

Experimental Part

General:

All reagents were purchased from commercial sources and used without further purification. *p*-tertbutylthiacalix[4]arene **1** was prepared according to the literature (Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971).

¹H NMR spectra were recorded at room temperature on a Bruker (300 MHz) NMR spectrometer.

FT-IR spectra were recorded on a Perkin Elmer spectrometer.

Mass spectra (MS(ES+)) were obtained on a MALDI-TOF Dynamo Finnigan mass spectrometer using 1,8,9-Trihydroxyanthracene or *p*-nitroaniline as matrix.

Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

Powder diffraction studies (PXRD) diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K α radiation with a scanning range between 3.8 and 40° using a scan step size of 2°/mn.

Synthesis

25,26,27,28-tetrakis[O-(4-cyano)benzyloxy]-5,11,17,23-tetra-*p*-tert-butyl-2,8,14,20-tetrathiacalix[4]arene **2**

A mixture of *p*-tert-butylthiacalix[4]arene **1** (0.50 g, 0.69 mmol), M₂CO₃ (13.90 mmol) [M = Na (1.47 g), K (1.91 g), Cs (4.53 g)], 4-(bromomethyl)benzotrile (2.18 g, 11.12 mmol), KI (catalytic amount) in dry acetone (35 mL) was refluxed for 7 days under argon. The solvent was evaporated to dryness and the residue was treated with 2M HCl (30 mL) and extracted with dichloromethane (3×30 mL). The organic layers were combined and dried over MgSO₄, before the solvent was evaporated. The residue was precipitated from a mixture of CHCl₃-MeOH (1/5, 30 mL) to afford the crude tetra-substituted product **2** as a mixture of conformers.

Na₂CO₃: 0.68 g (yield 83%). According to ¹H-NMR spectrum, the crude product was a mixture of all possible conformers with a ratio (*I,3-A*)/(*I,2-A*)/*C/PC* of 8/1/1/4.

K₂CO₃: 0.71 g (yield 87%). According to ¹H-NMR spectrum, the crude product consists of *1,3-alternate*, *1,2-alternate* and *partial cone* conformers in 6/1/1 ratio, respectively, with traces of *cone* conformer. The pure *1,3-alternate* conformer was obtained as a white powder by fractional recrystallisation from CH₂Cl₂-MeOH in 40% yield (0.33 g).

Cs₂CO₃: 0.72 g (yield 88%). According to ¹H-NMR spectrum, the crude product was composed of *1,3-alternate* and *1,2-alternate* conformers in 5/1.5 ratio, respectively, with traces of *partial cone* conformer.

For the *1,3-A* conformer:

Mp: 296-298 °C ; FTIR (KBr): $\nu_{C\equiv N} = 2229 \text{ cm}^{-1}$ (CN); MALDI TOF: 1181 *m/z* (M⁺), 1203 *m/z* (M⁺Na⁺); Elemental Analysis: % *calculated*: C: 73.18; H: 5.76; N: 4.74, % *found*: C: 73.39; H: 5.66; N: 4.62.

¹H-NMR (CDCl₃, 300 MHz, 25°C): δ (ppm) = 0.84 (s, 36H, *t*-Bu); 5.14 (s, 8H, OCH₂); 7.04 (d, 8H, J = 8.1 Hz, ArH[substituent]); 7.08 (s, 8H, ArH[calix]); 7.34 (d, 8H, J = 8.1 Hz, ArH[substituent]); ¹³C-NMR (CDCl₃, 300MHz, 25°C): δ (ppm) = 30.8, 34.1, 69.8, 111.5,

118.7, 128.1, 128.5, 128.6, 132.0, 142.5, 147.3, 155.9.
IR (KBr): $\nu_{\text{C}\equiv\text{N}} = 2229 \text{ cm}^{-1}$.

	Na ₂ CO ₃	K ₂ CO ₃	Cs ₂ CO ₃
<i>1,3-alternate</i>	8	6	5
<i>1,2-alternate</i>	1	1	1.5
<i>cone</i>	1	trace	-
<i>partial cone</i>	4	1	trace

Table TS1 Proportions of different conformers obtained for the synthesis of **2** using different alkali cations.

Crystallization conditions for **2**:

In a crystallization tube, a solution of compound **2** (3.0 mg, 0.0025 mmol) in CHCl₃ (0.5 mL) was layered with THF (0.25 mL). 1.0 mL of methanol was carefully added. Slow diffusion at room temperature produced colourless crystals suitable for X-ray diffraction after two months.

Crystallization of **2**-(AgNO₃)₁₀:

In a crystallization tube, a solution of compound **2** (3.0 mg, 0.0025 mmol) in CHCl₃ (0.50 mL) was layered with THF (0.25 mL). A solution of AgNO₃ (6.5 mg, 0.038 mmol) in MeOH (0.75 mL) was carefully added. Slow diffusion in the dark at room temperature produced colourless crystals suitable for X-ray diffraction after several days.

IR (KBr): $\nu_{\text{C}\equiv\text{N}} = 2253 \text{ cm}^{-1}$.