Porous Surfactants from Cone Conformers of Calix[5]arenes[1]

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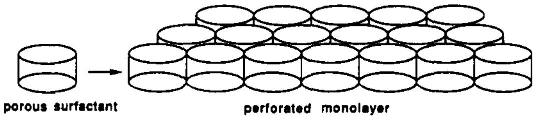
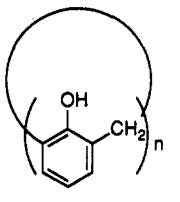
Received August 31, 1993•

Summary: This paper describes the synthesis and monolayer properties of two porous surfactants derived from the calix[5]arene framework that exist as stable cone conformers [i.e., 5,11,17,23,29-pentaformyl-31,32,33,34,35-pentakis(*n*-octyloxy)calix[5]arene (**1a**) and an *N,N*-dimethylthioamide derivative **2a**] plus calix[4]arene and calix[6]arene analogs. The introduction of **1a**, in and of itself, represents a significant advance in the calixarene area because it provides access to a wide-cavity calixarene that is amenable for further modification at its wider rim.

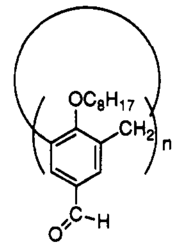
Calixarenes have proven to be versatile starting material for the synthesis of a broad range of host molecules and ligands.[2,3] The fact that they can be prepared in a variety of ring sizes also makes them attractive as frameworks for constructing "porous" surfactants and "perforated" monolayers.[4-6] We have recently chosen to explore the chemistry of calix[5]arenes for two reasons. First, examination of CPK molecular models suggests that their internal pore diameter (ca. 3.6 Å) should be ideally suited for the separation of gas mixtures that are of considerable current interest, e.g., H_2/N_2, H_2/CH_4, and H_2/CO.[7] Second, in contrast to the extensively investigated calix[4]arenes and calix[6]arenes, very little is known about the conformational stability of these intermediate cyclic pentamers.[8]



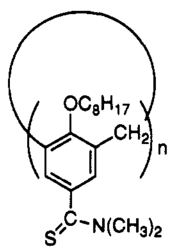
In this paper, we report the synthesis and monolayer properties of two porous surfactants derived from calix[5]arene (**1a**, **2a**), which exist as *stable cone conformers*. We also describe the synthesis and surfactant behavior of calix[4]arene and calix[6]arene analogs **1b**, **2b**, and **1c**, **2c**, respectively. The introduction of **1a**, in and of itself, represents a significant advance in the calixarene area because it provides access to a wide-cavity calixarene that is amenable for further modification at its wider rim.[9-11]



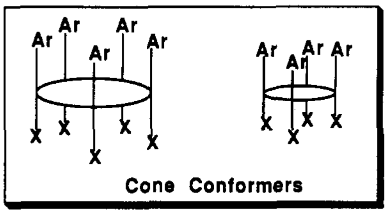
Calix[n]arene



1a, n=5 (cone)
b, n=4 (cone)
c, n=6



2a, n=5 (cone)
b, n=4 (cone)
c, n=6



Cone Conformers

Alkylation of calix[5]arene with 1-bromooctane, using procedures similar to those previously described,[5] afforded 31,32,33,34,35-pentakis(*n*-octyloxy)calix[5]arene in 91% isolated yield. A portion of this pentaether (0.071 g, 0.065 mmol), dissolved in 0.4 mL of $CHCl_3$, was added dropwise (100 min) to a stirred solution of $TiCl_4$ (1.75 g, 9.22 mmol), α,α-dichloromethyl methyl ether (2.12 g, 18.4 mmol), and $CHCl_3$ (1 mL) that was maintained at 45 °C under a nitrogen atmosphere.[12] Immediately after the addition was completed, the resulting reddish-brown mixture was cooled to 10 °C and poured onto 10 mL of ice-water. The organic layer, after being combined with $CHCl_3$ extracts of the aqueous phase, was washed with water and concentrated under reduced pressure. Purification by preparative TLC [$R_f = 0.2$, silica, $CHCl_3$/ether (9/1, v/v)] and recrystallization from diethyl ether afforded 22.5 mg (28%) of 5,11,17,23,29-pentaformyl-31,32,33,34,35-pentakis(*n*-octyloxy)calix[5]arene (**1a**), having a ^1H NMR spectrum that is shown in Figure 1.[13,14] The bridging methylene protons, which appear as two distinct doublets (δ 3.45 and 4.55, J_{AB}= 15.2 Hz), readily identify this structure as a cone conformer.[2,3] An analogous calix[4]arene (**1b**) displays very similar spectral features (Figure 1).[13] In sharp contrast, the bridging methylene protons

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• Abstract published in *Advance ACS Abstracts*, November 1, 1993.

[1] Supported by the Divison of Basic Energy Sciences and the Department of Energy (DE-FG02-85ER-13403).

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[13] Compound **1a**: mp 163-164 °C; ^1H NMR (90 MHz, $CDCl_3$, 55 °C) δ 0.85 (t, 15 H, CH_3), 1.3 (brs, 50 H, CH_2), 1.6-2.0 (brm, 10 H, CH_2), 3.45 (d, 5 H, ArCH, J_{AB} = 15.2 Hz), 3.85 (t, 10 H, OCH_2), 4.55 (d, 5 H, ArCH, J_{AB} = 15.2 Hz), 7.35 (s, 10 H, ArH), 9.65 (s, 5 H, CHO). Anal. Calcd for $C_{80}H_{110}O_{10}$: C, 78.01; H, 9.00. Found: C, 77.73; H, 8.99. Compound **1b**: mp 120-121 °C; ^1H NMR (90 MHz, $CDCl_3$, 55 °C) δ 0.90 (t, 12 H, CH_3), 1.35 (brs, 40 H, CH_2), 1.6-2.05 (brm, 8 H, CH_2), 3.30 (d, 4 H, ArCH, J_{AB} = 13.0 Hz), 3.95 (t, 8 H, OCH_2), 4.50 (d, 4 H, ArCH, J_{AB} = 13.0 Hz), 7.15 (s, 8 H, ArH), 9.55 (s, 4 H, CHO). Anal. Calcd for $C_{64}H_{88}O_8$: C, 78.01; H, 9.00. Found: C, 77.42; H, 8.88. Compound **1c**: mp 174-175 °C; ^1H NMR (90 MHz, $CDCl_3$, 55 °C) δ 0.85 (t, 18 H, CH_3), 1.3 (brs, 60 H, CH_2), 1.4-1.85 (brm, 12 H, CH_2), 3.80 (t, 12 H, OCH_2), 4.1 (s, 12 H, $ArCH_2$), 7.35 (s, 12 H, ArH), 9.50 (s, 6 H, CHO). Anal. Calcd for $C_{96}H_{132}O_{12}$: C, 78.01; H, 9.00. Found: C, 77.02; H, 8.74. The isolated yields of **1b** and **1c** from the alkylated calixarene precursors were 52% and 57%, respectively.

[14] Other formylated (noncone) and partially-formylated calix[5]arene compounds were also present in the product mixture; no effort was made to fully characterize these side products.

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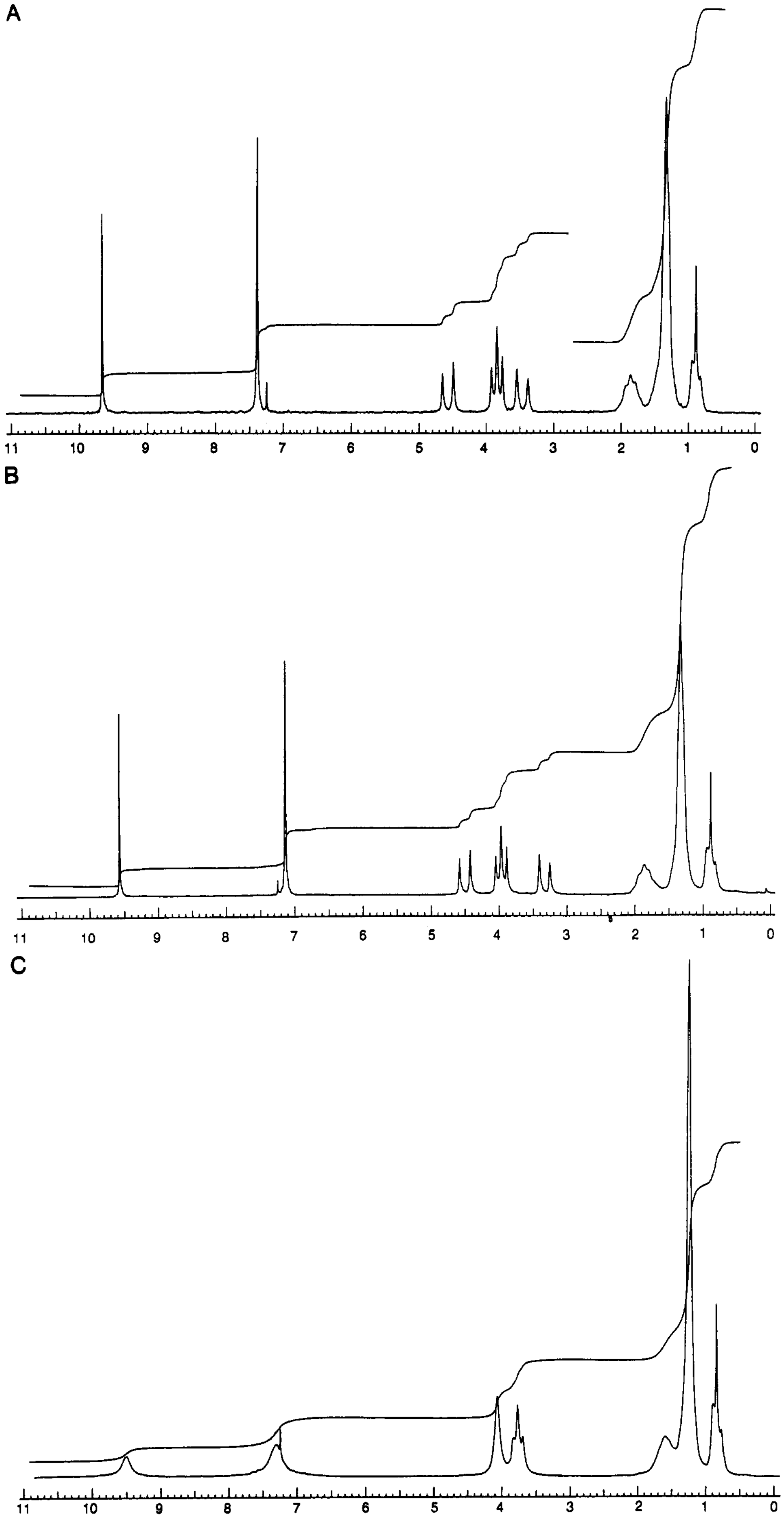

Figure 1. ^{1}H NMR (90 MHz, $CDCl_3$, 55 °C) spectra of (A) **1a**, (B) **1b**, (C) **1c**; residual solvent protons (δ 7.25) were used as an internal reference.

of the cyclic hexamer (**1c**) appear as a singlet (δ 4.1), which indicates that the aromatic units are free to rotate through the annulus of the calixarene.[2,3]

The feasibility of derivatizing **1a**, with retention of its cone conformation, was established by direct conversion to **2a**. Thus, a suspension of **1a** (22.5 mg, 18.3 mmol), dimethylamine hydrochloride (37.2 mg, 0.456 mmol), anhydrous sodium acetate (37.5 mg, 0.456 mmol), and elemental sulfur (14.6 mg, 0.456 mmol) in 2 mL of dry DMF was stirred at 50 °C for 15 h under nitrogen.[15] Subsequent cooling to room temperature, quenching with water, extraction with $CHCl_3$, concentration under reduced pressure, and purification by preparative TLC [$R_f = 0.62$, silica, $CHCl_3/CH_3OH$ (50/1, v/v)], followed by recrystallization from methanol, afforded 22.5 mg (81%) of **2a**.[16] By use of similar procedures, **1b** and **1c** were converted into **2b** and **2c**, respectively.[16]

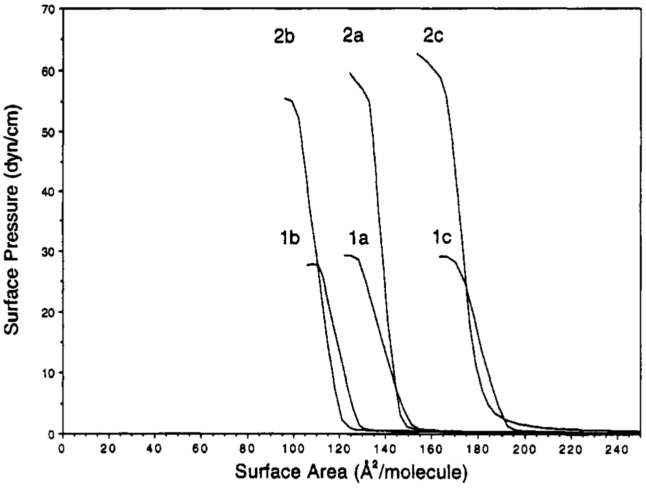

Figure 2. Surface pressure–area isotherms for monolayers of **1a**–**1c** and **2a**–**c** over a pure water subphase at 25 °C.

Each of the above calixarenes produced stable monolayers at the air–water interface (Figure 2).[17,18] The limiting area for **1a**, estimated by drawing a tangent from the condensed portion of the force–area isotherm to 0 dyn/cm, was 151 ± 2 Å^2/molecule; the limiting areas for **1b** and **1c** were 128 ± 2 and 190 ± 3 Å^2/molecule, respectively. Complete replacement of the aldehyde moieties with *N*,*N*-dimethylthioamide groups resulted in calixarenes that formed less compressible monolayers which were stable up to ca. 55 dyn/cm. The limiting areas for **2a**, **2b**, and **2c** were 144 ± 3, 119 ± 3, and 181 ± 3 Å^2/molecule, respectively. Efforts aimed at cross-linking such calixarene assemblies are now in progress.

The accessibility of wide-cavity calix[5]arenes, of the type described herein, raises entirely new prospects for the design and synthesis of novel classes of molecular hosts, ligands, and pores. Given the wealth of cone structures that has already emerged from the calix[4]arene framework, we expect that cone conformers of calix[5]arenes will lead to rich and rewarding new chemistry.[19,20]

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(16) Compound **2a**: mp 258–259 °C; ^{1}H NMR (90 MHz, $CDCl_2CDCl_2$, 140 °C) δ 0.85 (brt, 15 H, CH_3), 1.35 (brs, 50 H, CH_2), 1.7–2.1 (brm, 10 H, CH_2), 3.05 (brs, 30 H, CH_3N), 3.25 (d, 5 H, ArCH, J_{AB} = 15.2 Hz), 3.85 (t, 10 H, OCH_2), 4.6 (d, 5 H, ArCH, J_{AB} = 15.2 Hz), 6.9 (s, 10 H, ArH). Anal. Calcd for $C_{90}H_{135}N_5O_5S_5$: C, 70.77; H, 8.91; N, 4.58. Found: C, 70.53; H, 8.79; N, 4.70. Compound **2b**: mp 163–164 °C, ^{1}H NMR (90 MHz, $CDCl_3$, 55°C) δ 0.85 (brt, 12 H, CH_3), 1.35 (brs, 40 H, CH_2), 1.7–2.1 (brm, 8 H, CH_2), 2.75 (s, 12 H, CH_3N), 3.15 (d, 4 H, ArCH, J_{AB} = 13.0 Hz), 3.45 (s, 12 H, CH_3N), 3.85 (t, 8 H, OCH_2), 4.4 (d, 4 H, ArCH, J_{AB} = 13.0 Hz), 6.8 (s, 8 H, ArH). Anal. Calcd for $C_{72}H_{108}O_4N_4S_4$: C, 70.77; H, 8.91; N, 4.58. Found: C, 70.65; H, 8.88; N, 4.65. Compound **2c**: mp 240–241 °C, ^{1}H NMR (90 MHz, $CDCl_2CDCl_2$, 140 °C) δ 0.85 (brt, 18 H, CH_3), 1.35 (brs, 60 H, CH_2), 1.6–2.0 (brm, 12 H, CH_2), 3.05 (brs, 36 H, CH_3N), 3.8 (t, 12 H, OCH_2), 4.0–4.4 (brs, 12 H, $ArCH_2$), 6.9 (brs, 12 H, ArH). Anal. Calcd for $C_{108}H_{162}O_6N_6S_6$: C, 70.77; H, 8.91; N, 4.58. Found: 70.53; H, 8.76; N, 4.55. The isolated yields of **2b** and **2c** from the aldehydic calixarene precursors were 93% and 63%, respectively.

(17) Specific methods that were used to determine surface pressure–area isotherms were similar to those previously described: Conner, M.; Kudelka, I.; Regen, S. L. *Langmuir* **1991**, *7*, 982.

(18) A minimum of three isotherms were recorded for each surfactant; limiting areas are reported along with an error of one standard deviation.

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