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Short Note

5,11,17,23-Tetra-*tert*-butyl-25-(2'-pyridylmethylamidocarbonylmethyl)-calix[4]arene

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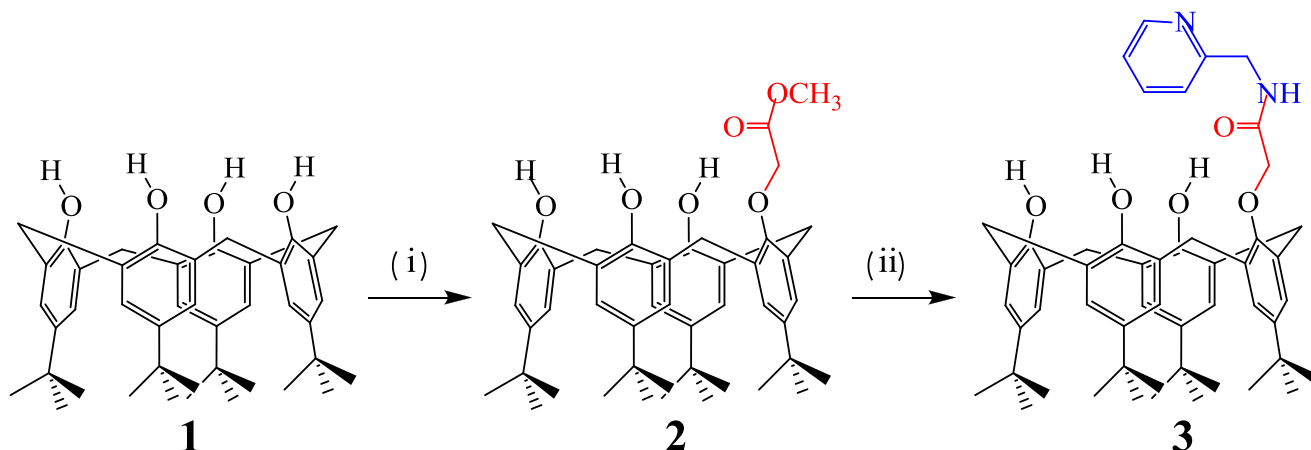
Abstract: 5,11,17,23-tetra-*tert*-butyl-25-(2'-pyridyl methyl amidocarbonylmethyl)-calix[4]arene (**3**) has been synthesized in the *cône* conformation through reaction of the corresponding mono-ester with 2-aminomethylpyridine (picolyamine) and characterised using ¹H NMR and MALDI-TOF mass spectral data as well as elemental analyses.

Keywords: calixarene; pyridine; amide

The present manuscript concerns a class of macrocycles widely used as complexing agents and as substrates for the construction of more elaborate receptors with broader applications. These macrocycles are the calix[n]arenes [1,2], macrocycles composed of n phenolic units (n = 4–20) connected by methylene bridges at positions ortho to the hydroxyl function. Their name derives from the perceived resemblance of the smallest calixarene, calix[4]arene, in its so-called *cone* configuration where all the hydroxyl groups are directed to the same side of the non-planar macrocycle, to the antique Greek vase known as a “*calix crater*” [3]. *Cone* calix[4]arene, in particular, may be considered as a ditopic receptor with a hydrophilic site defined by the hydroxyl groups and a hydrophobic cavity defined by the phenyl groups.

In earlier work [4,5], we have described the syntheses of several calixarene derivatives incorporating amido functional groups, including a tetra-amide derivative of calix[4]arene obtained from 2-aminomethylpyridine (picolyamine) which exhibited useful metal-ion binding properties [6]. The present work is part of our extended studies of this system aimed at evaluating the effect of varying the number of amido binding sites attached to the calix[4]arene scaffold.

Scheme 1. Synthesis of 5,11,17,23-tetra-tert-butyl-25-(2'-pyridylmethylamidocarbonylmethyl)-calix[4]arene (**3**). (i) K_2CO_3 , $BrCH_2CO_2CH_3$, acetone, reflux; 48 h (ii) $Py-CH_2-NH_2$, CH_3OH , $C_6H_5CH_3$, reflux, 5 days.



Experimental

All reagents and solvents for synthesis were commercial and used without further purification. All the reactions were performed under a N_2 atmosphere. TLC was carried out on Silica gel 60 F254 (Merck 1.05554.0001). SiO_2 (Geduran 1.11567) was used for column chromatography. 1H NMR spectra were recorded using a 300 MHz Bruker SY 200 instrument. Shifts (δ) are referenced relative to internal tetramethylsilane (TMS). Coupling constants J are given in Hertz. MALDI TOF mass spectra were measured on a Biflex Bruker instrument. Melting points were measured using an electrothermal Buchi 535 melting point (Mp) apparatus and are reported uncorrected. Elemental analyses were performed by the Microanalytical Service of the University of Strasbourg. 5,11,17,23-tetra-tert-butyl-25-(methoxycarbonylmethyl)-calix[4]arene **2** was prepared according to the literature [7].

Preparation of **3**: 5,11,17,23-tetra-tert-butyl-25-(methoxycarbonylmethyl)-calix[4]arene **2** (0.600 g; 0.90 mmol) was reacted with an excess of 2-(aminomethyl)pyridine (0.94 g; 1.79 mmol) in a refluxing 1:1 mixture of methanol–toluene (6 mL) for 5 days. The solvents were evaporated and the residue was chromatographed on a silica column using CH_2Cl_2/CH_3OH 96/04 as eluent. Pure **3** was obtained as a white solid (143 mg, 20%).

Melting point: 240–242 °C.

MALDI TOF mass spectrum: $m/z = 797.80$ ($[M+H]^+$).

1H -NMR (300 MHz, $CDCl_3$) (δ/ppm): 9.72 (t, $J = 5.0$ Hz, 1H, NH), 9.12 (s, 2H, OH), 8.86 (s, 1H, OH) 8.70 (d, $J = 7.5$ Hz, 1H, PyH_6), 7.72 (t, $J = 7.5$ Hz, 1H, PyH_5), 7.45 (d, $J = 7.5$ Hz, 1H, PyH_3), 7.20 (t, $J = 7.5$ Hz, 1H, PyH_4), 7.10 (s, 2H, ArHmetacalix), 7.07 (s, 4H, ArHmetacalix), 7.00 (d, $J = 1.5$ Hz, 2H, ArHmetacalix), 4.88 (d, $J = 5.5$ Hz, 2H, CH_2Py), 4.55 (s, 4H, $-CH_2OAr$), 4.25 (AB system, $J = 14.0$ Hz, 2H, Ar CH_2 Ar), 4.15 (AB system, $J = 14.0$ Hz, 2H, Ar CH_2 Ar), 3.53 (AB system, $J = 14.0$ Hz,

2H, ArCH₂Ar), 3.45 (AB system, $J = 14.0$ Hz, 2H, ArCH₂Ar), 1.23 (s, 9H, -C(CH₃)₃), 1.21 (s, 18H, C(CH₃)₃), 1.18 (s, 9H, -C(CH₃)₃).

Elemental analysis: Calculated for C₅₂H₆₄O₅N₂, C 78.35, H, 8.09; Found: C, 78.1, H, 8.08%.

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