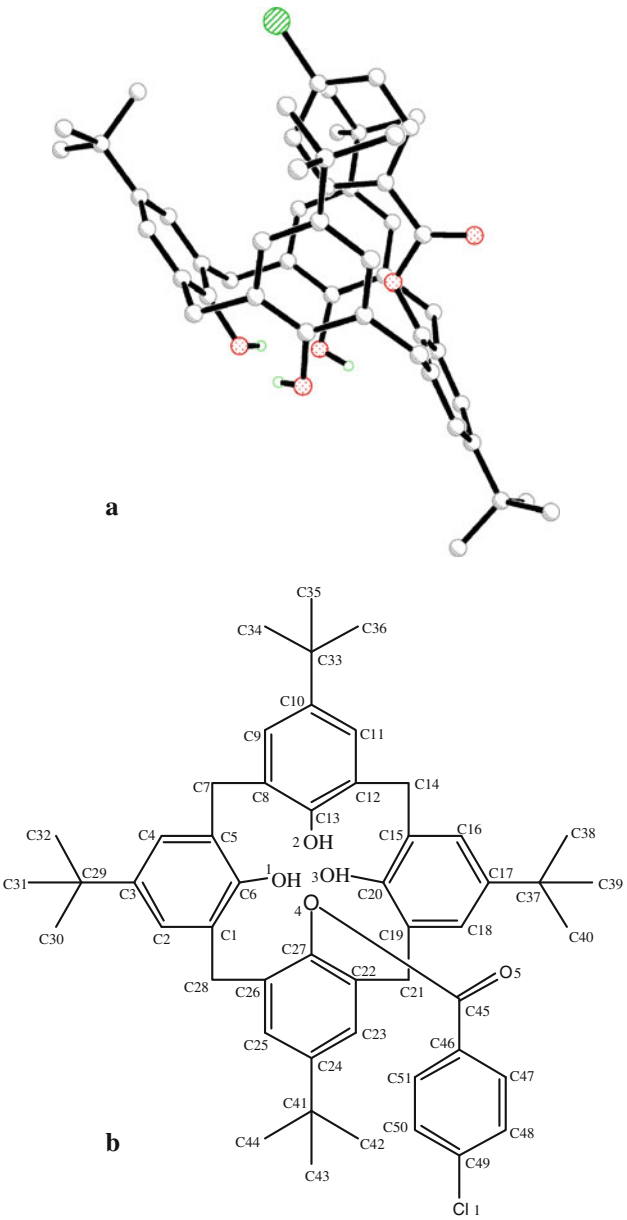


Fig. 4 The molecular structure of **5b** (**a**) and numeration of atoms (**b**) according to X-ray diffraction data

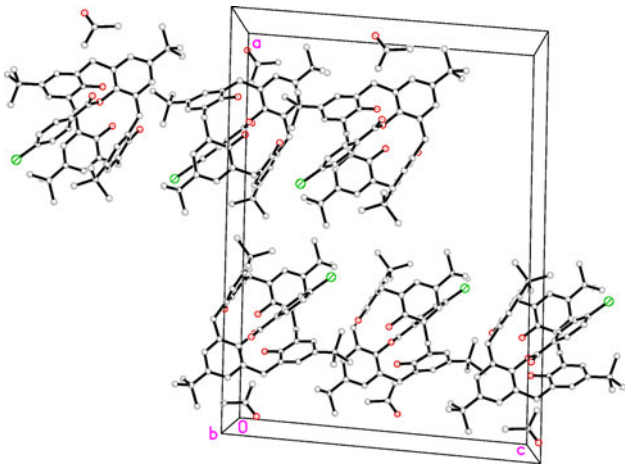


Fig. 5 The packing of **5b** molecules in the crystal phase

The solvent acetone molecules are situated between chains formed by molecules **5b** along the [001] crystallographic direction (Fig. 5). It can be assumed that they do not influence molecular structure of **5b**.

So mono functionalized trihydroxycalix[4]arenes may exist in *cone* conformation as well as *partial cone* conformation. Their ratio is determined of substitute and kind of solvents. Now we investigate the influence of these factors on the equilibrium in this process.

Conclusion

In this work it is shown that alkylation of monosodium salt of *p-tert*-butylcalix[4]arene in DMF goes selectively, leads to the monoalkyloxycalix[4]arenes in good yields and may be used as preparative method of monoalkylation. Reaction of monosodium salt with benzoyl chloride derivatives in these conditions leads to the 1,3-diacylated products, which transform into monoacyloxycalix[4]arenes by the treatment with sodium methoxide. It is established, that monoacylated calix[4]arenes in chloroform solution and in crystal phase adopts a *partial cone* conformation in which phenylacylic group is located inside of the macrocycle cavity.

References

1. Gutsche, C.D. (ed.): Calixarenes: an introduction. The Royal Society of Chemistry, Cambridge (2008)
2. Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J. (eds.): Calixarenes 2001. Kluwer Academic Publishers, Dordrecht (2001)
3. Lumetta, G.J., Rogers, R.D., Gopalan, A.S.: Calixarenes for separations. American Chemical Society, Washington (2000)
4. Rodic, R.V., Boyko, V.I., Kalchenko, V.I.: Calixarene in biomedical researches. Car. Mad. Chem. **16**, 1630–1655 (2009)
5. Nam, K.C., Kim, J.M., Park, Y.J.: Synthesis and structure identification of ABCH type calix[4]arenes: two step synthesis of asymmetrically substituted calix[4]arenes from monoalkyl calix[4]arenes. Bull. Korean Chem. Soc. **19**, 770–776 (1998)
6. Zheng, Y.-S., Luo, J.: Inherently chiral calixarenes: a decade's review. J. Incl. Phenom. Macrocycl. Chem. **71**, 35–56 (2011)
7. Li, Z.-Y., Chen, J.-W., Liu, Y., Xia, W., Wang, L.: The use of calixarenes in asymmetric catalysis. Curr. Org. Chem **15**, 39–61 (2011)
8. Li, Sh.-Y., Xu, Y.-W., Liu, J.-M., Su, Ch.-Y.: Inherently chiral calixarenes: synthesis, optical resolution, chiral recognition and asymmetric catalysis. Int. J. Mol. Sci. **12**, 429–455 (2011)
9. Boyko, V.I., Shivanyuk, A., Pyrozhenko, V.V., Zubatyuk, R.I., Shishkin, O.V., Kalchenko, V.I.: A stereoselective synthesis of asymmetrically substituted calix[4]arenecarbamates. Tetrahedron. Lett. **47**, 7775–7778 (2006)
10. Ray, K.B., Weatherhead, R.H., Pirinccioglu, N., Williams, A.: Enhanced alkaline hydrolysis of monoesterified 4-tert-butylcalix[4]arenes involving intramolecular electrophilic catalysis by phenolic hydroxy group. J. Chem. Soc., Perkin. Trans. **2**, 83–88 (1994)
11. Shu, C.-M., Chung, W.-S., Wu, S.-H., Ho, Z.-S., Lin, L.-G.: Synthesis of calix[4]arenes with four different "lower rim" substituents. J. Org. Chem. **64**, 2673–2679 (1999)
12. Groenen, L.C., Ruël, B.H.M., Casnati, A., Verboom, W., Pochini, A., Ungaro, R., Reinhoudt, D.N.: Synthesis of monoalkylated calix[4]arenes via direct alkylation. Tetrahedron **47**, 8379–8384 (1991)
13. Santoyo-González, F., Torres-Pinedo, A., Sanchéz-Ortega, A.: Regioselective monoalkylation of calixarenes. Synthesis of homodimer calixarenes. J. Org. Chem. **65**, 4409–4414 (2000)
14. Shang, S., Khasnis, D.V., Burton, J.M., Santini, C.J., Fan, M., Small, A.C., Lattman, M.: From a novel silyl p-tert-butylcalix[4]arene triether to mono-0-alkyl substitution: a unique, efficient, and selective route to mono-0-substituted calix[4]arenes. Organometallics **13**, 5157–5159 (1994)
15. Gutsche, C.D., Lin, L.-G.: Calixarenes 12. The synthesis of functionalized calixarenes. Tetrahedron **42**, 1633–1640 (1986)
16. Casnati, A., Arduini, A., Ghidini, E., Pochini, A., Ungaro, R.: A general synthesis of calix[4]arene monoalkyl ethers. Tetrahedron **47**, 2221–2228 (1991)
17. Matvieiev, Y.I., Boyko, V.I., Podoprigorina, A.A., Kalchenko, V.I.: Preparative synthesis of para-tert-butylcalix[4]arene monoalkyl ethers. J. Incl. Phenom. Macrocyclic Chem. **61**, 89–92 (2008)
18. See, K.A., Fronczek, F.R., Watson, W.H., Kashyap, R.P., Gutsche, D.C.: Calixarenes. 26. Selective esterification and selective ester cleavage of calix[4]arenes. J. Org. Chem. **56**, 7256–7268 (1991)
19. Gonzcilez, J.J., Nieto, P.M., Prados, P., Echavarren, A.M., de Mendoza, J.: Calix[4]arene sulfonates: palladium-catalyzed intermolecular migration of sulfonyl groups and isolation of a calixc4larene in a chiral 1,2-alternate conformation. J. Org. Chem. **60**, 7419–7423 (1995)
20. Chowdhury, S., Bridson, J.N., Georghiou, P.E.: Synthesis of calix[4]arene triflates and their unusual chemical reactivity in palladium-catalyzed reactions. J. Org. Chem. **65**, 3202–3299 (2000)
21. Casnati, A.: Calixarenes: from chemical curiosity to a rich source for molecular receptors. Gazz. Chim. Ital. **127**, 637–649 (1997)
22. Hanna, T.A., Liu, L., Angeles-Boza, A.M., Kou, X., Gutsche, C.D., Ejsmont, K., Watson, W.H., Zakharov, L.N., Incarvito, Ch.D., Rheingold, A.L.: Synthesis, structures, and conformational characteristics of calixarene monoanions and dianions. J. Am. Chem. Soc. **125**, 6228–6238 (2003)
23. Hamada, F., Kerr, D.R., Orr, G.W., Atwood, J.L.: Alkali metal salts of oxyanions of p-tert-butylcalix[4]arene. Supramol. Chem. **2**, 19–24 (1993)

24. Thuéry, P., Asfari, Z., Vicens, J., Lamare, V., Dozol, J.-F.: Synthesis and crystal structure of sodium and caesium ion complexes of unsubstituted calix[4]arene. New polymeric chain arrangements. Polyhedron **21**, 2497–2503 (2002)
25. Iwamoto, K., Araki, K., Shinkai, S.: Synthesis of all possible conformational isomers of o-alkyl-p-t-butylcalix[4]arenes. Tetrahedron **47**, 4325 (1991)
26. Sheldrick, G.M.: A short history of SHELX. Acta Crystallogr., Sect. A. **A64**, 112–122 (2008)
27. Margans, J.O., de Mendoza, J., Pons, M., Prados, P.: Are 1,3-Di-O-benzoylcalix[4]arenes an exception to the ^{13}C-NMR rule for conformational determination? J. Org. Chem. **62**, 4518–4520 (1997)