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Self-organization of discogenic molecules at the air-water interface

Nicholas C. Maliszewskyj (1), Paul A. Heiney (1), J. Kent Blasie (2), John P. McCauley, Jr. (2) and Amos B. Smith, III (2)

(1) Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, U.S.A.
(2) Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, U.S.A.

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Abstract. — The behavior of several species of discogenic molecules at the air-water interface has been determined by measuring surface pressure vs. molecular area isotherms. Alkylthiotriphenylene derivatives do not appear to form monolayers at the interfaces, due to lack of amphiphilic character. Two truxene derivatives were found to display molecular areas on the order of 65 Å², most likely due to the molecules lying «edge-on» to the water surface. Hexacyclens generally lie with the core group parallel to the surface of the water with the tail groups extending away from the interface; a higher density phase may correspond to conformational changes within the molecule.

1. Introduction.

The organization of amphiphilic molecules such as lipids and soaps into monolayers on water surfaces is a well known phenomenon [1]. Recently, it has become clear [2-7] that Langmuir monolayers can also be formed from the disc-shaped molecules of which discotic liquid crystals [8] are composed. Such molecules typically, but not universally, have flat, conjugated cores and 4-8 aliphatic tails. The bulk liquid crystalline phases may be nematic («N_d») or hexagonal-columnar («D_{hd}»), the latter structure consisting of a hexagonal array of columns of molecules. The column axis is approximately normal to the molecular core and the aliphatic tails extend more or less radially from the column axis. By contrast, surface pressure isotherm measurements have shown that several quite different conformations are possible for discogenic molecules at the air-water interface.

For phthalocyanines [3], benzenz hexa-n-alkanoates [2, 5], and hexacyclens [6, 7], the molecular areas extrapolated from measurements of spreading pressure \( \Pi \) versus area \( A \) are consistent with a model for a condensed phase in which the core lies flat in the surface, with the aliphatic tails projecting away from the surface. By contrast, the measured molecular area of several alkoxytriphénylene derivatives is much smaller than the area of such a
Scheme 1.

1a $X, R = SC_5H_{11}$
1b $X, R = SC_6H_{13}$
1c $X, R = SC_7H_{15}$
1d $X = COO(CH_2)_3CH_3$
   $R = OC_5H_{11}$
1e $X, R = OC_3H_{11}$

2a $R = COO(CH_2)_{12}CH_3$
2b $R = COOPhO(CH_2)_{10}CH_3$

3a-f

a $R = C_6H_4OC_{12}H_{25}$
b $R = C_6H_4OC_4H_9$
c $R = C_6H_5$
d $R = C_{17}H_{35}$
e $R = C_6H_4OC_{11}H_{23}$
f $R = C_5H_{11}$
molecule lying flat, implying that these molecules most likely are oriented « edge-on » to the air-water interface, with at least two tails penetrating into the subphase [4, 7]. Thermodynamic transitions between different conformations may be possible; in particular, benzene hexa-n-alkanoate isotherms have been interpreted both in terms of a structure for which the core lies parallel to the interface with the tails close packed [5], and in terms of a transition in which the entire molecule tilts from a conformation in which the core lies parallel (« flat ») to the interface to one in which it sits perpendicular (« edge-on ») to the interface at high compression [4].

We have measured surface pressure vs. molecular area isotherms at room temperature for three classes of thermotropic discotic mesogen as shown in Scheme 1: hexacyclens, truxenes, and triphenylenes. Thermal data and literature references for these compounds are given in table I. The goal was to further explore the role of molecular architecture in determining both liquid-crystal-phase structure and structure at the air-water interface.

Small quantities of solute ($\approx 10^{-3}$ g) were weighed on a Cahn electrobalance to an accuracy of $10^{-6}$ g. The hexacyclens 3a-3f and 4a-4d are quite hygroscopic [9, 10], and for these compounds it was necessary to remove water by heating the sample gently to 55 °C under dynamic vacuum for at least 36 hours before weighing to obtain reproducible results. After weighing, the solutes were dissolved in 10 ml of HPLC grade methylene chloride. Methylene chloride is known to be a good spreading solvent, immiscible in water and quite volatile (boiling point $\approx 40$ °C) [6]. The subphase for $\Pi - A$ measurements was water purified in a Millipore filtration system. A commercially available Lauda film balance was used to determine the surface pressure by the movable barrier/Langmuir float method to an accuracy of 0.1 mN/m. All measurements were performed at room temperature, $T = 21 \pm 3$ °C. After performing a cleaning sweep of the surface, 0.1 ml of the solution was spread on the interface and at least 10 min allowed for evaporation of the solvent. The film was then compressed at a barrier speed of 0.75 cm/min, so that the duration of an experiment was approximately 30 min. All measurements were made 3 times from different solutions and the reproducibility was within 5%.

In a typical $\Pi - A$ isotherm, steep rises in pressure are associated with a pure phase, while approximately horizontal regions are associated with coexistence between two phases. There is more than one convention for determining the molecular area from such isotherms. For example, the molecular area of 3a is variously reported as 160 Å² [7] and 225 Å² [6], even though the measured isotherms are quite similar. The difference lies in whether the molecular area is defined by the inflection point of the vertical rise in pressure corresponding to the condensed phase, or by the onset of that vertical rise. It is the former convention to which we adhere in this paper.

As recently observed [11], $\Pi - A$ isotherms in Langmuir films are in practice often performed away from thermodynamic equilibrium. We and others [2, 4, 5, 7] have in some cases observed a local maximum, or « bump », in spreading pressure vs. molecular area. Such a feature is an indication that the isotherm is in fact measuring a nonequilibrium process such as irreversible second layer formation or a hysteretic first order transition. With care, however, the isotherms are still useful tools for determining molecular surface areas close to monolayer completion.

2. Results.

We will discuss in turn our studies of triphenylene derivatives, truxene derivatives, and hexacyclens.

Triphenylene derivatives: The liquid crystalline properties of alkoxy- and alkylthio-triphenylene derivatives have been extensively studied [12-15]. $\Pi - A$ isotherms of
Table I. — Bulk transition temperatures and molecular areas at the water surface, derived at the inflection point of the first state of the condensed phase of the monolayer. References are given for the appearance of these compounds in the literature. Molecular areas are measured from the inflection points in the first « state » of the condensed monolayer phase from the isotherms in figures 1, 2, 4 and 5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bulk Liquid-Crystalline Phases</th>
<th>Reference</th>
<th>Area (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>K1 $\leftrightarrow$ K2 $\leftrightarrow$ D$_{hd}$ $\leftrightarrow$ I</td>
<td>[27]</td>
<td>17</td>
</tr>
<tr>
<td>1b</td>
<td>K $\leftrightarrow$ H $\leftrightarrow$ D$_{hd}$ $\leftrightarrow$ I</td>
<td>[13-15]</td>
<td>17</td>
</tr>
<tr>
<td>1c</td>
<td>K $\leftrightarrow$ D$_{hd}$ $\leftrightarrow$ I</td>
<td>[27]</td>
<td>21</td>
</tr>
<tr>
<td>1d</td>
<td>D$_{hd}$ $\leftrightarrow$ I</td>
<td>[27]</td>
<td>53</td>
</tr>
<tr>
<td>1e</td>
<td>K $\leftrightarrow$ D $\leftrightarrow$ I</td>
<td>[4,12]</td>
<td>68</td>
</tr>
<tr>
<td>2a</td>
<td>K $\leftrightarrow$ N$<em>{D}$ $\leftrightarrow$ D$</em>{rd}$ $\leftrightarrow$ D$_{hd}$ $\leftrightarrow$ I</td>
<td>[17-23]</td>
<td>63</td>
</tr>
<tr>
<td>2b</td>
<td>K $\leftrightarrow$ D$<em>{rd}$ $\leftrightarrow$ N$</em>{D}$ $\leftrightarrow$ D$<em>{rd}$ $\leftrightarrow$ N$</em>{D}$ $\leftrightarrow$ I</td>
<td>[17-23]</td>
<td>74</td>
</tr>
<tr>
<td>3a</td>
<td>K $\leftrightarrow$ T $\leftrightarrow$ I</td>
<td>[6], [7], [10]</td>
<td>159</td>
</tr>
<tr>
<td>3b</td>
<td>K $\leftrightarrow$ I</td>
<td>[10]</td>
<td>168</td>
</tr>
<tr>
<td>3c</td>
<td>glass $\leftrightarrow$ I</td>
<td>[10]</td>
<td>17</td>
</tr>
<tr>
<td>3d</td>
<td>K $\leftrightarrow$ I</td>
<td>[10]</td>
<td>122</td>
</tr>
<tr>
<td>3e</td>
<td>K $\leftrightarrow$ T $\leftrightarrow$ I</td>
<td>[10]</td>
<td>176</td>
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<tr>
<td>3f</td>
<td>K $\leftrightarrow$ I</td>
<td>[10]</td>
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<tr>
<td>4a</td>
<td>K $\leftrightarrow$ I</td>
<td>[10]</td>
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<tr>
<td>4b</td>
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<tr>
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<td>[10]</td>
<td>157</td>
</tr>
<tr>
<td>4d</td>
<td>K $\leftrightarrow$ I</td>
<td>[10]</td>
<td>112</td>
</tr>
</tbody>
</table>

Compounds 1a-1e are shown in figure 1. Our isotherm for 1e agrees within 6 % with the previous determination [4] of a 7-9 mN/m pressure and 70 Å² area per molecule at the inflection point. Compound 1d gives a similar molecular area, with a smaller compressibility in the condensed phase. This supports the hypothesis of an « edge on » arrangement for both compounds. The alkylthiotriphenylenes (1a-c) lack polarizable atoms which would serve to anchor the molecule to the surface, suggesting that they might be less likely to form.
monolayers on water. Indeed, the very small measured molecular areas for these compounds is smaller than the known area for packing of hydrocarbon chains attached to hydrophilic groups (≈ 18 Å²), leading us to conclude that these alkylthiotriphenylenes do not form Langmuir films [16].
Truxene derivatives: The liquid crystalline properties of the truxene derivatives, hexa-\(n\)-alkanoyloxytruxene (2a) and hexa-\(n\)-alkoxybenzoyloxytruxene (2b), are also well understood [17-23]. The spreading behavior of these mesogens is shown in figure 2. The \(\Pi - A\) diagrams all show the formation of relatively incompressible monolayers with surface pressures at the inflection point on the order of 17.5 mN/m. The areas measured at the inflection points of the isotherms are much smaller than would be expected if the molecules were assumed to lie with the cores flat on the surface (about 154 Å\(^2\) for 2a and 380 Å\(^2\) for 2b). The presence of highly electronegative oxygen atoms to serve as polar anchoring points to the water surface and relatively high surface pressures (\(\approx 20\) mN/m) coupled with non-negligible molecular areas indicate that the molecules are not being pulled into the subphase and are not so hydrophobic as to form oily droplets at the surface.

![Diagram of truxene derivatives](image)

**Fig. 2.** — \(\Pi - A\) isotherms for two derivatives of truxene cores. The low molecular areas of 2a and 2b are reminiscent of those of 1d and 1e and are consistent with a model in which the molecules lie edge-on to the water surface. The larger area of 2b can be attributed to the presence of bulky phenyl rings in the substituted tails.

The most plausible explanation of the observed molecular areas is that, like the benzene and triphenylene derivatives discussed above, the molecules lie edge-on to the interface. Taking the bulk core-core distance of 4.5 Å for the core-core distance in the Langmuir film, the corresponding long axis of the molecular projection on the water surface must be on the order of 15-20 Å, consistent with the transverse dimensions of the molecule. The «edge-on» hypothesis requires that two hydrocarbon tails penetrate the subphase to some extent. Figure 3 shows a possible conformation for 2a at the surface, and illustrates the manner in which the (hydrophobic) tails that penetrate the subphase most likely coil up so as to minimize their surface area [24]. The cross sectional area of the molecule shown in figure 3 is consistent with the measured molecular areas from figure 2.
**Fig. 3. — Model of 2a at the air-water interface, assuming an edge-on arrangement of the truxene cores at the interface. We postulate that the tails submerged in the water adopt a coiled structure to reduce the free energy of the hydrophobic hydrocarbon tails in direct contact with water.**

**Hexacyclen derivatives**: We have studied a variety of hexasubstituted [18]-N₆ azacrowns, or hexacyclens (Scheme 1); $\Pi - A$ isotherms are shown in figure 4 and 5. Among the hexacyclen compounds 3a-3f and 4a-4d, only 3a and 3e form liquid crystalline phases. The bulk mesophase structure of 3a is unclear, and has been variously described as tubular-columnar [25] or smectic [10]. The interfacial behavior of this molecule, however, is much more straightforward, and we have duplicated previous [6, 7] $\Pi - A$ isotherms.

Compounds 3a, 3b, and 3e are all similar to each other, sharing the same hexamide core and benzoyl linkage, and differing only in the length of the attached alkyl tail. Substitution of a hexamine core (amounting only to substituting the carbonyl functional group for a methylene linkage) produces 4a and 4b. All of these compounds display isotherms characteristic of a transition between a low-density, low-pressure state and a high-density, high-pressure state. The molecular areas in the low-density state are on the order of 160 Å², while those for the high-density state are either 50 or 100 Å². The transition between the two states generally involves a non-equilibrium «bump» as discussed above. The generally accepted [6, 7] interpretation of the low-density state is that the macrocycle core lies flat on the water surface and the alkyl tails project away from the water surface; a space-filling model of such an arrangement yields a molecular area in agreement with that observed.
Fig. 4. — II - A isotherms for derivatives of the hexamide core 3. Note the distinct second phase at low molecular areas for several of these compounds, corresponding either to multilayer formation or a more compact molecular conformation.
Fig. 5. — $\Pi - A$ isotherms for derivatives of the hexamine core 4. The second phase is clearly manifest in 4a and 4b.

It is conceivable that the high-density state corresponds to multilayer formation; ellipsometry measurements could help resolve this question. Alternatively, the second state may quite likely correspond to a conformational change in the monolayer. For example, there may be more than one conformation of the macrocycle core: an «expanded» conformation in which the nitrogen atoms are relatively far away from each other, and a «collapsed» conformation in which the core occupies much less volume. If we assume a conformation in which a collapsed macrocycle lies flat on the water surface and the alkyl tails are constrained to extend away from the water surface, thereby incorporating the known cross-sectional area per alkyl chain of $\sim 18 \text{ Å}^2$, then the minimum molecular area is approximately 110 $\text{Å}^2$, in good agreement with the measured areas for 3a, 3b and 4a. If we assume a linear conformation of the molecule [10], in which three chains group together on either end of the molecule, we calculate a molecular area of $\sim 55 \text{ Å}^2$, in reasonable agreement with our results for 3e and 4b.

Completely removing the alkyl tails leaves us with compounds 3c and 4c. Compound 4c has an isotherm with only a first state observable, whereas 3c has an isotherm with a measurable molecular area of $17 \text{ Å}^2$, smaller than that for a single alkyl chain, and certainly too small to support interpretation as a monolayer. As this compound is weakly soluble in water, the low molecular area for 3c most likely arises from the molecules dissolving into the subphase.

Finally, removing the phenyl ring and associated oxygen and leaving the alkyl tail gives compounds 3d, 4d, and 3f. Compounds 3d and 4d share similar spreading behavior, with
comparable areas per molecule and absence of a second state. The molecular areas associated with these two compounds appear to be consistent with the hexacyclen core laying flat on the water surface with the alkyl tails extending away from the subphase. As 3f is structurally similar to 3d and 4d, one would expect to see similar spreading behavior. However, the isotherm measured clearly displays the two state phenomenon observed in compounds such as 3a.

3. Conclusions.

A number of quite dissimilar conformations are possible for discogenic mesogens at the air-water interface. Depending on the details of the molecular structure, discogenic molecules with flat conjugated cores (such as benzene, triphenylene, or truxene derivatives) may either lie flat on the water surface with the tails extending away from the interface, or edge-on with two tails penetrating the subphase to some extent. In the hexacyclen compounds, which have quite flexible cores, the molecules may make a transition between a conformation with the cores lying flat on the water surface and a second state in which either the cores are collapsed (i.e. compressed such that the projection of the core on the water is as small as possible) and the alkyl chains are close packed, or in which the molecule is essentially linear (quite similar to the edge-on model for more rigid compounds).

De Gennes first suggested in 1971 [26] that elongated molecules at interfaces could form two-dimensional nematic phases, with short-range positional order and quasi-long-range orientational order. Discogenic molecules such as phthalocyanines and benzene-hexa-alkanoates lie with their core groups flat on the water surface, projecting roughly circular cross-sections on the water surface. These materials are therefore not good candidates for two-dimensional nematics. Fatty acid molecules exhibit tilted monolayer phases, projecting elliptical cross-sections on the water surface, but in this case the three-dimensional aspect of the molecules becomes more important, making them again inappropriate models for two-dimensional nematics. On the other hand, molecules such as the triphenylene and truxene alkanoates project elongated cross sections on the water surface due solely to the molecular shape. This raises the interesting possibility that similar compounds may exhibit two-dimensional liquid crystal phases. Future progress in understanding the structure of mesogenic compounds at the air-water interface will clearly rely on structural probes such as high resolution x-ray diffraction.

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References

[16] This interpretation was strengthened by the observation of a patchy structure when crossed polarizers were used to examine a deposition of density similar to that on the surface of the trough or on the surface of water in a Petri dish, suggesting that three-dimensional microcrystallites or oily droplets were floating on the water surface.
[24] Figure 3 actually shows a structure obtained via potential energy minimization of an isolated (gas phase) molecule, not including the effects of the air-water interface or the surrounding molecules. The energy was minimized using the conjugate gradient method in the Dreiding force field available on Polygraf, a product of Biodesign, Inc.
[27] Transition temperatures were measured in our laboratory using Differential Scanning Calorimetry.