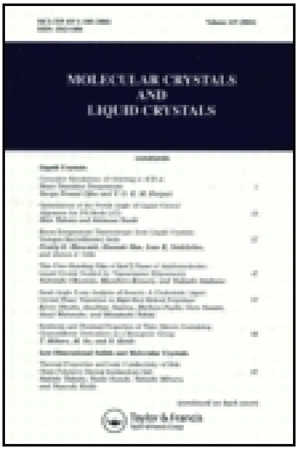

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Langmuir-Blodgett Films of Amphiphiles with Cyano Headgroups

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LANGMUIR-BLODGETT FILMS OF AMPHIPHILES WITH CYANO HEADGROUPS

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Abstract Surface pressure-area isotherms for a number of structurally related aromatic cyano derivatives were recorded. T15 (4-cyano-4"-n-pentyl-p-terphenyl) gave the most cohesive monolayer owing to a greater degree of intermolecular π orbital overlap. This compound gave Z-type multilayer deposition and an explanation for this transfer behaviour is proposed based on dipole-dipole interactions between adjacent layers. An X-ray diffraction study showed the layer thickness to be 20.5 ±0.5Å and a molecular packing model consistent with this value is presented. Preliminary comparisons are made with the monolayer and multilayer behaviour of long-chain alkyl cyanides.

1 INTRODUCTION

The main objectives of the work described in this paper were to investigate monomolecular layers of various amphiphilic cyano (CN) derivatives adsorbed at the water-air interface and, where possible, to prepare multilayer films using the Langmuir-Blodgett (LB) technique. Apart from an early report by Adam[1] that long-chain alkyl cyanides can give stable monolayers, very little attention (if any) has been given to the monolayer-multilayer behaviour of CN materials.

The majority of CN derivatives investigated here exhibit liquid crystalline behaviour in the parent bulk phase. A wide range of CN liquid crystals (LCs) are available and it has therefore been possible to investigate the influence of molecular design on the ability to form monolayers and/or multilayers. Also, it was considered of interest to check for any structural analogies between the LB films and the liquid crystal phases of the parent bulk materials.

2 EXPERIMENTAL DETAILS

The CN LC samples used here were kindly supplied by Professor G W Gray (Hull University) and BDH Chemicals Ltd. The alkyl cyanides were obtained commercially from Koch-Light Laboratories Ltd. Other chemicals and solvents used were the best available commercial grades.

Materials were spread from chloroform and/or toluene solutions onto the surface of water obtained from a Milli-Q purification system; no significant solvent effects were observed. The surface area of the monolayer was varied by using a motor-driven polytetrafluoroethylene-coated glass fibre barrier of constant perimeter. Monolayer compression rates were typically about 10 $Å^2$ $molecule^{-1}$ min^{-1}. An electronic feedback system was used to maintain the surface pressure at the required value. Substrates were prepared using conventional evaporation techniques and dipped at 2.5 mm min^{-1}.

X-ray diffraction profiles were recorded using a conventional Philips vertical powder diffractometer, employing Cu Kα radiation and narrow slits to permit measurements down to a scattering angle $2\theta \approx 1.5^{o}$ ($d_{max} \approx 60$ Å). The accuracy of our technique was confirmed by obtaining fair agreement with the literature value for a 55-layer LB film of cadmium stearate (observed layer thickness, 24.5 ± 0.5 Å; cf. the literature value of 25.3 ± 0.1 Å[2]).

3 EXPERIMENTAL RESULTS AND DISCUSSION

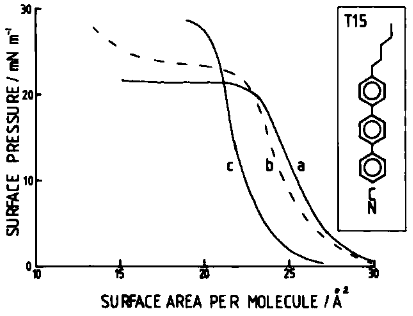
3.1 Surface pressure-area isotherms for T15

Figure 1 shows a selection of isotherm data for T15 together with its structural formula. As expected for an unionized monolayer the data were little affected by changes in pH or the addition of salts to the subphase. At 20°C (curve a) the monolayer is expanded and collapses at 22 mN m^{-1} with an average molecular area of 23 $Å^2$ $molecule^{-1}$. Consideration of a space-filling molecular model of T15 showed that this area is physically reasonable (estimated minimum cross-sectional area, about 20 $Å^2$ $molecule^{-1}$). The collapsed regions were unstable for $A_m \gtrsim 15$ $Å^2$ $molecule^{-1}$, rapidly reverting to the monolayer on increasing the surface area. However, the monolayer did become more condensed (curve b). Further condensation of the monolayer occurred on cooling to 8°C (curve c).

3.2 Deposition of multilayers of T15

Figure 2 shows the changes in T15 monolayer area with time at two different surface pressures. Although cooling the subphase to 8°C gave an increase in π_c (see Figure 1), no significant improvement in monolayer stability was obtained. Transfer of monolayers to an aluminium-coated glass slide was carried out at the higher pressure of 12 mN m^{-1} ($T \approx 22°C$; pH, about 5.7), since an intolerable degree of peeling-off of the deposited film was encountered at 6 mN m^{-1}.

Monolayer transfer was primarily observed on the upward strokes (Z-type deposition). A possible explanation for this deposition behaviour is schematically illustrated in Figure 3. Orientation of dipoles of adsorbed T15



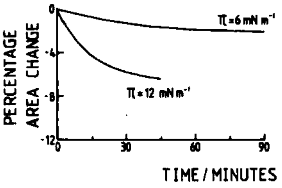


FIGURE 1. π-A isotherms of T15 (the structural formula is shown in the inset): curve a, first compression at 20°C; curve b, seventh compression at 20°C; curve c, subphase temperature reduced to 8°C (second compression).

FIGURE 2. Percentage change in T15 monolayer area with time at two different surface pressures, 6 and 12 mN m^{-1} (subphase temperature, 22°C).

molecules might induce a parallel orientation in an adjacent layer of molecules via dipole-dipole interactions, with this preferential configuration being to some extent propagated to subsequent layers. The CN dipole is collinear with the main molecular axis in T15 and its moment is relatively large, about 4 debye. It is well known that COOH amphiphiles tend to transfer on both strokes of the dipping cycle, resulting in a head-to-head configuration (Y-type deposition) via either hydrogen-bonded dimerization (unionized) or salt formation (ionized), depending on the subphase pH; neither is possible for CN derivatives.

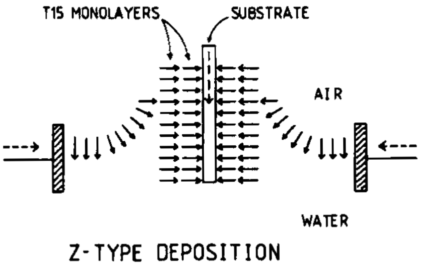


FIGURE 3. Schematic illustration of the model proposed to explain Z-type multilayer deposition of T15. The arrows are used to represent T15 molecules and to indicate dipole directions. The substrate is on its downward stroke and is wetted by the meniscus. Further explanation is given in the text.

If no gross rearrangement of the T15 molecules occurs either during or after deposition and the multilayer film has a Z-type structure, then it might well form the basis of a novel piezoelectric or pyroelectric device since it presumably would possess a permanent dipole moment. An analysis of the film structure was made using X-ray diffraction and the results obtained will now be described.

3.3 X-ray diffraction study of the T15 Langmuir-Blodgett film

The X-ray diffraction profile for a 16-layer T15 film was measured using the method outlined in Section 2 one week after deposition. Only one Bragg peak was observed corresponding to a layer spacing of 20.5 ± 0.5 Å. Since no peak corresponding to twice this spacing was found, it may be assumed that the observed peak is the first-order layer reflection. This strongly suggests that the constituent layers are arranged in a unidirectional (Z-type) configuration and that any gross rearrangement of the molecules must be negligible for the present film for the duration of the experiment.

It is of interest to note that there appears to be a structural link between the T15 LB film and the bulk nematic phase which has an unusual structure[3], consisting of two coexisting mass density fluctuations with incommensurate wavelengths of 20.4 Å and 30.7 Å corresponding respectively to something less than the molecular length (ℓ = 22 Å) and to the CN "bilayer" spacing (about 1.4ℓ). It is thought that the 20.4 Å repeat distance probably results from monolayer formation[3], which is consistent with the observed LB layer spacing, suggesting therefore that closely similar local molecular packing exists in regions of the bulk nematic and the LB film.

Figures 4(a) and 4(b) together show how the T15 molecules might pack together within the layers. Figure 4(a) shows that this packing arrangement is consistent with the observed layer thickness. Improved agreement with experiment may be obtained if allowance is made for some interpenetration of the CN groups and the alkyl tails between adjacent layers; up to about 2 Å can be accommodated. It should be noted that, if this were the case, then the alkyl groups would act to reduce dipole repulsion between neighbours via screening. An orthogonal view (Figure 4(b)) shows that some staggering of the CN head groups is possible, which would again help to reduce dipole repulsion.

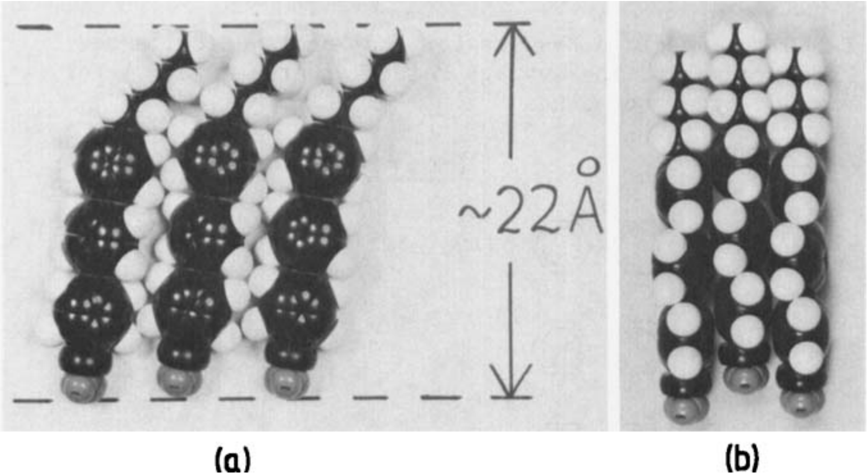


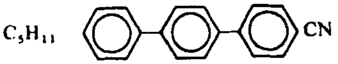
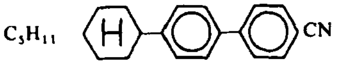
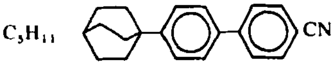
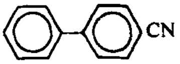
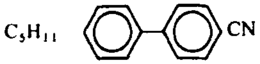
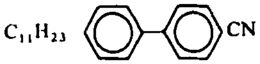
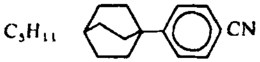
FIGURE 4. Molecular space-filling models of T15 indicating a possible packing arrangement within a single layer as illustrated by two orthogonal views: (a) the model layer thickness is about 22 Å; (b) it should be noted that some staggering of the CN head groups is possible. Further explanation is given in the text.

It is important to point out that the molecular packing is probably significantly more disordered than that indicated in Figures 4(a) and 4(b). For example, the alkyl chains may be conformationally disordered and also the molecules may be rotationally disordered in an analogous way to that observed in the highly ordered smectic phases. Moreover, it is highly probable that water is retained in the vicinity of the CN head groups.

3.4 Surface pressure-area isotherms of some other liquid crystal cyano derivatives

π-A isotherms were recorded for a number of other structurally closely related LC CN compounds in an attempt to understand those factors responsible for monolayer cohesion in the T15 monolayer; this should allow us to predict

TABLE 1. Specimen Results for the Monolayer Collapse Pressure π_c and the Average Molecular Area A_c at π_c for various cyano compounds

	Compound	π_c (mNm^{-1})	A_c (Å^2 molecule^{-1})
A	 [T15] K(131)N(240)I	22	23±1
B	 K(96)N(222)I	≈0	—
C	 K(160)N(270)I	≈0	—
D	 K(87)I	≈0	—
E	 K(24)N(35.3)I	4.5	34±2
F	 K(53)S_A(57)N(57.5)I	5.0	36±2
G	 K(62)N(100)I	≈0	—
H	$C_{16}H_{33}CN$	30	20
I	$C_{18}H_{37}CN$	35	19

Bulk transition temperatures are given in degrees Celsius ,  and  indicate phenyl, cyclohexane and BCO groups respectively. K denotes crystal; S_A denotes smectic A; N denotes nematic; I denotes isotropic liquid. Compound D has a virtual monotropic transition, N(-45)I. The sub-phase temperature is about 20°C, the pH about 5.8.

possible structural improvements. Results for a selection of materials studied are summarized in Table 1. All monolayers were spread onto a water subphase to which no salt had been intentionally added.

As mentioned earlier in the introduction, T15 (compound A in Table 1) gave the most stable monolayer of all the aromatic materials investigated here. The replacement of a phenyl ring in T15 by a much bulkier ring system should have a marked effect on the molecular packing. Indeed, substitution of a cyclohexane or BCO group, compounds B and C respectively, gave monolayers which were unable to offer any significant resistance to barrier compression ($\pi_c \approx 0$); the molecules were expelled and the bulk phase was observed to form, presumably as a result of reduced packing efficiency compared with that of T15. This behaviour is consistent with the observation that the introduction of cyclohexane or BCO groups suppresses the formation of CN LC smectic phases[4] which have the constituent molecules arranged in layers. Strong intermolecular forces in the bulk phases may be achieved of course by adopting the CN "bilayer" configuration.

Figure 5 shows the π-A isotherms for all the alkyl CN biphenyl monolayers investigated here, plotted together for easy comparison. Although the steepness of the curves increases on increasing the length of the alkyl tail, indicating some improvement in intermolecular attraction, the collapse points are not significantly affected (4.5 ± 0.5 mN m^{-1}, 36 ± 2 Å^2 molecule^{-1}). This marked reduction in π_c compared with the value for T15 clearly demonstrates the importance of π orbital overlap in conferring good cohesion in aromatic systems. In fact π_c for compound E was found to be the same as its equilibrium

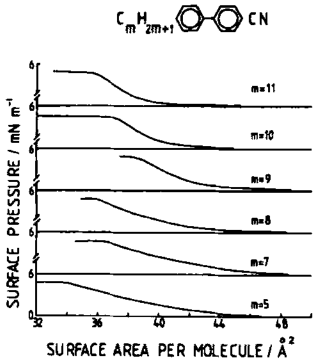
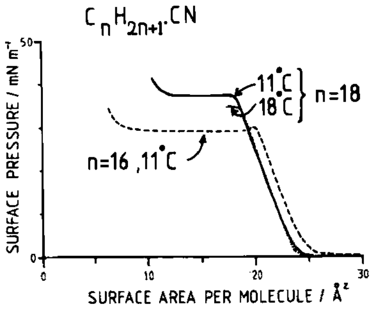


FIGURE 5. Comparison of the π-A isotherms for the 4-cyano-4'-n-alkyl-p-biphenyls (subphase temperature, 20°C). The number m of carbon atoms in individual alkyl tails is indicated in the figure.

spreading pressure within experimental error. The increase in A_m relative to that for T15 (about 23 Å^2 molecule^{-1}) indicates that the CN biphenyl cores are (in each case) tilted further from the layer normal at the collapse point. Although this increased tilting reduces the dipole repulsion between neighbours, concomitant reduction in π orbital overlap also occurs. With reference to the result for compound D, it appears that the presence of an alkyl group is necessary in order to allow a finite monolayer collapse pressure for the CN biphenyls. Replacement of a phenyl ring in compound E by a BCO group (compound G) reduced π_c to approximately zero, analogously to the situation observed for the three-ring systems (compounds A and C).

3.5 Alkyl cyanides

For comparison, the monolayer-multilayer behaviour of some



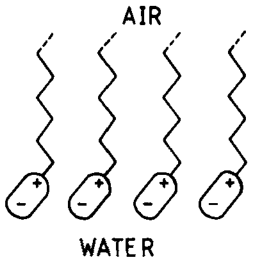


FIGURE 6. π-A isotherms for two alkyl cyanides.

FIGURE 7. Probable packing arrangement for alkyl cyanide molecules in a compressed monolayer.

alkyl cyanides were investigated. π-A isotherms for $C_{16}H_{33}CN$ and $C_{18}H_{37}CN$ were recorded and are shown in Figure 6 and are consistent with the results reported by Adam[1]. Note that, as expected, either cooling the subphase or increasing the chain length produces an increase in π_c.

The $C_{18}H_{37}CN$ monolayer was particularly stable (-dA/dt $\lesssim$ 1% hour). This stability probably results from efficient packing of the alkyl chains and the tilting of the cyano groups with respect to the layer normal which reduces the intermolecular dipole-dipole repulsive forces; the probable molecular packing arrangement is schematically illustrated in Figure 7.

Although the π-A curves were insensitive to the presence of $CdC\ell_2$ in the subphase, good monolayer transfer was achieved onto a hydrophobic gold-coated glass substrate during each stroke (Y-type deposition) with a 2.5 10^{-4} M

$CdC\ell_2$ aqueous subphase (to give an even number of layers) and poor quality Z-type deposition was observed with no $CdC\ell_2$ present. Further studies are in progress aimed at understanding reasons for this marked change in deposition behaviour.

4 CONCLUDING REMARKS

We have demonstrated that it is possible to prepare moderately stable monolayers of CN derivatives with extended π electron systems and short alkyl chains. Relatively uncommon Z-type deposition, involving parallel orientation of adjacent layers, was observed for T15. A simple model has been proposed to explain this behaviour based on dipole-dipole interactions. Results of a subsequent X-ray diffraction study were consistent with Z-type structure being retained in the T15 LB film. It would obviously be of interest to study the surface potentials of these multilayer films as a function of thickness. Space-filling molecular models of T15 have been used to describe a possible packing arrangement for the molecules in the LB film based on our X-ray results.

Comparison of the monolayer-forming ability of various closely related CN derivatives has clearly demonstrated the importance of π orbital overlap in determining monolayer cohesion in aromatic systems. Therefore it would be of interest to add a fourth phenyl ring to T15 in an attempt to improve monolayer stability whilst maintaining Z-type deposition. Alternatively, by analogy with the biphenyl series, an increase in length of the alkyl tail should also produce some improvement in monolayer cohesion, albeit less marked. Interestingly, increased alkyl chain length in the

CN terphenyls is known to produce smectic (layered) phases in the parent bulk[5], and we are planning to explore this route. Further Langmuir-Blodgett studies using both established and new families of liquid crystalline materials, including COOH and ester derivatives for example, should improve our understanding in both areas.

ACKNOWLEDGEMENTS

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