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X-RAY CRYSTAL STRUCTURES AND ISOSTRUCTURALITY CALCULATION OF CALIX[4]ARENES WITH LOWER RIM PROPYL AND CARBOXYLIC ACID OR MIXED CARBOXYLIC ACID AND ESTER SUBSTITUENTS INVOLVING SOLVENT COMPLEXES WITH METHANOL AND ETHANOL

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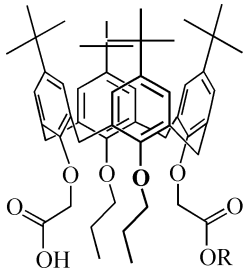
X-ray crystal structures of two calix[4]arenes are reported. They feature aside from two distal *n*-propyl units, two ethyl acetate or mixed ethyl acetate and acetic acid groups as the characteristic substituents of the lower rim hydroxylic hydrogens. The structures are compared by making use of isostructurality calculations. In case of the semi-ester, solvates with methanol and ethanol as the guest solvents are involved. The carboxy function of the semi-ester does not form a dimer but an intramolecular hydrogen bond to a propoxy group. The solvates can be described as isostructural in spite of the different solvent molecules.

K e y w o r d s: calix[4]arenes, solvate, inclusion compound, crystal structure, supramolecular interaction, hydrogen bonds, isostructurality calculation.

Since more than two decades, calix[4]arenes are a very active field in supramolecular chemistry [1]. Much of the interest in this particular class of compounds derives from the potential use in a wide variety of applications such as chemical separation, sensoring or catalysis [2]. In most cases, this depends not only on the basket-like character of the molecules but also on the presence of appropriate functional groups attached to the upper and lower rims. The groups may be helpful for conformational freezing of the calix framework, in improving inclusion selectivity, or they may be effective as a linkage group for the generation of functional devices [3]. In these respects, both lower rim site *n*-propyl and acetic acid substituents have proven to be very useful [4].

Here, we describe for the first time the detailed preparation of two calix[4]arenes featuring, aside from two distal *n*-propyl units, mixed acetic acid and ester (**1**) or two acetic acid groups (**2**) [5, 6] as the other characteristic substituents of the lower rim hydroxyls (Scheme 1). We report the X-ray crys-



1 (R = Et)
2 (R = H)
3 (**2** · MeOH)
4 (**2** · EtOH)

Scheme 1. Compounds studied in this paper

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tal structures of the unsolvated calixarene **1** and of **2** in the form of solvent complexes with methanol **3** and ethanol **4**, including also an in-depth isostructurality calculation study [7] of the compounds under discussion.

EXPERIMENTAL

Synthesis. Melting points (m.p.) were determined using a microscope heating stage PHMK Rapido (VEB Wägetechnik) and are uncorrected. IR spectra were obtained using a Perkin-Elmer 1600 FT-IR instrument. NMR spectra were recorded on a Bruker AVANCE DPX 400 at 25 °C. Chemical shifts are reported in ppm with TMS as an internal standard (δ = 0 ppm). The elemental analyses were performed with a Heraeus CHN rapid analyzer.

The calixarenes **1** and **2** were synthesized from 5,11,17,23-tetra-*tert*-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-dipropoxycalix[4]arene (diester of **1**) [8] by partial or full hydrolysis with potassium hydroxide, respectively, referring to protocols not being detailed described in the literature [5, 6].

For the preparation of **1**, a mixture containing the calixarene diester (3.40 g, 3.76 mmol), powdered potassium hydroxide (2.54 g, 45.27 mmol), ethanol (70 ml) and *iso*-propanol (40 ml) was heated for 3 h at reflux, then cooled and treated with concentrated hydrochloric acid until the precipitation of a solid was complete. The precipitate was filtered, dried and recrystallized from chloroform/ethanol (1:1) to yield 3.06 g (93 %) of **1** as a white solid, m.p. 238—240 °C. IR (KBr, cm^{-1}): 3248 (OH), 3053, 2965, 2934, 2872 (CH), 1761, 1738 (C=O), 1632 (C=C), 1480 (CH), 1391, 1381, 1363, 1303, 1241, 1198, 1127, 1060, 1004, 873; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (s, 18H, $C(CH_3)_3$), 1.00 (t, 6H, J = 7.2 Hz, $CH_2CH_2CH_3$), 1.28 (t, 3H, J = 6.4 Hz, OCH_2CH_3), 1.36 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$), 1.93 (m, 4H, $CH_2CH_2CH_3$), 3.24 (d, 2H, J = 13.2 Hz, $ArCH_2Ar$), 3.25 (d, 2H, J = 12.4 Hz, $ArCH_2Ar$), 3.72 (m, 2H, OCH_2CH_2), 3.92 (m, 2H, OCH_2CH_2), 4.24 (s, 2H, $COOCH_2CH_3$), 4.25 (d, 2H, J = 12.8 Hz, $ArCH_2Ar$), 4.56 (s, 2H, OCH_2COOH), 4.91 (s, 2H, OCH_2COCH_2), 4.93 (d, 2H, J = 14 Hz, $ArCH_2Ar$), 6.52 (d, 2H, J = 1.6 Hz, ArH), 6.63 (d, 2H, J = 1.6 Hz, ArH), 7.17 (d, 4H, J = 7.6 Hz, ArH), 11.41 (s, 1H, COOH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.3 ($CH_2CH_2CH_3$), 14.2 (CH_2CH_3), 23.0 ($CH_2CH_2CH_3$), 29.7, 31.0, 31.6, 31.7 ($C(CH_3)_3$, $ArCH_2Ar$), 33.6, 34.0, 34.2 ($C(CH_3)_3$), 60.4 ($COOCH_2CH_3$), 70.9, 72.5 (OCH_2CO), 78.4 (OCH_2CH_2), 124.6, 125.2, 125.8, 125.9, 131.8, 132.6, 134.9, 135.3, 145.0, 145.7, 147.3, 151.0, 151.3, 154.4 (ArC), 169.9, 170.7 (CO); Anal. Calcd for $C_{56}H_{76}O_8$: C, 76.68; H, 8.73. Found: C, 76.80; H, 8.71.

For the synthesis of **2**, powdered potassium hydroxide (2.34 g, 44.56 mmol) was added to the monoester **1** (3.00 g, 3.42 mmol) suspended in ethanol (120 ml). The mixture was heated for 7 h at reflux, cooled and treated with concentrated hydrochloric acid until the precipitation of a solid was complete. The precipitate was filtered, dried and recrystallized from ethanol to yield 2.54 g (87 %) of **2** as a white solid, m.p. = 270—272 °C. IR (KBr, cm^{-1}): 3251 (OH), 3051, 2960, 2905, 2876 (CH), 1767, 1742 (C=O), 1638 (C=C), 1485 (CH), 1392, 1367, 1338, 1303, 1242, 1199, 1131, 1056, 999, 871; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (s, 18H, $C(CH_3)_3$), 0.91 (t, 6H, J = 7.2 Hz, $CH_2CH_2CH_3$), 1.34 (s, 18H, $C(CH_3)_3$), 1.89 (m, 4H, $CH_2CH_2CH_3$), 3.28 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 3.92 (t, 4H, J = 8 Hz, OCH_2CH_3), 4.27 (d, 4H, J = 12.8 Hz, $ArCH_2Ar$), 4.65 (s, 4H, OCH_2CO), 6.57 (s, 4H, ArH), 7.17 (s, 4H, ArH), 11.44 (s, 2H, COOH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.9 (CH_2CH_3), 22.7 (CH_2CH_3), 31.0, 31.6 ($C(CH_3)_3$), 31.3 ($ArCH_2Ar$), 33.3, 33.7 ($C(CH_3)_3$), 72.0 (OCH_2CO), 79.2 (OCH_2CH_2), 125.2, 126.2, 131.8, 134.6, 145.8, 147.4, 149.9, 152.9 (ArC), 169.8 (CO)); Anal. Calcd for $C_{54}H_{72}O_8$: C, 76.38; H, 8.55. Found: C, 76.36; H, 8.67.

X-ray structural study. Crystals suitable for X-ray diffraction were obtained by slow evaporation of solution of the corresponding calixarene in chloroform/ethanol (1:1), methanol and ethanol for **1**, **3** and **4**, respectively. The intensity data were collected on a Bruker APEX II diffractometer with MoK_α radiation (λ = 0.71073 Å) using ω- and φ-scans. Reflections were corrected for background, Lorentz and polarization effects. Preliminary structure models were derived by application of direct methods [9] and were refined by full-matrix least squares calculation based on F^2 for all reflections [10]. All hydrogen atoms were included in the models in calculated positions and were refined as

Table 1

Crystal data and selected details of the data collection and refinement calculations for compounds **1**, **3** *and* **4**

Compound	**1**	**3**	**4**
Temperature, K	93(2)	153(2)	93(2)
Empirical formula	$C_{56}H_{76}O_8$	$C_{54}H_{72}O_8 \cdot CH_4O$	$C_{54}H_{72}O_8 \cdot C_2H_6O$
Formula weight	877.17	881.16	895.18
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a, b, c, Å	13.7017(5), 15.4580(7), 23.9092(11)	25.5244(8), 21.4404(7), 21.0158(7)	25.5776(13), 21.3161(11), 21.0211(9)
α, β, γ, deg.	90.0, 90.0, 90.0	90.0, 113.585(1), 90.0	90.0, 113.176(2), 90.0
V, Å^3	5064.0(4)	10540.3(6)	10536.1(9)
Z	4	8	8
D_c, g/cm^3	1.151	1.111	1.129
Data collection			
Collected reflections	30352	116063	121338
θ-limits, deg.	1.6—27.6	0.9—27.6	0.9—27.3
Unique reflections	6437	24453	23713
Refined parameters	625	1229	1229
F values used [$I > 2\sigma(I)$]	4357	14968	16651
Final R-Indices			
$R(=\Sigma\|\Delta F\|/\Sigma\|F_o\|)$	0.0638	0.0637	0.0565
wR on F^2	0.1860	0.2196	0.1732
GOOF on F^2	1.014	1.050	1.021
Final $\Delta\rho_{max}$ / ρ_{min}, e/Å^3	0.54 / –0.49	0.59 / –0.43	0.58 / –0.53

constrained to bonding atoms. In the present crystal structures, the calixarene skeleton itself is perfectly ordered whereas the *tert*-butyl and propoxy groups show higher displacement parameters or are disordered over several positions even at low temperatures. In the structure of **3**, some of these fragments have proven to be difficult to model and therefore were only refined isotropically. The crystal data and experimental parameters are summarized in Table 1.

Crystallographic data for the structures in this paper including atomic coordinates, thermal parameters, bond lengths and valent angles have been deposited with the Cambridge Crystallographic Data Centre (deposition Nos.: **1**, CCDC-695422; **3**: CCDC-695424; **4**: CCDC-695423) and are freely available from http://www.ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

The molecular structures of **1** and **3** are shown in Figs. 1 and 3 whilst Fig. 2 and 4 illustrate the crystal packings of **1** and **4**, respectively. The conformation of the calixarene framework may be described by a set of angles which define the inclination of the aromatic rings with respect to the mean plane given by methylene carbon atoms C(7), C(14), C(21) and C(28). These angles correlate with the dihedral angles between pairs of opposite arene rings. These parameters together with relevant torsion angles are summarized in Table 2. Information regarding hydrogen bonds geometry is listed in Table 3. Results of the isostructurality calculations are presented in Table 4.

The crystal of the solvent-free semi-ester **1**, incorporating no guest molecule, reveals the orthorhombic space group $P2_12_12_1$. The calixarene framework adopts an extremely pinched cone conformation with the corresponding interplanary angles A/C and B/D of 7.44 and 84.44°, respectively (Table 2). The centroid-to-centroid distance between the facing aromatic rings B and D is 5.5 Å. Surpris-

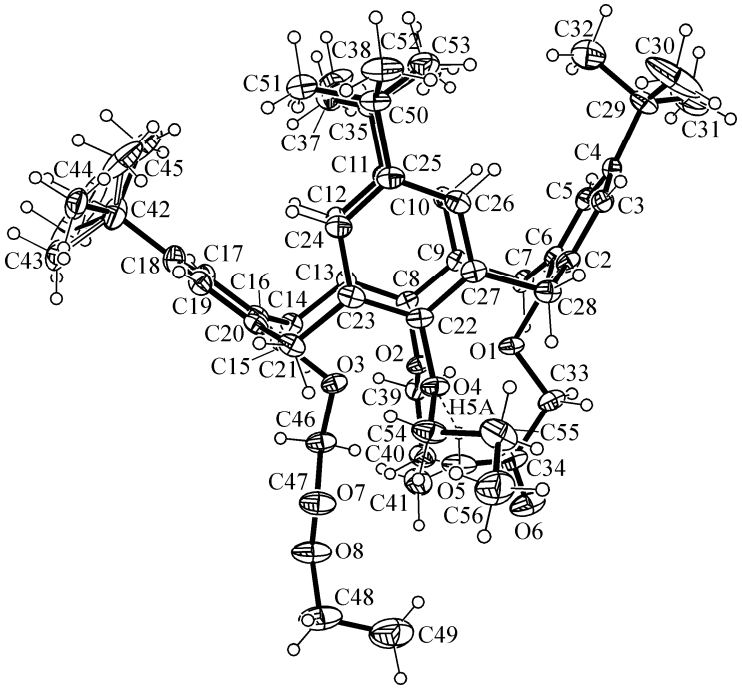


Fig. 1. Molecular structure of **1**, shown with 30 % probability displacement ellipsoids and numeration of atoms. Broken line indicates hydrogen bonding

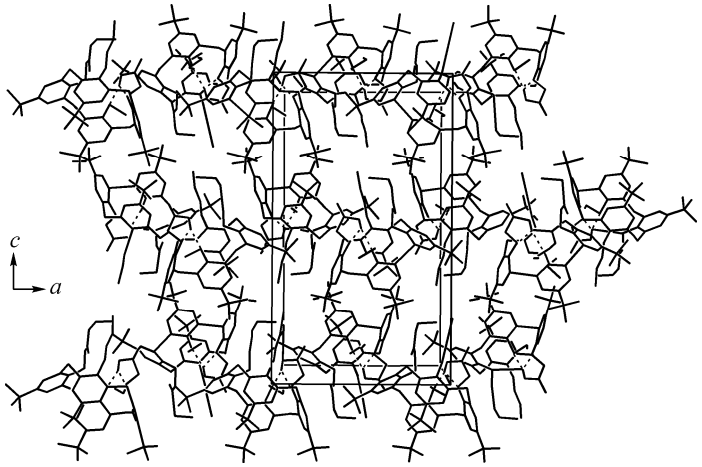


Fig. 2. Packing arrangement of **1** in stick style, viewed along the crystallographic *b* axis. Bold and light molecules refer to different planes in the diagram; broken lines represent hydrogen bonds

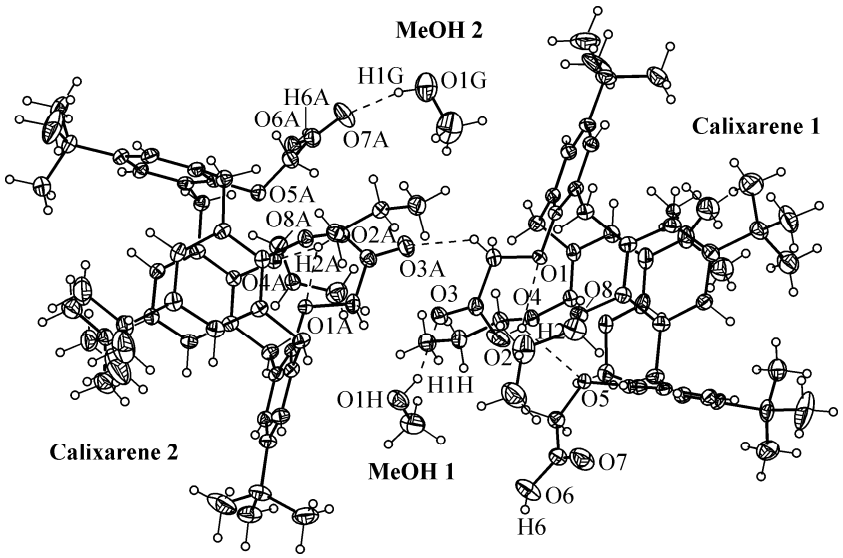


Fig. 3. Molecular structure of **3**, shown with 30 % probability displacement ellipsoids and numeration of atoms. Broken lines indicate hydrogen bonds

Table 2

Selected conformational parameters of the calixarene molecule in the crystal structures of compounds **1**, **3** *and* **4**

Compound	**1**	**3**(1)	**3**(2)	**4**(1)	**4**(2)
		Interplanar angles (°)[a]			
mpla[b]/*A*	49.9(1)	45.8(1)	39.8(1)	45.6(1)	44.8(1)
mpla/*B*	83.3(1)	84.8(1)	89.6(1)	89.0(1)	86.6(1)
mpla/*C*	48.9(1)	55.0(1)	51.0(1)	54.8(1)	52.1(1)
mpla/*D*	89.3(1)	87.2(1)	88.3(1)	83.9(1)	88.4(1)
A/*C*	81.2(1)	79.3(1)	89.2(1)	79.6(1)	83.1(1)
B/*D*	7.4(2)	8.1(1)	2.1(1)	7.2(1)	5.1(1)
		Torsion angles (°)			
O(1)—C(33)—C(34)—O(5)	–30.7(6)				
C(33)—C(34)—O(5)—H(5A)	–7.2(7)				
O(1)—C(33)—C(34)—O(2)		14.8(3)		–17.9(3)	
C(33)—C(34)—O(2)—H(2)		–1.8(4)		–2.0(4)	
O(5)—C(46)—C(47)—O(6)		–175.2(2)		173.1(2)	
O(1A)—C(33A)—C(34A)—O(2A)			–22.6(3)		–22.1(3)
C(33A)—C(34A)—O(2A)—H(2A)			–1.0(4)		–6.6(5)
O(5A)—C(46A)—C(47A)—O(6A)			13.5(3)		13.0(3)

[a] Aromatic rings: ring *A*: C(1)…C(6); ring *B*: C(8)…C(13); ring *C*: C(15)…C(20); ring *D*: C(22) …C(27).
[b] Best plane through atoms C(7), C(14), C(21) and C(28).

ingly, the lower rim carboxy group is not involved in the common dimer formation [11, 12] but is engaged in a bifurcated intramolecular hydrogen bond with oxygen atoms of neighbouring propoxy groups [O(5)…O(1) = 2.706(5) Å, O(5)…O(4) = 2.698(5) Å] (Fig. 1) yielding a O(1)—C(33)—C(34)—O(5) torsion angle of 30.7°. Furthermore, some weak intermolecular hydrogen bonds [13] stabilize the conformation of the molecule (Table 3). Hence, in spite of the presence of strong hydrogen donor and acceptor sites, the packing structure (Fig. 2) is controlled by weak C—H…O [13] and C—H…π interactions [14] including van der Waals forces. The intermolecular distances between the calixarene aromatic core centroids, coming to 10.72, 10.81 and 11.13 Å, do not indicate a layer-type structure but a molecular arrangement essentially following close packing requirements [15].

Crystallization of the dicarboxylic acid **2** from methanol and ethanol gives inclusion structures **3** and **4**, respectively, which proved to have similar unit cell dimensions (Table 1) and identical space group symmetries (monoclinic $P2_1/c$). The asymmetric units contain two crystallographically independent calixarene molecules which are bridged by strong hydrogen bonds via two alcoholic guest molecules [16, 17] leading to a calixarene:alcohol stoichiometric ratio of 2:2 (Fig. 3). The calixarenes are in the cone conformation and show again nearly coplanar (A/C) and orthogonal (B/D) behaviour concerning the angles of the corresponding arene units (Table 2). A closer examination of the crystal structure of **3** (**2**·MeOH) reveals that the crystallographically independent 1:1 host-guest entities differ in their modes of non-covalent interaction. The carboxylic hydrogen H(2) of the calixarene-1 (*see* Fig. 3) is involved in formation of a trifurcated intramolecular hydrogen bond to the oxygens O(1), O(4) and O(5) [d(O…O) 2.638(2)—2.874(3) Å]. The carboxylic oxygen O(3) acts as an acceptor site for binding of an alcohol guest [O(1H)…O(3) 2.714(3) Å]. Its oxygen O(1H) is associated with the carboxylic hydrogen H(6A) of the calixarene-2. The carboxylic hydrogen H(2A) of the calixarene-2 molecule forms a less symmetric bifurcated hydrogen bond [O(2A)…O(1A) 2.716(3), O(2A)…O(8A) 2.696(2) Å], while oxygen O(3A) takes part in the formation of a weak C—H…O hydrogen bond [C(33)…O(3A) 3.397(3) Å] to a methylene hydrogen of a neighbouring calixarene molecule.

T a b l e 3

Hydrogen-bonding geometry (Å, deg.) *for* **1**, **3** *and* **4**

Atoms involved	Symmetry	Distances (Å)		Angle (deg.)
		D…A	H…A	D—H…A
	1			
O(5)—H(5A)…O(4)	*x*, *y*, *z*	2.698(5)	1.92	154
O(5)—H(5A)···O(1)	*x*, *y*, *z*	2.706(5)	2.29	111
C(21)—H(21A)…O(6)	–0.5+*x*, 2.5–*y*, 2–*z*	3.419(6)	2.64	135
C(30)—H(30C)…O(6)	1.5–*x*, 2–*y*, –0.5+*z*	3.487(8)	2.68	140
C(7)—H(7B)…O(2)	*x*, *y*, *z*	2.901(5)	2.44	108
C(14)—H(14B)…O(2)	*x*, *y*, *z*	2.894(5)	2.44	107
C(21)—H(21B)…O(6)	–0.5–*x*, 2.5–*y*, 2–*z*	3.420(6)	2.65	135
C(28)—H(28B)…O(4)	*x*, *y*, *z*	2.899(5)	2.46	107
C(44)—H(44A)…*centroid*(A)[a]	–1+*x*, *y*, –0.5+*z*	3.615(7)	2.66	164
C(43)—H(43C)…*centroid*(B)[a]	–1+*x*, *y*, –0.5+*z*	3.827(6)	2.96	148
C(56)—H(56C)…*centroid*(C)[a]	0.5+*x*, 2.5–*y*, 2–*z*	3.677(7)	2.91	136
C(32)—H(32A)…*centroid*(D)[a]	1–*x*, –0.5+*y*, 1.5–*z*	3.575(7)	2.74	144
	3			
O(2)—H(2)…O(1)	*x*, *y*, *z*	2.638(2)	2.12	119
O(2)—H(2)…O(4)	*x*, *y*, *z*	2.874(3)	2.30	126
O(2)—H(2)…O(5)	*x*, *y*, *z*	2.870(3)	2.44	113
O(6)—H(6)…O(1G)	1+*x*, *y*, *z*	2.651(3)	1.82	167
O(1H)—H(1H)…O(3)	–1+*x*, *y*, *z*	2.714(3)	1.92	154
O(2A)—H(2A)…O(1A)	*x*, *y*, *z*	2.716(2)	2.24	116
O(2A)—H(2A)…O(8A)	*x*, *y*, *z*	2.696(2)	1.97	144
O(1G)—H(1G)…O(7A)	*x*, *y*, 1+*z*	2.787(3)	2.00	157
O(6A)—H(6A)…O(1H)	*x*, *y*, –1+*z*	2.561(2)	1.74	171
C(21A)—H(21C)…O(6A)	*x*, *y*, *z*	3.329(3)	2.44	150
C(53B)—H(53E)…O(2A)	*x*, *y*,*z*	3.410(3)	2.65	134
C(33)—H(33B)…O(3A)	1+*x*, 1.5– *y*, 0.5+*z*	3.397(3)	2.56	143
	4			
O(2)—H(2)…O(1)	*x*, *y*, *z*	2.646(2)	2.15	117
O(2)—H(2)…O(8)	*x*, *y*, *z*	2.845(2)	2.19	135
O(2)—H(2)…O(5)	*x*, *y*, *z*	2.875(2)	2.52	107
O(6)—H(6)…O(1G)	1+*x*, 1.5–*y*, 0.5+*z*	2.558(2)	1.73	167
O(1H)—H(1H)…O(3)	–1+*x*, 1.5–*y*, –0.5+*z*	2.749(2)	1.93	165
O(2A)—H(2A)…O(1A)	*x*, *y*, *z*	2.694(2)	2.23	114
O(2A)—H(2A)…O(8A)	*x*, *y*, *z*	2.749(2)	2.01	147
O(1G)—H(1G)…O(7A)	*x*, *y*, *z*	2.805(3)	2.01	156
O(6A)—H(6A)…O(1H)	*x*, *y*, *z*	2.585(2)	1.75	174
C(21A)—H(21C)…O(6A)	*x*, *y*, *z*	3.311(3)	2.41	151
C(53A)—H(53C)…O(2A)	*x*, *y*, *z*	3.427(3)	2.64	137
C(33)—H(33A)…O(3A)	1+*x*, *y*, *z*	3.370(3)	2.56	140

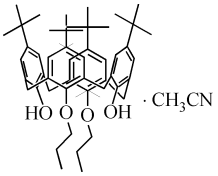
[a] *Centroid* means the centre of gravity of a corresponding aromatic ring as specified in Table 2.

Table 4

Molecular isometricity indexes comparing the calixarene molecules in space group $P2_1/c$ at different levels

$I(m)$ calculation	36 Heavy atoms	42 Heavy atoms	50 Heavy atoms	$I(m)$ calculation	36 Heavy atoms	42 Heavy atoms	50 Heavy atoms
3(1)/**3**(2)	97.850	90.726	57.036	**3**(1)/**5**[a]	67.950	68.136	—
3(1)/**4**(1)	94.267	95.047	71.306	**3**(2)/**5**	70.117	67.905	—
3(1)/**4**(2)	96.300	85.387	78.801	**4**(1)/**4**(2)	91.533	88.720	90.058
3(2)/**4**(1)	92.600	94.229	66.045	**4**(1)/**5**	67.217	61.517	—
3(2)/**4**(2)	98.067	87.609	65.734	**4**(2)/**5**	71.033	71.053	—

[a] Chemical formula of compound **5** [18]:



Inclusion formation of **2** with ethanol instead of methanol, yielding the complex **4**, leads only to a slight change in the calixarene conformation which, however, does not affect the packing structures. The crystal structures of both inclusion compounds, **3** and **4**, are characterized by layered arrangement of calixarene molecules extending parallel to the crystallographic *bc*-plane (Fig. 4). Interlayer association is carried out by the solvent molecules. Because of the occurrence of two independent calixarene molecules, the stacking order of molecular layers has to be described as …ASBS… (A, B = calixarene-1 and calixarene-2, respectively; S = solvent). The shortest intra-layer distances between calixarene aromatic core centroids are 10.53 and 11.62 Å whereas their inter-layer distance is 12.20 Å. It is worth mentioning that the layer structures of **3** and **4** deviate from packing modes recently discussed in the literature [18]. In another recent paper [19] it was demonstrated that a pair of similar calixarenes show drastically different affinity towards the formation of capsules, although molecular dynamic simulations predict very similar geometrical parameters. However, in the present cases of compounds, the formation of a strong intramolecular H-bond caused by the lower rim carboxylic group effectively influences the calixarene cavity resulting in a rather compact molecular geometry and prevents the formation of a capsule.

The cell similarity indices (π) as well as the molecular isometricity indices [I(*m*)] were estimated, covering in addition to the present compounds **1**, **3** and **4** a further known inclusion species **5** (see Table 4), which is the 1:1 acetonitrile inclusion of the synthetic intermediate dipropoxycalix[4]arene [20]. The cell similarity index (π) has been calculated as $\pi = [(a + b + c)/(a' + b' + c') - 1]$, where *a*, *b*, *c*, and *a*′, *b*′, *c*′ are the orthogonalized lattice parameters of the compared crystals [7]. In the event

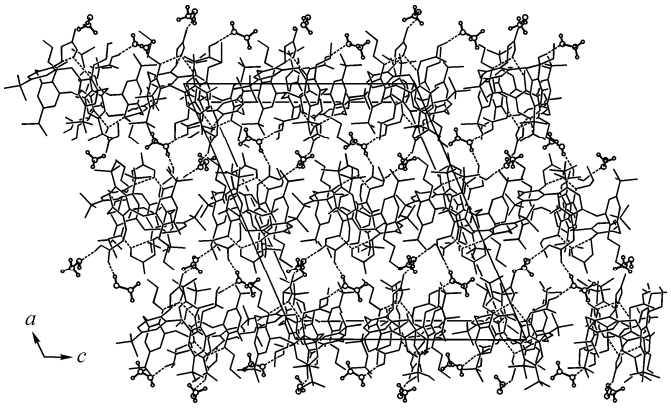


Fig. 4. Packing diagram of **3**, viewed along the crystallographic *b* axis. The calixarene molecules are represented in stick style, the solvent molecules are specified in ball-and-stick mode; broken lines represent hydrogen bonds

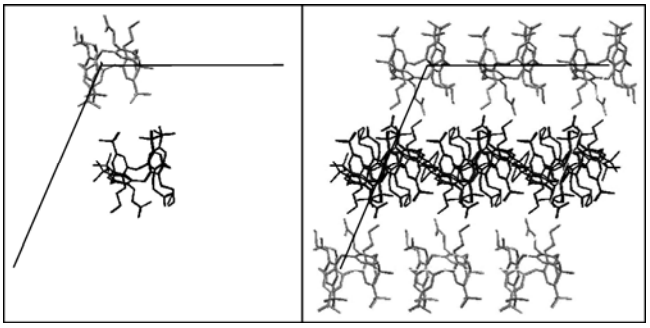


Fig. 5 (*left*). Superimposed packing arrangements of **3** and **4** involving two crystallographically independent calixarene molecules (1 and 2) in the crystal structure. Both molecular conformation and placement in the cell are more similar to the calixarenes-2 at the $a = 0$ sheet than calixarenes-1 at the $a = 1/2$ sheet

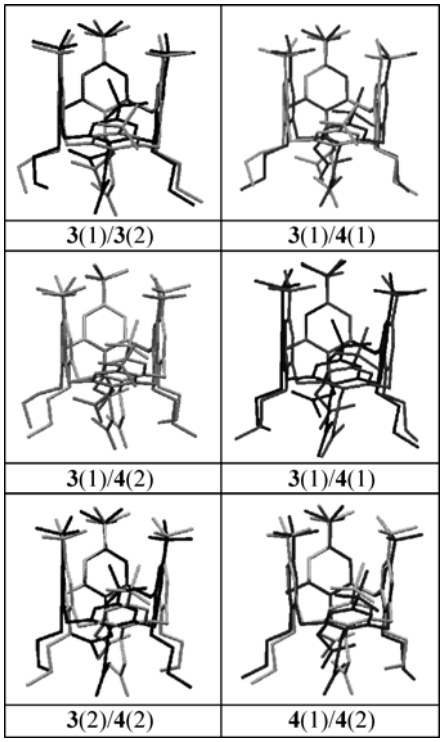


Fig. 6 (*right*). Comparison of the molecular conformations of calixarene **2** in its two complexes **3** and **4**. To enhance the differences in the molecular conformation, the aryl rings of the calixarenes in the back of the reader are superimposed on the figures

of great similarity of the two unit cells, the value of π is close to zero [21]. For the calculation of the isostructurality index [I(*s*)], the distance differences between the crystal coordinates of identical non-H atoms within the same section of the related structures were used [7], taking into account both the differences in the geometry of the molecules and the positional differences caused by rotation and translation. The molecular isometricity calculations were carried out by least-squares fitting of the positions occupied by the identical heavy atoms of the two related molecules [22].

Although **3**, **4** and **5** all crystallize in the same space group $P2_1/c$, only the cells of **3** and **4** are similar. The lower rim CH_2COOH substitution in **3** and **4**, in addition to the *n*-Pr substituents in **5**, cause different crystallographic packing, giving rise to a change in the number of host molecules in the asymmetric unit from one to two. Thus, cell similarity can only be calculated for **3** and **4**, being $\pi = 0.00223$. In the compounds **3** and **4**, the two crystallographically independent calixarene molecules are affected differently by the guest molecules that are MeOH and EtOH, respectively. The calixarenes-1 at the $a = 1/2$ sheet are more different in placement than the calixarenes-2 at the $a = 0$ sheet (Fig. 5). This is also true for the molecular isometricity. The isostructurality index for all 65 heavy atoms in case of the calixarene-1 is 37.352 % while for calixarene-2 it is 98.973 %.

Molecular similarity is examined within the asymmetric unit in case of $Z' = 2$ and among all cone conformational molecules that crystallize in space group $P2_1/c$ (Table 4 and Fig. 6). Since there are chemical differences between the calixarene in **5** and the isostructural pairs **3** and **4**, the molecular conformational comparison consists of three levels: (1) Comparison of 36 heavy atoms (no lower rim substituents, terminal methyl groups of the mostly rotating *tert*-butyl groups are also omitted from the calculation). (2) Comparison of 42 heavy atoms (*n*-Pr lower rim substituents are included, but terminal methyl groups of the mostly rotating *tert*-butyl groups are omitted from the calculation). (3) Comparison of 50 heavy atoms (both *n*-Pr and CH_2COO lower rim substituents are included, but terminal methyl groups of the mostly rotating *tert*-butyl groups are omitted from the calculation).

The following facts and conclusions can be drawn from the data (Table 4). (1) The substituents highly influence the conformation of the semi-rigid calixarene framework [**5** compared with **3**(1), **3**(2), **4**(1) and **4**(2)]. Hence, it is obvious that in case of the chemically identical substitution [**3**(1)—**4**(2)], the conformations of the calixarenes are largely conformable. (2) Taking into account the flexible propyl groups (42 heavy atoms), we observe a drop in the *I*(*m*) value. Thus, the presence of a guest mole-

cule has a smaller influence on the calixarene conformation than the substituents. (3) It also happens that a rather small chemical change in the guest molecule, from MeOH in **3** to EtOH in **4**, has a somewhat greater effect on one of the two crystallographically independent calixarene molecules. (4) Considering the carboxymethoxy units (50 heavy atoms) in the calculations, the values of $I(m)$ remain constant or do even increase in some cases. This observation corresponds to the interactions in the crystals of **3** and **4**, in particular demonstrated by the strong hydrogen bonds involving the carboxyl groups. By way of contrast, the propyl moieties display only weak van der Waals type interactions in the crystals, subjected to conformational effects due to the higher flexibility in the present complexes.

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