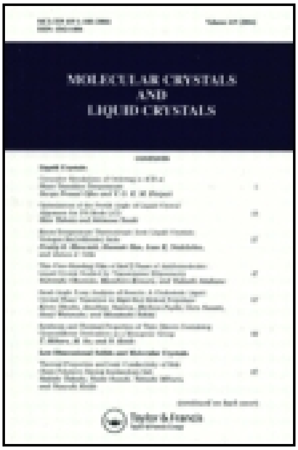

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SNPP and SMAP as Candidate Materials for Langmuir-Blodgett Films for Non-Linear Optics

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SNPP and SMAP as Candidate Materials for Langmuir-Blodgett Films for Non-Linear Optics

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(*S*)-*N*-(4-nitrophenyl)-prolinyl stearate (SNPP) and 2,4-dinitrophenyl-1-alanine stearyl ester (SMAP), stearyl derivatives of the molecules NPP and MAP (which form non-centrosymmetric crystals), have been prepared and studied as candidate materials for Langmuir-Blodgett films for non-linear optics. Pressure-area isotherms were determined under various conditions of sub-phase pH and temperature for both materials, separately and in mixtures with other film-forming species. Surface layers of the pure materials were at best metastable, and Langmuir-Blodgett films deposited from mixtures did not incorporate any SNPP or SMAP. Molecular modelling showed that in SNPP the hydrophobic tail appears to prevent stable film formation by preferring to lie over the weakly hydrophilic nitro group, while in SMAP the orientation of the tail is more favourable but the two nitro groups appear to destabilize the film.

Keywords: Langmuir-Blodgett film; isotherm; non-linear optics

1. INTRODUCTION

Langmuir-Blodgett films offer the advantage for non-linear optics that one can control the packing of layers and hence ensure the absence of centrosymmetry essential for dipole-allowed quadratic response. However, this flexibility is acquired at the cost of having to design molecules that exhibit high NLO response while being able to form stable multilayer films. One approach to this problem is to take molecules that form crystals with high NLO response and modify them to make them amphiphilic. We have previously reported(1) using this approach by making stearyl derivatives of the molecules DAN (**1**), NPP (**2**) and MAP (**3**), denoted SDAN (**4**), SNPP (**5**) and SMAP (**6**). In these molecules,

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* Corresponding Author.

the stearyl chain provides a hydrophobic "tail", leaving the NLO-active chromophore to provide the hydrophilic "head". Of these derivatives, SDAN was most promising, and we described its properties in some detail. We reported only briefly on SNPP and SMAP, and so in the present paper we report on them in more detail.

We report mainly on the isotherms for deposition of Langmuir films of the molecules, separately and in mixtures with good monolayer-forming molecules. In either case, stable films are not obtained. Molecular modelling of the SNPP and SMAP molecules shows that this is probably attributable to the position at which the stearyl moiety is attached.

2. EXPERIMENTAL

SNPP was synthesized by amination of 4-fluoro-nitrobenzene with D-proline in ethanol followed by esterification with stearic acid. SMAP was synthesized from 2,4-dinitro-fluorobenzene by reaction with D-alanine in ethanol followed by esterification with stearyl alcohol. The materials were crystalline solids at room temperature and gave satisfactory NMR, IR and micro-analytical data after purification by column chromatography on silica gel. UV-visible spectra of both materials in ethanol and chloroform solution showed an absorption cut-off below 450 nm. This means that neither absorbs any second-harmonic light generated at 532 nm from the fundamental of a Nd: YAG laser at 1.064 μm. Both materials exhibited second-harmonic generation from the powder(2). This indicates that the crystals are non-centrosymmetric, and encourages the belief that they could form stable non-centrosymmetric Langmuir-Blodgett films instead of trying to rearrange into some energetically more favourable centrosymmetric structure.

The experimental methods used to study the isotherms of Langmuir floating monolayers are described in detail elsewhere, as are the techniques used in depositing and studying Langmuir-Blodgett films(3). A Joyce-Loebl dual A-B trough was used, under conditions designed to minimize problems with impurities without using full clean-room facilities.

3. SNPP

Isotherms for pure SNPP were studied on a water sub-phase. Since SNPP does not contain an acid or other easily ionizable group, the common procedure of adding cadmium ions to the sub-phase to aid stability was not adopted. Figure 1 shows isotherms measured at a sub-phase temperature of 20 °C for several values of sub-phase pH. (Through a quirk of the software that controls the operation of the trough, data points are not recorded on horizontal plateau regions, which are therefore indicated by broken lines in this and later isotherms.) For surface pressures up to about 10 mN/m, the curves exhibit gently sloping liquid regions essentially independent of pH. At higher pressures, corresponding to areas per molecule below about 37 Å^2, there is a change of behaviour that is not clearly identifiable as liquid or solid, with somewhat greater dependence on pH.

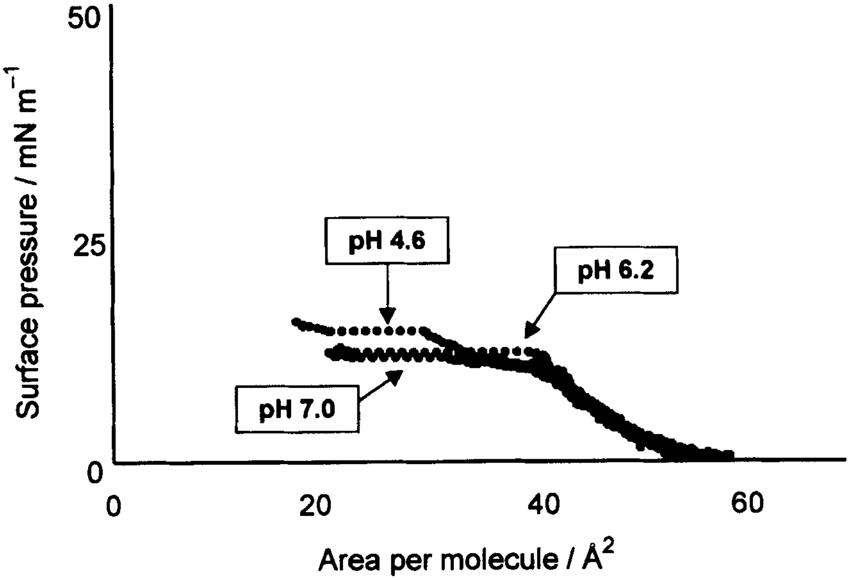


FIGURE 1 SNPP isotherms at a sub-phase temperature of 20 °C and different pH values

Isotherms determined on lowering the sub-phase temperature successively to 16 °C, 12 °C and 8 °C at various values of pH are shown in Figures 2, 3 and 4. These isotherms give clear plateau regions as the surface pressure increases, followed by solid-like behaviour, and show a stronger dependence on pH than at 20 °C. The areas per molecule obtained by extrapolating the linear portion of the solid curve to zero surface pressure increase as the temperature decreases, being 13 – 14 Å^2 at 16 °C, 14 – 16 Å^2 at 12 °C, and 17 – 20 Å^2 at 8 °C. These values are smaller than the value of about 22 Å^2 that might have been expected from stearic acid itself. Evidently the films become more stable as the temperature decreases, but the apparent solid region seems to comprise multiple layers that collapse through the plateau region.

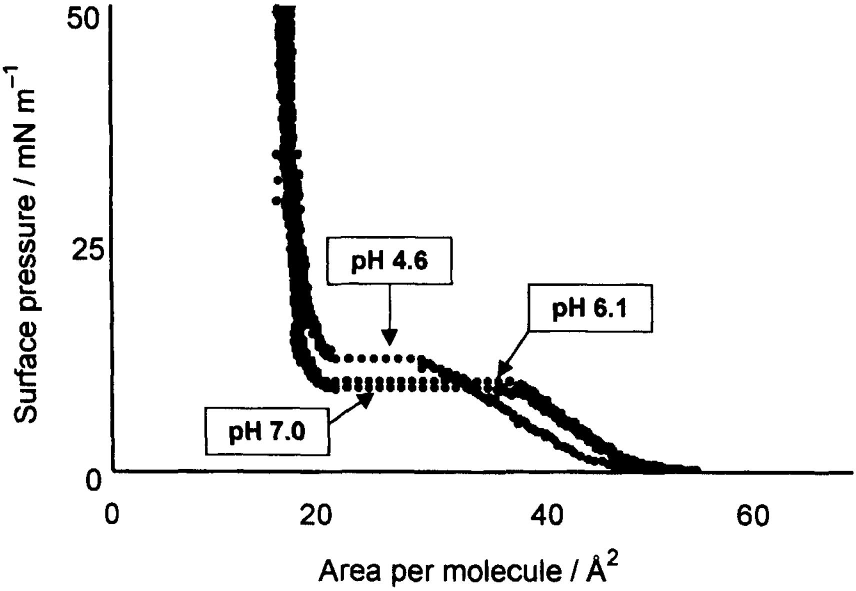


FIGURE 2 SNPP isotherms at a sub-phase temperature of 16°C and different pH values

In order to confirm this interpretation, the film area was studied as a function of time at fixed pressure. At the highest temperatures, the films collapsed to their minimum working area before a stable pressure could be established. At the lowest temperatures, measurements of film area could be performed, as shown in Figure 5, where the films are clearly seen to be unstable. Indeed, collapse of the monolayers was visible to the naked eye in the form of yellowish striations on the water surface.

The instability might have been caused by significant solubility of SNPP in water. This possibility was ruled out by sonicating about 0.5 g of the material with 50 cm^3 of water and filtering off residual SNPP. Determination of the UV/visible spectrum of the filtrate showed no sign of absorption that could be assigned to SNPP.

Further experiments were carried out to explore the possibility that films containing SNPP could be stabilized in mixtures with good film-forming species, as is found to occur with other species.(4) Mixtures were first prepared in equimolar proportions with stearic acid ($C_{17}H_{35}CO_2H$) and studied under conditions suited to deposition of stearic acid alone, viz. a sub-phase temperature of 20 °C, a pH of 5.5 and cadmium ions in the sub-phase at a concentration of 1.36 (±0.05) × 10^{-3} mol dm^{-3}. An isotherm of such a mixture is shown in Figure 6, with one for

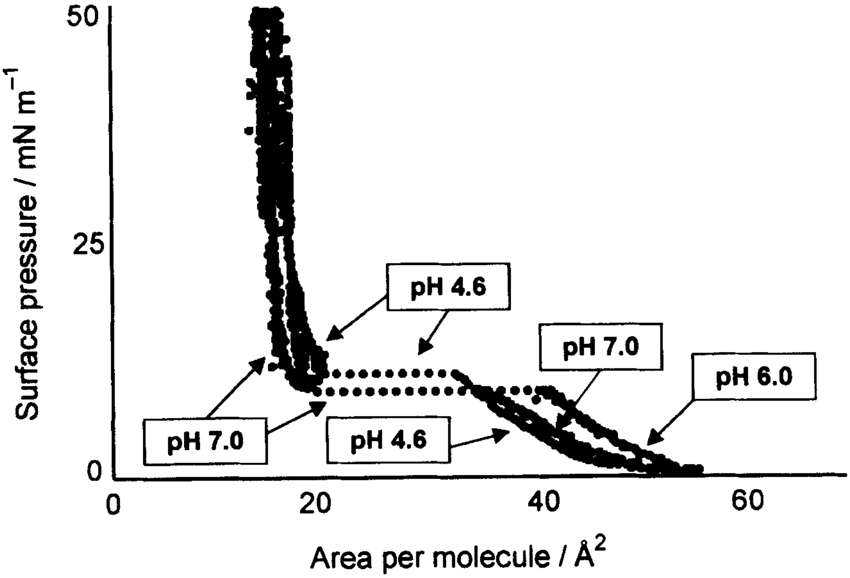


FIGURE 3 SNPP isotherms at a sub-phase temperature of 12°C and different pH values. The plateau regions coincide for pH 6.0 and 7.0

pure stearic acid for comparison. The isotherm for the mixture clearly shows contributions from both components, suggesting that they were immiscible. In the solid regions both isotherms extrapolate to essentially the same area per molecule of 22 Å^2, as appropriate to stearic acid alone. Depositing Langmuir-Blodgett films of the mixed material provided further evidence that the materials were immiscible. Optical micrographs of the films after deposition clearly revealed a fairly uniform distribution of yellow SNPP globules over the surface, perhaps having been squeezed out of the film by the stearic acid.

Since SNPP is a longer molecule than stearic acid, having the NPP group as well as the stearyl group, experiments were also carried out with the longer molecule behenic acid ($C_{21}H_{43}CO_2H$). Deposition under conditions suited to deposition of behenic acid alone gave isotherms very similar to that for the mixture in Figure 6. The extrapolated area per molecule was 20 Å^2, more appropriate to behenic acid alone, without evidence of any effects attributable to the SNPP.

4. SMAP

Isotherms for SMAP were studied under the same range of conditions as for SNPP. In this case there was no evidence of incipient solid film formation, even

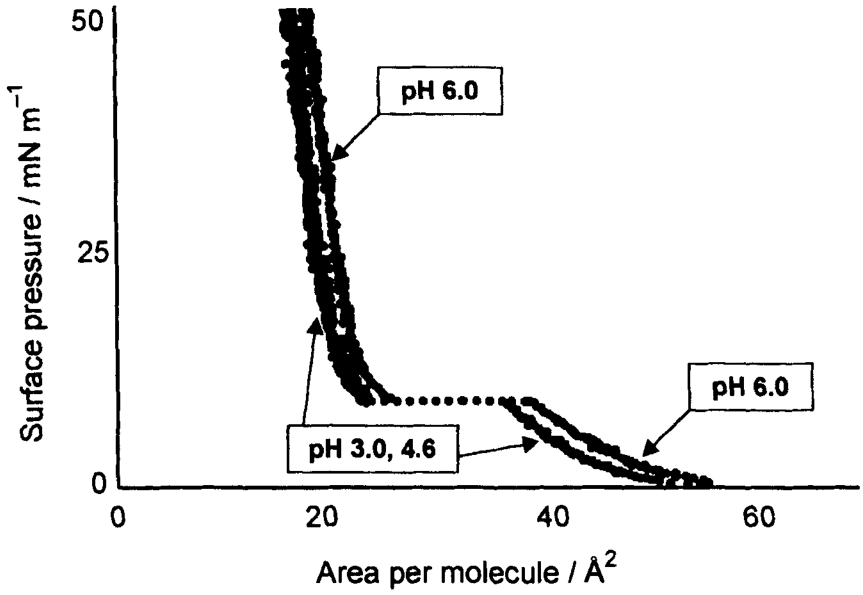


FIGURE 4 SNPP isotherms at a sub-phase temperature of 8 °C and different pH values. All the plateau regions coincide, and the points for pH 3.0 and 4.6 largely overlap

at the lowest temperature. Figure 7 shows isotherms taken at a sub-phase temperature of 8 °C and various values of pH: only a liquid region is seen for areas per molecule as low as 10 $Å^2$. Although there is again little dependence on the sub-phase pH, the highest curves for SMAP lie at the lowest sub-phase pH, in contrast to those for SNPP, which show the opposite tendency.

Equimolar mixtures of SMAP with behenic acid were also studied. In this case, conditions suited to deposition of behenic acid alone were adjusted to increase the chances of successful formation of the mixed film. The sub-phase temperature was set lower than usual at 10 °C and the barrier compression rate was halved to 1 $cm^2\ s^{-1}$. These precautions produced an isotherm for the mixed film that differed from that for behenic acid alone, as shown in Figure 8, but not in the way found for the SNPP mixtures with stearic acid and behenic acid. In the case of SMAP the isotherms appeared to be consistent with miscibility between SMAP and behenic acid, as shown by their similar shape to that for behenic acid alone. If so, the extrapolated area per molecule should be a weighted average of those for the separate components.(5) In fact it was found to be 16 $Å^2$ for the mixture, as opposed to about 20 $Å^2$ for behenic acid alone, implying an unrealistically small area per molecule of perhaps 12 $Å^2$ for SMAP. This indicates that the

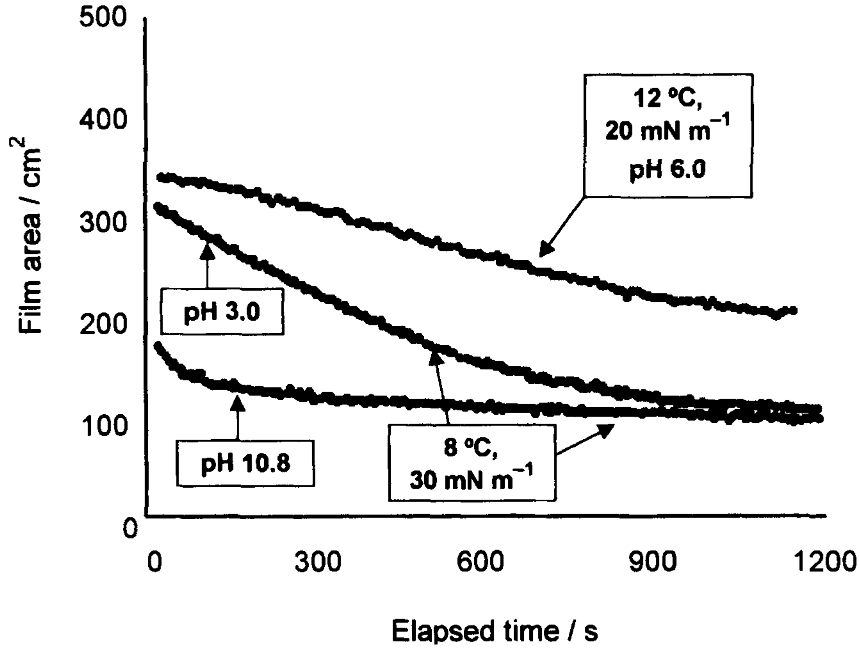


FIGURE 5 Area per molecule versus time plots for SNPP at various sub-phase temperatures, pH values and surface pressures

SMAP molecules are not contributing as expected in a mixed film. They are probably squeezed out of the floating monolayer by the behenic acid, perhaps encouraging a degree of collapse leading to the low area per molecule.

Further mixed films were prepared with OMPBA, another film-forming molecule with an octadecyl chain that we have studied for possible non-linear optics applications.(3) The conditions used in measuring isotherms resembled those used for the films with behenic acid, but at a sub-phase temperature of 15°C. As with behenic acid, the isotherms appeared to be consistent with miscibility between the components, but again the areas per molecule were lower than those for OMPBA or behenic acid under similar conditions, presumably because the SMAP molecules were squeezed out of the film. The fate of the SMAP was investigated by UV/visible spectroscopy. A solution of the equimolar mixture in chloroform showed absorption bands characteristic of both separate components, at approximately 346 nm for SMAP and 440 nm for OMPBA. A Langmuir-Blodgett film containing four layers was then deposited from the mixture at a surface pressure of 30 mN m^{-1} and a dipping speed of 5 mm min^{-1}. The film deposited from the SMAP/OMPBA mixture showed a broad absorption band from 400 to

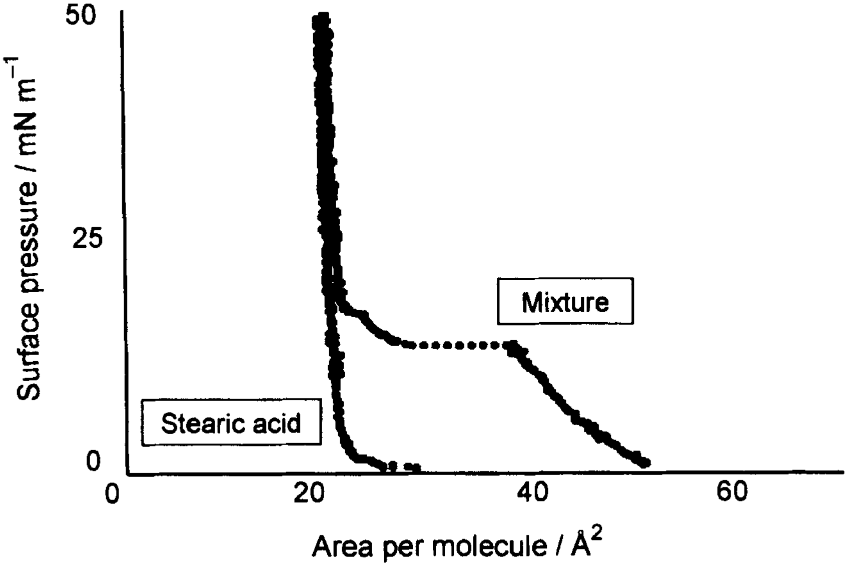


FIGURE 6 Isotherms of 1:1 SNPP:stearic acid and pure stearic acid

500 nm similar to that for a pure OMPBA film four layers thick, but showed no absorption around 350 nm. Hence it appears that the SMAP molecules are not only forced out of the film but also are not transferred to the substrate (at least, not permanently).

5. MODELLING

Evidently, neither SNPP nor SMAP forms stable Langmuir films under the range of conditions used here, either alone or in the mixtures studied here. Neither molecule appears to cohere well with itself or with the other molecules. One contributory factor is that neither molecule has a strongly hydrophilic group in its head. Modest hydrophilic character is imparted by the nitro groups, but is apparently not very effective given that SMAP, with two nitro groups, seems to form less stable films than SNPP, with one. The molecules have the same hydrophobic tails as the archetypal film-forming molecule stearic acid, but these enhance film stability only if they can pack effectively. Given the rather bulky head groups to which the tails are attached, it is not evident how effective the packing can be relative to stearic acid. Hence we have performed simple molecular modelling to explore the preferred molecular arrangements by energy minimization.

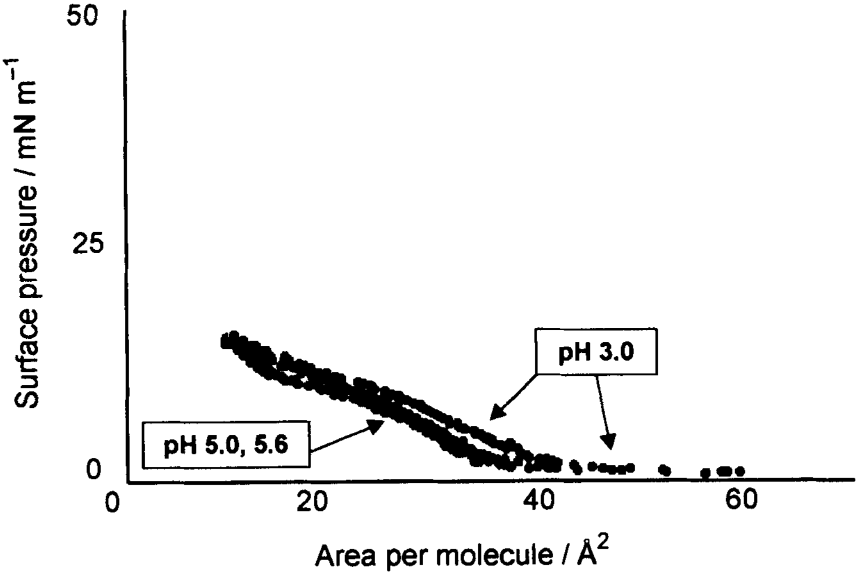


FIGURE 7 SMAP isotherms at a sub-phase temperature of 8 °C and different pH values. The sets of points for pH 5.0 and 5.6 largely overlap, except below 20 A^{2}per molecule, where those for pH 5.0 lie distinctly higher, approaching those for pH 3.0

The structure thus found for SNPP is shown in Figure 9. The alkyl chain is seen to lie across the nitro group. This makes it difficult to satisfy simultaneously the different requirements of the two groups. The hydrophobic tail prefers to lie out of the water sub-phase, while the weakly hydrophilic nitro group prefers to lie in the water. As a result, the two groups frustrate their respective preferences, and formation of a stable floating monolayer is hindered.

The structure found for SMAP is shown in Figure 10. The alkyl chain now lies away from the benzene ring, so that the hydrophobic tail could lie out of the water while the two nitro groups could lie on the water sub-phase. Compression of molecules with such an arrangement might then form a herringbone structure.(6) However, the presence of two electronegative nitro groups in the surface is likely to mean that compression of SMAP films induces unfavourable electrostatic repulsions that lead to instability. Stability of films can also be influenced by hydrogen bond formation, as we have shown elsewhere.(7) In SMAP this might have been possible between the amino group and the *ortho* nitro group, but the model structure shows that such a process is not likely to be favoured in the minimum energy structure.

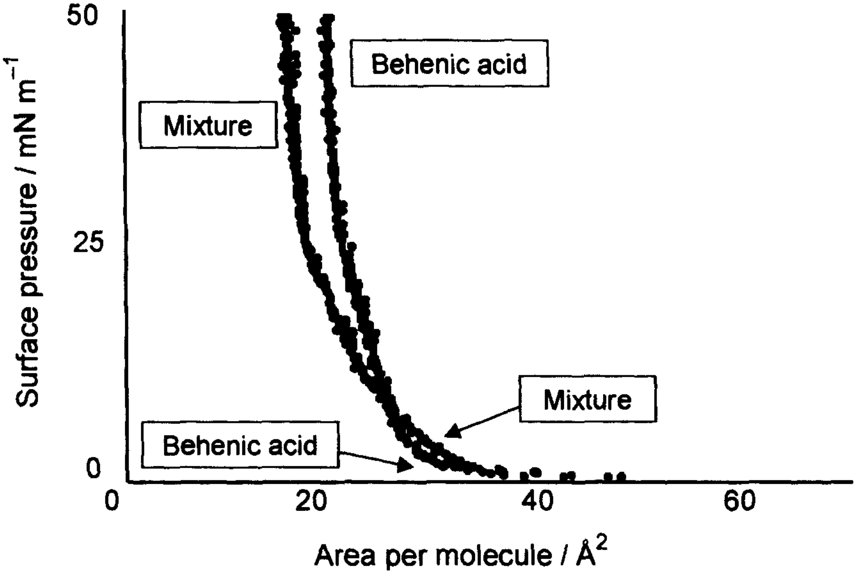


FIGURE 8 Isotherms of 1:1 SMAP:behenic acid and pure behenic acid

6. DISCUSSION

We have shown in some detail that SNPP and SMAP do not form stable Langmuir films under a wide variety of conditions of sub-phase temperature and pH. Mixtures with stearic acid, behenic acid and (for SMAP) OMPBA could give stable Langmuir films, but did not give Langmuir-Blodgett films that contained SNPP or SMAP. Modelling the structures of the molecules shows that neither adopts an arrangement favourable to film formation, owing to mutually incompatible dispositions of the head and tail groups in SNPP and electrostatic repulsions between the nitro groups in SMAP. The modelled structures suggest different accessibilities of the nitro groups to the aqueous sub-phase, which is consistent with the observation of opposite (rather weak) dependences of the SNPP and SMAP isotherms on sub-phase pH (although in SMAP the ester group could also respond to pH changes).

Nevertheless, even unsatisfactory attempts to prepare Langmuir and Langmuir-Blodgett films can provide insights into improved strategies. In the present case, the first improvement is to use a more effective hydrophilic group than the nitro group. In effect, attempting to use the nitro group both as an acceptor group in the NLO chromophore and as a hydrophilic functional group to help film for-

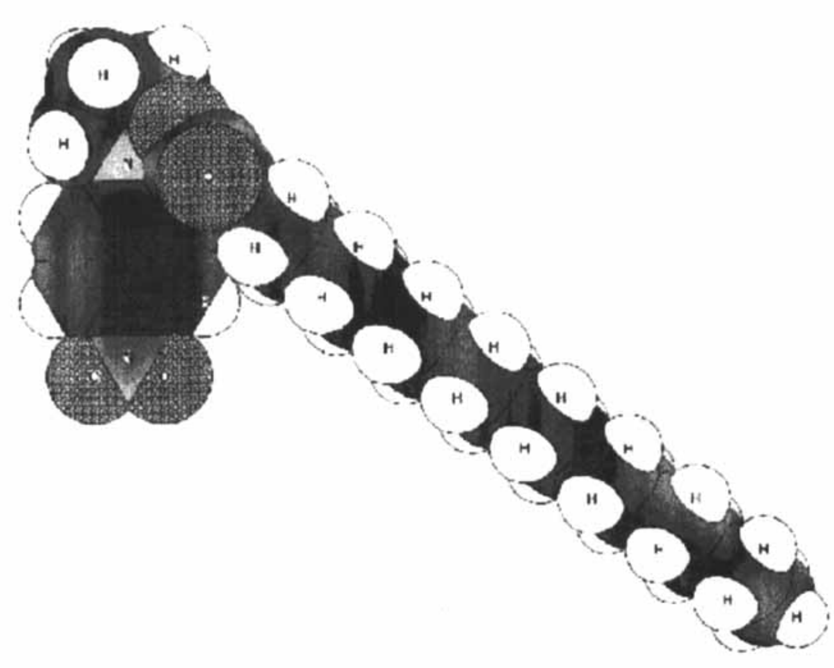


FIGURE 9 Computer model of the energy-minimized SNPP molecule

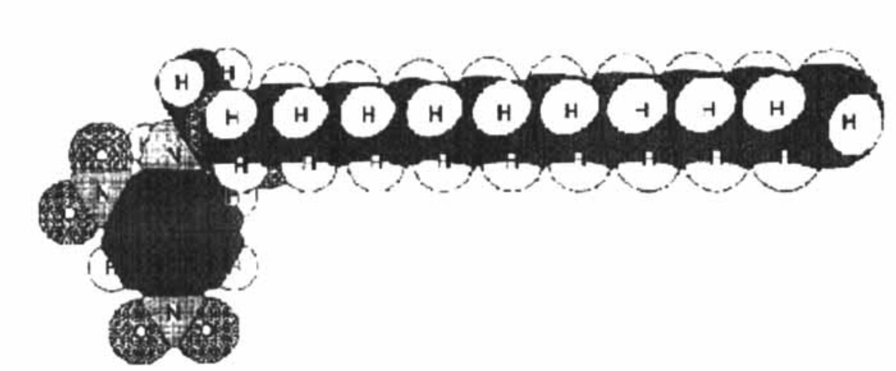
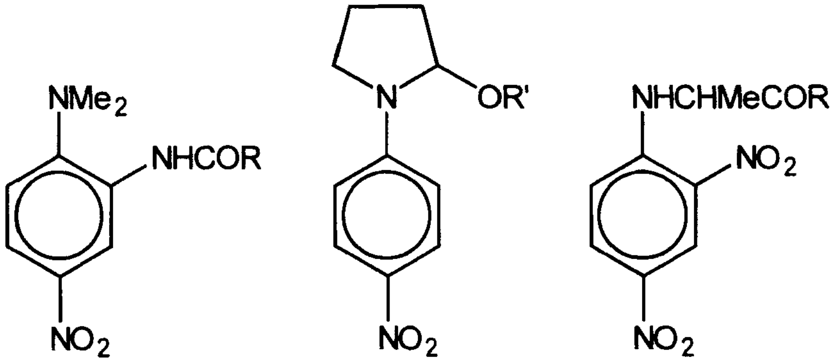


FIGURE 10 Computer model of the energy-minimized SMAP molecule

mation is too greedy, and relying on two nitro groups to enhance the hydrophilic effect proves counterproductive. The second improvement is to ensure that the hydrophobic tail lies well clear of the hydrophobic head so that they do not frustrate each other's attempts to lie in their preferred phases. Simple structural modelling of proposed amphiphilic molecules is clearly helpful to ensure that the necessary structure is energetically favourable before effort is committed to synthesis. More generally, stability of films like these depends critically on the van der Waals attractions between the long tails, and for this purpose, the molecular structure must allow effective packing. Otherwise, molecules need to be devised that have rather specific interactions between molecules, perhaps of the sort characteristic of molecular recognition.



1: DAN, R = CH_3 **2**: NPP, R' = H **3**: MAP, R" = CH_3O

4: SDAN, R = $C_{17}H_{35}$ **5**: SNPP, R' = $C_{17}H_{35}CO$ **6**: SMAP, R" = $C_{18}H_{37}O$

MOLECULAR STRUCTURES

Acknowledgements

This paper is dedicated to the memory of the late Edgar Silinsh, whose science and company always gave pleasure.

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