Crystallization of (012) Oriented Calcite Single Crystals Underneath Monolayers of Tetra(carboxymethoxy)calix[4]arenes

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Synthesis

Melting points were determined with a Electrothermal melting point apparatus and were uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX 500 spectrometer in CDCl$_3$ at room temperature (unless stated otherwise) with residual solvent.

Mass spectra were recorded with a Micromass VG Autospec X, Voyager DE spectrometer. Elemental analysis were carried out with a Perkin-Elmer 240 elemental analyzer. All reagents were reagent grade and used without further purification.

5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetrahydroxycalix[4]arene:

was prepared in 34 % yield by analogy to the standard procedure of the t-butylicalix[4]arene.$^{[1]}$ m.p. 249-251ºC (Toluol); $^1$H NMR (500 MHz, 25ºC, TMS: $\delta$ = 9.97 (s, 4 H, OH), 7.18-7.16 (m, 5 H, Tol), 6.99 (s, 8 H, ArH), 4.23 (s, 4 H, Ar-CH$_2$), 3.46 (s, 4 H, ArCH$_2$), 2.36 (s, 3 H, TolCH$_3$), 1.57 (s, 8 H, CCH$_2$), 1.23 (s, 24 H, CH$_3$), 0.54 (s, 36 H, CH$_3$). $^{13}$C NMR (125 MHz) $\delta$ = 146.28 (ArCO), 143.05 (ArCO$_2$), 129.04, 128.23, 127.61 (ArCCH$_2$), 126.39 (ArCH), 125.30, 57.26 (CH$_2$(CH$_3$)$_3$), 37.79 (C(CH$_3$)$_3$), 32.35 (C(CH$_3$)$_3$), 32.29 ((CH$_3$)$_2$C), 31.66 ((CH$_3$)$_3$C), 31.32 (CH$_2$Ar), 21.47.

MS (DCI, isobutane): m/z (%) 872.4 (95) [M]+, 801.5 (100); elemental analysis calcd for C$_{60}$H$_{88}$O$_4$ ⋅ C$_7$H$_8$: C 83.35; H 10.02; found: C 83.51, H 9.92.

5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(ethoxycarbonyl-methoxy)calix[4]arene:

The product was prepared according to a slightly modified procedure.$^{[2]}$ To a well-stirred suspension of 5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetrahydroxycalix[4]arene (14.29 g, 14.8 mmol) in anhydrous acetone (400 mL) was added ethyl bromoacetate (30 mL, 270 mmol) and potassium carbonate (34.5 g, 250 mmol). The mixture was refluxed for 4 d under an argon stream. After filtration, the filtrate was extracted with dichloromethane (3 × 50 mL). The combined organic layers were concentrated in vacuo and the residue was diluted in dichloromethane (300 mL). The solution was washed with hydrochloric acid (50 mL, 1 N) and water (3 × 100 mL). After drying over sodium sulfate, the organic layer was concentrated in vacuo. Subsequently the crude product was recrystallized from ethanol to give the desired product in 73 % yield: m.p. 143 – 145ºC; $^1$H NMR (500 MHz, 25ºC, TMS: $\delta$ = 6.74 (s, 8 H, ArH), 4.82 (s, 4 H, Ar-CH$_2$), 4.79 (s, 8 H, OCH$_2$COO), 4.19 (quart, $J$ = 7.1 Hz, 8 H, OCH$_2$CH$_3$), 3.17 (d, $J$ = 13.0 Hz, 4 H, Ar-CH$_2$), 1.53 (s, 8 H, CCH$_2$C), 1.27 (t, $J$ = 7.1 Hz, 12 H,OCH$_2$CH$_3$), 1.09 (s, 24 H, CH$_3$), 0.69 (s, 36 H, CH$_3$).

$^{13}$C-NMR (125 MHz) $\delta$ = 170.51 (COO), 153.05 (ArCO), 144.34 (ArCOC), 133.05 (ArCCH$_2$), 126.14 (ArCH), 71.42 (OCH$_2$CH$_3$), 60.27(OCH$_2$CH$_3$), 57.19 (CH$_2$(CH$_3$)$_3$), 37.79 (C(CH$_3$)$_3$), 32.30 (C(CH$_3$)$_3$), 32.17 (C(CH$_3$)$_3$), 31.78 (C(CH$_3$)$_3$), 31.18 (CH$_2$Ar), 14.18 (CH$_3$).


MS (DCI; ammonia): \( m/z \) (%) 1234.9 (100) [M + NH\(_4\)]\(^+\); elemental analysis calcd. for C\(_{76}H_{112}O_{12}\): C 74.96, H 9.27; found: C 74.96, H 9.08.

The product was prepared according to a slightly modified procedure.\(^3\) To a solution of 5,11,17,23-tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(ethoxy-carbonylmethoxy)calix[4]arene (1.72 g, 1.41 mmol) in tetrahydrofuran (70 mL) was added an aqueous solution of tetramethylammonium hydroxide (25 %, 36 mL, 100 mmol). After 24 h under reflux the suspension was concentrated under reduced pressure, the residue was dissolved in a 1:1 mixture of chloroform/water, washed with hydrochloric acid (2 × 30 mL) and water (3 × 30 mL). The organic layer was concentrated in vacuo and the crude product was recrystallized from acetonitrile (80 mL) to yield the final product in 86 % yield: m.p. 251-252ºC (CH\(_3\)CN); \(^1\)H NMR (500 MHz, 50ºC, TMS: \( \delta = 6.90 \) (s, 8H, ArH), 4.59 (br s, 12 H (ArCH\(_2\), CH\(_2\)COO), 3.25 (d, \( ^2J = 7.1 \) Hz, 4 H, ArCH\(_2\)), 1.96 (s, 3 H, CH\(_3\)CN), 1.55 (s, 8 H, CCH\(_2\)C), 1.14 (s, 24 H, CH\(_3\)), 0.66 (s, 36 H, CH\(_3\)).

\(^13\)C-NMR (125 MHz) \( \delta = 145.91 \) (ArCO), 132.99 (ArC\(_t\)Oc), 126.53 (ArCH, ArCCH\(_2\)), 72.62 (OCH\(_2\)), 57.23(CH\(_2\)C(CH\(_3\))\(_3\)), 37.98 (C(CH\(_3\))\(_2\)), 32.34 (C(CH\(_3\))\(_3\), 31.64 (C(CH\(_3\))\(_3\)), 31.05(C(CH\(_3\))\(_3\)), 30.66 (CH\(_2\)Ar), 1.91 (CH\(_3\)CN).

MALDI-MS (matrix 2,5-dihydroxybenzoic acid): \( m/z \) 1127 [M + Na\(^+\)], 1141 [M + K\(^+\)]; elemental analysis calcd for C\(_{76}H_{112}O_{12}\) ⋅ CH\(_3\)CN: C 73.33, H 8.70, N 1.22; found: C 73.67, H 9.05, N 1.11.

Calcium complex of 5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(carboxymethoxy)calix[4]arene (2):
5,11,17,23-Tetrakis-(1,1,3,3-tetramethylbutyl)-25,26,27,28-tetra(carboxymethoxy)calix[4]arene (55 mg, 0.05 mmol) was suspended with calcium hydroxide (7.4 mg, 0.1 mmol) in H\(_2\)O (5 mL). The suspension was treated ultrasonically and centrifuged. The pellet was suspended in H\(_2\)O (5 mL), treated ultrasonically and was centrifuged. The wet residue was dissolved in DMSO (5 mL) and crystallized at 98ºC. Colourless crystals were obtained after 3 days. 

\(^1\)H NMR (500 MHz, 50ºC, TMS): \( \delta = 7.07 \) (d, \( ^2J = 19.1 \) Hz, 8 H, ArH), 4.27, 3.35 (dd, \( ^2J = 12.3 \) Hz, 8 H, ArCH\(_2\)), 5.10, 3.96 (dd, \( ^2J = 14.3 \) Hz, 8 H, CH\(_2\)COO), 1.52 (s, 8 H, CCH\(_2\)C), 1.21 (s, 24 H, CH\(_3\)), 0.48 (s, 36 H, CH\(_3\)).

\(^13\)C-NMR (125 MHz) \( \delta = 175.50 \) (COO), 150.12 (ArCO), 147.41(ArC\(_t\)Oc), 134.45 (ArCCH\(_2\)), 126.72 (ArCH), 77.87 (OCH\(_2\)), 57.23 (CH\(_2\)C(CH\(_3\))\(_3\)), 40.97 (CSO), 38.05 (C(CH\(_3\))\(_2\)), 32.31 (C(CH\(_3\))\(_3\)), 31.47 (C(CH\(_3\))\(_2\)), 31.07 (C(CH\(_3\))\(_3\)), 30.72 (CH\(_2\)Ar).

Elemental analysis calcd. for [Ca (C\(_{68}H_{92}O_{12}Ca) (DMSO)\(_2\) (H\(_2\)O) ] ⋅ (DMSO)\(_2\)\(_5\): C 60.33, H 7.90; found: C 58.72, H 7.94.