

Structure of Discotic Liquid Crystalline Compounds at the Air–Water Interface

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We have used grazing incidence X-ray diffraction and X-ray specular reflectivity to study the behavior of platelike hexaalkoxytriphenylene derivatives at the air–water interface. The data are consistent with a two-dimensional columnar mesophase, wherein the molecules are arranged “edge-on” to the water surface, with intercolumnar spacings of 13–19 Å. We propose a molecular conformation in which hydrophobic tails lie parallel to the water surface so as to allow the hydrophilic oxygen atoms to directly contact the water surface. In equimolar mixtures of two disubstituted amphiphilic isomers of a triphenylene derivative, we see direct evidence for structural self-organization and intercolumnar order. We also present indirect evidence for orientational self-organization in symmetrically substituted triphenylene derivatives.

1. Introduction

Self-organizing systems have attracted substantial interest as a means of producing highly ordered materials, often with useful electronic or optical properties. Research on these systems is moving from relatively simple compounds that are organized on short length scales to larger structures formed by complex macromolecules. To understand the relationships between molecular structure, intermolecular nanostructure, and macroscopic properties, it is important to obtain a detailed structural characterization at all of these length scales.

Grazing incidence X-ray diffraction (GID) and X-ray specular reflectivity (XR) are now widely recognized as powerful tools for structural characterization of molecules adsorbed at the air–liquid interface.¹ These techniques have primarily been applied to the investigation of rodlike amphiphilic molecules.^{1,2} The present paper deals with nanostructure elucidation of Langmuir films of platelike discotic liquid crystalline compounds (DLC) that are known to form organized films at the air–water interface with novel structural properties. We have used liquid surface X-ray scattering techniques to study monolayer Langmuir films of platelike alkoxy-triphenylene derivatives.

DLC's are composed of disk-shaped molecules, most often consisting of a rigid π -conjugated core to which are attached 6–8 flexible hydrocarbon chains.³ The bulk liquid crystalline phases can be nematic or columnar;^{4,5} the columnar phase is characterized by long-range intercolumnar order (usually hex-

agonal or rectangular) and short-range structural order within each column. The thin-film properties of disk-shaped molecules have not been studied in as much detail as their three-dimensional properties. The structures of monolayer films at the air–water interface have been inferred primarily on the basis of indirect techniques, particularly pressure–area (Π – A) isotherm measurements.^{6,7} These measurements indicated that discotic mesogens adopt in general one of two types of packing at the air–water interface. Large, flexible cores with long substituents and highly polar anchor groups will favor a conformation with the cores parallel (“face-on”) to the interface. Alternatively, strong π – π interactions of the cores may lead to cofacial packing with the planes of the cores perpendicular (“edge-on”) to the interface. These monolayer Langmuir films can be transferred to solid substrates, and it is most often found that the edge-on structure inferred for the Langmuir films is indeed transferred to the substrate, with columns lying parallel to the interface. The characteristic 15–20 Å in-plane spacings of these columns have been clearly observed via GID and atomic force microscopy. Furthermore, XR measurements on a variety of multilayer LB DLC films^{6,8–10} show a layer repeat spacing of 15–20 Å, consistent with that expected for regular columns parallel to the substrate.

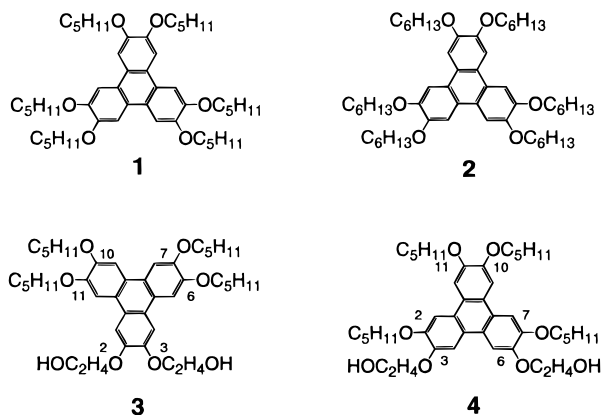
In the present study, we chose to investigate two sets of model DLC alkoxy-triphenylene derivatives (Scheme 1). The bulk structure and phase behavior of compounds **1** and **2** have been well characterized.^{5,11–13} They are not manifestly amphiphilic, but nevertheless have been shown to form stable Langmuir films.¹⁴ Compounds **3** and **4** have been modified with hydrophilic C₂H₄OH tails to increase their amphiphilic character; they have recently been shown to display an unusual capacity for

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SCHEME 1



self-organization at the air–water interface,¹⁵ as discussed in more detail below.

2. Experimental Details

Two sets of X-ray scattering measurements were performed at beam line X22B of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. We employed the Harvard/BNL liquid surface diffractometer¹⁶ with incident wavelengths of $\lambda = 1.545 \text{ \AA}$ or $\lambda = 1.549 \text{ \AA}$. A sealed and thermostated Langmuir trough equipped with a Wilhelmy balance was supported by a vibration isolation stage on the diffractometer. A flat silicon block just under the water surface at the position of the X-ray beam served to reduce the amplitude of capillary waves. The temperature in the trough during the measurements was kept constant at 18°C .

The monochromatic X-ray beam was deflected toward the water surface via Bragg reflection from a Ge(111) crystal. The GID angle of incidence was chosen as $0.87\alpha_c$, where $\alpha_c = 0.138^\circ$ is the critical angle for total external reflection from the pure water surface. The scattered beam was measured by a NaI scintillation detector. The instrumental resolution was always determined primarily by the slits between the sample and the detector. These slits were always set to optimize the resolution in the scattering plane while increasing the signal by lowering the resolution out of the scattering plane; this resulted in a somewhat different slit configuration for GID and XR measurements. A beam monitor after the slits defining the beam, but before the sample, provided a precise normalization factor for the incident beam intensity. Calibrated attenuators between the sample and the detector were inserted and removed as necessary during the course of an XR scan to keep the measured intensity within the linearity regime of the detector.

Millipore water was used as a subphase. The monolayers were spread from 10^{-3} to 10^{-4} M chloroform solutions. Pressure–area (Π – A) isotherms were measured for each compound before each scattering measurement and were all essentially identical with previous observations.^{6,14–15} A typical isotherm displayed a low-pressure segment at large molecular areas, a rapid rise beginning around $90 \text{ \AA}^2/\text{molecule}$, and a collapse pressure of ~ 40 – 50 mN/m . A typical extrapolated molecular area at full compression was 60 – 80 \AA^2 , which agrees well with the area calculated for a molecule in the edge-on configuration.^{6,14–15} Compounds **3** and **4**, and their mixture were measured at constant pressure of 30 mN/m . We observed that, if we controlled the pressure, the area per molecule might decrease by as much as 3 – $4 \text{ \AA}^2/\text{molecule}$ during the time scale of a typical XR or GID measurement, indicating that structural relaxations on the order of 4 – 5% might be taking place. Measurements on compounds **1** and **2** were made either at

constant surface pressure of 9 and 14 mN/M , in which case the area typically relaxed by 1 – $2 \text{ \AA}^2/\text{molecule}$, or while maintaining a constant area of the order 60 – $80 \text{ \AA}^2/\text{molecule}$, in which case the surface pressure typically dropped by 5% during the course of a measurement. The XR and GID patterns obtained did not depend sensitively on whether the area or the pressure was maintained during the measurement.

3. Measurements on Compounds 1 and 2

We first discuss the results of our measurements on compounds **1** and **2**, which differ only in the lengths of their side chains (C_5H_{11} vs C_6H_{13}). The 70 \AA^2 area per molecule obtained from Π – A measurements, as well as the columnar structures observed in GID and AFM studies of Langmuir films of similar molecules,^{6,8–10} led us to anticipate that these molecules would adopt an edge-on configuration at the air–water interface, with regular columns parallel to the surface.

GID measurements are made with the X-ray momentum transfer in or close to the plane of the air–water interface.¹ The GID pattern of an ideal two-dimensional liquid-crystalline columnar structure, given by the Fourier transform of the in-plane electron density at the interface, should consist of two sets of features. First, we expect a set of equally spaced (H00) Bragg peaks, at multiples of $q_{xy} \approx 2\pi/14 \text{ \AA}$, arising from a 14 \AA intercolumnar spacing. In practice, the structure factors of the higher-order peaks are very weak, and they are often unobservable even in three-dimensional discotic liquid crystals, so they might be unobservable in the present case. Second, there should be a broad (001) peak at $q_z \approx 2\pi/3.5 \text{ \AA}$, arising from intracolumnar correlations; since this peak is quite weak in 3D liquid crystals, it might well be unobservably weak in a Langmuir film.

If the in-plane structure were crystalline, rather than liquid crystalline, the pattern above should be modified in two ways: the (001) peak should be sharp, and there should be an entire set of (HOL) peaks arising from intercolumnar correlations of molecular positions. (We also note that true long-range order in either a columnar phase or liquid crystalline phase is not possible in two dimensions, but our limited resolution did not allow us to observe the power-law cusps expected under these circumstances.^{17,18})

In fact, for both compounds **1** and **2** the GID measurements yielded a single (100)-type diffraction peak. The peak positions were, respectively, $2\theta = 6.55^\circ$ and $2\theta = 6.09^\circ$ (Figure 1), corresponding to intercolumnar distances of 13.9 and 14.5 \AA for **1** and **2**. As discussed below, 14 \AA is somewhat smaller than expected for columns of triphenylene derivatives with five or six carbons per chain but still physically reasonable. This observation unambiguously establishes the existence of 14 \AA columns and is consistent with what we expect for a two-dimensional liquid-crystalline columnar phase. We searched for, but did not observe, the (001) and other (HOL) peaks at higher angles. However, we cannot rule out the possibility that our structural order is crystalline and that the (HOL) and (OOL) peaks are unobservably weak because of structure factor effects. Indeed, preliminary Brewster angle microscopy measurements¹⁹ on **1** at room temperature reveal a mosaic of birefringent domains with a nonzero shear modulus, consistent with expectations for a crystalline rather than a liquid crystalline structure.

Specular X-ray reflectivity measurements record X-rays scattered with the momentum transfer strictly perpendicular to the air–water interface.¹ The XR profile is determined by the Fourier transform of the gradient of the electron density perpendicular to the water surface. The reflectivity is given in

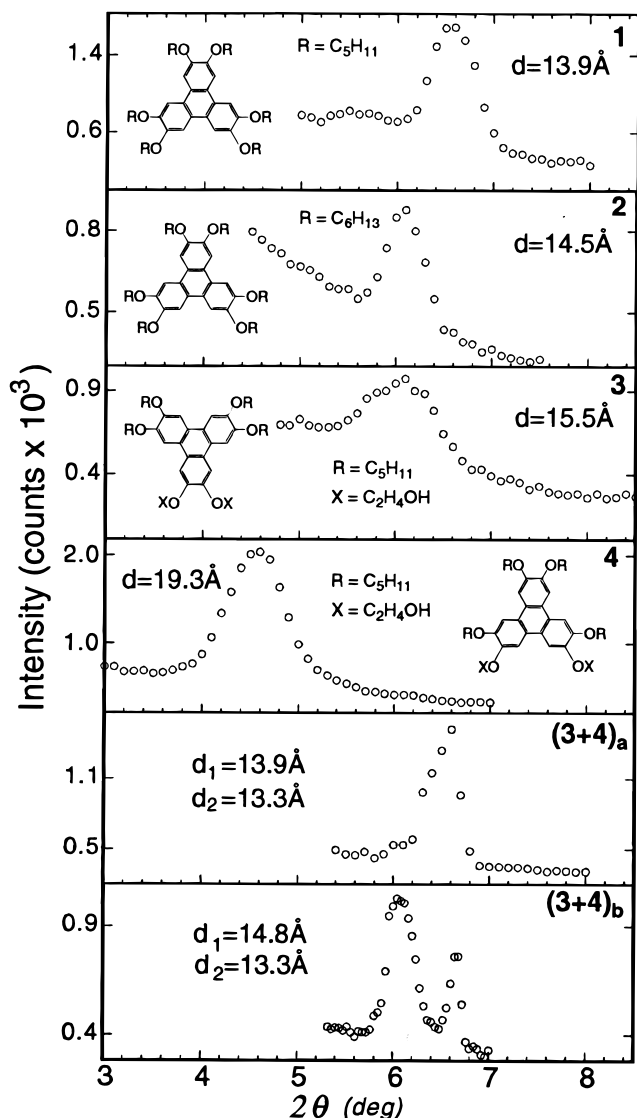


Figure 1. Grazing incidence X-ray diffraction peaks from compounds 1–4 and equimolar mixtures of 3 and 4, all spread on pure water. The intercolumnar spacings d corresponding to GID peak positions are indicated. The molecular structures of 1–4 are shown in corresponding insets. The (3 + 4)_a and (3 + 4)_b diffraction patterns were measured approximately 2 and 0.5 h after spreading, respectively.

the Born approximation by

$$\frac{R(q_z)}{R_F(q_z)} = \left| \int \rho'(z) e^{iq_z z} dz \right|^2 \quad (1)$$

where R/R_F is the measured reflectivity divided by the Fresnel reflectivity calculated for a perfect, sharp interface, $\rho(z)$ is the electron density as a function of height z , $\rho'(z) = d\rho(z)/dz$ is the gradient of the electron density, $q_z = (4\pi \sin \theta)/\lambda$ is the momentum transfer perpendicular to the interface, q_z/q_c is the normalized vertical scattering vector, and q_c is the scattering vector at the critical angle of incidence.

The data cannot in general be uniquely inverted to yield the electron density profile. A common approach to XR data analysis,²⁰ which we have adopted, is to model the film by a stack of uniform slabs, or boxes, each with a different electron density ρ_i and thickness L_i . The effect of capillary waves on the water surface is modeled by a single Gaussian roughness,

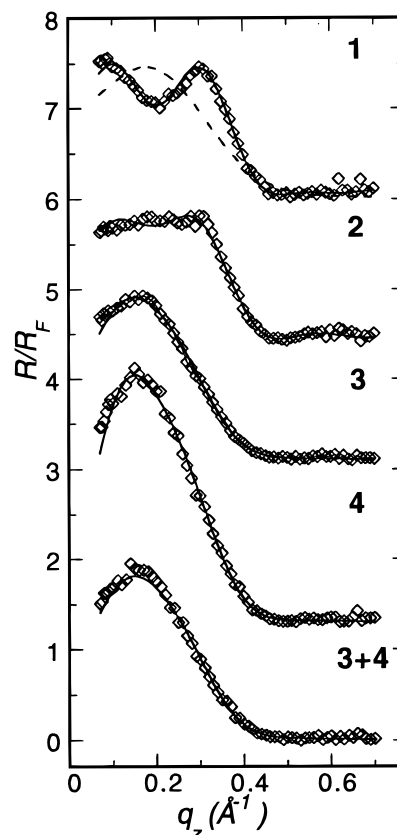


Figure 2. Measured (squares) and calculated (solid lines) X-ray reflectivities from compressed monolayers of compounds 1–4 and an equimolar mixture of 3 and 4 over pure water. R/R_F is the measured reflectivity normalized to the Fresnel reflectivity.

σ , for all interfaces. The reflectivity is then given by

$$\frac{R(q_z)}{R_F(q_z)} = \left| \sum_{i=1}^N \left(\frac{\rho_i - \rho_{i-1}}{\rho_0} \right) e^{-iq_z L_i} e^{-q^2 \sigma^2 / 2} \right|^2 \quad (2)$$

where ρ_0 is the density of the subphase. We used one-, two-, and three-box models to describe our films. The XR data were analyzed using least-squares fits to multibox models, with the constraints that the electron density per unit area be consistent with molecular areas derived from Π – A isotherm measurements and that the box thicknesses be consistent with plausible structural models of the films.

Figure 2 shows the XR data for all compounds together with representative model fits. Although we anticipated that 1 and 2 would form edge-on structures, the exact conformation of the tails was unknown, and we hoped that XR could clarify this question. However, our first, and unexpected, result was that the 1 and 2 XR data (Figure 2, top, Table 1) could not be described by a single-box model. The dashed curve through the XR profile of 1 (Figure 2, top) displays the best possible using eq 2 with $N = 1$. Although a single box model can reproduce the position of the minimum in any curve with a single minimum, the single-box fits to 1 and 2 fail badly at low q_z , indicating that the model breaks down at large distances. To obtain a theoretical curve in even qualitative agreement with the data, it was always necessary to incorporate a second box representing a low-occupancy (30% for 1 and 20% for 2) second layer. This implies that the pressure relaxation observed at high surface pressure is largely due to second layer formation. Indeed, Brewster angle microscopy measurements¹⁹ indicate that multilayer islands are present in carefully spread films even at

TABLE 1: Fitted Parameters for the Box Model of Electron Density Corresponding to the X-ray Reflectivity Curves in Figure 2^a

compound	1	2	3	4	3 + 4
no. of boxes	3	3	2	2	2
A [\AA^2]	66	81.9	60	60	60
ρ_i/ρ_s	1.64	1.74	1.48	1.77	1.48
L_1 [\AA]	4.0	5.5	13.2	12.8	13.1
ρ_2/ρ_s	1.41	0.98	0.1	0.17	0.1
L_2 [\AA]	8.2	6.5	16.4	15.4	16.3
ρ_3/ρ_s	0.37	0.21			
L_3 [\AA]	15.7	15.0			
σ [\AA]	2.65	2.8	3.8	3.8	3.8

^a A is the calculated area/molecule, ρ_i/ρ_s represents the normalized (to the electron density of water) electron density of box i , L_i is the thickness of box i , and σ is a surface roughness parameter.

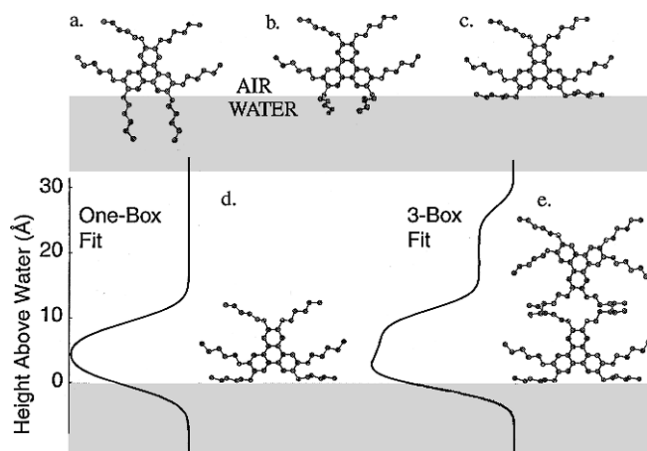


Figure 3. Possible conformations of hexapentyloxytriphenylene (**1**) at the air–water interface. (a) A model in which the tails are fully extended. (b) A model with the tails “coiled” in the water. (c) The conformation suggested by the XR measurements and molecular simulations, in which the tails are parallel to the water surface and the oxygen atom is in contact with the water. (d) The best electron density profile derived from a one-box fit, with a corresponding single-layer molecular conformation. (e) The best electron density profile derived from a three-box fit to XR data with a corresponding bilayer molecular conformation (the second layer has only 30% occupancy for **1** and 20% for **2**).

low pressure. Our best fits to the data were obtained using a three-box model, wherein the first box of 12–13 Å thickness is subdivided into a relatively high-density, thin slab contacting the water surface followed by a lower-density, thicker slab (Table 1). However, the three-box model increases the quality of the fit only slightly, and some improvement is to be expected merely due to the introduction of more free parameters.

We now return to the question of tail conformation. In principle one could imagine a number of possible molecular conformations. First, the tails could be fully extended, forming a “sun shape” with two or three of the terminal methyl groups contacting water surface. This conformation is energetically implausible, since the methyl groups are not particularly hydrophilic, and would imply a fairly thick 17–18 Å layer, in disagreement with our measured 12 Å thickness. Second, the tails adjacent to the water surface could still be fully extended and project down into the water, as shown in Figure 3a. This is energetically unfavorable for hydrophobic aliphatic tails. Third, the tails adjacent to the water surface could somehow “coil up” inside the subphase so as to minimize their exposure to the water (Figure 3b). Fourth, the tails adjacent to the water surface could bend or twist out of the way so that the core itself, or the ether linkage to the tails, is in contact with the water (Figure 3c).

To help distinguish between the latter two models, we performed simple molecular simulations.²¹ (Our goal was not to perform a complete ab initio analysis of the molecular conformation at the air–water interface but rather to filter out obviously inappropriate conformations.) We found that it is virtually impossible to “coil up” an alkyl tail so as to minimize contact with the water surface, but that a highly favorable conformation for the molecules, consistent with the XR data, is one in which the tails closest to the water surface lie parallel to the interface without projecting into it, exposing the hydrophilic oxygen atom to the water (Figure 3c). The molecular conformation is almost planar, and the side chains in positions 2, 7, 10 and 11 are somewhat flexible, thus increasing the entropy.

An alternative explanation of the ~12 Å thickness of the first fully occupied molecular layer of **1** and **2** could be a “sun model” with sharply tilted molecules. Low-temperature X-ray diffraction data²² from bulk **1** yield an intercolumnar distance of 18.95 Å which allows us to estimate the tilt angle as $\phi = 45\text{--}50^\circ$ from the normal to the water surface. However, such a model should increase the area per molecule substantially. This is inconsistent with previous and current Π – A isotherms,^{6,14–15} even when the possibility of 20–30% second layer occupancy is included.

4. Measurements on Compounds **3** and **4**

We now discuss the results of our measurements on compounds **3** and **4**. We expect that the substituted hydrophilic $\text{C}_2\text{H}_4\text{OH}$ groups should almost always be adjacent to the water surface. Thus, **3** and **4** should display more strongly amphiphilic behavior, and form more stable monolayers, than **1** or **2**. Furthermore, by controlling the placement of the $\text{C}_2\text{H}_4\text{OH}$ groups during the synthesis of the molecule it is possible to control the molecular orientation relative to the interface.¹⁵ The “2,3-isomer” **3** has the two functionalized tails immediately adjacent to each other, leading to a structure that can be schematically thought of as a triangle with the vertex pointing toward the water, while the “3,6-isomer” **4** has the two functionalized tails further away, leading to a triangle with the base pointing toward the water (Scheme 1).

Henderson et al.¹⁵ previously found that 1:1 mixtures of isomers **3** and **4** had properties quite different from those of either pure compound. The bulk liquid-crystalline mesophase range was dramatically increased in the mixture, and the molecular area at the air–water interface was lower for the mixture than for the sum of the individual compounds. These effects were rationalized in terms of an *intracolumnar* alternation of the two isomers in either the bulk DLC phase or the thin film: alternating up and down triangles can pack more efficiently within a given column than a sequence of molecules with the same orientation. Thus, we were interested in determining the structure of **3**, **4**, and their equimolar mixture at the air–water interface.

As was for the case of **1** and **2**, GID measurements of pure **3** or **4** always yielded one Bragg peak. These results were reproducible even between measurements separated by several months. We obtained reasonable intercolumnar spacings of 15.5 and 19.3 Å from **3** and **4**, respectively. If we now consider GID measurements on the 1:1 **3** + **4** mixture, the model presented above would predict that the (unobserved) (001) peak should be at somewhat higher q_{xy} than that in the pure compounds, but that the (100) peak in the mixture should be at roughly the average of the two pure compound positions. However, the GID from the mixture was quite different from that expected, showing unambiguous evidence of *intercolumnar* order.

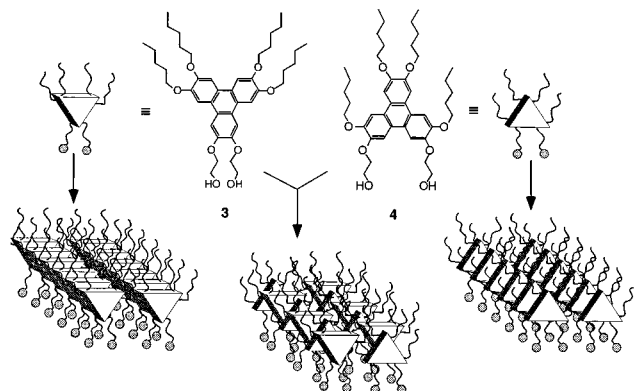


Figure 4. Schematic diagram of molecular order proposed in Langmuir films of a 1:1 mixture of **3** and **4**. Each molecule tends to lie with its hydroxy groups adjacent to the water and is represented schematically by a triangle. When the compounds are mixed they can pack more efficiently by alternating up and down triangles in both the intracolumnar and intercolumnar directions, resulting in a smaller intercolumnar distance in the mixture than in the pure compounds.

An initial measurement on the equimolar mixture of **3** and **4**, performed roughly 2 h after spreading the solution on the surface, and after a reflectivity measurement, resulted in an asymmetric single peak at $2\theta = 6.6^\circ$ (Figure 2e). This feature could be analyzed as arising from two broad peaks at 6.4° and 6.6° (yielding corresponding intercolumnar distances of 13.9 and 13.3 Å). When we repeated the measurement on a freshly spread film (roughly 30 min after the film was spread), we observed two adjacent peaks at $2\theta = 6.0^\circ$ and 6.6° (Figure 2f), neither of which is a peak position of one of the pure compounds. Such a pattern might originate from the coexistence of two different columnar structures or from a noncolumnar unit cell with unequal lattice parameters, such as a distorted hexagonal lattice.² The latter option should yield unit cell areas of 180–220 Å², which are significantly larger than the ~ 70 Å² molecular areas determined by Π -A isotherms, even if we include the possibility of 20–30% second layer formation. A more plausible explanation is that isomers **3** and **4** can pack more efficiently via an intercolumnar alternation of the two compounds, that this can happen in more than one way, and that we have observed the coexistence of these different phases. We note that the time scale for self-organization of these compounds is quite long, on the order of 4–8 h.¹⁵ Thus, it is not unexpected that our two measurements, made at different time intervals on the order of 0.5–2 h after spreading the monolayers, resulted in quantitatively different patterns.

Self-organization of a binary mixture of two compounds, such as **3** and **4**, could take place in a number of ways. The first model, proposed by Henderson et al., on the basis of Π -A isotherms,¹⁵ consists of an *intracolumnar* alternation of up and down isomers in a two-dimensional columnar liquid crystal, such that the molecular area was reduced. The effect on the diffraction pattern would be a shift in the (unobserved) (001) peak to higher angles. Second, each column could contain only one isomer, with an alternation of **3** and **4** from column to column in a columnar liquid crystal, such that the intercolumnar distance was reduced. This would move the (100) peak to higher angles and also result in a weak superlattice (1/2 0 0) peak, which has not been observed. Third, there could be an alternation of the up and down isomers both within the column and between the columns, as shown schematically in Figure 4. If the structure were liquid crystalline, the columns would be free to slide past each other, and there should be no (HOL) peaks and no superlattice peak. However, it is possible that the intercolumnar distance could still be reduced if there were short-

range correlations in isomer position from column to column. Finally, if the structure were crystalline, the isomers could be ordered both in their intracolumnar and intercolumnar positions. In this case, we would expect to observe both an increase in the (001) and (100) angles and also the presence of (HOL) peaks, although such peaks could be rendered unobservably weak by structure factor effects or stacking faults.

The observation that the intercolumnar spacings of both pure **3** and pure **4** are larger than any of the *d* spacings measured in the 1:1 mixture (Table 1) shows clearly that the area reduction in the mixture cannot arise solely from an *intracolumnar* alternation of up and down isomers. Some ordering must also be present on the intercolumnar length scale. It is most natural to assume a combination of both intracolumnar and intercolumnar order in either a crystalline or liquid crystalline phase, as shown in Figure 4, but our measurements did not allow us to determine more precisely the exact nature of this order.

The XR data and analysis of compounds **3** and **4** and the equimolar **3** + **4** mixture were similar to those of **1** and **2**. The data were best fitted with two boxes, where the first box of ~ 13 Å thickness represents a completely occupied monolayer of edge-on molecules and the second box of ~ 15 – 16 Å thickness corresponds to a second molecular layer with only $\sim 10\%$ occupancy (Table 1). The relatively smaller second layer occupancy compared to **1** and **2** is consistent with the enhanced monolayer stability that we anticipate for **3** and **4**. Since the short OH-terminated tails of **3** and **4** almost certainly contact the water surface, there is no necessity for the “splay” of the tails adjacent to the water surface that was observed for **1** and **2**, and indeed the fits were not significantly improved by the introduction of a third box. The larger electron density for the first layer of **4** and the consequential higher total number of electrons calculated per molecule of **4** indicate a significantly higher hydration level of **4** compared to **3**. This is consistent with the expected orientation of **4**, which leaves substantially more volume available near the water interface for binding of the water molecules than does **3**. The electron density profile of the equimolar 1:1 mixture of **3** and **4** is very similar to that of **3**.

5. Summary and Discussion

The analysis of our XR and GID data has led to an unambiguous determination of the edge-on columnar conformation of both symmetric and selectively functionalized triphenylene derivatives at the air–water interface. The XR data also indicated, unexpectedly, the formation of a partial second layer in all compounds studied.

Our diffraction measurements on the equimolar **3** and **4** mixture imply at least short-range intercolumnar order of the molecular positions, so that up and down triangles can align from one column to another, leading to a more efficient packing. It is unclear at this point whether the 1:1 ratio of **3** and **4** is truly “special,” as simple structural models would predict. Preliminary calorimetry measurements on bulk mixtures of **3** and **4** have been inconclusive;²² further structural and thermodynamic work on both bulk phases and thin films would be required to settle this question.

Our preferred model for **1** and **2** indicates that two hydrocarbon tails of each molecule most likely lie on the water surface such as to expose the hydrophilic oxygen atoms to water. This may help to explain the long-standing mystery¹⁴ of why alkoxytriphenylene derivatives form stable Langmuir monolayers while alkylthio derivatives do not: the sulfur atoms which substitute for the oxygen atoms in the alkylthio derivatives are less capable of hydrogen bonding, making the monolayer structure less stable to multilayer or droplet formation.

We note, finally, that the 13.9–14.5 Å intercolumnar spacings measured for **1** and **2** are significantly smaller than the corresponding 18–20 Å intercolumnar spacings measured in the three-dimensional hexagonal columnar (D_{hd}) phases of **1**, **2**, and other triphenylene derivatives with five or six carbons per tail.^{5,23–25} This could possibly arise if all the tails extended directly away from the air–water interface, but as we have seen the layer thicknesses are also somewhat smaller than expected. It seems more likely that films of **1** or **2** self-organize on short length scales, alternating “up” and “down” triangle orientations so as to minimize tail–tail overlap both between columns and between adjacent molecules in the same column. The local order is similar to that proposed for equimolar mixtures of **3** and **4**, and shown in Figure 4, with the difference that molecules of **1** (or **2**) can rapidly reorient between the up and down triangle orientations. This kind of orientational self-organization is not possible a D_{hd} phase, because each column is surrounded by six equivalent columns. Alternating the molecular orientations is equivalent to a two-dimensional antiferromagnetic Ising model, which is frustrated on a triangular or hexagonal lattice. However, the two-dimensional system is not frustrated, and our short intercolumnar distances indicate that such an alternation of orientations is probably taking place.

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