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Preparation of Series of Calix[6]arenes and Calix[8]arenes derived from p-n-alkylphenols.

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Abstract. The preparation of series of p-n-alkylcalix[6]arenes and p-n-alkylcalix[8]arenes by p-n-alkylphenol-formaldehyde condensations in basic conditions is described.

For their interest in supramolecular chemistry[1] a large variety of macrocyclic compounds have been synthetized and their properties investigated as for instance crown-ethers[2], cryptates[3], cyclophanes[4], and cycloamyloses[5]. Peculiar concern has been paid to the design of multi-armed receptor molecules[6]. Multi-armed molecules refer to molecules in which long chains are attached to a central unit, giving to the molecule thus produced chemical and physical properties different from those of individual precursors[7].

The present Note reports the preparation of series of calixarenes[8] with six and eight units, 1 and 2 respectively, derived from p-n-alkylphenols substituted by linear hydrocarbon chains containing 8,10,14,16 and 18 carbons. Calixarenes were prepared by condensing the corresponding p-n-alkylphenols[9] with formaldehyde (CH_2O) in basic conditions[10]. They were selectively separated from the crude mixture by crystallization.

Preparation of the calixarenes 1 and 2. A typical procedure is given for p-n-decylcalixarenes 1-C10 and 2-C10 : a mixture of 11.72 g (50 mmoles) of p-n-decylphenol, 4.01 g (130 mmoles) of CH_2O, and 0.65 ml of 13N aqueous potassium hydroxyde (0.8 mmole) in 60 ml of tetralin was heated at 150°C under nitrogen for 4 hrs in a 250 ml flask equipped with Dean-Stark collector. The tetralin was evaporated under vacuum to yield a slurry yellow mixture which was precipited with 100 ml of acetone. 4.83 g of a white powder was filtered. This powder was shown to contain two products as detected by tlc (Merck plates 60 F_{254}, 230-240 mesh, using hexane-chloroform 66:33 as eluent). The solid was suspended in 150 ml of ethyl acetate. The solid part was separated by succion and dried under high vaccuum. This solid corresponds to pure 2-C10. Rf = 0.75. mp > 300°C. ^1H nmr ($CDCl_3$) in ppm from tms : 0.60-1.65 (m, 19H, aliphatics), 2.18-2.28 (broad t, aromatic-CH_2-aliphatics), 3.16 (s, large, 1H, aromatic-CH_AH_B-aromatic), 4.13 (s large, 1H, aromatic-CH_AH_B-aromatic), 6.72 (s, 2H, aromatics), 9.39 (s, 1H, phenolic-OH) 10% yield. Evaporation of the remaining solvent left a residue containing only 1-C10. Rf = 0.63. mp 204-205°C. ^1H nmr ($CDCl_3$) : 0.68-1.69 (m, 19H, aliphatics), 2.12-2.58 (broad t, aromatic - CH_2-aliphatic), 3.74 (s, 2H, aromatic-CH_2-aromatic), 6.85 (s, 2H, aromatics), 10.27 (s, 1H, phenolic-OH). 12% yield.

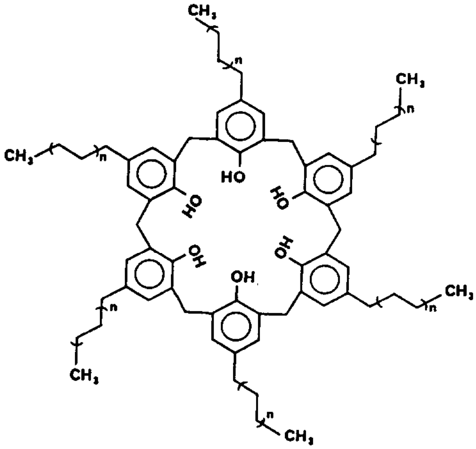
p-n-Octylcalixarenes 1-C8 and 2-C8 have already been described[11]. We also produced them in our reaction conditions[9] and used them as standard for the rest of the series. Analytical data were in agreement with the proposed structures of 1 et 2.

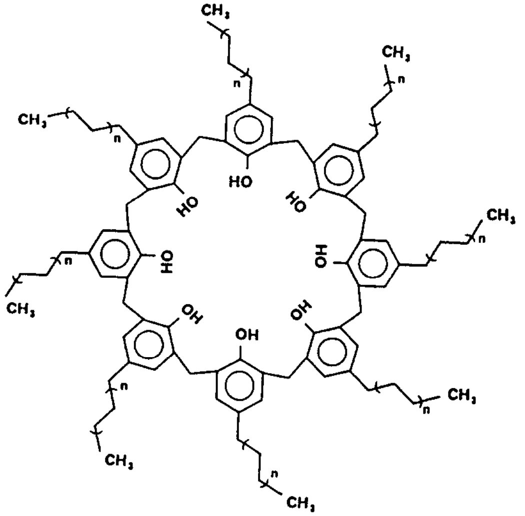
Physical data. We noted that the calix[6]arenes 1 are melting at lower mps (from 110-111°C to 230-231°C) than of calix[8]arenes 2 (from 270-271°C to 350-365°C).

^1H nmr ($CDCl_3$) spectra of calix[6]arenes 1 present three single peaks for methylenes (from 3.61 to 3.83 ppm), aromatics (from 6.91 to 7.02 ppm), and phenolic-OH (from 10.27 to 10.30 ppm). ^1H mmr spectra of calix[8] arenes 2 present four single signals for methylenes (two large singlets at ca 4.10 ppm and 3.10 ppm, aromatics (from 6.71 to 6.93 ppm) and phenolic-OH (from 9.30 to 9.54 ppm).

At 56°C in $CDCl_3$ the aromatic-CH_AH_B-aromatic resonances of p-n-octylcalix[8]arene <u>2-C8</u> show a singlet at 3.59 ppm. At 28°C the singlet splits into two broad singlets at 3.27 and 4.10 ppm. At-6°C one observes an AB system with J_{AB} = 12.2Hz. The temperature of coalescence is 35°C leading to a ΔG_{35} value equal to 14.8 kcal/mole[12]. No coalescence is observed in pyridine-d_5 from-20°C to 37°C. According to Gutsche[8], this behaviour is rationalized by the presence of intramolecular H-bond arrays, due to neighbouring of phenolic-OH, and rigidifying calix[8]arene in poor H-bonding solvent such as $CDCl_3$. On the reverse, in the presence of solvent such as pyridine-d_5 able to H-bond the phenolic-OH, the effect desappears[8].

Unfortunately, preliminary investigations with the polarized microscope show that 1 and 2 do not present tubular[13] nor columnar[14] mesophases. We are presently testing their behaviour as membrane surfactants[15].





n = 3, 4, 5, 6, 7, 8

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