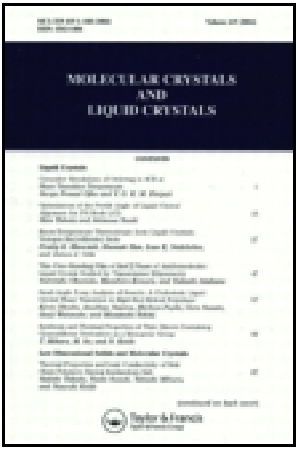

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Structure of Mesogenic 4′-Hexadecyloxy-3′-Nitrobiphenyl-4-Carboxylic Acid (ANBC-16) at the Air--Water Interface

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STRUCTURE OF MESOGENIC 4′-HEXADECYLOXY-3′-NITROBIPHENYL-4-CARBOXYLIC ACID (ANBC-16) AT THE AIR–WATER INTERFACE

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The Langmuir film behavior of an amphiphilic thermotropic mesogen at the air–water interface has been studied from surface pressure–molecular area isotherms. The isotherms exhibited a transition from an expanded to a condensed phase and on further compression also indicated the formation of an unstable monolayer, evidenced through a pronounced hysterisis observed during the decompression cycle. This phenomenon is explained on the basis of stronger hydrophobic forces dominating the orientation in the condensed phase. Increase in the limiting molecular area at lower temperatures provides supporting evidence for the observed loss of a stable condensed phase, which is attributed to the dissolution of the molecules into the aqueous subphase.

Keywords: liquid crystals; Langmuir films; hydrophobic forces

INTRODUCTION

Liquid crystal compounds have been shown to yield easily well-controlled organized monolayers [1,2] and multilayers [3] at the air-water interface. Their organization at the interface depends on the liquid crystal (LC) molecule–LC molecule interactions and the LC–aqueous subphase interactions, as well as the compressing state of the film. Most thermotropic liquid crystal molecules are small rodlike lipids that are insoluble in water. These short rigid rods, whose interparticle interactions are considered simpler than those between surfactants and polymers, may therefore form different phases on the air–water interface and are ideal to study. Thus,

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because of their weak interlayer coupling and strong in-plane interactions, these materials can be successfully modeled as a collection of weakly coupled 2-D systems.

4′-n-alkoxy-3′-nitrobiphenyl-4-carboxylic acids, ANBC-n, (where n is the number of carbon atoms in the alkoxy group) are known as unique thermotropic liquid crystalline compounds exhibiting remarkable polymesomorphism. An optically isotropic D phase [4,5] which is not related to the conventional smectics A, B, or C appears in the hexadecyloxy derivative between the smectic A and C forms and as a high temperature form in addition to the smectic C form for the octadecyloxy derivative. From the X-ray studies [6] and NMR spectroscopy [7], several structural models for the D phase have proposed that micelles are arranged in harmony with a cubic symmetry to make the D phase optically isotropic but are different in shape and packing of the micelles from each other. The compound 4′-n-hexadecyloxy-3′-nitro-biphenylcarboxylic acid (ANBC-16) was historically one of the first ANBCs from a set of four compounds with very similar chemical structures and nearly equal molecular size, found to show this smectic D, or S_D, phase. The molecule of ANBC-16 consists of a nitrobiphenylcarboxylic acid core and an n-hexadecyloxy chain (Figure 1). Since most molecules are dimerized in the solid and liquid crystalline phases [8] owing to intermolecular bonding, the system in the bulk consists of a "molecule" that has a long core at its center and two terminal alkoxy chains. The acid core and the alkoxy chains have been shown to play different roles in the formation of the various mesophases, with the chains resembling solvent in the D phase [9]. Also, the alkoxy chain length (n) is a key factor for determining the phase behavior; when $n \geq 16$, the D phase appears on both heating and cooling and its temperature region becomes wider with increasing (n) [10]. Thus the molecular organization of the core

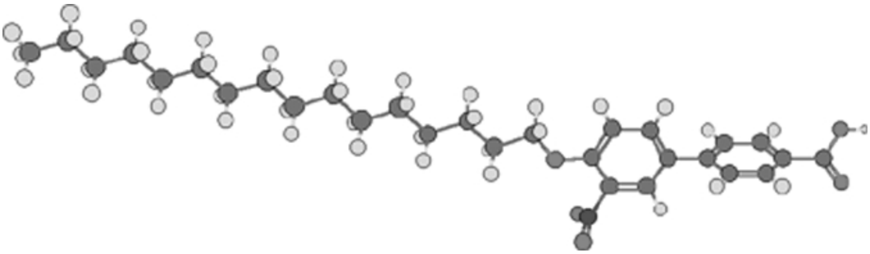

FIGURE 1 Energy minimized molecular model of mesogenic ANBC-16 calculated using CS-MOPAC (version 3.5.1) depicting the nitrobiphenyl core and the hexadecyloxy tail. The Carbon atoms are depicted in Dark-Grey, the Hydrogen atoms in Light-Blue, the Nitrogen atoms in Dark-Blue, and the Oxygen atoms in Red. (See Color Plate VIII).

and the tail in the 3-D bulk of ANBC-16 has been investigated in greater detail, taking into account the phase structure, formation, and behavior of the different mesophases.

We present in this paper the investigation into the structure and phase formation at the air–water interface and the effect of reduced dimensionality on the molecular organization of the core and the tail portions of the mesogen.

EXPERIMENTAL DETAILS

4′-n-hexadecyloxy-3′-nitrobiphenyl-4-carboxylic acid (ANBC-16) was prepared with the established method of Gray et al. [11]. The sample was identified to be ANBC-16 from ^{1}H NMR and mass spectroscopy. The sample was recrystallized several times from ethanol and the purity of the sample was confirmed by DSC, thin-layer chromatography, and elemental analysis.

Surface pressure–molecular are (π–A) isotherms of the liquid crystal sample were obtained using a computer-controlled double barrier Langmuir trough, KSV 5000 (KSV Chemical Corporation, Finland) made of Teflon with internal dimensions $37.5 \times 24\,\text{cm}^2$. Spreading solutions of the samples were prepared in chloroform (HPLC grade) with concentrations ranging from 0.7–2 mg/mL and the volume of the solution spread ranging from 100–150 µL. The solutions were spread uniformly over ultrapure water subphase (Milli-Q with resistivity 18.2 MΩ cm) using a microsyringe, and the solvent was allowed to evaporate for at least 30 min prior to compression. The monolayers were compressed at a rate of 0.3 cm/s. The surface pressure was measured by a Wilhelmy plate with a precision of ± 0.1 mN/m. The subphase temperature was controlled to within an accuracy of ± 0.1°C. The pH of pure water in equilibrium with atmospheric CO_2 was 5.5 ± 0.1.

RESULTS AND DISCUSSION

Figure 2 indicates the π–A isotherm of ANBC-16 at 22.3°C. The first compression profile shows a phase transition plateau with an inflection of about 21.04 $(A°)^2$/molecule and 6.1 mN/m. The transition plateau means the occurrence of a definite expanded state (point (a)) before the inflection point. The onset area of 25.42 $(A°)^2$/molecule for the expanded state is consistent with the enhanced interaction and steric hindrance between the mesomorphic tail containing the hexadecyloxy group, leading to coherence at larger areas and formation of an expanded state. After passing the transition plateau region, the appearance of an intermediate phase of onset area 17.67 $(A°)^2$/molecule and sustaining an onset pressure of 6.89 mN/m is

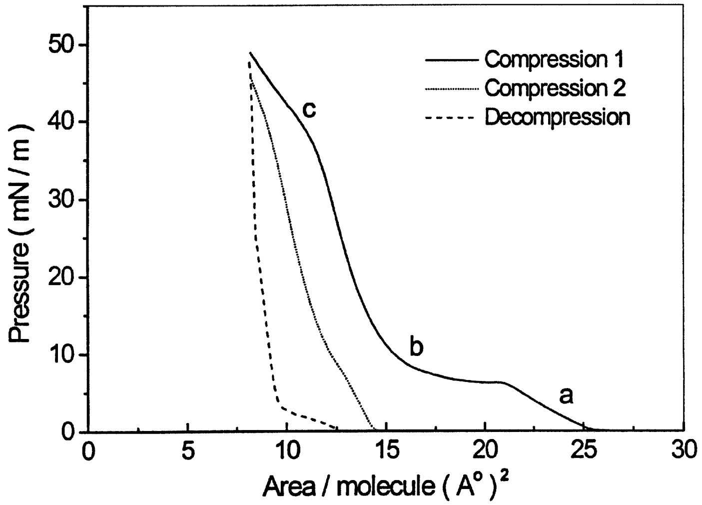

FIGURE 2 Surface Pressure–molecular Area (π–A) isotherms at 22.3°C for two successive compressions alongwith the decompression cycle for ANBC-16. The subphase is water at pH 5.5.

observed (point (b)). The possible orientation of this intermediate corresponds to a surface structure with the core on the water surface and the tail alkyl chains progressively directing away from the water surface. The intermediate then transforms into a condensed region at ca. 11.43 $(A°)^2$/molecule at a higher surface pressure of 37.01 mN/m (point (c)). The condensed region of the isotherm located at 11.43 $(A°)^2$/molecule suggests that the structure corresponds to the removal of the hexadecyloxy segment in the main chain from the water surface, leading to the closest packing of the core. This is in agreement with the area occupied by the core of the molecule, evidenced from the energy-minimized structure of ANBC-16 (shown in Figure 1), to be 10.8 A°. This appears as the logical arrangement since the core consists of two polar groups, the –COOH and $-NO_2$ linkages, and hence the orientation of the core would be lying flat down on the water surface with the tail alkoxy chain perpendicular to the water surface (Figure 3a). On further compression, the pressure increases linearly without exhibiting any collapse pressure, indicating the possibility of dissolution of the molecules in the subphase, leading to an unstable condensed state. The pronounced hysteresis observed for the decompression and the second compression profiles in Figure 2 lends further support to the above. The area of 8.2 $(A°)^2$/molecule at the highest surface pressure of 48.4 mN/m corresponds to the squeezing out of the benzene ring containing the $-NO_2$ group from the water surface with the –COOH group submerged

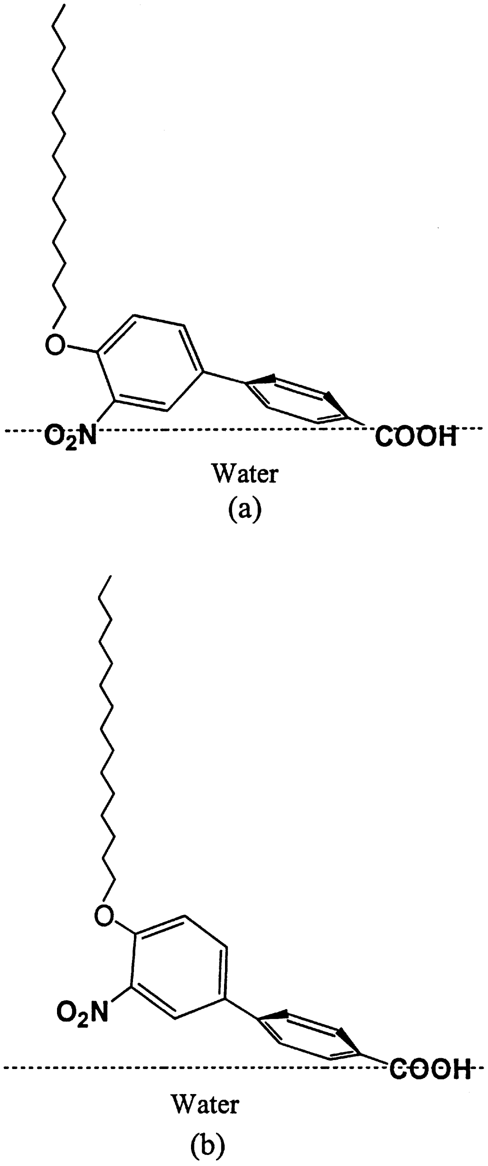

FIGURE 3 (a) Possible orientation of ANBC-16 at point (b) in Figure 2. One of the phenyl rings of the biphenyl core arranges in a plane perpendicular to the other. (b) Possible orientation of ANBC-16 at point (c) in Figure 2.

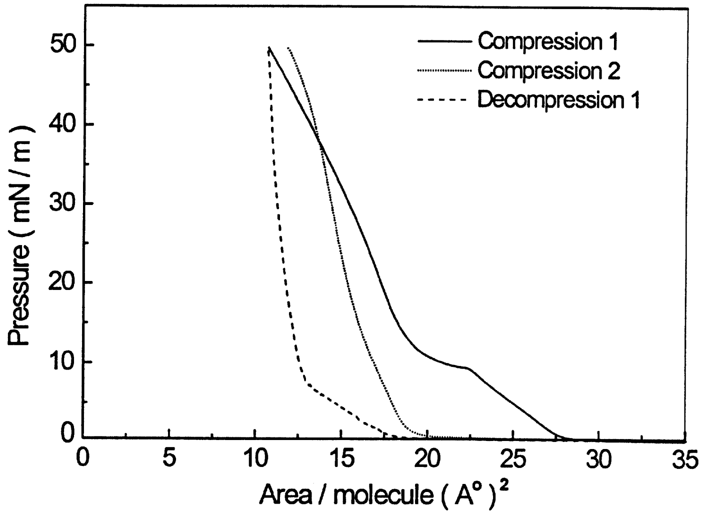

FIGURE 4 Surface Pressure–molecular Area (π–A) isotherm for ANBC-16 at 10°C.

still inside the subphase. This can be explained by the lower polarity of the nitro group compared to the carboxylic acid group and the ability of the acid group to bind to water through extended hydrogen bonding. Thus sustained compression pulls out the nitro group from the subphase, resulting in the associated benzene ring projecting away from the water surface (Figure 3b). Since the entire weight of the molecule rests now only on the carboxylic acid group and the resulting orientation makes the upward hydrophobic force greater than the hydrophilic one, the imbalance and the shear weight of the molecule is responsible for dissolution in the subphase and loss of the condensed phase.

Figure 4 shown the π–A isotherm at 10°C and indicates higher onset area for the expanded state as well as increase in the limiting area at highest surface pressure. The decrease in the temperature decreases the solubility of the molecule in the subphase and hence the process of dissolution at higher compressions is hindered, resulting in the high molecular areas obtained as compared to Figure 2. The transition between the expanded to the condensed state remains unaffected, but the transition plateau occurs with an inflection around 22.71 $(A^{\circ})^2$/molecule. An increase of 1.67 $(A^{\circ})^2$/molecule compared to that obtained at a higher temperature is due to the increase in the number of molecules on the surface.

In conclusion, the behavior of the thermotropic mesogen at the air-water interface revealed a phase transition from an expanded to a condensed state is explained on the basis of the extent of interaction between the mesomorphic tail and the orientation of the polar core. Further compression resulted in a loss of structure due to increase in the hydrophobic forces and subsequent dissolution in the aqueous subphase.

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