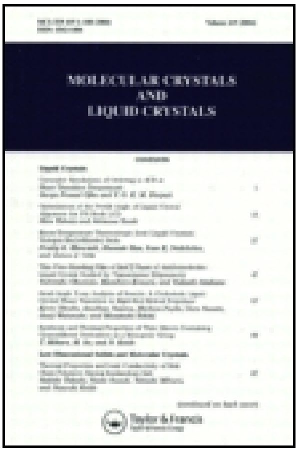

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Langmuir Monolayers of p-Octadecylbishomooxacalix[4]Arene

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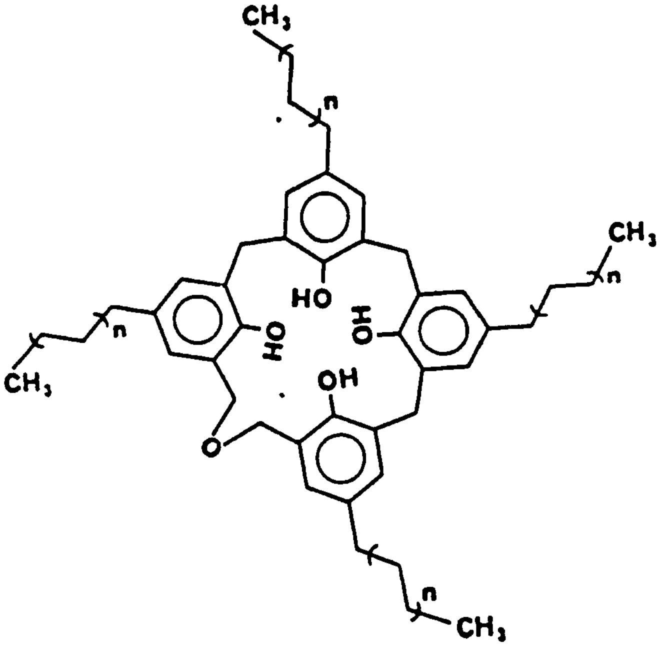
Abstract Langmuir-Blodgett (LB) monolayers of p-octadecylbis homooxacalix[4]arene 1 were formed at the air-water interface, in the presence of sodium hydroxide, with a solid state packing. The structure of the solid state was investigated by X ray diffraction techniques and the molecular packing was modeled by minimum energy calculations.

INTRODUCTION

Calixarenes[1] are organic compounds obtained by cyclization of 2-hydroxy 1,3-phenylenemethylene units. This typical arrangement creates a central cavity whose structure is unique. These molecules ,in addition, can form inclusion compounds with neutral or organo-metallic complexes with cationic species. Their easy preparation and transformation into various derivatives make them attractive for designing supramolecular entities. Recently, calixarenes have been chosen to develop a new class of monolayer forming-materials. Surfactant behavior of mercurated calix[6]arene at the water-air has been reported by Regen et al[2]. The same authors described ultrathin monolayers and vesicular membranes from calix[6]arene[3]. Calixarene esters showed monolayer behavior characteristic of their ring size, selectively responding to metal ions[4]. Langmuir monolayers of octadecylcalix[4]arene with solid state packing were obtained on water containing sodium hydroxide[5].

We present here our results on the formation monolayers of p-octadecylbishomooxacalix[4]arene <u>1</u>[6]. The molecular organisation of <u>1</u> in the solid state was determined. Atom-atom calculations of packing energies permitted a visualization of the monolayer arrangement.



<u>1</u>

FIGURE 1 p-octadecylbishomooxacalix[4]arene <u>1</u>

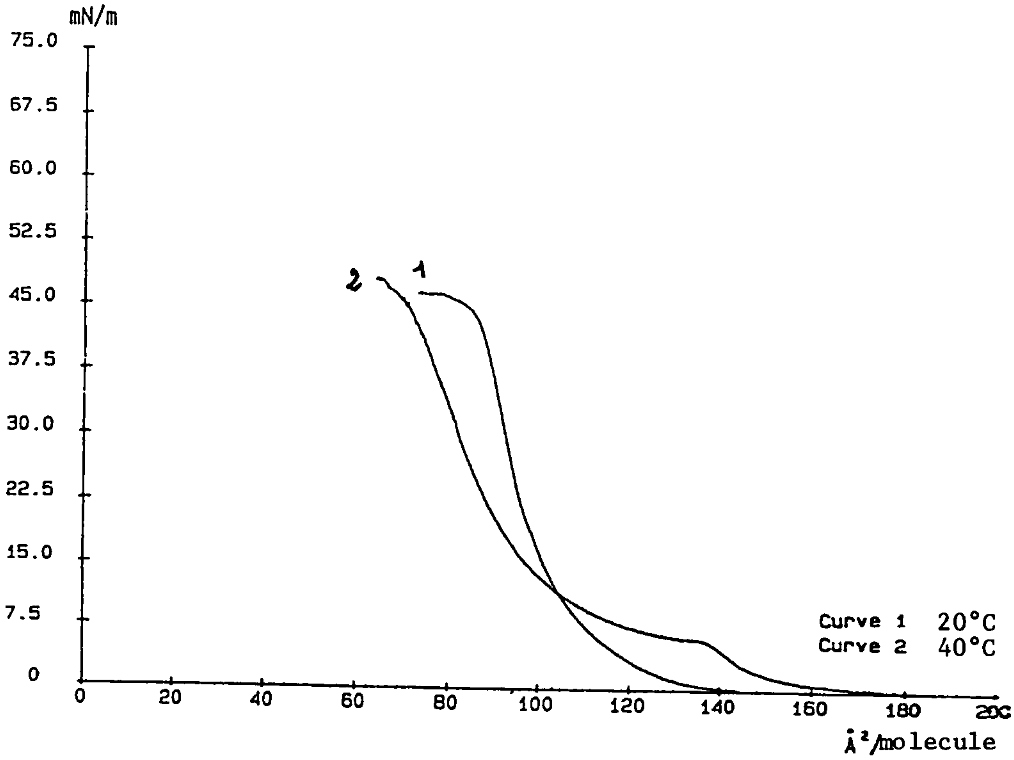


FIGURE 2 Surface pressure area isotherms.

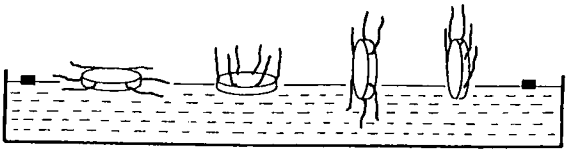


FIGURE 3 Possible arrangement of discotic liquid crystals at the gas-water interface according to Laschewsky[9].

RESULTS AND DISCUSSION

Langmuir Monolayer Measurements

Surface pressure area isotherms were measured on a pure water subphase or on 0.001 M NaOH at 20°C or at 40°C[4]. The measured limiting area of 1 on pure water phase is about 65 Å^2/molecule. This value is too small for close packing considering that the limiting area of p-octadecylphenol is 24 Å^2/molecule[5]. This probably is due to the fact that 1 is not amphilic enough to build a monolayer. This was overcome by using a basic aqueous subphase (0.001 M NaOH). Curve 1 in Figure 1 shows the behavior of 1 at 20°C. The limiting area is about 106 A^4/molecule as shown by extrapolation of linear part of π-A back to π =0. The collapse pressure for the condensed phase is about 43 mN/m. Curve 2 in Figure 1 shows the behavior of 1 on 0.001M NaOH at 40°C. There seems to be a transition phase between the expanded and the condensed phases. Such a transition phase has been explained by Langmuir[7] who assumed that some molecules in the expanded liquid like film become organized into clusters or two-dimensional micelles. Another explanation is by Kirwood[8], who proposed that hindered molecular rotation might lead to the discontinuity of compressibility associated with the onset of the transition. Amphiphilic self-organisation as "amphotropic systems[9]", described for LB- films of discotic liquid crystalline monolayers at the gas-water interface, may also be assumed (Figure 3).

Molecular Organisation of Solid 1

Optical observations have been carried out with a Leitz polarizing microscope equipped with a Mettler FP 82 hot stage.

A homogeneous thin film of crystallites of 1 was deposited between two glass slides. Starting from an isotropic phase at temperature higher than 71°C, the temperature was decreased to develop textures as is usually done to show evidence of characteristic textures of liquid crystals. Birefringent objects which did not change with temperature were observed. Nevertherless, after several cycles, 70°C ⇌ 50°C, we were able to observe classical spherulitic textures. The sample was left overnight at 50°C and was shown to be stable with time. It seems that this thermal process accelerates some crystallization effects leading to the stable classical lamellar structure. X-ray diffraction patterns (WAXD) were therefore recorded. Powder samples of 1 in Lindeman capillaries were diffracted at different temperatures from 71°C to 41°C. X-ray diffraction peaks, located in the low Bragg angle region exibit a series of sharp reflections with reciprocical spacing in the ratio 1:2:3, indicative of a well-developed lamellar structure of 25.7 Å at each temperature. In the wide angle region another series of sharp reflections are observed and are evidence of a well-developed short range organization in the layer structure. A similar molecular arrangement in layer structures has been already observed for sulphonated calixarenes[10,11]. The long induction time for compound 1 to crystallize is reminiscent of the transition phase observed in curve 2 in Figure 1.

Packing Energy Calculation of Solid 1

The calculation of the packing energy of solid 1 was performed by using an atom-atom potential method on molecule 1, previously calculated by the MM2 field method. The latter calculation was done on molecule 1 in which a mirror plane was assumed for the macroring part. This mirror plane was hypothesized to pass through the oxygen atom and the opposite carbon in the ring. This geometry was chosen based on ^{1}H nmr of the parent isopropylbishommooxacalix[4]arene. The calculated energy of isolated 1 is -40.25 kcal/mole. The geometry of the molecule is shown in Figure 4. It is noted that the length is equal to 27 Å which approximately corresponds to the distances separating two organic layers in the solid state structure of 1. The molecule-molecule interaction is split into the sum of different independent contributions which are the attractive, repulsive, electrostatic and polarization energies.

$$E = E_{rep} + E_{disp} + E_{el} + E_{pol}$$

All calculations involve pairwise evolution of non-bonded interactions between atoms composing the molecules in the crystal. Among the most used potential functions describing such interactions is the sixth power function which consists of a repulsive exponential part, and an attractive portion:

$$E = \sum_i \sum_j A \exp(-B R_{ij}) - C R_{ij}^{-6} + \sum_i \sum_j q_i q_j / R_{ij} - 1/2 \sum_i \sum_j \alpha_i (\epsilon_i)^2$$

where A, B and C are empirical parameters, R is the distance between atoms i and j, α_i is the mean polarizability attributed to atom i and ϵ_i is the electric field created at atom i by all other molecules. We assumed as hypothesis for the calculation a regular arrangement of the molecules in order to describe the whole monolayer by symmetry operations and translations. The calculations on several packing hypothesis were run taking into account 25 molecules. The minimization procedure involved the a and b paramaters of the pseudo-cell and lead to the surface area per molecule. The results are given in table I and in Figure 5.

TABLE I Packing energy calculation of monolayer made of 25 molecules

Packing hypothesis	Energy	Surface area/molecule
One molecule in the unit cell	-17.84	150
Two molecules in the unit cell (rotation of 180° around 1/4a, 1/4b and translation along c	-21.97	130

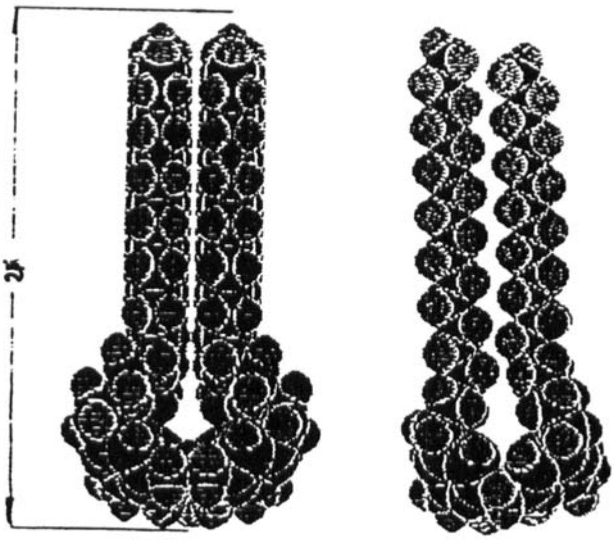


FIGURE 4 Conformation of 1 according to MM2 calculations

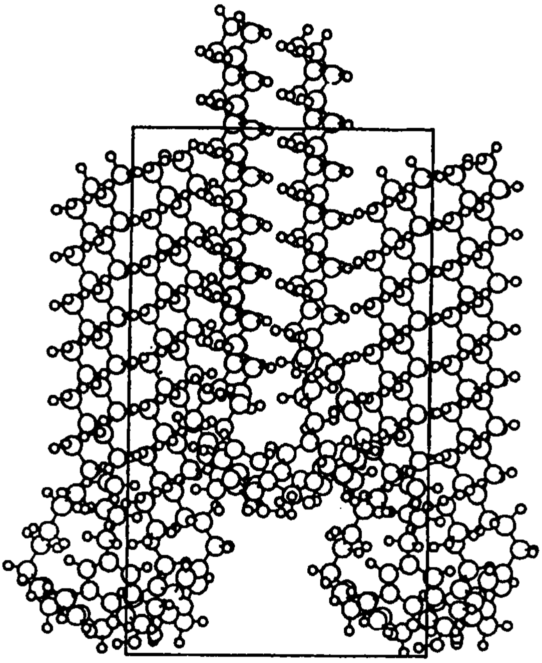


FIGURE 5 Molecular packing of 1 in the monolayer structure

CONCLUSIONS

In this communication we have shown that p-octadecylbishomooxacalix[4]arene 1 forms stable monolayers with the solid state packing on alkaline subphases. This solid state packing was shown to be similar in geometry to the solid state packing of powdered 1. A model of this packing has been presented. In this model the aliphatic chains are elongated to form layers separated by 27A and the pseudo-cell has been proposed. The results presented here with others presented on p-octadecylcalix[4]arene directed us to the study of parent calixarenes with six and eight phenolic units. This study is currently under investigations.

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