Investigation of Bulk Properties and Monolayer Behaviour of Amphiphilic Mesogens: Structural Variations of the Head Group

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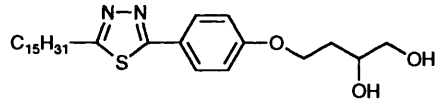
Non-ionic amphiphilic compounds—butane-1,2,3-triol derivatives, 2-hydroxycarboxylic acids and carboxylic acids—incorporating rigid aromatic structural units like 1,4-disubstituted benzene, 4,4'-disubstituted biphenyl or the 2-phenyl-1,3,4-thiadiazole have been prepared. In most cases these compounds exhibit smectic liquid crystalline phases which can be stabilized by the addition of water. Their mesomorphic properties are compared with those of the structurally related 1,2-diol derivatives. Surprisingly, also some ω-(4-alkylphenoxy)alkanoic acids which have no thermotropic mesophases were found to aggregate to lyotropic mesophases in the presence of water. Most of the new compounds form stable monolayers at the air–water interface. The force–area isotherms of the thiadiazole derivatives have been recorded and it was found that they strongly depend on the chemical structure of the head group.

The main basis for the self-organization of 'conventional' liquid crystals to thermotropic mesophases is the form-anisotropy of the individual molecules. However, amphiphilic molecules also aggregate to ordered supramolecular assemblies such as micelles, bilayers, monomolecular layers at interfaces and lyotropic liquid crystalline phases.[1]



1c

Recently we have reported,[2–4] that amphiphilic 1,2-diol derivatives such as **1**, *i.e.* amphiphilic compounds incorporating rigid structural units of classic calamitic mesogens like biphenyl, phenylthiadiazole or phenylpyrimidine not only exhibit thermotropic liquid crystalline phases but also form lyotropic mesophases and stable monomolecular layers at the air–water interface. In this way, the combination of structural characteristics of non-amphiphilic liquid crystalline materials and surfactants gave rise to amphotropic behaviour bridging the long existing gap between these two kinds of materials. In order to investigate the influence of variations of the head groups on the molecular self-organization, we have synthesized non-ionic amphiphiles in which the 1,2-diol group is replaced by structurally related hydrophilic head groups. Special attention was drawn to the investigation of the 2-hydroxy carboxylic acids **2**, the diastereoisomeric butane-1,2,3-triol derivatives **3b** and **4b** and the carboxylic acids **6**. The molecular self-organization of these new materials as bulk materials and as thin films at the air–water interface was investigated.

Results and Discussion

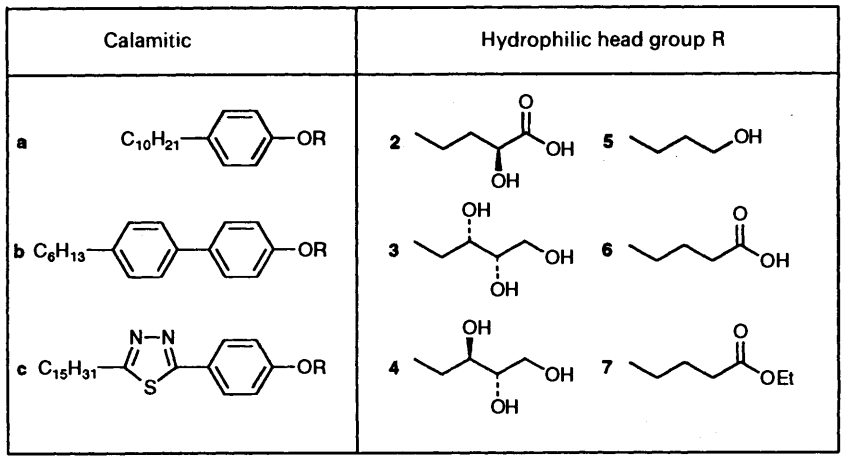
Synthesis.—The synthesis of the 2-hydroxycarboxylic acids **2** was carried out according to Scheme 1. Thereby (*S*)-malic acid was used as starting material, from which the chiral alcohol **9** was obtained in a three-step synthesis.[5,6] Compound **9** was etherified with 4-decylphenol **10a**,[7] 4'-hexyl-4-hydroxybiphenyl **10b**[8] or 2-(4-hydroxyphenyl)-5-pentadecyl-1,3,4-thiadiazole **9c**[9] using the Mitsunobu method[10] and subsequent saponification yielded the substituted (*S*)-2-hydroxycarboxylic acids **2a–c**. The influence of an additional hydroxy group on the molecular self-organization was investigated for the case of the two diastereoisomeric butane-1,2,3-triols **3b** and **4b** each in its enantiomerically pure form. The synthesis of these compounds was achieved starting from L-ascorbic acid as outlined in Scheme 2. Thereby ascorbic acid was transformed into the three-fold protected L-threitol **14** according to literature procedures.[11,12] In order to obtain the diastereoisomeric L-erythrol derivative **16** the configuration of the 2-hydroxy group of methyl L-threonate **12**[11] was inverted by means of a Mitsunobu esterification with 3,5-dinitrobenzoic acid.[10,13] The resulting 3,5-dinitrobenzoate **15** was transformed into the three-fold protected L-erythrol **16** as described in Scheme 2. Compounds **14** and **16** were used in Mitsunobu etherifications with appropriate phenols **10** and after hydrolytic cleavage of the protective groups the triols **3b** and **4b** were obtained.

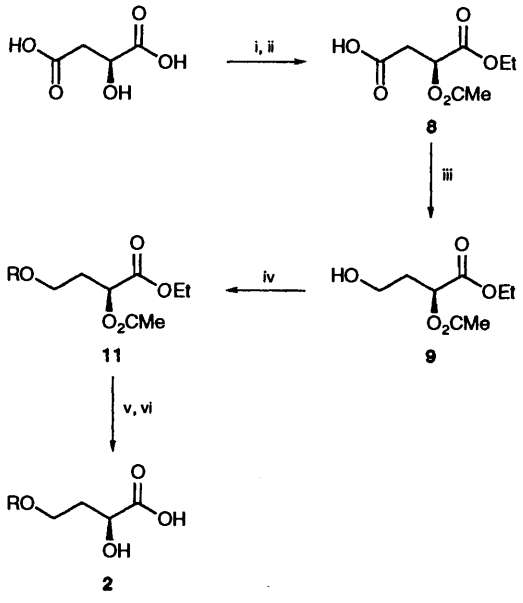
Compounds **5c**, **7c**, **19** and **20** were synthesized by etherification of appropriate 4-substituted phenols **10** with 3-bromopropanol, or ethyl ω-bromoalkanoates in the presence of potassium carbonate. Alkaline saponification of ethyl 4-[4-(5-pentadecyl-1,3,4-thiadiazol-2-yl)phenoxy]butanoate **7c** gave the carboxylic acid **6c**.

The 3-(4-nonyloxyphenyl)propionic acid **18** was synthesized starting from 3-(4-hydroxyphenyl)propionitrile[14] which was etherified with nonyl bromide. The resulting 3-(4-nonyloxyphenyl)propionitrile was saponified to give the desired carboxylic acid.

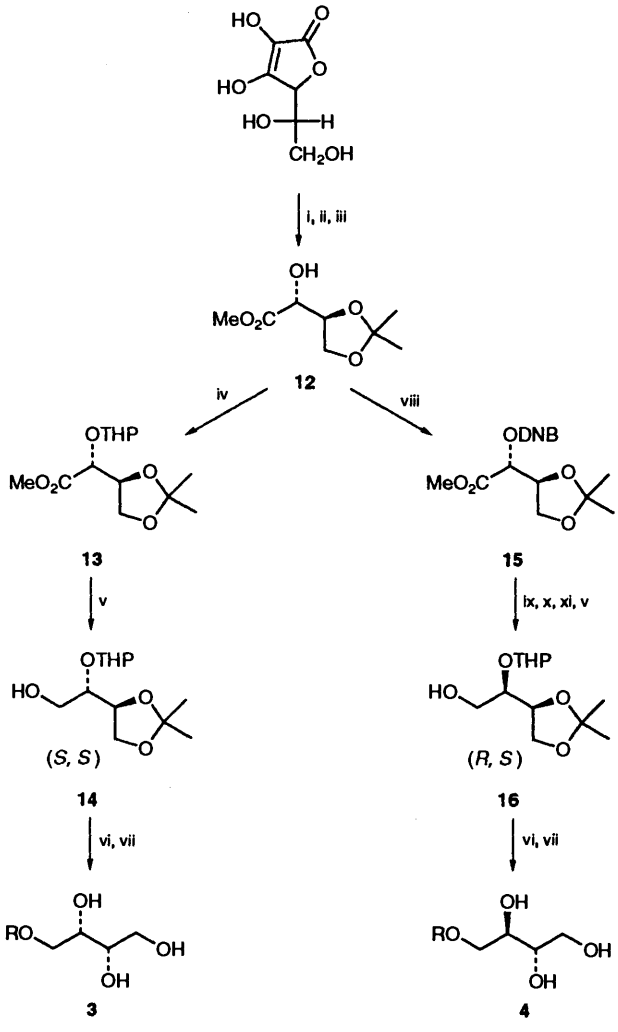
Thermotropic Properties.—Tables 1–3 contain the transition temperatures of the new amphiphilic materials as well as those of the comparable 1,2-diol derivatives **1**.[4] In most cases the smectic A-phase was formed on cooling from the isotropic liquid. Some compounds exhibit further smectic phases. Only the carboxylic acids **6a**, **6c** as well as compounds **5c** and **7c** are crystalline solids.

The amphiphilic diols **1** and the corresponding 2-hydroxycarboxylic acids **2** differ from each other only in the formal replacement of the primary alcoholic hydroxy group by a carboxylic acid group. However, the nature of the hydrogen bonding in simple alcohols differs significantly from that





Scheme 1 *Reagents:* i, MeCOCl; ii, EtOH; iii, BH_3·THF; iv, ROH (**10**), Ph_3P, EtOOC–N=N–COOEt, THF; v, KOH, MeOH; vi, H^+

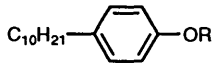


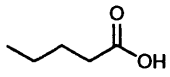
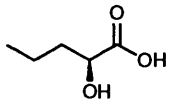
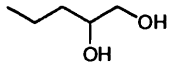
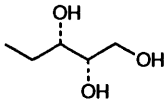
Scheme 2 *Reagents:* i, 2,2-dimethoxypropane, acetone, Py·TosOH; ii, H_2O_2, $CaCO_3$; iii, $NaHCO_3$, H_2O, Me_2SO_4; iv, DHP, Py·TosOH; v, $LiAlH_4$; vi, ROH (**10**), Ph_3P, EtOOC–N=N–COOEt, THF; vii, MeOH, H_2O, Py·TosOH; viii, 3,5-dinitrobenzoic acid, Ph_3P, EtOOC–N=N–COOEt, THF; ix, KOH, H_2O; x, $NaHCO_3$, Me_2SO_4; xi, Py·TosOH, DHP

observed in carboxylic acids. While the latter form cyclic dimers, alcohols prefer larger associates due to the cooperative nature of the hydrogen bonding in alcohols.[15] Therefore it was of special interest to combine both kinds of hydrogen bonding functional groups near to each other in one molecule and to investigate how this influences their mesomorphic properties. If one compares the clearing temperatures of the carboxylic acids **6** with those of the 2-hydroxycarboxylic acids **2**, the latter exhibit the higher mesophase stabilities. This reveals the additional stabilizing influence of the hydroxy group, which is also evident from the comparison of the diol derivatives **1** with the triol derivatives **3** and **4**. An increase in the number of hydrogen bonds between the polar head groups enhances the mesophase stability. Contrasting the diastereoisomeric triol derivatives **3b** and **4b** indicates that not only the number but also the relative configuration of the hydroxy groups influences the mesomorphic properties. The thermotropic clearing temperature of the *erythro*-diastereoisomer **4b** is slightly higher than that of the *threo*-diastereoisomer **3b**. This observation is in agreement with findings observed for amphiphilic carbohydrate derivatives and other multihydroxy compounds whose mesomorphic properties largely depend on their configuration.[16] The DSC traces, obtained by heating samples of the diastereoisomeric compounds **3b** and **4b** are given in Fig. 1. It is evident that the melting process takes place over a certain temperature range by several phase transitions. The high temperature phase is a smectic A-phase with a typical oily-streaks texture.

The precise structure of the various low temperature phases is not elucidated yet, but polarizing microscopic investigations suggest that at least the phase, directly below the smectic A-phase could be a low temperature mesophase.[17] The phase

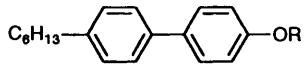
Table 1 Transition temperatures[a] (°C) of the amphiphilic 4-decylphenyl derivatives

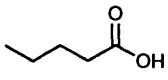
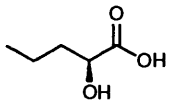
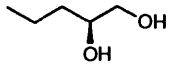
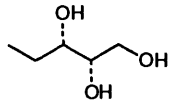
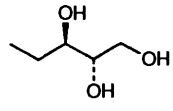


Compound	R	Phase transition/°C	
		Water-free state	Water-saturated state
6a		cr 65 is	cr 64 S_A 89 is
2a		cr 100 (S_A 92) is	cr 58 S_A 240 is
1a[b]		cr 68 S_A 75 is	cr 47 S_A 141 is
3a		cr 88 S_A 139 is	cr 63 S_A 201 is

[a] Determined using a hot-stage polarizing microscope; abbreviations: cr = crystalline, S_A = smectic A phase, is = isotropic liquid. [b] See ref. 4.

Table 2 Transition temperatures[a] (°C) of the amphiphilic biphenyl derivatives



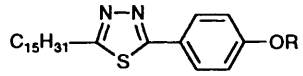
Compound	R	Phase transition/°C	
		Water-free state	Water-saturated state
6b		cr 157 S_A 158 is	cr 115 S_A 235 is
2b		cr 159 S_A 212 is	cr 116 S 264 is
1b[b]		cr 148 S_A 178 is	cr 90 S_A 206 is
3b		cr 123 S_X 146 S_A 220 is	cr 78 S 225 is
4b		cr 147 S_X 157 S_A 223 is	cr 98 S 225 is

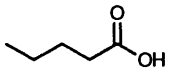
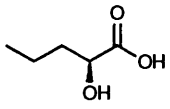
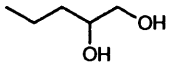
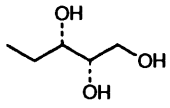
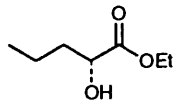
[a] S = unidentified lyotropic smectic phase/s, S_X = unidentified higher ordered thermotropic smectic phase. For an explanation of the other abbreviations see Table 1. [b] This homochiral butane-1,2-diol derivative was synthesized according to the procedure given in ref. 4, starting from (*S*)-1,2-*O*-isopropylidene butane-1,2,4-triol and **10b**.

transition is indicated by the formation of birefringent platelet areas with transparent platelets overlapping each other in the originally pseudoisotropic areas.

The heating traces of both compounds possess a striking similarity, but it is clearly visible that the phase transitions of the *erythro*-diastereoisomer **4b** generally take place at higher temperatures. Therefrom we may conclude that the attractive intermolecular interactions—especially hydrogen bonding—between the single molecules depend on the relative configuration of the hydroxy groups, whereby these attractive interactions are stronger for the *threo*-diastereoisomer **3b**. Furthermore the difference of the transition temperatures in both diastereoisomers increases with increasing order within the phases. This indicates that these attractive interactions are directed. As one would expect, the importance of these interactions increases with increasing order of the phases.

Table 3 Transition temperatures[a] (°C) of the amphiphilic 2-phenyl-1,3,4-thiadiazole derivatives



Compound	R	Phase transition/°C	
		Water-free state	Water-saturated state
6c		cr 125 is	cr 108 S 234 is
2c		cr 105 S_A 119 is	cr 84 S_A 183 is
1c[b]		cr 99 S_C 112 S_A 133 is	cr 70 S_A 156 is
3c		cr 110 (S_X 106 S_C* 109) S_A 184 is	cr 83 S_A 246 is
7c		cr 178 is	
5c		cr 94 is	

[a] Abbreviations: S_C = smectic C phase, S_C* = chiral smectic C phase. For an explanation of the other abbreviations see Tables 1 and 2. [b] See ref. 4.

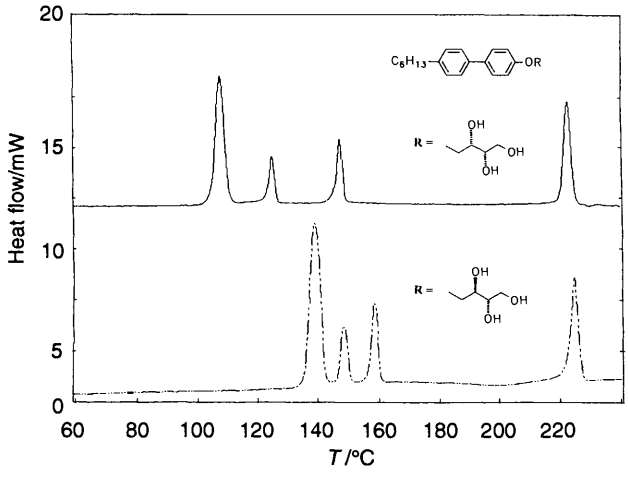


Fig. 1 Second heating DSC thermograms (10 °C min^{-1}) of the diastereoisomeric triol derivatives **3b** (upper curve) and **4b** (lower curve)

Lyotropic Properties.—It is well known that the liquid crystalline phases of amphiphilic diol compounds can be influenced by addition of water.[3] Although the water absorption is limited, a depression of the melting temperatures and an increase of the clearing temperatures has mostly been observed.* We determined the transition temperatures by heating contact preparations in sealed capillaries with excess water on a heating stage and observation of the samples between crossed polarizers of a polarizing microscope. Therefore only the clearing temperatures could be determined accurately. Phase transitions between different mesophases could hardly be detected due to the poor orientation of the samples in the capillaries, making the textural investigations extremely difficult. Only in those cases, when crystallization takes place markedly below 100 °C, did we succeed in observing the textures of the mesophases by polarizing microscopy of mixtures between cover glasses. The compounds investigated in this way generally exhibit smectic phases, often smectic A-phases which are indicated by the formation of large pseudoisotropic areas separated by oily streaks. Fan-like textures are seldom observed. The transition temperatures of the water-saturated samples of the newly synthesized compounds are collected in the Tables 1–3. If one compares the transition temperatures of the water-free samples with those of the water-saturated samples, it is obvious that the addition of water leads to a significant mesophase stabilization not only for diols and triols but also for hydroxycarboxylic acids and even for the simple carboxylic acids **6**. It is a rather surprising finding that even the mesophase of the simple carboxylic acids can be stabilized by addition of water. This is especially evident from the transition temperatures of the 4-(4-decylphenoxy)butanoic acid **6a** (Table 1). The pure compound **6a** is a crystalline solid which shows no mesomorphic behaviour, but addition of water causes the induction of a smectic A-phase.

The comparison with other carboxylic acids of similar structure is given in Table 4. It clearly shows that the presence of at least one additional oxygen atom in close proximity to

* Due to the limited water take up of the diol compounds, the rigidity of the molecules and their poor solubility in water, they do not form lyotropic mesophases consisting of curved aggregates such as cubic and hexagonal phases. Only lamellar phases have been observed. Additionally a continuous increase of the clearing temperature upon addition of water occurs. In other words one could say, that in the case of amphiphilic diols there is no borderline between thermotropic and lyotropic liquid crystalline phases. Therefore we use the descriptors of thermotropic phases (S_A, S_C, *etc.*) also to describe the mesophases of the water containing samples of amphiphilic diols incorporating calamitic structural units.

Table 4 Influence of different substituents on the mesomorphic behaviour[a] of amphiphilic carboxylic acids

Compound	R	Phase transition/°C	
		Water-free state	Water-saturated state
17	C_5H_{11}—C$_6$H$_4$—$(CH_2)_2CO_2H$	cr 71 N 81 is	cr 67 is
18	$C_9H_{19}O$—C$_6$H$_4$—$(CH_2)_2CO_2H$	cr 77 is	cr 73 is
19	$C_{10}H_{21}$—C$_6$H$_4$—OCH_2CO_2H	cr 97 is	cr 69 S 129 is
6a	$C_{10}H_{21}$—C$_6$H$_4$—$O(CH_2)_3CO_2H$	cr 65 is	cr 64 S_A 89 is
20	$C_{10}H_{21}$—C$_6$H$_4$—$O(CH_2)_4CO_2H$	cr 63 is	cr 63 is

[a] N = nematic phase. For an explanation of the other abbreviations see Tables 1 and 2.

the carboxylic acid group is essential for the occurrence of liquid crystallinity after addition of water.

The 3-phenylpropionic acid **18**, *i.e.* a compound without this additional ether oxygen atom, does not form any enantiotropic or monotropic mesophase either as a pure sample or after addition of water. Investigation of the *trans*-3-(4-pentylcyclohexyl)propionic acid **17** which also lacks the essential ether oxygen reveals that the thermotropic nematic phase of this compound[18] is even suppressed by addition of water. Furthermore, the distance between carboxylic acid group and ether oxygen atom is likely to be important. It should not be longer than three methylene units. Compound **20** with a butylene spacer between the ether oxygen and the carboxylic acid group also does not form any liquid crystalline phase after addition of water. Probably, these observations could be interpreted in the following way. The mesogenic dimers of carboxylic acids are partly broken by incorporation of water molecules into the hydrogen bonds between the carboxylic acid groups.[15] This should lead to a less pronounced rod-like shape of the mesogenic dimers, thus decreasing their mesophase forming ability. However, water molecules also could mediate additional hydrogen bonds between neighbouring dimers. If these intermolecular interactions are strong enough, they should give rise to a layered structure. The number of such intermolecular hydrogen bonds in simple carboxylic acids is small, but it could be greatly increased by an additional ether oxygen atom in close proximity to the carboxylic acid group. This ether oxygen atoms acts as an efficient proton acceptor and can participate in the formation of a hydrogen bonding network with water molecules. Consequently, mesophase stabilization or mesophase induction by addition of water is observed only for compounds bearing both of these structural features. In this way the ω-phenoxyalkanoic acids **6a** and **19** bridge the gap between the two structural types of mesophase forming compounds, calamitic and amphiphilic materials.

In the case of the ethyl carboxylate **7c** and the primary alcohol **5c** neither thermotropic nor lyotropic mesomorphism could be observed. Both compounds lack the ability to form large hydrogen bonding networks or stable dimers. This demonstrates once again the stabilizing influence of hydrogen bonding for liquid crystal formation.

Monolayer Behaviour.—In the study of the monolayer properties at the air–water interface we have focussed our interest on the group of substances containing a 2-phenyl-1,3,4-thiadiazole unit (Table 3). Our special interest arose from the investigation of monolayers of 1,2-diols incorporating this aromatic structural unit.[4] We have found that the replacement of a biphenyl or phenylpyrimidine rigid core in amphiphilic diol compounds by the 2-phenyl-1,3,4-thiadiazole moiety led to a special kind of F–A isotherm. These are characterized by the appearance of two different condensed films. The study under consideration aimed to find out if this effect is restricted to the 1,2-diols **1**. In Figs. 2 and 3 we compare the force–area isotherms of the substances listed in Table 3. At first glance we may classify two types of curve. The first type shows only one condensed film: these curves are obtained from the substances with the primary hydroxy group (**5c**), with the carboxylic acid group (**6c**) and those with the ethyl carboxylate group (**7c**). It is well established that in the case of simple long chain primary alcohols, acids and the corresponding ethyl esters the cross-sectional area of the alkyl chain determines the molecular dense packed area.[19] Therefore we expect, in the case of the thiadiazole derivatives **5c**–**7c**, this area to be determined by the dense packed rigid aromatic cores. The second type results from the investigation of substances with hydrophilic head groups consisting of two or more functional groups (1,2-diol **1c**, 2-hydroxycarboxylic acid **2c**, triol **3c**). The same type of curve is observed for compound **21** with the bulky 1,2-*O*-isopropylidene

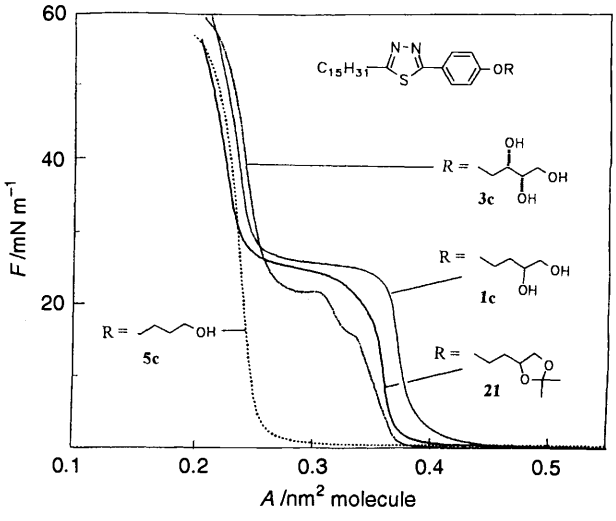


Fig. 2 F–A isotherms of compounds **1c**, **3c**, **5c** and **21** at 20 °C

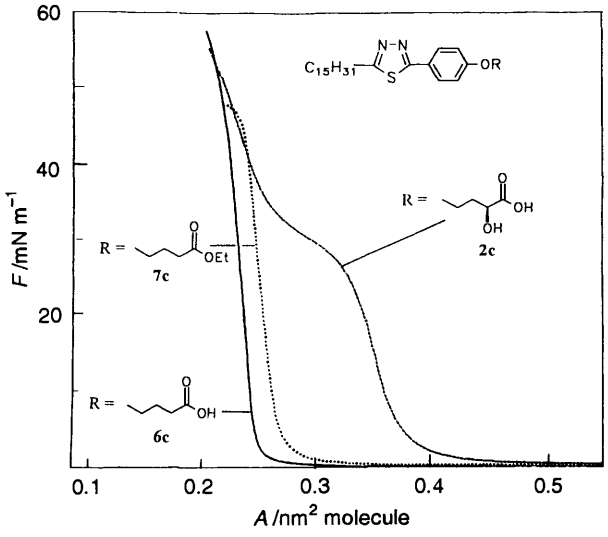


Fig. 3 F–A isotherms of compounds **2c**, **6c** and **7c** at 20 °C

head group. All of these compounds form two condensed films with a transition from one condensed film to another one.

The more condensed film could be compressed to a molecular area of about 0.22 nm^2. This area corresponds to that observed in the films of compounds with a single functional group as head group and should also be determined by the dense packed rigid aromatic cores. However the 1,2-diol group may occupy approximately the same area (A_k = 0.20–0.22 nm^2) as investigations of simple 1,2-alkanediols have proved.[20] Therefore, we assume, that the high area condensed film (A = 0.4 nm^2) may result from packing problems, probably because the two different structural units—rigid core and hydrophilic head group—prefer to arrange in a different manner.[21] Since they are fixed to each other by a very short spacer they cannot arrange independently, thus giving rise to larger cross section area (high area condensed films). Further increasing the lateral pressure probably influences the molecular conformation and/or the molecular packing in such a way that a low area film with closely packed rigid units results.

Although some questions still remain unanswered, our investigations indicate that the molecular self-organization of the compounds described strongly depends on the chemical structure of the hydrophilic headgroups.

Experimental

Confirmation of the structures of intermediates and products was obtained by ^1H and ^{13}C NMR spectroscopy (Bruker WP 200 spectrometer), IR spectroscopy (Specord 71 IR) and MS (AMD 402, electron impact, 70 eV). Microanalyses were performed using a Carlo-Erba 1102 elemental analyser. Transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and Perkin-Elmer Series 1020 data station). Pressure–area isotherms were recorded using a home-built film balance equipped with a Teflon-coated Langmuir trough (60 × 10 cm) and a continuous Wilhelmy type measuring system (reproducibility was within ±0.5 mN m^{-1}).[22] The width of the filter paper plate was about 35 mm. The Langmuir trough was thermostatted and enclosed in a thermostatted Perspex box. The temperature of the experimental system was 20 °C and was controlled to within ±0.1 K. The relative humidity within the box was higher than 95%. The substances were dissolved in chloroform. Typically, the solutions were between 1 and 2 mmol dm^{-3}. The measurements were started 10 min after spreading. The films were compressed with a velocity of 0.08 nm^2 mol^{-1} min^{-1}. The spreading solvent was chromatography grade chloroform stabilized by a small amount of purified methanol. It was distilled immediately prior to use. Water used for measuring the surface properties and the lyotropic properties was of Millipore quality. The purity of all compounds was checked by thin layer chromatography (Merck, silica gel 60 F_{254}). Light petroleum–ethyl acetate mixtures were used as eluents and the spots were detected by UV irradiation and/or by means of bromothymol blue solution. The final compounds were additionally checked by HPLC analysis (Merck-Hitachi; RP18 column) and were found to be >98% pure.

The phenols **10a–c** were synthesized according to literature procedures.[7–9] 3-Bromopropanol, ethyl bromoacetate, ethyl 4-bromobutanoate, (*S*)-malic acid, diethyl azodicarboxylate, ascorbic acid (all from Merck) and ethyl 5-bromopentanoate (Lancaster) were used as received.

(S)-*Ethyl 2-Acetoxy-4-hydroxybutanoate* **9**.—A solution of BH_3·THF (C_4H_8O) (2.39 mol dm^{-3} solution in THF; 42 cm^3, 0.1 mol) was added dropwise over a 40 min period to a stirred solution of (*S*)-2-acetoxybutanedioic acid 1-ethyl ester **8**[5] (19 g, 0.10 mol) in dry THF (60 cm^3) kept under an argon atmosphere at −18 °C. The mixture was allowed to equilibrate to ambient temp. and was stirred at room temp. overnight. Then excess BH_3·THF was destroyed by dropwise addition of water (60 cm^3) to the mixture at 0 °C. Afterwards potassium carbonate (24 g, 0.17 mol) was added. The mixture was stirred for 10 min. The solution was decanted and the residue was washed twice with diethyl ether (100 cm^3). The aqueous phase was separated and extracted twice with diethyl ether (150 cm^3). The organic solutions were combined and washed with brine (60 cm^3), dried (sodium sulfate) and concentrated under reduced pressure. The residue was distilled to give **9** as a colourless oil. Yield 10.2 g (53%); b.p. 117–120 °C/0.55 Torr (lit.,[5] b.p. 89.5 °C/0.12 Torr);* $[\alpha]_D$ −51.8 (*c* 1.8, EtOH) [lit.,[5] $[\alpha]_D$ −52.3 (*c* 2.3, ethanol)]. On the basis of IR and NMR spectroscopic findings the substance corresponds in all respects with the compound described in ref. 5.

(S)-*Ethyl 2-Acetoxy-4-[4-(5-pentadecyl-1,3,4-thiadiazol-2-yl)phenoxy]butanoate* **11c**.—*Typical procedure for Mitsunobu etherification.* 2-(4-Hydroxyphenyl)-5-pentadecyl-1,3,4-thiadiazole **10c** (1.17 g, 3.0 mmol) and triphenylphosphine (1.2 g, 4.5 mmol) were dissolved in dry THF (15 cm^3). After addition of **9** (0.86 g, 4.5 mmol) the mixture was cooled to 0–5 °C. At this temperature diethyl azodicarboxylate (0.78 g, 4.5 mmol) was added dropwise within 5 min to the stirred mixture. The solution was stirred for an additional 24 h at room temp. Afterwards the solvent was evaporated off and the residue was crystallized twice from methanol–water (9:1) to remove the triphenylphosphine oxide. The crude product was repeatedly recrystallized from methanol to leave white crystals. Yield 1.23 g (73%); m.p. 80 °C (Found: C, 66.0; H, 8.45; N, 5.1; S, 5.6. $C_{31}H_{48}N_2O_5$ requires C, 66.39; H, 8.63; N, 5.00; S, 5.72%); $\delta_H(CDCl_3)$ 0.84 (3 H, t, CH_3), 1.1–1.4 (27 H, m, CH_2, CH_3CH_2O), 1.79 (2 H, m, CH_2), 2.11 (3 H, s, CH_3CO_2), 2.30 (2 H, m, CH_2CH), 3.07 (2 H, t, CH_2-thiadiazole), 4.11 (2 H, t, CH_2O), 4.19 (3 H, q, CH_2CH_3), 5.21 (1 H, dd, CH), 6.92 (2 H, d, Ar) and 7.83 (2 H, d, Ar).

(S)-*Ethyl 2-Acetoxy-(4-decylphenoxy)butanoate* **11a**.—Prepared as before from 4-decylphenol **10a** (0.70 g, 3.0 mmol). Yield

* 1 Torr ≈ 133 Pa.

0.9 g (68.7%), oil, which was used as crude product for the saponification to yield **2a**.

(S)-*Ethyl* 2-*Acetoxy*-4-(4′-*hexylbiphenyl*-4-*yloxy*)*butanoate* **11b**.—Prepared as before from 4′-hexylbiphenyl-4-ol **10b** (0.76 g, 3.0 mmol). Yield 0.50 g (39.2%); m.p. 59 °C (Found: C, 73.4; H, 8.2. $C_{26}H_{36}O_4$ requires C, 73.21; H, 8.04%); δ_H(200 MHz; $CDCl_3$) 0.89 (3 H, t, CH_3), 1.3 (3 H, t, CH_3CH_2O), 1.3–1.5 (6 H, m, CH_2), 1.63 (2 H, m, CH_2), 2.14 (3 H, s, CH_3CO_2), 2.34 (2 H, m, CH_2CH), 2.63 (2 H, t, $CH_2C_6H_4$), 4.12 (2 H, t, CH_2O), 4.22 (3 H, q, CH_2CH_3), 5.25 (1 H, dd, CH), 6.93 (2 H, d, Ar), 7.22 (2 H, d, Ar) and 7.47 (4 H, dd, Ar).

(S)-2-*Hydroxy*-4-[4-(5-*pentadecyl*-1,3,4-*thiadiazol*-2-*yl*)-*phenoxy*]*butanoic Acid* **2c**.—Compound **11c** (1.12 g, 2.0 mmol) was dissolved in methanol (30 cm^3). Potassium hydroxide (0.56 g, 10 mmol; dissolved in 3 cm^3 water) was added and the obtained mixture was stirred and refluxed for 15 min. After cooling to room temp. the solvent was evaporated and the residue was suspended in dilute sulfuric acid (50 cm^3; 1 mol dm^{-3}). This mixture was extracted with chloroform (3 × 50 cm^3). The chloroform extract was washed with dilute sulfuric acid (50 cm^3; 1 mol dm^{-3}), water (50 cm^3) and brine (50 cm^3), dried (sodium sulfate) and concentrated under reduced pressure. The residue was crystallized from toluene and twice recrystallized from this solvent. Yield 0.60 g (61%); transitions (°C) cr 105 S_A 119 is (Found: C, 66.2; H, 8.5; N, 5.6; S, 6.4. $C_{27}H_{42}N_2O_4S$ requires C, 66.09; H, 8.63; N, 5.71; S, 6.53%); ν_{max}(Nujol)/cm^{-1} 3406 (OH), 1764 (C=N), 1707 (C=O), 1600 (C=C), 1513, 1298, 1250, 1226, 1168, 1104 and 1046; δ_H(200 MHz; [$^2H_6$]DMSO) 0.83 (3 H, t, CH_3), 1.01–1.29 (24 H, m, CH_2), 1.71 (2 H, m, CH_2), 1.87–2.19 (2 H, m, CH_2CH), 3.07 (2 H, t, CH_2-thiadiazole), 4.11–4.17 (3 H, m, CHO, CH_2O), 7.07 (2 H, d, Ar) and 7.85 (2 H, d, Ar); *m/z* 490 (M^+, 35%), 307 (64), 294 (76), 288 (39), 276 (64) and 192 (68).

(S)-4-(4-*Decylphenoxy*)-2-*hydroxybutanoic Acid* **2a**.—Prepared as before from **11a** (0.81 g, 2.0 mmol). Yield 0.42 g (62%); transitions (°C) cr 100 (S_A 92) is (Found: C, 71.5; H, 9.4. $C_{20}H_{32}O_4$ requires C, 71.39; H, 9.59%); ν_{max}(Nujol)/cm^{-1} 3421 (OH), 1707 (C=O), 1596 (C=C), 1500, 1238, 1214, 1186, 1088 and 1064; δ_H(200 MHz; [$^2H_6$]DMSO) 0.84 (3 H, t, CH_3), 1.22–1.41 (14 H, m, CH_2), 1.84–2.13 (2 H, m, CH_2CH), 2.48 (2 H, t, $CH_2C_6H_4$), 4.12 (2 H, t, CH_2O), 4.08 (1 H, dd, CH), 6.80 (2 H, d, Ar) and 7.06 (2 H, d, Ar); *m/z* 336 (M^+, 10%), 234 (33) and 107 (100).

(S)-4-(4′-*Hexylbiphenyl*-4-*yloxy*)-2-*hydroxybutanoic Acid* **1b**.—Prepared as before from **11b** (0.85 g, 2.0 mmol). Yield 0.43 g (60%); transitions (°C) cr 159 S_A 212 is (Found: C, 74.0; H, 8.0. $C_{22}H_{28}O_4$ requires C, 74.13; H, 7.92%); ν_{max}(Nujol)/cm^{-1} 3436 (OH), 3398 (OH), 1711 (C=O), 1594 (C=C), 1493, 1247, 1223, 1200, 1104, 1067, 1033 and 809; δ_H(200 MHz; [$^2H_6$]DMSO) 0.85 (3 H, t, CH_3), 1.20–1.41 (6 H, m, CH_2), 1.57 (2 H, m, CH_2), 1.89–2.14 (2 H, m, CH_2CH), 2.57 (2 H, t, $CH_2C_6H_4$), 4.07–4.17 (3 H, m, CH_2O, CH), 6.98 (2 H, d, Ar), 7.22 (2 H, d, Ar) and 7.53 (4 H, dd, Ar); *m/z* 356 (M^+, 30%), 254 (63) and 183 (100).

Methyl 3,4-O-*Isopropylidene*-2-O-*tetrahydropyran*-2-*yl*-L-*threonate* **13**.—A solution of **12** (9.5 g, 50 mmol),[11] 3,4-dihydro-2*H*-pyran (6.3 g, 75 mmol) and pyridinium toluene-*p*-sulfonate (0.5 g, 2.0 mmol) in dry dichloromethane (80 cm^3) was stirred at room temp. for 5 h. After this period the reaction mixture was diluted with dichloromethane (200 cm^3). The solution was washed twice with brine and dried (sodium sulfate). Evaporation of the solvent under reduced pressure gave an oily residue which was further purified by Kugelrohr distillation to yield pure **13** as a colourless oil. Yield 12.0 g (88%); b.p. 78–83 °C/0.01 Torr; compound **13** exhibits the same ^1H NMR spectrum as that reported in ref. 12.

1,2-O-*Isopropylidene*-3-O-*tetrahydropyran*-2-*yl*-L-*threitol* **14**.—The reduction of **13** (9.0 g, 33 mmol) was carried out with lithium aluminium hydride (0.72 g, 19 mmol) as described by Schmidt and co-workers.[12] Yield 6.8 g (90%); b.p. 123 °C/0.03 Torr; compound **14** exhibits the same ^1H NMR spectrum as that reported in ref. 12.

4-O-(4-*Decylphenyl*)-L-*threitol* **3a**.—**3a** was prepared from **14** (0.74 g, 3.0 mmol) and 4-decylphenol **10a** (0.47 g, 2.0 mmol) according to the general procedure for Mitsunobu etherification as described for the synthesis of **11c**. After evaporation of the solvent an oily residue was obtained which was washed twice with a methanol–water mixture (9:1, 10 cm^3) to remove the triphenylphosphine oxide. This crude product (0.38 g, 1.0 mmol) was dissolved in wet ethanol (20 cm^3, containing 5% water). After addition of pyridinium toluene-*p*-sulfonate (50 mg, 0.2 mmol) the solution was refluxed for 3 h. Removal of the solvent under reduced pressure gave a residue which was dissolved in ethyl acetate (50 cm^3) and washed with water, saturated aqueous sodium hydrogen carbonate, water, and brine successively. After drying (sodium sulfate) the solvent was evaporated and the residue crystallized from light petroleum (b.p. 65–80 °C). **3a** was repeatedly recrystallized from methanol–water (9:1) to leave white crystals. Yield 0.37 g (55%); transitions (°C) cr 88 S_A 139 is (Found: C, 71.2; H, 9.95. $C_{20}H_{34}O_4$ requires C, 70.97; H, 10.13%); δ_H(200 MHz; [$^2H_6$]DMSO) 0.84 (3 H, t, CH_3), 1.22 (14 H, m, CH_2), 1.55 (2 H, m, CH_2), 2.50 (CH_2-Ar and solvent), 3.35–4.12 (6 H, m, CH_2O, CHO), 4.48 (2 H, m, CH_2OH, CHO*H*), 4.66 (1 H, d, CHO*H*), 6.80 (2 H, d, Ar) and 7.06 (2 H, d, Ar); *m/z* 338 (M^+, 9%), 234 (77) and 107 (100).

4-O-(4′-*Hexylbiphenylyloxy*)-L-*threitol* **3b**.—Prepared as described for **3a** from **14** (0.74 g, 3.0 mmol) and 4′-hexylbiphenyl-4-ol **10b** (0.51 g, 2.0 mmol). Yield 0.44 g (61%); transitions (°C) cr 137 S_X 154 S_A 229 is (Found: C, 73.65; H, 8.5. $C_{22}H_{30}O_4$ requires C, 73.71; H, 8.44%); ν_{max}(KBr)/cm^{-1} 3320 (br, OH), 2900, 1590, 1480 and 1440; δ_H(200 MHz; [$^2H_6$]DMSO) 0.84 (3 H, t, CH_3), 1.26 (6 H, m, CH_2), 1.55 (2 H, m, CH_2), 2.50 (2 H, t, CH_2Ar), 3.35–4.12 (6 H, m, CH_2O, CHO), 4.55 (2 H, m, br, CH_2OH, CHO*H*), 4.74 (1 H, d, br, CHO*H*), 6.99 (2 H, d, Ar), 7.20 (2 H, d, Ar), 7.49 (2 H, d, Ar) and 7.54 (2 H, d, Ar).

4-O-[4-(5-*Pentadecyl*-1,3,4-*thiadiazol*-2-*yl*)*phenoxy*]-L-*threitol* **3c**.—Prepared as described for **3a** from **14** (0.74 g, 3.0 mmol) and 2-(4-hydroxyphenyl)-5-pentadecyl-1,3,4-thiadiazole **10c** (0.70 g, 2.0 mmol). Yield 0.61 g (62%); transitions (°C) cr 110 (S_X 106 S_C* 109) S_A 184 is (Found: C, 65.9; H, 9.1; N, 5.6; S, 6.40. $C_{27}H_{44}N_2O_4S$ requires C, 65.82; H, 9.00; N, 5.69; S, 6.51%); δ_H(200 MHz; [$^2H_5$]pyridine) 0.86 (3 H, t, CH_3), 1.27 (24 H, m, CH_2), 1.79 (2 H, m, CH_2), 3.12 (2 H, t, CH_2-thiadiazole), 4.3–4.8 (6 H, m, CH_2O, CHO), 7.14 (2 H, d, Ar) and 8.02 (2 H, d, Ar).

Methyl 3,4-O-*Isopropylidene*-2-O-(3,5-*dinitrobenzoyl*)-L-*erythronate* **15**.—A solution of diethyl azodicarboxylate (8.9 g, 51 mmol) in dry THF (45 cm^3) was added dropwise to a stirred solution of methyl 3,4-*O*-isopropylidene-L-threonate **12**[11] (9.5 g, 50 mmol), 3,5-dinitrobenzoic acid (10.8 g, 51 mmol) and triphenylphosphine (13.4 g, 51 mmol) in dry THF (125 cm^3) under an argon atmosphere. The temperature of the reaction mixture was kept below 10 °C during the addition. Then the reaction mixture was stirred for a further 10 h at room temp. Afterwards the solvent was evaporated off under reduced

pressure and the residue was crystallized twice from methanol–water (9:1) and once from light petroleum (b.p. 60–85 °C) to give pure **15** as white needles. Yield 13.3 g (69%); m.p. 109 °C; $[\alpha]_D$ −18.2 (*c* 3.02, $CHCl_3$) (Found: C, 46.8; H, 4.2; N, 7.4. $C_{15}H_{16}N_2O_{10}$ requires C, 46.88; H, 4.20; N, 7.29%); δ_H(200 MHz; $CDCl_3$) 1.37 (3 H, s, CH_3), 1.40 (3 H, s, CH_3), 3.81 (3 H, s, CH_3O), 4.16 (1 H, d, CH_2O), 4.17 (1 H, d, CH_2O), 4.60–4.68 (1 H, m, CHO), 5.42 (1 H, d, $CHCO_2$), 9.19 (2 H, s, Ar) and 9.24 (1 H, s, Ar).

1,2-O-*Isopropylidene*-3-O-(*tetrahydropyran-2-yl*)-L-*erythritol* **16**.—A solution of **15** (11.3 g, 30 mmol) in THF (30 cm^3) was added to a solution of potassium hydroxide (3.7 g, 65 mmol) in water (30 cm^3). This mixture was stirred for 12 h at 25 °C. Then sodium hydrogen carbonate (22.5 g, 0.27 mol) was added followed by dimethyl sulfate (33.2 g, 0.26 mol). Stirring was continued for 2 h at 40 °C. After the solution had been filtered, the residue was washed with THF (30 cm^3). The solutions were combined and the THF was distilled off at reduced pressure while keeping the temperature below 40 °C. The residue was extracted with chloroform (5 × 50 cm^3). The combined extracts were dried over sodium sulfate and the solvent was evaporated off under reduced pressure. The crude product was purified by vacuum distillation leaving methyl 3,4-*O*-isopropylidene-L-erythronate as a colourless oil. Yield 3.75 g (66%); b.p. 78–83 °C/0.01 Torr. This product was used in the next step without further purification. As described for the synthesis of **13** methyl 3,4-*O*-isopropylidene-L-erythronate (3.61 g, 19.0 mmol) was tetrahydropyranylated to give methyl 3,4-*O*-isopropylidene-2-*O*-(tetrahydropyran-2-yl)-L-erythronate. Yield 4.74 g (91%). This compound (4.66 g, 17.0 mmol) was reduced [12] with lithium aluminium hydride to give **16** as a colourless, viscous oil. Yield 3.56 g (85%); b.p. 143 °C/0.10 Torr; $[\alpha]_D$ −9.2 (*c* 9.6, EtOH) (Found: C, 58.4; H, 9.0. $C_{12}H_{22}O_5$ requires C, 58.52; H, 9.00%); ν_{max}(film)/cm^{-1} 3420 (OH), 2920 (CH), 1450 and 1375; δ_H(200 MHz; $CDCl_3$) 1.24, 1.30, 1.32 [6 H, 3 s, $C(CH_3)_2$], 1.35–1.87 (6 H, m, $[CH_2]_3$, THP), 2.76 (0.4 H, br, OH), 3.31–3.97 [7.6 H, m, OH, CH_2OH, CH_2O THP, OC*H*CH_2OH, $CH_2OC(CH_3)_2$], 4.08 [0.6 H, m, *H*$COC(CH_3)_2$], 4.28 [0.4 H, m, *H*$COC(CH_3)_2$], 4.49 (0.4 H, m, OC*H*O THP) and 4.69 (0.6 H, m, OC*H*O THP).

4-O-(4′-*Hexylbiphenyl-4-yl*)-L-*erythritol* **4b**.—Prepared as described for **3b** from **16** (0.74 g, 3.0 mmol) and 4-hexyl-4′-hydroxybiphenyl **10b** (0.51 g, 2.0 mmol). Yield 0.45 g (63%); transitions (°C) cr 146 S_X 153 S_A 229 is (Found: C, 73.6; H, 8.5. $C_{22}H_{30}O_4$ requires C, 73.71; H, 8.44%); ν_{max}(KBr)/cm^{-1} 3320 (br, OH), 2900 (C–H), 1590, 1480 and 1440; δ_H(200 MHz; [$^2H_6$]DMSO) 0.84 (3 H, t, CH_3), 1.27 (6 H, m, CH_2), 1.56 (2 H, m, CH_2), 2.56 (2 H, t, CH_2-Ar), 3.35–3.80 (4 H, m, CH_2OH, C*H*OH), 3.96 (1 H, dd, CH_2O-Ar), 4.18 (1 H, dd, CH_2O-Ar), 4.44 (1 H, t, br, CH_2OH), 4.71 (1 H, d, br, CHO*H*), 4.96 (1 H, d, CHO*H*), 6.99 (2 H, d, Ar), 7.20 (2 H, d, Ar), 7.40 (2 H, d, Ar) and 7.53 (2 H, d, Ar).

Ethyl 4-[4-(5-*Pentadecyl*-1,3,4-*thiadiazol*-2-*yl*)*phenoxy*]*butanoate* **7c**.—2-(4-Hydroxyphenyl)-5-pentadecyl-1,3,4-thiadiazole **10c** (3.5 g, 9.0 mmol) were dissolved in dry acetone (50 cm^3). Potassium carbonate (12.4 g, 90 mmol) and potassium iodide (0.5 g, 3.0 mmol) were added to the solution, followed by addition of ethyl 4-bromobutanoate (3.51 g, 18 mmol). The mixture was then stirred under reflux for 16 h. After cooling to room temp. ethyl acetate (100 cm^3) was added and the suspension was filtered. The solid residue was washed once with dichloromethane (50 cm^3), the solutions were combined and the solvent was distilled off using a rotary evaporator. An oily residue was obtained, which was dissolved in ethyl acetate (100 cm^3). The solution was washed with two 20 cm^3 portions of dilute hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate and brine, successively, and then dried (sodium sulfate). Evaporation of the solvent gave a solid residue, which was recrystallized several times from ethanol to give pure **7c**. Yield 3.5 g (77%); m.p. 78 °C (Found: C, 69.15; H, 9.3; N, 5.5; S, 6.4. $C_{29}H_{46}N_2O_3S$ requires C, 69.28; H, 9.22; N, 5.57; S, 6.38%); δ_H(200 MHz; $CDCl_3$) 0.85 (3 H, t, CH_3), 1.20–1.43 (27 H, m, CH_2, CH_3CH_2O), 1.76 (2 H, m, CH_2), 2.11 (2 H, m, $CH_2CH_2CO_2$), 2.50 (2 H, t, CH_2CO_2), 3.08 (2 H, t, CH_2-thiadiazole), 4.04 (2 H, t, CH_2O), 4.13 (2 H, q, CH_3CH_2O), 6.92 (2 H, d, Ar) and 7.83 (2 H, d, Ar).

4-[4-(5-*Pentadecyl*-1,3,4-*thiadiazol*-2-*yl*)*phenoxy*]*butanoic Acid* **6c**.—Compound **6c** was prepared by saponification of **7c** (3.0 g, 6 mmol) according to the procedure given for **2c**. Yield 2.1 g (74%), m.p. 127 °C (Found: C, 68.2; H, 8.85; N, 5.8; S, 6.85. $C_{27}H_{42}N_2O_3S$ requires C, 68.32; H, 8.92; N, 5.90; S, 6.75%); δ_H(200 MHz; [$^2H_6$]DMSO) 0.84 (3 H, t, CH_3), 1.15–1.35 (22 H, m, $[CH_2]_{11}$), 1.70–2.07 (4 H, m, CH_2), 2.55 (2 H, t, CH_2CO_2), 2.55 (2 H, t, CH_2CO_2), 3.08 (2 H, t, CH_2-thiadiazole), 4.08 (2 H, t, $CH_2OC_6H_4$), 7.07 (2 H, d, Ar) and 7.85 (2 H, d, Ar).

3-[4-(5-*Pentadecyl*-1,3,4-*thiadiazol*-2-*yl*)*phenoxy*]*propanol* **5c**.—Compound **5c** was prepared by etherification of 2-(4-hydroxyphenyl)-5-pentadecyl-1,3,4-thiadiazole **10c** (3.5 g, 9.0 mmol) with 3-bromopropanol (2.5 g, 18 mmol) according to the procedure given for **7c**. Yield 3.0 g (75%), m.p. 94 °C (Found: C, 69.6; H, 9.4; N, 6.0; S, 7.0. $C_{26}H_{42}N_2O_2S$ requires C, 69.91; H, 9.48; N, 6.28; S, 7.16%); δ_H(200 MHz; $CDCl_3$) 0.85 (3 H, t, CH_3), 1.15–1.37 (23 H, m, OH, $[CH_2]_{11}$), 1.70–1.83 (4 H, m, $[CH_2]_2$), 2.06 (2 H, m, CH_2), 3.08 (2 H, t, CH_2-thiadiazole), 3.86 (2 H, t, CH_2OH), 4.16 (2 H, t, $CH_2OC_6H_4$), 6.95 (2 H, d, Ar) and 7.83 (2 H, d, Ar).

4-*Decylphenoxyacetic Acid* **19**.—Compound **19** was prepared by etherification of 4-decylphenol (**10a**) (2.1 g, 9.0 mmol) with ethyl bromoacetate (3.0 g, 18.0 mmol) according to the procedure given for **7c** followed by saponification of the ethyl decylphenoxyacetate according to the procedure given for **2c**. Yield 1.9 g (73%), m.p. 97 °C (Found: C, 74.0; H, 9.9. $C_{18}H_{28}O_3$ requires C, 73.92; H, 9.66%); δ_H(200 MHz; $CDCl_3$) 0.87 (3 H, t, CH_3), 1.25 (14 H, m, $[CH_2]_7$), 1.56 (2 H, m, CH_2CH_2-Ar), 2.53 (2 H, t, CH_2-Ar), 4.64 (2 H, s, CH_2O-Ar), 6.82 (2 H, d, Ar), 7.09 (2 H, d, Ar) and 9.86 (1 H, s, CO_2H); *m*/*z* 292 (M^+, 28%), 165 (100) and 107 (25).

4-(4-*Decylphenoxy*)*butyric Acid* **6a**.—Compound **7a** was prepared by etherification of 4-decylphenol (**10a**) (2.1 g, 9.0 mmol) with ethyl 4-bromobutyrate (3.5 g, 18.0 mmol) according to the procedure given for **7c**. The crude product was saponified as described for **2c** to give **6a** as a white solid. Yield 1.3 g (45%), m.p. 65 °C (Found: C, 75.0; H, 10.0. $C_{20}H_{32}O_3$ requires C, 74.94; H, 10.07%); δ_H($CDCl_3$) 0.87 (3 H, t, CH_3), 1.25 (14 H, m, $[CH_2]_7$), 1.56 (2 H, m, CH_2), 2.09 (2 H, m, CH_2), 2.48–2.61 (4 H, m, CH_2-Ar, CH_2CO_2), 3.98 (2 H, t, CH_2O-Ar), 6.79 (2 H, d, Ar), 7.07 (2 H, d, Ar) and 10.24 (1 H, br, CO_2H); *m*/*z* 320 (M^+, 11%), 234 (33) and 107 (100).

5-(4-*Decylphenoxy*)*pentanoic Acid* **20**.—Compound **20** was prepared by etherification of 4-decylphenol (**10a**) (2.1 g, 9.0 mmol) with ethyl 5-bromopentanoate (3.8 g, 18.0 mmol) as described for **7c** followed by saponification of ethyl 5-(4-decylphenoxy)pentanoate according to the procedure given for **2c**. Yield 1.9 g (65%), m.p. 63 °C (Found: C, 75.6; H, 10.05. $C_{21}H_{34}O_3$ requires C, 75.39; H, 10.25%); δ_H(200 MHz; $CDCl_3$) 0.86 (3 H, t, CH_3), 1.24 (14 H, m, $[CH_2]_7$), 1.55 (2 H, m, CH_2), 1.82 (4 H, m, $[CH_2]_2$), 2.40–2.55 (4 H, m, CH_2-Ar, CH_2CO_2),

3.93 (2 H, t, CH_2O-Ar), 6.78 (2 H, d, Ar) and 7.06 (2 H, d, Ar).

3-(4-*Nonyloxyphenyl*)*propionic Acid* **18**.—Compound **18** was obtained by saponification of 3-(4-nonyloxyphenyl)propionitrile. The latter was prepared by Mitsunobu etherification of 3-(4-hydroxyphenyl)propionitrile[14] (1.5 g, 10.0 mmol) with nonanol (2.2 g, 15.0 mmol) according to the procedure given for **11c**. Yield 2.4 g (88%), m.p. 40 °C (Found: C, 79.1; H, 9.7; N, 5.05. $C_{18}H_{27}NO$ requires C, 79.06; H, 9.96; N, 5.13%); δ_H(200 MHz; $CDCl_3$) 0.87 (3 H, t, CH_3), 1.27 (14 H, m, $[CH_2]_7$), 1.76 (2 H, m, CH_2CH_2O-Ar), 2.56 (2 H, t, CH_2-Ar), 2.87 (2 H, t, CH_2CN), 3.91 (2 H, t, CH_2O-Ar), 6.84 (2 H, d, Ar) and 7.12 (2 H, d, Ar); *m/z* 273 (M^+, 24%), 147 (45) and 107 (100).

3-(4-Nonyloxyphenyl)propionitrile (0.5 g, 1.8 mmol) was suspended in a solution of potassium hydroxide (10.1 g, 0.18 mol) in water (30 cm^3). After the addition of ethanol (15 cm^3) the mixture was stirred at reflux temp. for 8 h. Evaporation of the solvent gave an off-white residue which was dissolved in water and afterwards acidified by careful addition of concentrated hydrochloric acid. The precipitate was filtered off, washed with water (2 × 20 cm^3) and recrystallized from methanol–water to give pure **18** as a white crystalline material. Yield 0.3 g (57%), m.p. 77 °C (Found: C, 74.0; H, 9.64. $C_{18}H_{28}O_3$ requires C, 73.92; H, 9.66%); δ_H(200 MHz; $CDCl_3$) 0.87 (3 H, t, CH_3), 1.26 (14 H, m, $[CH_2]_7$), 1.75 (2 H, m, CH_2CH_2O-Ar), 2.63 (2 H, t, CH_2-Ar), 2.88 (2 H, t, CH_2CO_2), 3.90 (2 H, t, CH_2O-Ar), 6.80 (2 H, d, Ar) and 7.09 (2 H, d, Ar); *m/z* 292 (M^+, 20%), 166 (62) and 107 (100).

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