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Alignment of a nematic liquid crystal using substituted calixarene Langmuir–Blodgett films

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The alignment of a nematic liquid crystal (5CB) induced by several substituted calixarene-based films is reported. Calixarene molecules consisting of four or six moieties and different substituents (acyl and azobenzene groups) were synthesized. Films of such molecules were deposited using a Langmuir–Blodgett technique onto glass plates and were characterized using atomic force microscopy. These treated plates were used to prepare liquid crystal cells, and the overall alignment studied. In the case of photosensitive molecules, photoinduced reorientation experiments were undertaken and are reported. It is shown that it is not important to have a large number of interacting sites on the surface to induce a reorientation of the liquid crystal.

1. Introduction

Calixarenes are macrocyclic compounds, well known for their size-related selectivity in binding cations as well as organic guest molecules. Up to now, they have been studied mostly for use in sensor devices [1, 2]. Recently, Ichimura and co-workers [3] reported a reorientation of a liquid crystal (LC) induced by such a cyclic molecule substituted with a photosensitive azobenzene group, during illumination with UV radiation. In addition, these molecules are known to form organized molecular films either self-assembly monolayers (SAM) or Langmuir–Blodgett films (LB), and to host molecules within their bucket-like shape. This feature makes calixarene-based molecules attractive for aligning a LC on exotic substrates such as optical fibres, which is our long term goal. A preliminary study of the alignment properties is thus timely: specifically, is the LB technique suitable and does the bucket shape of the molecules play a specific role in the LC alignment. In this paper we report on the LC alignment properties of five substituted calixarenes, of which two are photosensitive. It is shown that molecular geometry and size play an important role in the LC alignment. The reorientation of the LC via photoisomerization of the calixarene films is confirmed, and the role and the number of photosensitive substituents are discussed.

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Prior to the fabrication of the LC cell, and to check the alignment obtained, the topography of the films was characterized using atomic force microscopy (AFM).

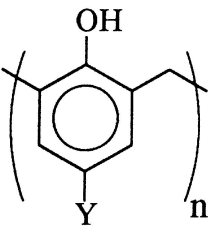
The paper is organized in two main parts: the preparation and characterization of the films is described in §2; experimental results are reported in §3. It is worth noting that it is beyond the scope of this paper to optimize the LC alignment or the efficiency of the photoinduced alignment.

2. Material and film preparation

We have chosen to study LC alignment induced by five different calixarenes. Two of them have the same substituent but contain a differing number of moieties (Calix 1 and Calix 2). The others have the same number of moieties, but are functionalized with either an acyl group (Calix 3), or five (Calix 4) or two (Calix 5) azobenzene groups. Their structures and their acronyms are shown in table 1.

The synthesis of Calixarenes 1 and 2 involved the reaction of *p*-*tert*-butylphenol with formaldehyde according to the methods of Gutsche *et al.* [4] leading to *p*-*tert*-butylcalix[4]arenes and *p*-*tert*-butylcalix[6]arenes. Treatment of these compounds with aluminium chloride gave Calix 1 and Calix 2 according to the procedure described by Bocchi *et al.* [5]. Calixarene 3 was synthesized by the Fries rearrangement procedure [6].

Table 1. Structures of the calixarenes studied and the acronyms used for reference.



Acronym	Substituent Y	Number of moieties <i>n</i>
Calix 1	H	4
Calix 2	H	6
Calix 3	COC ₁₁ H ₂₃	6
Calix 4	5 × N=N-∅-C ₃ H ₇ , 1 × H	6
Calix 5	2 × N=N-∅-C ₃ H ₇ , 4 × H	6

Starting from various amounts of the diazonium salt of *p-n*-propylaniline, Calix 4 and Calix 5 were obtained following a general procedure described previously [7]. All these products were identified by IR and NMR spectroscopy and elemental analysis.

The films were deposited using the LB technique on microscope slides (Mettler) cleaned using a UV treatment [8]. The LB films were produced using a KSV 5000 trough containing demineralized water with conductivity lower than 0.1 $\mu\text{S cm}^{-1}$. The calixarenes were diluted in chloroform (0.5 mg ml^{-1}) then spread onto the water subphase. The films were deposited onto the glass slides at a constant surface pressure of 20 mN m^{-1} , with a compression speed of 1.5 mm s^{-1} and a dipping speed of 2 mm s^{-1} . The topography of the films obtained was analysed using an atomic force microscope working in the contact mode (Autoprobe CP, Parck Scientific Instrument) at ambient temperature and pressure.

To check the induced alignment, the LC was inserted in a cell consisting of two identically treated slides, separated by two mylar spacers (DuPont de Nemour, 15 μm) and glued using an epoxy compound. The cell was filled by capillary action with the nematic liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl (5CB, Merck) in the isotropic phase. The alignment was checked by visual inspection through a polarizing microscope (Olympus BX50), looking for the classical black cross in the case of homeotropic alignment (conoscopic observation) and using the crystal rotation method [9] to determine the pretilt angle in the case of a planar alignment.

In the case of photosensitive materials (Calix 4 and Calix 5), UV absorption spectra were recorded using a spectrophotometer (Lambda 19, Perkin-Elmer) working

in transmission in the wavelength range 240–410 nm, in order to study the interaction between the calixarene molecule and 5CB.

3. Experimental results

3.1. Alignment

We report only our preliminary observations of the LC cells, i.e. homeotropic or planar, homogeneous or not. In the case of planar alignment, a more comprehensive study was undertaken to measure the pretilt angle, since a visual inspection does not allow for discrimination between a planar and a tilted optical axis. The results are gathered in table 2. A random alignment was observed in the case of films prepared with the calixarene molecule containing 4 phenolic residues (Calix 1), whereas the other films induced homogeneous alignment. The simplest (Calix 2) yields a planar alignment (0° pretilt angle) whereas the molecules with substituents (Calix 3, 4 and 5) induce a homeotropic alignment.

AFM topography reveals no notable differences between the different calixarene films, even though they induce clearly different alignments of the LC. To illustrate this, three AFM images are shown for Calix 1, 2 and 4 which induce, respectively, a random alignment (figure 1), a homogeneous planar alignment (figure 2) and a homogeneous homeotropic alignment (figure 3). Moreover these images show that the films have not spread homogeneously over the glass slides (not monolayer films), but the obtained alignments are homogeneous. Thus, according to these AFM images, the various alignments obtained cannot be explained by differences in the surface morphologies. Moreover, the comparison between different molecules underlines the importance of the molecular geometry for these systems.

For all the calixarenes synthesized, the adhesion onto the slides is achieved via the OH group [10]. The only difference between Calix 1 and Calix 2 lies in the overall geometry: thus, Calix 1 is smaller and looks like a truncated cone, slightly opened, whereas Calix 2 is much more opened. The phenol groups (backbone of the cone) are almost perpendicular to the substrate for Calix 1 but almost parallel to it for Calix 2. A π -stacking between the phenol of calixarene and 5CB is highly probable and can explain the planar alignment induced by Calix 2.

Table 2. Observed alignments of 5CB on the calixarene films.

Alignment layer	Observed alignment
Calix 1	not homogeneous
Calix 2	planar
Calix 3	homeotropic
Calix 4	homeotropic
Calix 5	homeotropic

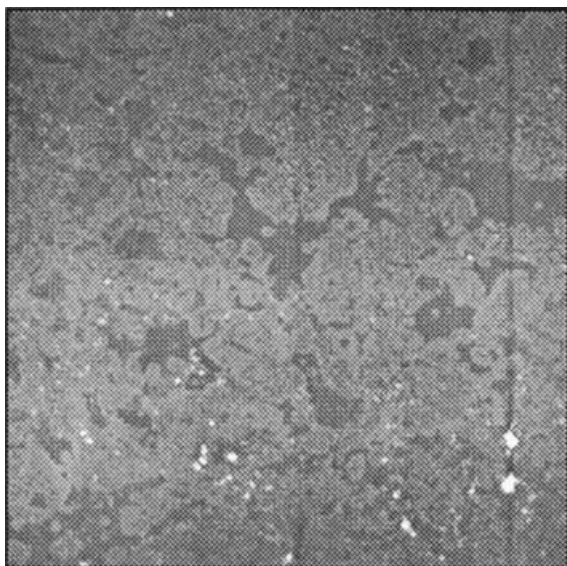


Figure 1. A $35 \times 35 \mu\text{m}^2$ Calix 1 film area scanned using AFM. Homogeneous alignment of the LC has not been observed using this substrate.

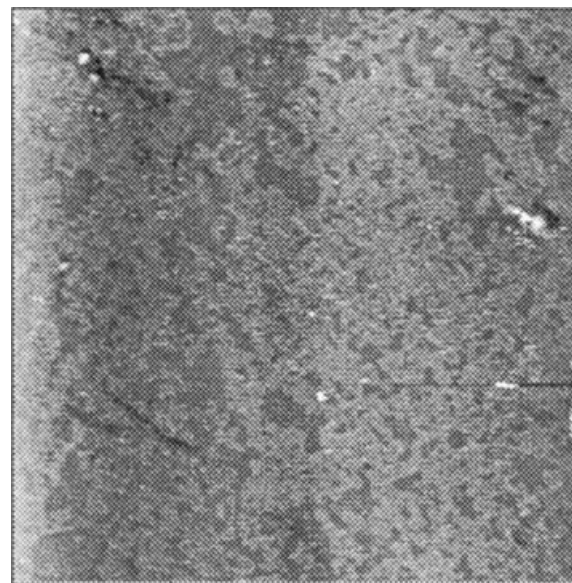


Figure 3. As figure 2, but the film is prepared using Calix 4. This film induces a homeotropic alignment of the LC.

Thus, the first 5CB layer, on the Calix 2 film is aligned in a planar fashion and induces the bulk alignment, figure 4(a). In the case of the Calix 3 film, which possesses long aliphatic chains, the homeotropic orientation can be explained by analogy with Stegemeyer's model [11], figure 4(b). The AFM analysis reveals a similar surface morphology to the other calixarene molecules (i.e. a partial wetting of the slide) which means that a homogeneous homeotropic alignment can be induced by only a few surface sites, and is propagated through the whole surface and bulk via the collective behaviour of the liquid crystal.

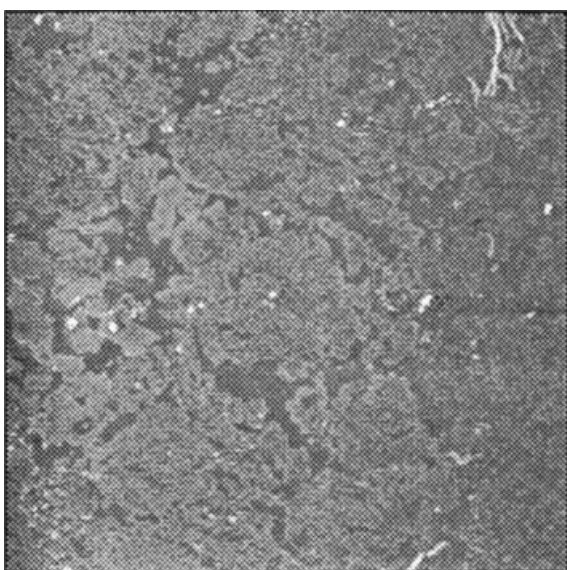


Figure 2. As figure 1, but the film is prepared using Calix 2. This film induces a planar alignment of the LC.

3.2. photoinduced LC reorientation

The two films prepared using Calix 4 and Calix 5 were photosensitive and could potentially reorient the LC when illuminated with UV light. Thus we performed some preliminary photoinduced reorientation experiments. These two films homeotropically align the LC under normal conditions while under UV light one might expect a transition towards a tilted or planar alignment. The isomerization was achieved by illuminating the sample through a pinhole ($\varnothing 400 \mu\text{m}$) using a mercury lamp (Lot Oriel, 100 W) polarized by a Glan-Taylor, placed 30 cm away from the pinhole, with no other optical components. The reorientation effects were observed through the polarizing microscope. As mentioned already and noted in table 2, before UV irradiation the cell was homeotropically aligned (figure 5). The transition towards a tilted or planar alignment was observed after two hours for Calix 5 (figure 6), whereas it occurred only after eight hours of illumination for Calix 4.

These response times are definitely longer than those usually reported; however, they were not optimized, and the process takes place on a film and not in the bulk, so the amount of energy available in the photosensitive film is reduced by loss through the glass and the pinhole (no special focusing optics). In addition, one can understand that to have an efficient LC reorientation, it is important that most of the azo groups on the same molecule are transformed simultaneously. The poor quality of the observed reorientation in figure 6 is partly due firstly to the depolarization of the beam by the pinhole and secondly to the heterogeneity of the LB deposited film as shown using AFM. It was beyond the

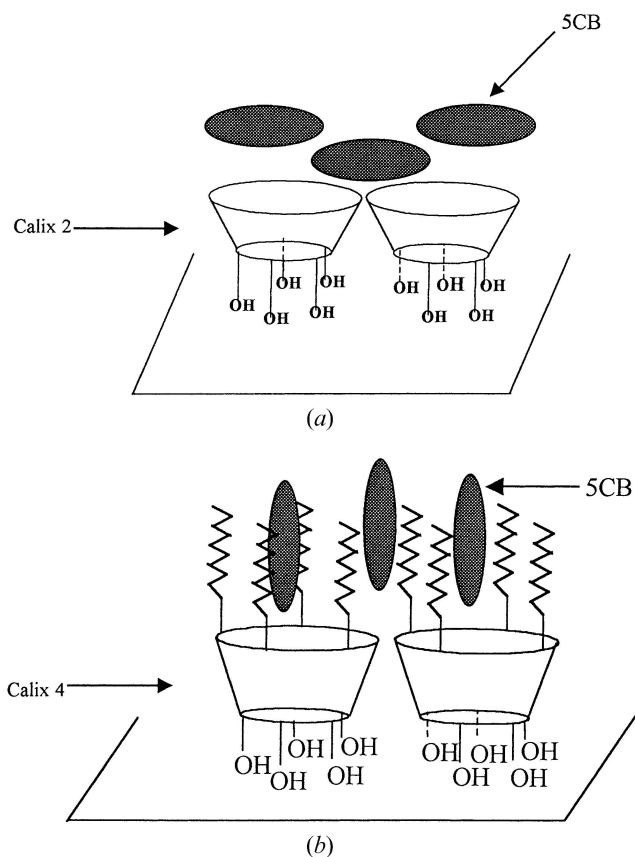


Figure 4. Schematic representations of the geometry of the calixarenes deposited on the surface and the interaction with the LC molecules. Both calixarenes are bound to the surface via the OH group. Calix 2 (a) is much more opened than Calix 3 (b); as a result the molecular interactions are between the cores of each molecule (a) whereas for Calix 3 the LC molecule and the alkyl chains interact.

scope of this study to optimise this. It is important to note that the reorientation occurs strictly in the illuminated region of the film.

For the Calix 5 film, two processes were observed: one reversible and the other irreversible. The reorientation which occurred after two hours was reversible and is likely to be a classical *trans-cis* isomerization process. The reorientation becomes irreversible for UV exposure times longer than eight hours. This may either be a crosslinking process analogous to that reported for example for polyvinylcinnmate [12, 13], or an intermolecular interaction involving aromatic rings such as cyclo-additions [14, 15]. Rather than proceeding further with this second irreversible process, we have focused on the fact that the orientational transition is experimentally easier to achieve with the Calix 5 film than with the Calix 4. This may be explained in terms of steric hindrance: the conformational change requires free



Figure 5. LC cell homeotropically aligned by the calixarene film (Calix 5, polarizing microscope $\times 20$, between crossed polarizers), before UV illumination.

volume which is available in the case of two azobenzene groups (Calix 5) but not in the case of 5 groups on the same calixarene (Calix 4).

However, another effect can play a role in this reorientation process, as can be seen from the absorption spectra. Although it occurs for both Calix 4 and Calix 5, it is more apparent for the molecule having two azobenzene groups (Calix 5). The UV absorption spectra for pure Calix 5 (dissolved in chloroform) and pure 5CB are shown in figure 7(a). The peak around 360 nm accounts for both the *trans-cis* transition and the $\pi \rightarrow \pi^*$ transition. The spectrum recorded for two mixtures of Calix 5 and 5CB (two different molar concentrations) are shown in figures 7(b) and 7(c). In addition, in these figures is plotted the linear combination of the spectra of the pure materials, chosen to reproduce the concentration of the mixture experimentally studied. It is clear that the presence of 5CB decreases the intensity of the 360 nm peak. This reduction may be assigned to a close

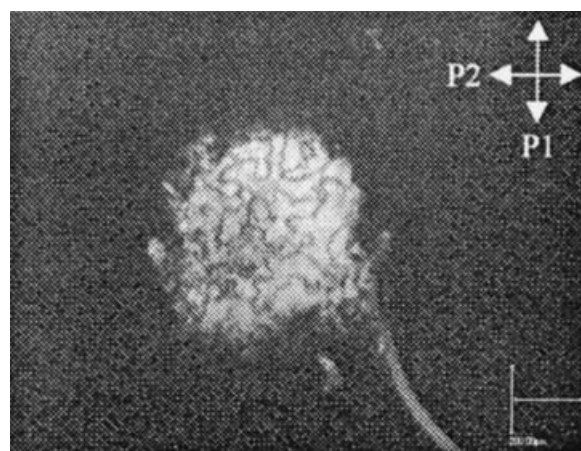


Figure 6. Same cell as figure 6 after UV irradiation.

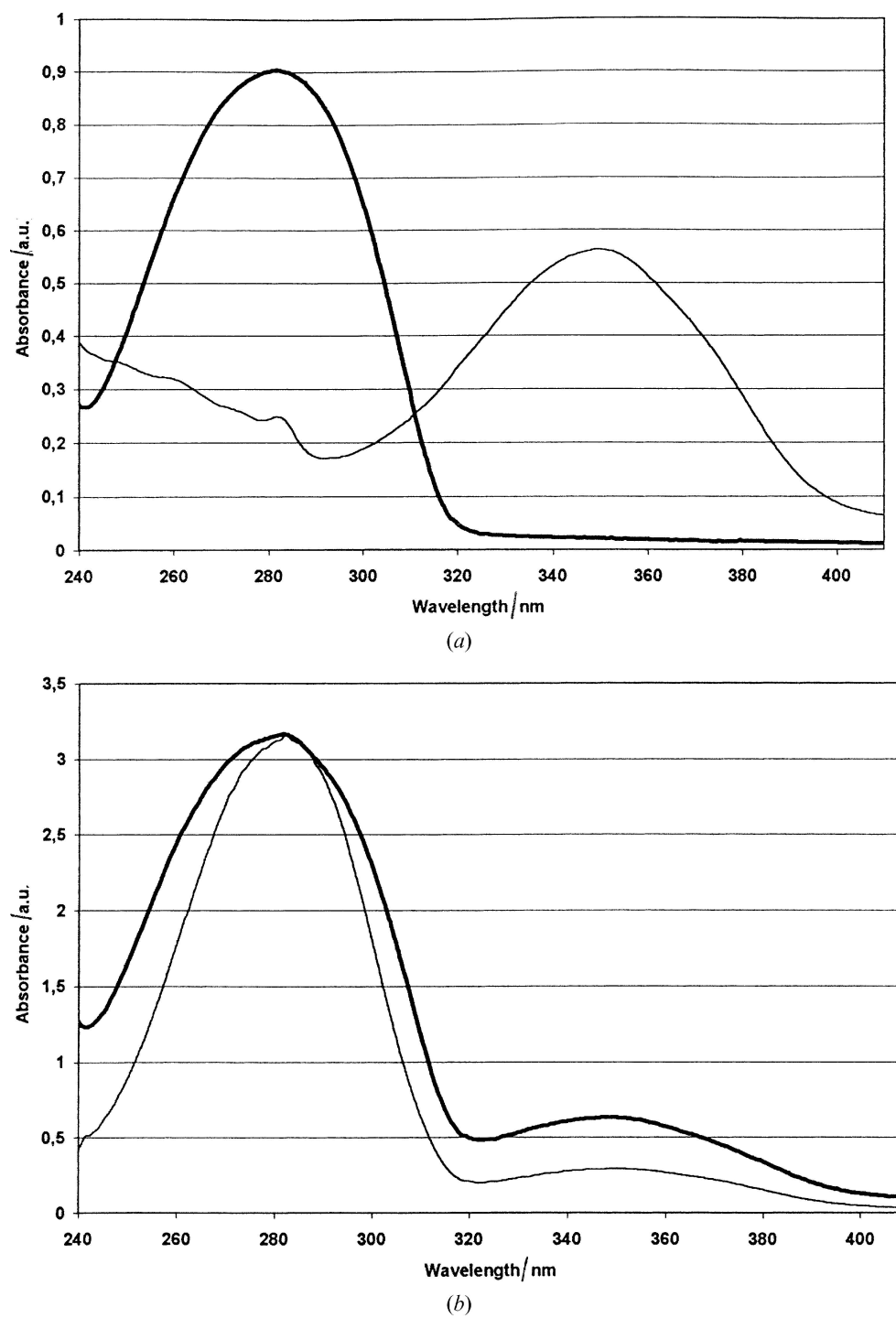


Figure 7. The UV absorption spectra of: (a) the pure materials Calix 5 and 5CB (bold); (b) the mixture Calix 5 + 3 × (5CB) and the calculated spectrum (bold) obtained from a linear combination of the spectra of the pure materials; (c) as (b) with essentially the same amount of both molecules.

correlation between the benzene rings of 5CB and the azobenzene function (π -stacking) [3]. The 5CB molecule close to the Calixarene film is therefore associated with the photosensitive group and reversibly rotates with it as

it is isomerized from *trans* to *cis*: the molecules in the bulk liquid crystal follow this reorientation via the elasticity of the LC. This association enhances the reversibility of the reorientation.

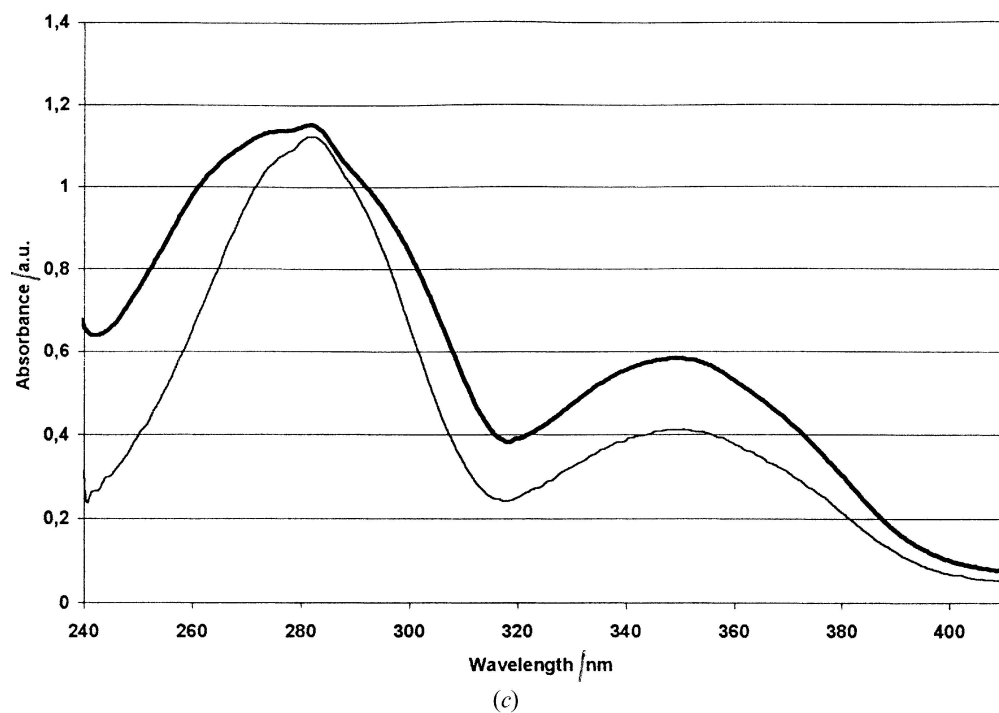


Figure 7. (Continued.)

Finally, it is noteworthy that it is not necessary to have many interaction sites between the liquid crystal and the alignment film to induce an efficient reorientation. Indeed, Calix 5 having only two photosensitive groups is much more efficient in terms of effecting reorientation than the film having 5 interacting sites. In the case of the Calix 5 film, the molecular area has been determined from the surface pressure isotherms and it is estimated that there are two sites per 160 nm^2 (average area of Calix 5).

4. Conclusion

Calixarene-based molecules have been synthesized and thin films prepared using the Langmuir–Blodgett technique. These films have been tested as alignment agents for liquid crystals. Depending on the molecular geometry (how widely opened the bucket-like shape is), it has been shown that both homeotropic and planar alignments can be induced. However, the interaction between the liquid crystal molecule and the calixarene substituents seems to be an essential component of the process yielding the macroscopic alignment of the LC.

Photosensitive azobenzene substituents have also been studied. It has been shown that a photoinduced reorientation occurs and there are similarities with the photoinduced reorientation already observed in polyvinylcinnamate materials, namely the observation of a reversible and an irreversible isomerization process; the latter may be assigned to a crosslinking reaction between

azo groups. The reversible process is enhanced by a close association between 5CB and the azo-groups (π -stacking). Clearly, our results hold specifically for 5CB. However, having identified the interactions which play a major role in the alignment, and considering the fact that calixarenes are easily functionalized, this study opens a wide range of possible alignment films with specific properties for differing liquid crystals. Furthermore, we have confirmed that the Langmuir–Blodgett technique generates films that can align liquid crystals: a further investigation on using this technique on an optical fibre is underway. Finally, it is worth noting that it is not essential to have many interacting surface sites to achieve good LC alignment.

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