TECHNICAL REPORT OF DOE-PROGRAM DE-FG02-85ER-13403

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Summary

Our research over this past grant period has focused on (i) developing methods for making *in situ* permeation measurements at the air-water interface, (ii) defining the structural and conformational behavior of selected calix[4]arenes, (iii) defining the metal complexation properties of certain upper-rim functionalized calix[4]arenes, and (iv) synthesizing a broad series of polymerizable calixarenes, to be used for constructing perforated monolayers and multilayers. The following is a brief summary of our efforts:

(i) In Situ Permeation Measurements At The Air-Water Interface. In order to be able to define the porosity of perforated monolayers, directly at the air-water interface, we have developed a method which enables us to measure the loss of organic molecules from the aqueous phase into air; i.e., a quantitative method for following pervaporation from water. A schematic illustration of our device is shown in Figure 1. In essence, a Teflon trough is charged with an aqueous subphase that contains one or more of the desired organic permeants; e.g., tetrahydrofuran (THF). The trough is then enclosed in a plexiglass box that is equipped with a removable lid and a nitrogen inlet and outlet. The outlet is connected to a six-port valve which leads to a Varian 6000 gas chromatograph, equipped with a HP-5 30 M X 0.64 mm megabore capillary column and a flame ionization detector. Experiments that are now in progress are aimed at analyzing, quantitatively, the permeation rate of THF (and related ethers) through the air-water interface, and also through monolayers of calixarenes that have been assembled at the air-water interface.

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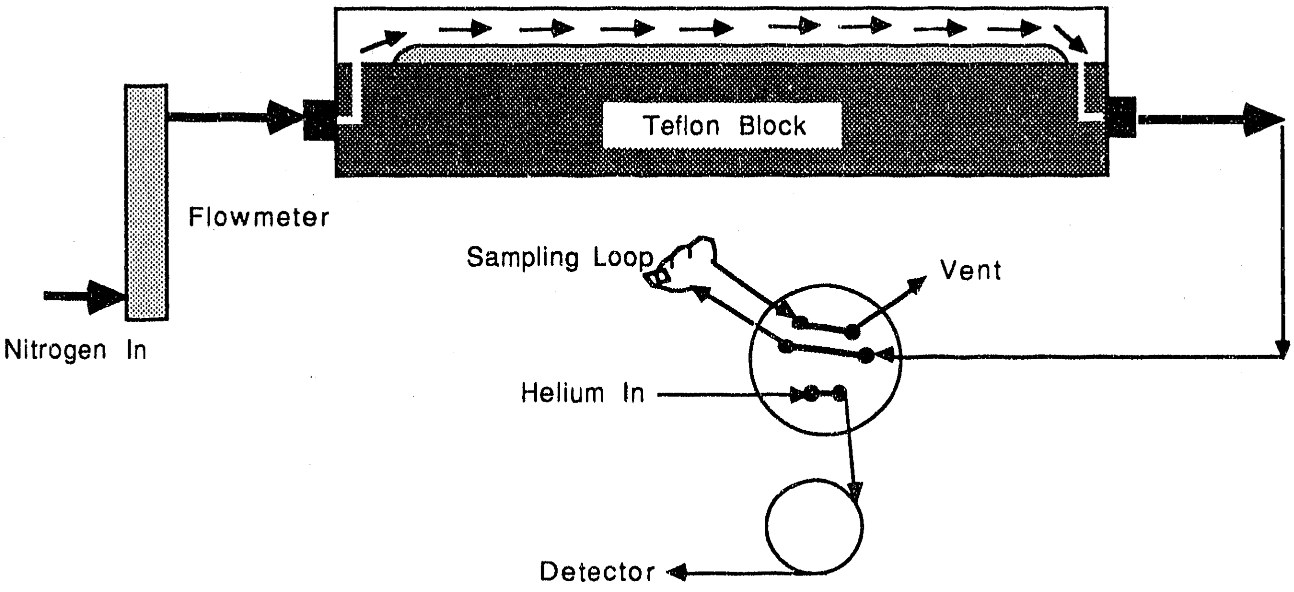
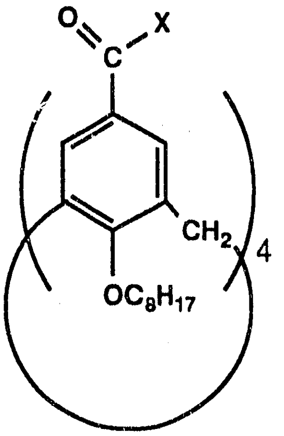
Figure 1

In-Situ Permeation Experiments



(ii) Pinched-Cone Conformers of Calix[4]arenes. During the course of our studies dealing with the construction of perforated monolayers, we had need for the tetrasubstituted calix[4]arenes **I** and **II**. While the synthesis of these compounds proved to be straightforward, it soon became apparent that both compounds showed unusual spectral properties. Our principal findings, which have recently appeared in the *Journal of the American Chemical Society*, provide the first direct evidence that pinched-cone conformers can play a major role in the overall structure and dynamics of the calix[4]arene framework. In brief, the cone conformational isomer of 5,11,17,23-tetracarboxy-25,26,27,28-tetra-*n*-octylcalix[4]arene (**I**) and 5,11,17,23-tetracarboxamido-25,26,27,28-tetra-*n*-octylcalix[4]arene (**II**) have been synthesized and found to exist as equilibrating C_{2v} structures. Evidence in support of this conclusion has been obtained from

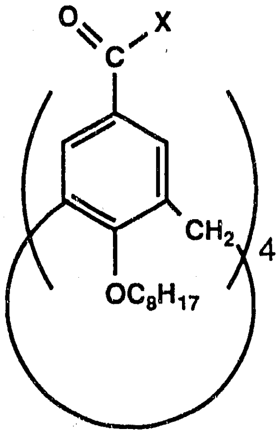
variable temperature ^1H NMR spectroscopy, using $CDCl_2CDCl_2$ as the solvent. These findings represent the first experimental evidence for the existence of C_{2v} conformational isomers of a calix[4]arene *in solution.* The free energy of activation for the interconversion, calculated from the temperature at which the aromatic protons coalesce from two singlets to one, was 14.1 kcal mol^{-1} for **I** at 45°C, and 13.3 kcal mol^{-1} for **II** at -4°C. The *appearance* of **I** and **II** as C_{4v} isomers in DMSO-d_6, together with a large deuterium isotope effect on T_c in $CDCl_2CDCl_2$ (T_c is raised ~25° for **I** and ~19° for **II**) and the *appearance* of a methyl ester analog of **I** as a C_{4v} structure in $CDCl_2CDCl_2$, provide strong evidence that internal hydrogen bonding contributes, significantly, to the barrier for interconversion.



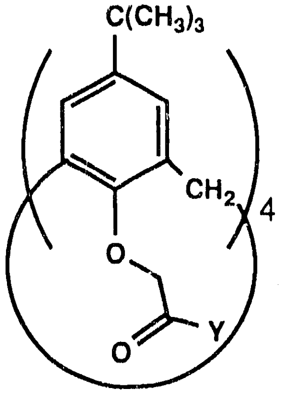
I, X=OH
II, X=NH_2
III, X=OCH_3

(iii) Synthesis and Alkali Metal Binding Properties of "Upper-Rim" Functionalized Calix[4]arenes. Calixarenes are receiving considerable attention as starting material for the preparation of novel hosts, ligands and pores. Of special interest, in this regard, has been the use of the *cone*-conformer of calix[4]arenes. Previous studies have shown that certain lower rim (phenolic side) ester and amide derivatives of calix[4]arene cones are effective in extracting alkali metal picrates from water into chloroform, and that sodium salts are strongly favored. To date, no effort has been made to examine the extracting behavior of upper-rim analogs. Because of the splay that is inherent in the calix[4]arene framework, one might expect that placement of ligands on the upper rim could result in stronger binding toward larger metal ions, and that extraction of potasium or cesium salts might be favored.

The fact that calix[4]arenes have moderate flexibility, however, makes it difficult to predict their precise complexation and selectivity features. In order to probe this issue, we have synthesized calixarenes **I-III**, and have compared their extracting behavior with those previously reported for a lower-rim functionalized ester (**IV**).



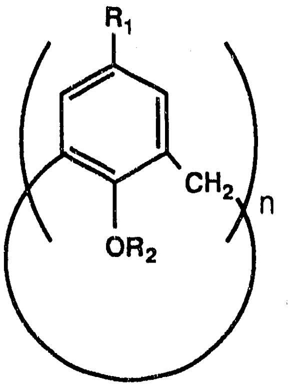
I, X=CH_3
II, X=OCH_3
III, X=NH_2



IV, Y=$OC(CH_3)_3$

Alkylation of 25,26,27,28-tetrahydroxycalix[4]arene with 1-bromooctane afforded the corresponding tetra-*n*-octyloxyether, which was readily isolated as the *cone* isomer. Friedel-Crafts acylation (CH_3COCl) of this tetraether afforded 5,11,17,23-tetraacetyl-25,26,27,28-tetrakis-(1-*n*-octyloxy)calix[4]arene (**I**); subsequent haloform oxidation, and esterification (CH_2N_2), yielded 5,11,17,23-tetracarboxymethyl-25,26,27,28-tetrakis-(1-*n*-octyloxy)calix[4]arene (**II**). 5,11,17,23-Tetracarboxamido-25,26,27,28-tetraoctyloxycalix[4]arene (**III**) was prepared by bromination of the starting tetra-*n*-octyloxyether (NBS), followed by sequential displacement with cyanide and hydrolysis. Calix[4]arenes **I-III** proved to be effective in extracting Li^+, Na^+, K^+, and Cs^+ picrates from water into chloroform. Unlike the extracting behavior of a previously reported lower-rim ester derivative, however, each showed similar extractability of sodium and potassium picrates, but significantly reduced efficacy toward lithium and cesium salts. Equilibrium extraction constants (K_e) for each calix[4]arene type have been obtained and are described in the enclosed manuscript.

(iv) Synthesis Of Novel Polymerizable Calixarenes. The following calixarenes have been synthesized, and are now being investigated in connection with their potential use as materials for perforated monolayer construction:



I, $R_1 = CH_2SH$; $R_2 = n\text{-}C_4H_9$; n=6
II, $R_1 = CH_2SH$; $R_2 = n\text{-}C_8H_{17}$; n=4
III, $R_1 = CONHCH_2CH_2SSCH_3$; $R_2 = C_8H_{17}$; n=4
IV, $R_1 = CONHCH_2CH_2SSCH_3$; $R_2 = C_8H_{17}$; n=6

The details of these syntheses will described in the next progress report.

Publications:

(i) "Pinched-Cone Conformers of Calix[4]arenes", M. Conner, V. Janout, and S. L. Regen, *J. Am. Chem. Soc.*, **1991**, *113*, 9670.

(ii) "Synthesis and Alkali Metal Binding Properties of "Upper-Rim" Functionalized Calix[4]arenes", *J. Org. Chem.*, submitted for publication.

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