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Chiral Sulphur-containing Molecules in Langmuir–Blodgett Films

Christian Georges, T. John Lewis, J. Patrick Llewellyn, Susanna Salvagno, D. Martin Taylor and Charles J. M. Stirling*
Institute of Molecular and Biomolecular Electronics, University College of North Wales, Bangor, Gwynedd

Viola Vogel
Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen-Nikolausberg, Federal Republic of Germany

Long, straight alkane chains have been functionalised with sulphur-containing groups at the chain-end, near the chain-end and at the mid-chain. The behaviour of such compounds in Langmuir films has been investigated. Several gave stable monolayers from which molecular areas have been determined. Surface potential (ΔV) measurements carried out simultaneously with the pressure–area (π–A) isotherms provided an important insight into the surface behaviour of some of the compounds. On compression, changes in the ΔV–A characteristics were clearly visible, well before any significant changes occurred in the π–A curves. New evidence presented here suggests also that the previous interpretation of the π–A behaviour of $C_{10}H_{21}SO(CH_2)_{10}CO_2H$ in terms of molecular orientation was incorrect, dissolution of the monolayer in the water subphase at higher pressure being the most likely explanation. Attempts at depositing chiral L.B. multilayers of (+)-$C_{18}H_{37}SO$-*p*-tolyl were not successful because of crystallite formation on the quartz support. Multilayers of (+)-*S*-octadecyl cysteine were deposited successfully, albeit with a monolayer of stearic acid interposed every seven monolayers of the chiral compound. No optical rotation was observed in the films.

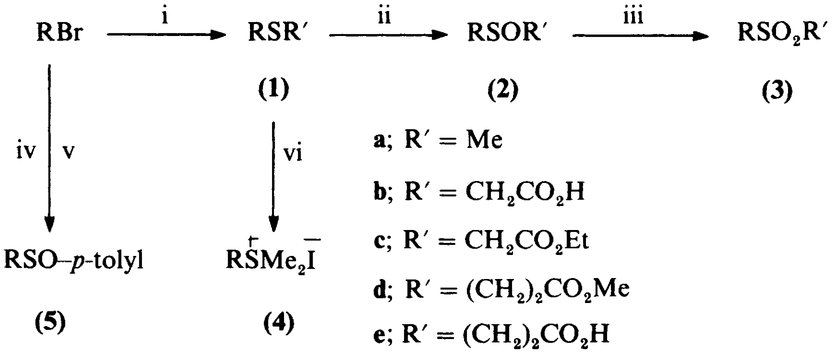
There has been a considerable upsurge of interest in the formation and behaviour of Langmuir–Blodgett (L.B.) films because of their ability to deliver, on solid supports, specifically ordered two-dimensional arrays of molecules containing a variety of functions.[1,2] Among the wide range of functions incorporated in this way are those exhibiting interesting optical properties. Dye and photochromic molecules have been so prepared and have important practical potential. Recently we reported on a preliminary study of a range of sulphur-containing compounds that were suitable for L.B. film deposition.[3] Previously, molecules with functional groups containing sulphur had scarcely been studied in mono- and multi-layer form, despite the fact that they show marked differences in dipole strength and hydrophilicity. Further, several types of sulphur-containing groups are chiral or prochiral.

The objective of the work reported here was the preparation and characterisation of L.B. films composed of chiral molecules. Such films, particularly if they can be prepared from pure enantiomers, are expected to have interesting optical properties as well as show specific adsorption.[4] Because of the large dipole moment[5] and strong optical rotatory power of the sulphoxide moiety[6] we have been particularly concerned to obtain a pure enantiomer of a long-chain compound containing this function. Also, many amino acids occur naturally in pure enantiomeric form and can be modified to give substrates suitable for L.B. film deposition. One such substrate we have investigated was the *S*-octadecyl derivative of cysteine, because both a pure enantiomer and the racemic mixture of this compound were easily prepared.

When constructing multilayers of bifunctional molecules, careful consideration must be given to the polarities of the two polar groups and to their relative location in the molecule, since the presence of the second polar function may be detrimental to film formation and/or deposition. This problem was addressed in the present work by synthesising and characterising a series of alkanoic acids in which sulphur-containing functions were located either near the terminal acid group or in the mid-chain position.

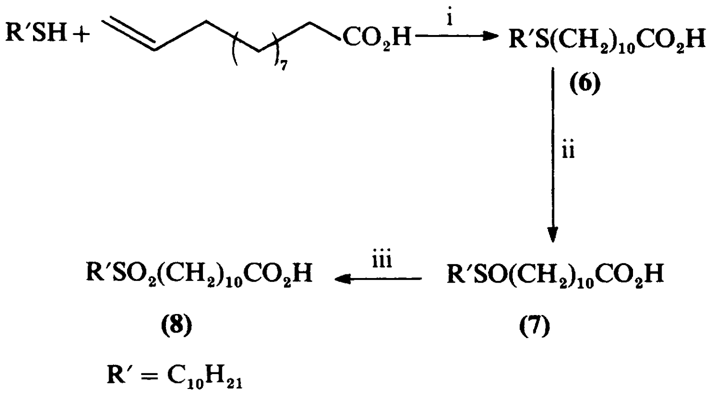
Substrates

Preliminary studies were made with the octadecyl systems obtained by the routes of scheme 1 [R = $(CH_2)_{17}Me$],



Scheme 1. *Reagents*: i, RSNa–EtOH; ii, *m*-chloroperbenzoic acid; iii, $KMnO_4$–H_2O–AcOH; iv, Mg–Et_2O; v, menthyl toluene-*p*-sulphinate; vi, MeI–MeOH.

were extended to substrates with sulphur functions close to the carboxy head group. Preparation of centre-chain functionalised substrates was based on the photoaddition of thiols to undecenoic acid[7] (scheme 2).



Scheme 2. i, *hν*; ii, *m*-chloroperbenzoic acid; iii, $KMnO_4$–H_2O–AcOH.

Finally the cysteine derivatives (**9a**) and (**9b**) were prepared (scheme 3).

$$\mathrm{RBr} + \bar{\mathrm{S}}\mathrm{CH_2\,CH(NH_2)CO_2^-} \longrightarrow \mathrm{RSCH_2CH(NH_2)CO_2^-}$$

(9) **a**; $R = (CH_2)_{17}Me$; (+)
b; $R = (CH_2)_{17}Me$; (±)

Scheme 3

Because of the crucial requirements for purity of film substrates, all products were repeatedly flash or radially chromatographed to constant m.p., elemental analysis and chromatographic behaviour (t.l.c. and/or g.l.c.). It was established in all conversions that there was no contamination by the starting material of the previous preparation.

Film Preparation and Characterisation

Pressure-area (π–A) characteristics of monolayers were obtained by injecting solutions of the compounds on to the surface of water in a continuous barrier trough of the type described by Blight *et al.*[8] The trough was thermostatically controlled through a metal base plate and the whole apparatus was located on vibration-damping mounts. Water in the trough was purified by percolation through reverse osmosis, activated carbon and mixed-bed deionisation cartridges and buffered at pH 5.8 ± 0.1 for most experiments.

To understand further the behaviour of these films, surface potential measurements[9] were carried out on the floating monolayers using the vibrating plate capacitor method, which has an absolute accuracy of *ca.* 10 mV.[10]

Deposition of films on to quartz discs for optical examination and on to glass microscope slides for more general evaluation was by automated dipping at a film pressure maintained constant by feedback from a Wilhelmy plate-pressure sensor and electrobalance.

Measurements on the deposited L.B. films were made to determine the rotation of plane-polarised light from an He–Ne laser using a Glan Thompson analyser and a photomultiplier.

Results and Discussion

Results from the π–A characteristics of all compounds studied are given in table 1. Most of the sulphur-functionalised compounds gave reproducible monolayers at *ca.* 17 °C with almost featureless π–A characteristics,[3] from which molecular areas were estimated by extrapolation from the high-pressure portion of the curve. However, further work has shown that care must be taken in interpreting these values since monolayers of (**4**), (**2b**), (**7**) and (**8**) are unstable when compressed, so that the molecular areas determined depend on both the rate of compression and the maximum pressure applied.

Prochiral Compounds

Further measurements at a lower temperature (*ca.* 13 °C) on compounds (**2b**) and (**2e**) revealed the existence of phase transitions at pressures between 5 and 8 mN m^{-1} (fig. 1), which were not present in the earlier work at higher temperature.[3] With two methylene spacers between the sulphoxide group and the carboxylic headgroup (**2e**), the π–A characteristic is of the classic stearic acid type. At 13.7 °C, the molecular areas in the low- and high-pressure phases are, respectively, 30 and 27 Å^2. When only one methylene spacer is present (**2b**), the low-temperature transition is much more marked and has almost developed into a plateau. The solid-phase molecular area in this case is 23 Å^2. Interestingly, the sulphoxide (**2e**) with two intervening methylene groups gives a very

Table 1. Molecular areas for the sulphur-containing compounds determined from the π–A characteristics

compound[a]		molecular area/Å^2	aqueous phase	
			T/°C	pH
RSMe	**(1a)**	20.8	17	5.8
$RSCH_2CO_2H$	**(1b)**	26.5	17	5.8
$RSCH_2CO_2Et$	**(1c)**	26.4	17	5.8
$RS(CH_2)_2CO_2Me$	**(1d)**	23.9	25	4.8
$RS(CH_2)_2CO_2H$	**(1e)**	22.0	26	4.7
RSOMe	**(2a)**	19.7	17	5.8
$RSOCH_2CO_2Et$	**(2c)**	27.2	17	5.8
$RSO(CH_2)_2CO_2Me$	**(2d)**	28.4	26	4.9
RSO_2Me	**(3a)**	32.6	17	5.8
$RS^+Me\ I^-$	**(4)**	17.8[c]	17	5.8
SO-*p*-tolyl	**(5)**[b]	indeterminate because of crystallisation (see text)		
$RSOCH_2CO_2H$	**(2b)**	20.1[c]	17	5.8
$RSO(CH_2)_2CO_2H$	**(2e)**	27.0	14	*ca.* 5.5
$R^1S(CH_2)_{10}CO_2H$	**(8)**	24.9	17	5.8
$R^1SO(CH_2)_{10}CO_2H$	**(7)**	indeterminate because of monolayer instability (see text)		
$R^1SO_2(CH_2)_8CO_2H$	**(8)**	25.2	17	5.8
$RSCH_2CH(NH_2)CO_2H$	**(9a)**	26.0	20	7.8
$RSCH_2CH(NH_2)CO_2H$	**(9b)**	28.6	20	7.9

[a] $R = C_{18}H_{37}$; $R^1 = C_{10}H_{21}$. [b] Molar rotation $[M]_D^{25} + 491°$. [c] Unstable monolayer.

stable film, which showed no change in pressure when the monolayer area was held constant for 10 min. By contrast, the surface pressure of the sulphoxide (**2b**) fell from 21 to 16 mN m^{-1} in 8 min. The reason for this difference is not clear unless the greater rigidity of the methylene link between the two polar groups in the sulphoxide (**2b**) makes packing more difficult.

The surface potentials of these compounds measured at the same time as the pressure isotherms showed no major difference from those obtained at higher temperature except that the main features are shifted to larger molecular areas, *e.g.* the shoulder in the plot for the sulphoxide (**2b**) now occurs at 50 instead of 40 Å^2.

At large molecular spacings the surface potential is apparently independent of molecular area (fig. 1) but is slightly more negative than for clean water. When the molecular area is reduced below *ca.* 80–100 Å^2, a large positive change occurs in the surface potential. Note that for the sulphoxide (**2e**) the increase in ΔV is more gradual than for the sulphoxide (**2b**), although the maximum in potential is similar for both, *i.e.* *ca.* 350 mV.

While the isotherms of the sulphoxides (**2b**) and (**2e**) are typical of those observed in compounds with only one polar headgroup, the mid-chain sulphoxide (**7**) shows behaviour (fig. 2) typical of bifunctional molecules. The large area per molecule at which the surface pressure begins to increase suggests that at low surface pressures both polar groups of the molecule are anchored in the aqueous surface. On increasing the pressure, the molecular area gradually decreases to *ca.* 130 Å^2, approximately the area of the prone molecule. Further compression causes a significant reduction in area with very little change of surface pressure. Previously,[3] this was interpreted as being due to the

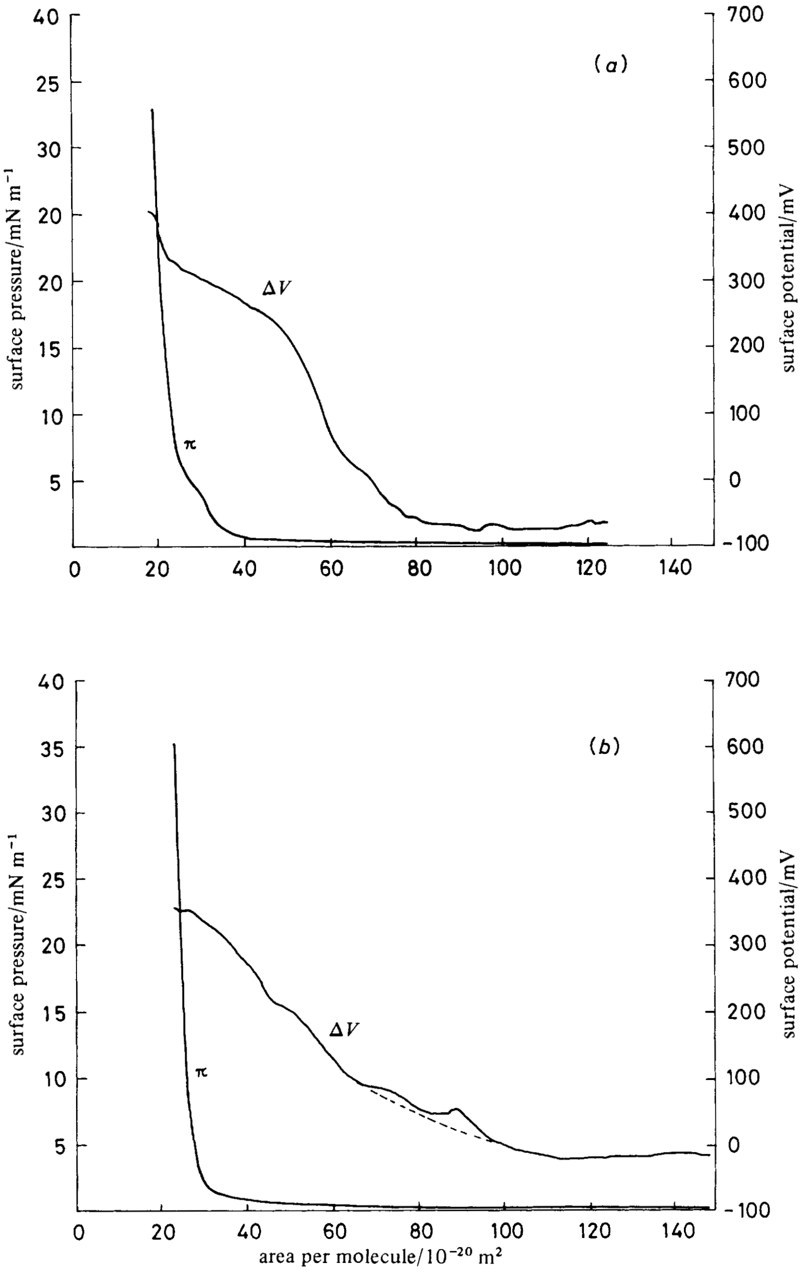


Fig. 1. π–A and ΔV–A characteristics for (*a*) $C_{18}H_{37}SOCH_2CO_2H$ and (*b*) $C_{18}H_{37}SO(CH_2)_2CO_2H$. The small bumps in the surface potential plots probably arise from islands of condensed material in the monolayer, see ref. (13). The sub-phase was pure water and the compression rate was 5 Å^2 molecule^{-1} minute^{-1}. $T = 13.3$ °C.

sulphoxide group lifting from the aqueous surface, a mechanism already suggested by others to describe the behaviour of hydroxyoctadecanoic acids[11] and hydroxyhexadecanoic acids.[12] If the sulphoxide group were indeed lifting from the water, a rapid change in surface potential should also occur, reflecting a rapid change in

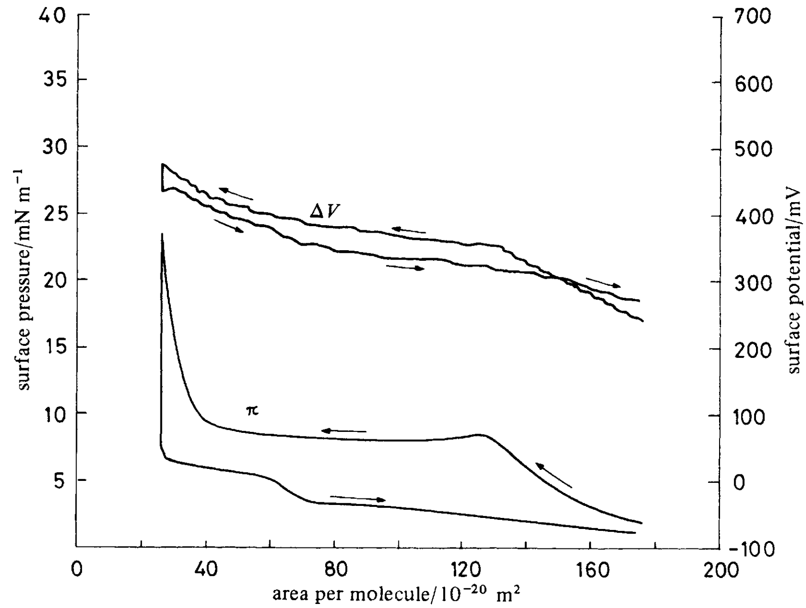


Fig. 2. π–A and ΔV–A characteristics for the mid-chain sulphoxide $C_{10}H_{21}SO(CH_2)_{10}CO_2H$.

surface dipole moment. As can be seen in fig. 2, ΔV rises steadily when the film is first compressed but reaches an almost constant potential when molecular area decreases below *ca.* 130 Å^2.

Furthermore, films of this mid-chain sulphoxide are unstable at high pressures. For example, when the molecular area is held constant at *ca.* 26 Å^2 per molecule, corresponding to a surface pressure of 24 mN m^{-1}, the pressure falls rapidly. Also, when a compressed film is subsequently expanded, the plateau region is shorter (see fig. 2), suggesting loss of material from the monolayer. It is probable, therefore, that at low pressure the molecules of the sulphoxide (7) lie flat on the surface, and are easily compressed until the minimum area of the prone molecule is achieved at *ca.* 130 Å^2 per molecule. Thereafter, on further compression, the material goes into solution, since no evidence for stacking or crystallite formation was obtained from close visual examination of the sub-phase surface in reflected light. Contamination of the platinum reference electrode in the sub-phase during the course of several experiments provides further evidence of dissolution.

The rapid rise in pressure at low molecular area ($<$40 Å^2) must then occur when the dissolution rate decreases below the compression rate because of an increasing concentration of dissolved molecules immediately below the sub-phase surface.

From the surface potential plots in fig. 1 and 2 we have calculated the product ΔVA, which is proportional to $\mu_{\perp}$, the effective molecular dipole moment,[10] *i.e.* the component perpendicular to the water surface. In fig. 3 this product is plotted as a function of molecular area for the sulphoxides (**2b**), (**2e**) and (**7**), together with the corresponding data for stearic acid from Harkins and Fischer.[13]

The mid-chain sulphoxide (**7**) in the prone configuration appears to have the largest effective dipole moment. Dissolution, as would be expected, produces an almost linear decrease in the apparent moment because of the loss of molecules from the floating monolayer.

Interestingly, the near chain-end sulphoxides have a negative dipole moment at large area, presumably because of the dominant effect of the sulphoxide group. On compression of the monolayer, a large positive change in $\mu_{\perp}$ occurs, so that at small

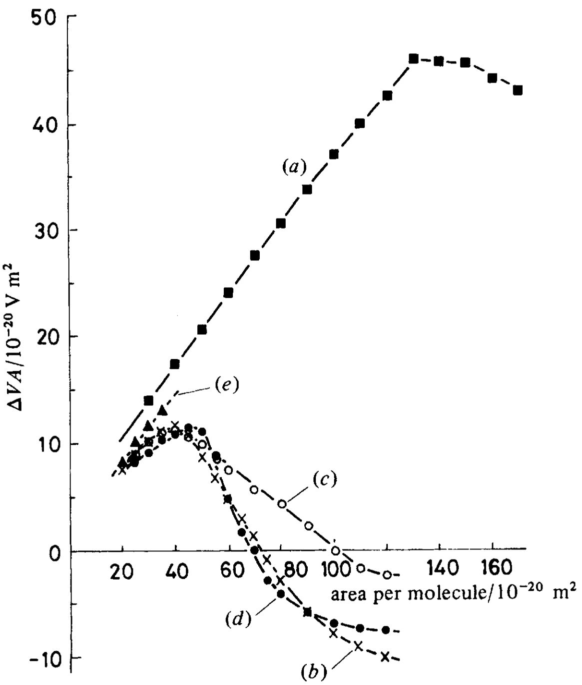


Fig. 3. Plots of ΔVA as a function of average molecular area A. The curves were obtained for (*a*) $C_{10}H_{21}SO(CH_2)_{10}CO_2H$ at 19.0; (*b*) for $C_{18}H_{37}SO(CH_2)_2CO_2H$ at 13.7; (*c*) and (*d*) for $C_{18}H_{37}SOCH_2CO_2H$ at 19.2 and 13.3, respectively; (*e*) for stearic acid at 17 °C [from ref. (13)].

molecular separation the effective moment approaches that for stearic acid. Again this is to be expected, because when these compounds assume a vertical orientation the sulphoxide dipole is directed almost horizontally and so makes very little contribution to the overall vertical moment.

Chiral Compounds

Octadecyl *p*-tolyl sulphoxide (**5**) is one of the compounds that we have been able to prepare in pure enantiomeric form. The π–A curves for a racemic mixture and the pure (+)-enantiomer are given in fig. 4. The general features of both curves are reproducible and show a number of common features, in particular a considerable plateau and hysteresis as observed for the mid-chain sulphoxide (**7**) (fig. 2). Although this behaviour was thought initially to arise from molecular orientation on the surface, further work has suggested that it may arise from stacking or crystallite formation. Consistent with this view is the fact that successive compression–expansion cycles on the pure enantiomer cause a displacement of the major features of the π–A curve to lower areas. Furthermore, crystallites were visible on the water surface at high monolayer pressures.

The results of fig. 4 show that collapse of the racemic film is initiated at a lower pressure (*ca.* 22 mN m^{-1}) than for the pure enantiomer (*ca.* 38 mN m^{-1} on the first compression cycle) and that the process is reversible in the former case. Thus racemic and enantiomeric forms of this compound show different behaviour, presumably corresponding to different interactions in the monolayer.

Amino acids occur naturally as pure enantiomers, but apart from a few notable exceptions[14] their incorporation in L.B. films has hardly been studied. We have now

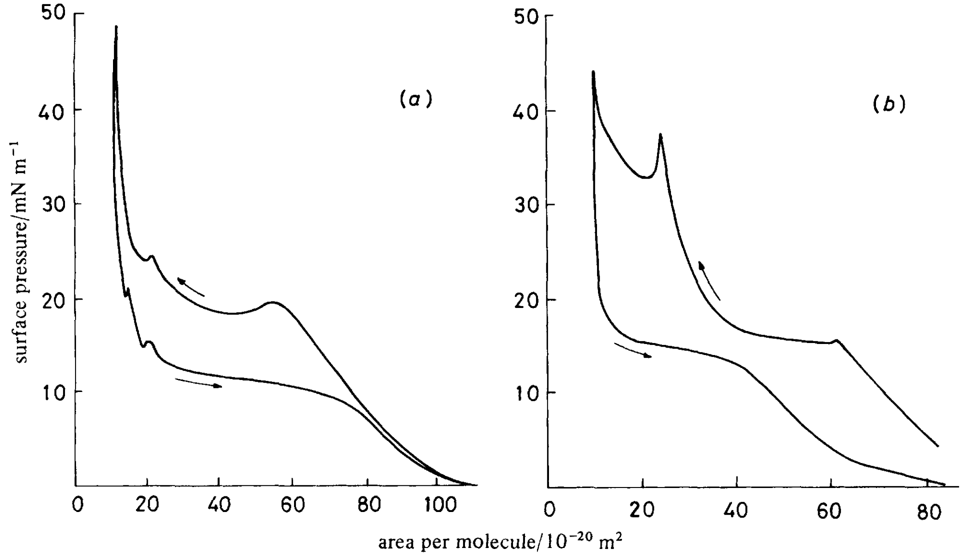


Fig. 4. π–A characteristics of (*a*) a racemic mixture and (*b*) the (+)-enantiomer of $C_{18}H_{37}SO$-*p*-tolyl at 21.5 °C.

prepared robust films of *S*-octadecylcysteine (**9**) in both racemic and enantiomerically pure forms. As can be seen in fig. 5, the two forms again show different behaviour, though not as marked as with the sulphoxide (**5**). The difference this time is confined to low pressures, where the pure compound undergoes a much sharper transition on entering the condensed phase.

L.B. Film Deposition

Multilayers of the chiral compounds were deposited on to quartz discs for optical examination. Ten layers of the (+)-sulphoxide (**5**) were deposited on each side of the disc at a surface pressure of 20 mN m^{-1}. Optical examination of the films indicated optical activity in that an apparent rotation of the plane of polarisation of the incident light was detected. Microphotography of the deposited layer showed it to be composed of a large number of acicular crystallites *ca.* 1–10 μm in length lying in the plane of the quartz disc and partially aligned with the dipping direction. Dichroism is therefore the most likely explanation for the observed optical rotation. Further efforts were made at various dipping pressures and dipping rates to improve film quality, but without success.

Films of *S*-octadecylcysteine (**9**) also deposited as crystallites initially, although there was no indication of crystallite formation in the floating monolayer. The problem was overcome by first depositing a monolayer of stearic acid on to the substrate. This allowed up to 7 layers of *S*-octadecylcysteine to be deposited at a pressure of 30 mN m^{-1}, after which a further layer of stearic acid was deposited. Continuing in this way, a 28-layer film of the cysteine derivative was prepared. Optical rotation was not observed, but this is not surprising since the molar rotation of cysteine is considerably smaller than that of the sulphoxide (**5**).

Conclusions

A wide variety of achiral sulphur-containing compounds has been prepared, and most readily form monolayers. Pure enantiomers of some sulphoxides could not be prepared

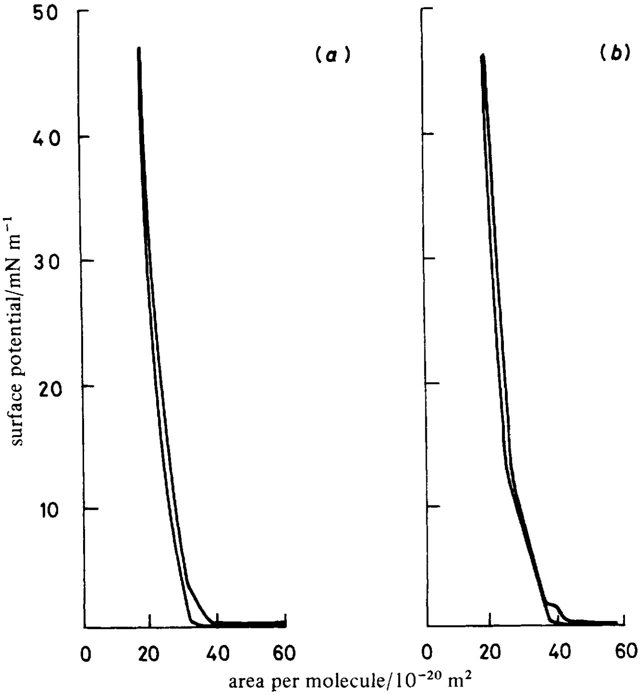


Fig. 5. Surface behaviour of (*a*) a racemic mixture and (*b*) the (+)-enantiomer of octadecylcysteine at 20.5 °C.

by resolving racemic mixtures of the sulphoxides because the long octadecyl chain imparts almost identical physical properties to both diastereoisomers. The asymmetric oxidation of sulphides was also unsuccessful. No optical activity was observed in L.B. films obtained from an enantiomerically pure sulphoxide, nor from an enantiomerically pure amino acid. In the former case the monolayer crystallised on the water sub-phase and on the quartz substrate during deposition, while in the second case optical rotation, if present, was too small to be measured. The chiral species did show significant differences in their π–A behaviour compared with racemic mixtures.

It has been shown that the sulphoxide group has a strong attraction for the aqueous sub-phase; the mid-chain sulphoxide group does not lift off the water surface during compression. Not unexpectedly, when the sulphoxide moiety is located near the terminal acid group, the molecule behaves as if it contained only one polar group.

Experimental

Unless otherwise stated, extractions were carried out with dichloromethane and extracts were dried over Na_2SO_4. Solids were recrystallised to constant m.p. and were homogeneous by t.l.c. Light petroleum refers to the fraction of b.p. 40–60 °C. Flash chromatography was according to Still's procedure.[15] N.m.r. spectra were consistent with the assigned structures. Temperatures are in °C.

11-*Decylthioundecanoic Acid* (**6**).—M.p. 63–64 °C (lit.,[16] m.p. 68 °C) (Found: C, 70.3; H, 12.0. Calc. for $C_{21}H_{42}O_2$: C, 70.4; H, 11.7%).

The following two compounds were prepared from compound (**6**) by the general procedures described by Smith and Hernestam:[16]

11-*Decylsulphinylundecanoic Acid* (**7**).—M.p. 87–88 °C (Found: C, 67.6; H, 11.6. $C_{21}H_{42}O_3S$ requires C, 67.4; H, 11.2%).

11-*Decylsulphonylundecanoic Acid* (**8**).—M.p. 112–114 °C (Found: 64.4; H, 10.6. $C_{21}H_{42}O_4S$ requires C, 64.6; H, 10.8%).

Methyl Octadecyl Sulphide (**1a**).—Methanethiol (54 mmol) was added to a solution of sodium (1.21 g) in ethanol (100 cm^3). Octadecyl bromide (54 mmol) in ether (20 ml) was then added with efficient stirring. Sodium bromide was filtered off, and after evaporation of the filtrate the residue was recrystallised to give the *sulphide* (88%) m.p. 29–31 °C (Found: C, 76.1; H, 13.2. $C_{19}H_{40}S$ requires C, 76.0; H, 13.3%).

Methyl Octadecyl Sulphoxide (**2a**).—The preceding sulphide (0.16 mol) was added to *m*-chloroperbenzoic acid (0.15 mol) in chloroform (150 cm^3) at 0 °C. Oxidation was rapid and two further portions (0.34 mol in all) were added. The mixture was extracted with aqueous sodium hydrogen carbonate and evaporation of the chloroform extracts gave the crude sulphoxide (2.433 g). T.l.c. and ^{1}H n.m.r. spectroscopy showed the presence of sulphide, sulphoxide and sulphone which were separated by flash chromatography on Kieselgel eluting with toluene–ether (3:1). The *sulphoxide* (18%) was washed from the column with methanol and had m.p. 84–86 °C (from hexane) (Found: C, 71.8; H, 12.4. $C_{19}H_{40}OS$ requires C, 72.1; H, 12.6%).

Methyl Octadecyl Sulphone (**3a**).—The sulphide (**1a**) in ethanoic acid (10 cm^3) was treated individually with an excess of saturated aqueous potassium permanganate at 60 °C. Excess reagent was destroyed with sodium metabisulphite and extraction of the reaction mixture with chloroform gave the title sulphone m.p. 97 °C (from hexane) (Found: C, 68.4; H, 11.8. $C_{18}H_{40}O_2S$ requires C, 68.7; H, 12.1%).

Octadecylthioethanoic Acid (**1b**).—Octadecyl bromide (16.7 g; 50 mmol) in ether was added dropwise to an ethanolic solution of mercaptoethanoic acid (1 mol dm^3; 57.5 mmol) containing sodium ethoxide (120 mmol) at 20 °C. When the ensuing precipitation was complete, filtration and evaporation of the filtrate gave a residue which was treated with aqueous hydrochloric acid and extracted. Evaporation of the extracts gave a residue, a portion of which (2 g) was flash chromatographed on light petroleum–ether (3:1) to give octadecyl bromide (0.79 g) and then with pure ether to give the *sulphide* (0.86 g) m.p. 76 °C raised to 82 °C (from hexane) (Found: C, 69.8; H, 11.5. $C_{20}H_{40}O_2S$ requires C, 69.8; H, 11.6%).

Dimethyl(octadecyl)sulphonium Iodide (**4**).—The sulphides (**1a**)–(**1g**) in methanol (50 cm^3) were treated with methyl iodide (0.21 ml) in methanol (20 ml) and the mixture was refluxed for 21 h. Evaporation of the reaction mixture gave a residue, which on treatment with ether gave the title *sulphonium* salt (654 mg, 19%) m.p. 78–81 °C raised to 83.7 °C (from methanol) (Found: C, 54.6; H, 9.5. $C_{20}H_{43}IS$ requires C, 54.3; H, 9.7%).

(±)-*Octadecyl* p-*Tolyl Sulphoxide* (**5**).—Octadecylmagnesium bromide [from octadecyl bromide (7.23 g, 21.7 mmol) and magnesium (0.527 g)] in ether (170 cm^3 at reflux) was treated with ethyl toluene-*p*-sulphinate[17] (2 g, 10.9 mmol). After 1 h, an excess of dilute hydrochloric acid was added and separation and evaporation of the organic phase gave a residue (5.01 g) m.p. 53–54 °C. Flash chromatography eluting with light petroleum–ether (1:1) gave first octadecan-1-ol, m.p. 50–61 °C and then the title *sulphoxide* (7.8%) m.p. 66–68 °C (from hexane) (Found: C, 76.5; H, 11.2. $C_{35}H_{44}OS$ requires C, 76.4; H, 11.2%).

(+)-*Octadecyl* p-*Tolyl Sulphoxide* (**5**).—The previous procedure was followed using (−)-methyl toluene-*p*-sulphinate[18] ($[\alpha]_D^{19}-202°$). The title *sulphoxide* (34%) m.p. 66–68 °C was crystallised to constant rotation $[\alpha]_D^{25}+96°$ (*c* 0.841, $CHCl_3$) from hexane (Found: C, 76.2; H, 10.85%).

Ethyl Octadecylthioethanoate (**1c**).—Ethyl mercaptoethanoate (49.2 mmol) was added to a solution of sodium (49.2 mmol) in ethanol (50 cm^3). Octadecyl bromide (16.39 g, 49.2 mmol) in ether (100 cm^3) was added dropwise with stirring, and when the reaction was complete sodium bromide was filtered off and the filtrate was concentrated under reduced pressure. Extraction of the residue with ether and distillation of the extracts gave the crude *ester* (67%) b.p. 204 °C at 0.3 mmHg (Found: C, 70.1; H, 12.1. $C_{22}H_{44}O_2S$ requires C, 71.0; H, 11.8%).

Ethyl Octadecylsulphinylethanoate (**2c**).—The preceding sulphide (**1c**) (8 mmol) in chloroform (30 cm^3) at 0 °C was treated with *m*-chloroperbenzoic acid (8 mmol) in chloroform (60 cm^3). After 16 h, the mixture was washed with aqueous sodium hydrogen carbonate and evaporation of the organic layer gave material (2.966 g) m.p. 72.5°. A portion (2.004 g) was flash chromatographed on silica eluting with toluene–ether (3:1) to give first a trace of a sulphone and then the *sulphoxide* (**2c**) (1.343 g) m.p. 79 °C (from hexane) (Found: C, 68.2; H, 11.6. $C_{22}H_{44}O_3S$ requires C, 68.0; H, 11.3%).

Octadecylsulphinylethanoic Acid (**2b**).—The preceding sulphoxide ester (**2c**) (6.536 g) in ethanol (150 ml) was treated with sodium hydroxide (1 equiv.) in ethanol–water (50% v/v; 20 cm^3). After 16 h, the mixture was neutralised (HCl), the solvent was removed and extraction of the residue gave the acid (**2b**) (5.37 g, 89%) m.p. 101–102 °C (from dichloromethane) (Found: C, 66.7; H, 11.2. $C_{20}H_{40}O_3S$ requires C, 66.7; H, 11.1%).

Methyl 3-Octadecylthiopropanoate (**1d**).—Methyl 3-mercaptopropanoate (30 mmol) in methanol (10 cm^3), was treated with methanolic sodium methoxide (1 mol dm^{-3}; 30 mmol). The mixture was stirred for 30 min at 20 °C and then octadecyl bromide (30 mmol) in ether (40 cm^3) was added. The mixture was left for 30 h under N_2 and filtered. The filtrate containing the crude *ester* was washed with methanol and ether and then flash chromatographed in ethyl ethanoate–light petroleum (2:98). The pure ester had m.p. 45.5 °C (from hexane) (Found: C, 70.9; H, 11.6. $C_{22}H_{44}O_2S$ requires C, 70.9; H, 11.9%). The ester (6 mmol) in ether (40 cm^3) was stirred vigorously with sodium hydroxide (10 mmol) and water (20 cm^3). Addition of an excess of aqueous hydrochloric acid gave a homogeneous organic phase which, after having been dried and evaporated, gave the *acid* (**1e**) m.p. 79.4 °C (from hexane) (lit.,[19] m.p. 78–79 °C) (Found: C, 70.2; H, 11.3. Calc. for $C_{21}H_{42}O_2S$: C, 70.3; H, 11.8%).

Methyl 3-Octadecylsulphinylpropanoate (**2d**).—The ester (**1d**) (11.2 mmol) in ether (20 cm^3) was treated with *m*-chloroperbenzoic acid (13.63 mmol) in ether (40 cm^3) at 20 °C. After 16 h, the mixture was filtered and flash chromatography of the crude product gave the title *sulphoxide*, m.p. 81.4 °C (from hexane) (Found: C, 68.0; H, 11.5. $C_{22}H_{44}O_3S$ requires C, 68.0; H, 11.4%); $\nu_{max.}$($CHCl_3$) 1040 cm^{-1} (S=O).

3-Octadecylsulphinylpropanoic Acid (**2e**).—The acid (**1e**) (2.3 mmol) in ether (30 cm^3) was treated with *meta*-chloroperbenzoic acid (2.3 mmol) in ether (25 cm^3). After 1 h, the precipitated solid was filtered off and recrystallisation of the residue from chloroform gave the pure *acid*, m.p. 92–93 °C (Found: C, 67.3; H, 11.4. $C_{21}H_{42}O_3S$ requires C, 67.3; H, 11.3%); $\nu_{max.}$($CHCl_3$) 1050 cm^{-1}.

(+)-R-*Octadecylcysteine* (**9a**).—(+)-(*R*)-Cysteine hydrochloride (Aldrich; 1.75 g, 0.01 mol) in aqueous sodium hydroxide (2 mol dm^{-3}; 15 ml, 0.03 mol) was stirred for 7 days at 20 °C with octadecyl bromide (3.339, 0.01 mol). Acidification and filtration of the reaction mixture gave the crude *amino acid*, $[\alpha]_D^{20}$ 5.2° (EtOH) m.p. 189 °C (decomp.) raised to 193 °C (from AcOH) (Found: C, 67.7; H, 11.35; N, 3.8. $C_{21}H_{43}NO_2S$ requires C, 67.5; H, 11.6; N, 3.8%). The (±)-cysteine isomer (**9b**) was obtained similarly from (±)-cysteine and had m.p. 170 °C (from ethanoic acid) (Found: C, 67.5; H, 11.6%).

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