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Formation of columnar hexagonal mesophases near room temperature from functionalised [9]aneNS$_2$ (1,4-dithia-7-azacyclononane)

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Oligo(benzoate) derivatives, (R)[9]aneNS$_2$, of 1,4-dithia-7-azacyclononane [R = OC-C$_6$H$_4$-4-OR′ (**1**) [R′ = C$_3$H$_7$ (**a**) C$_8$H$_{17}$ (**b**)], OC-C$_6$H$_4$-4-O$_2$C-C$_6$H$_4$-4-OC$_8$H$_{17}$ (**2**), OC-C$_6$H$_4$-4-O$_2$C-C$_6$H$_4$-4-O$_2$C-Z, Z = C$_6$H$_4$-4-OC$_8$H$_{17}$ (**3**), C$_6$H$_3$-3,4-(OR′$_2$)$_2$ (**4**) [R′ = C$_4$H$_9$ (**a**), C$_8$H$_{17}$ (**b**), C$_{12}$H$_{25}$ (**c**)], C$_6$H$_2$-3,4,5-(OC$_{12}$H$_{25}$)$_3$ (**5**)] have been synthesised. Compound **3** displays monotropic nematic and smectic phases, while **5** shows an enantiotropic columnar hexagonal phase (Col$_h$) just above room temperature as characterised by X-ray scattering experiments. Dilatometry suggests a model for the packing of molecules of **5** in the mesophase. An alternative route to these compounds has been developed *via* the preparation of the protected species **6** [R = OC-C$_6$H$_4$-4-OC(O)OMe], which can be deprotected using aqueous NH$_3$ to give **7** [R = OC-C$_6$H$_4$-4-OH], followed by reaction with the appropriate acid chloride or anhydride. Oligo(benzoate) derivatives, (R)$_2$[9]aneN$_2$S, of 1-thia-4,7-diazacyclononane [R = OC-C$_6$H$_4$-4-OC(O)OMe (**8**), OC-C$_6$H$_4$-4-OH (**9**) OC-C$_6$H$_4$-4-O$_2$C-C$_6$H$_4$-4-OC$_8$H$_{17}$ (**10**), OC-C$_6$H$_4$-4-O$_2$C-C$_6$H$_2$-3,4,5-(OC$_{12}$H$_{25}$)$_3$ (**11**)] have been prepared as transesterification products.

Introduction

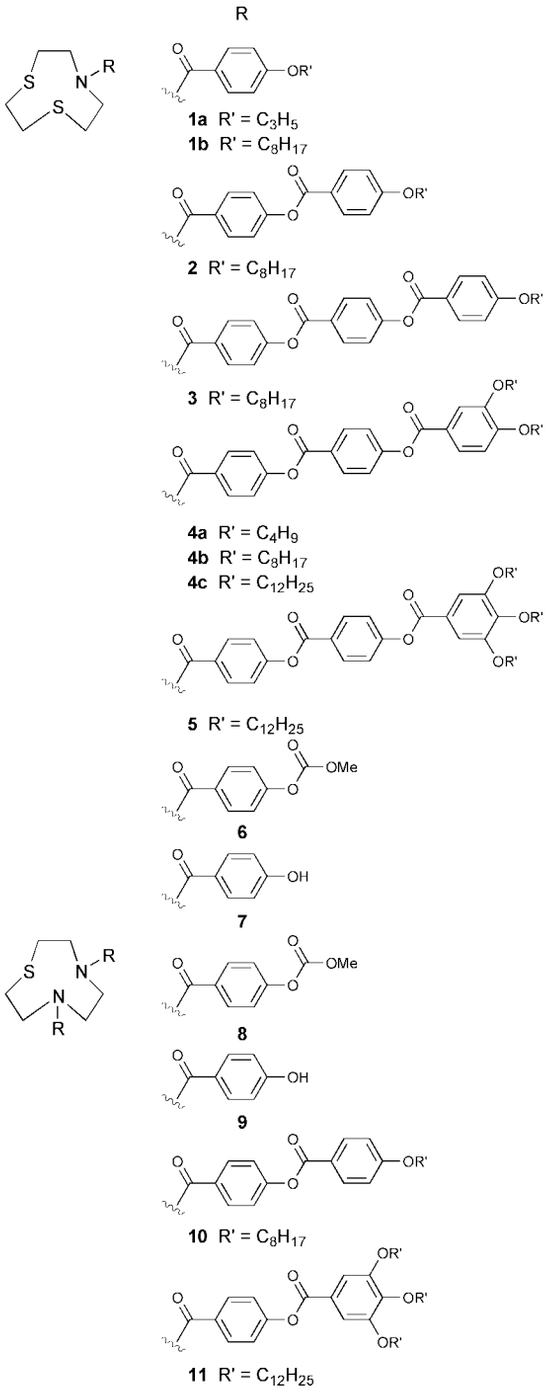
The incorporation of macrocyclic ligands into liquid crystal arrays is of increasing interest. Most of this work has focused on phthalocyanines[1] and porphyrins[2] which generally form columnar phases, although more recently low-temperature nematic phases have been observed.[3] The symmetric di-functionalisation of polyaza macrocycles to give a range of columnar mesophases has also been reported,[4,5] the formation of columnar phases reflecting the shape and symmetric topology of these systems. In contrast, lower symmetry mono-functionalised crown systems are very rare, Shinkai and co-workers having reported novel functionalised oxy-crowns.[6] We were, therefore, interested in probing the variation in mesophase behaviour of macrocycles incorporating only one mesogenic side group. As part of our studies on thioether crown liquid crystals,[7] we now report the synthesis and characterisation of oligo(benzoate)derivatives of monofunctionalised [9]aneNS$_2$ and the study of their liquid-crystalline properties using polarising optical microscopy, differential scanning calorimetry (DSC), X-ray scattering and dilatometry. The synthesis of related derivatives of [9]aneN$_2$S is also reported.

Results and discussion

Synthesis

Reaction of [9]aneNS$_2$ (1,4-dithia-7-azacyclononane)[8] with 1.5 molar equivalents of the appropriate acid chloride or acid anhydride for 12 h at room temperature in freshly distilled CH_2Cl_2 in the presence of pyridine affords the compounds **1**–**5** in good yields after column chromatography on silica. For example, **3** was prepared by treatment of [9]aneNS$_2$ with 4″-[4′-(4-octyloxybenzoyloxy)benzoyloxy]benzoic acid anhydride and pyridine in a 2 : 3 : 3 molar ratio in freshly distilled CH_2Cl_2 for 16 h at room temperature. The solvent was removed *in vacuo* and the crude product purified by column chromatography to afford **3** as a colourless solid which was crystallised from toluene–*n*-hexane. The infra-red spectrum of **3** exhibits two bands at 1733 and 1630 cm^{-1} corresponding to the carbonyl stretching modes of an ester and an amide group, respectively. The ES mass spectrum of the product shows an ion peak at *m*/*z* = 636 consistent with **3**.

The ^{1}H NMR spectrum of **3** provides further information about the macrocyclic moiety. Each of the methylene groups of the ring is inequivalent and gives rise to a fairly broad multiplet due to the low symmetry of the molecule imposed by the amide group. Analysis of the {H,H}-COSY ^{1}H NMR spectrum allows the assignment of each methylene group to individual multiplets. The macrocyclic methylene group closest in space to the amide carbonyl O-centre is shifted towards higher frequency and appears at 3.98 ppm. This resonance couples to the adjacent macrocyclic methylene group which appears at 3.18 ppm. A second pair of NCH_2CH_2 protons can be assigned to the signals at 3.71 and 3.43 ppm, while resonances at 3.06 and 2.95 ppm are due to the protons of the methylene groups situated between sulfur atoms. Furthermore, three pairs of aromatic resonances due to three different AA′XX′ spin systems are assigned to individual aromatic resonances, in accord with the cross couplings observed in the {H,H}-COSY ^{1}H NMR spectrum of **3** and the $^3J(H_A,H_X)$ coupling constants. Thus, the phenyl ring adjacent to the amide group gives rise to AA′XX′ multiplets at 7.63 and 7.31 ppm with $^3J(H_A,H_X) = 8.45$ Hz. Similar resonances at 8.29 and 7.39 ppm with $^3J(H_A,H_X) = 8.63$ Hz are assigned to the aromatic protons of the next aromatic ring along, while the resonances at 8.17 and 7.01 ppm with $^3J(H_A,H_X) = 8.80$ Hz are



attributed to the protons of the outer phenyl ring. The $^{13}C\{^1H\}$ NMR spectrum of **3** reveals six signals corresponding to the methylene carbon atoms of the macrocyclic ring.

Tuffin and co-workers have reported[5c] the esterification of phenol derivatives of azacrown ethers with benzoic acids using *N*,*N*′-dicyclohexylcarbodiimide in the presence of a catalytic amount of 4-pyrrolidinopyridine. An alternative approach to *N*-functionalised [9]aneNS$_2$ derivatives such as **3** is by reaction of [9]aneNS$_2$ with 4-methoxycarbonyloxybenzoic acid chloride and Et$_3$N in a 2 : 3 : 3 molar ratio in freshly distilled CH_2Cl_2 which gives **6** as a colourless solid after column chromatography. The ^{1}H NMR spectrum of **6** shows six distinct macrocyclic methylene resonances due to the inequivalence of all six methylene groups. The singlet at 3.93 ppm corresponds to the methyl protons of the methoxycarbonyloxy protecting group. Deprotection of **6** was carried out using NH$_3$(aq) to give **7** as a colourless solid which was crystallised from EtOH. The infra-red spectrum of **7** reveals a band at 3165 cm^{-1} indicative of the stretching vibration of the phenolic hydroxy group, while the EI mass spectrum of **7** shows a molecular ion peak at *m*/*z* = 283 as expected. The ^{1}H NMR spectrum of **7** confirms the absence of the methyl resonance at 3.93 ppm observed in the ^{1}H NMR spectrum of **6**. Recrystallisation of **7** from EtOH at −15 °C afforded colourless, diamond-shaped crystals suitable for single crystal X-ray diffraction studies. The structure of **7** shows two independent molecules in the asymmetric unit which are very similar and are related by an approximate, non-crystallographic inversion centre: one of these is shown in Fig. 1. Each molecule in the asymmetric unit is linked to two symmetry equivalents of itself by two C=O···H–O hydrogen-bonds, giving two independent chains of molecules running along the *c* direction (see Table 1). Seven out of nine torsion angles of the macrocyclic ring are less than 90° reflecting a very distorted conformation (Table 1). This contrasts with the regular [333] conformation found for [9]aneS$_3$.[9a] The mean planes containing the amide functions, C1P—C10—O10—N7 and C1PA—C10A—O10A—N7A are tilted with respect to their adjacent phenyl group by 111.2 and 119.8°, respectively.

Compound **7** is a useful precursor for further functionalisation. Thus, reaction of **7** with HOOC-C$_6$H$_4$-4-O$_2$C-C$_6$H$_2$-3,4,5-(OC$_{12}$H$_{25}$)$_3$ in the presence of *N*,*N*′-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine in CH_2Cl_2 affords **5** in high yield after column chromatography on silica followed by crystallisation. Likewise, reaction of **7** with 3,4-disubstituted and 3,4,5-trisubstituted alkoxybenzoyloxybenzoic acids using *N*,*N*′-dicyclohexylcarbodiimide and a catalytic amount of 4-pyrrolidinopyridine leads to the formation of **3**, **4a**–**c** and **5**. As before, the introduction of the amide group into the macrocycle causes the inequivalence of the macrocyclic methylene groups for all these compounds.

Few *N*-functionalised derivatives of [9]aneN$_2$S have been reported in the literature.[9b] Reaction of [9]aneN$_2$S with 4-methoxycarbonyloxybenzoic acid chloride affords **8**, the ^{1}H NMR spectrum of which reveals three resonances at 3.93, 3.80 and 2.88 ppm corresponding to the protons of three distinct sets of macrocyclic methylene groups with an integration ratio of 4 : 4 : 4. The resonance at 3.93 ppm is partially obscured by the singlet due to the methyl protons of the 4-methoxycarbonyloxy protecting group. The $^{13}C\{^1H\}$ NMR spectrum of **8** shows the expected ten signals. Deprotection of **8** using NH$_3$(aq) affords **9** as a colourless crystalline solid which was crystallised from EtOH. The infra-red spectrum of **9** reveals a new band at 3278 cm^{-1} due to the O–H stretching vibration of the phenolic group, and a resonance at 1610 cm^{-1} corresponding to an amide carbonyl stretching vibration. The EI mass spectrum of **9** shows the expected molecular ion peak at *m*/*z* = 386, and elemental analytical data are consistent with **9**. Unfortunately, no NMR data could be obtained due to the insolubility of the compound in all common organic solvents.

The reaction of **9** with 4′-(4-octyloxybenzoyloxy)benzoic acid using *N*,*N*′-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine as a catalyst was carried out according to the method for the synthesis of **4**. The infra-red spectrum of the colourless product obtained shows two bands at 1733 and 1648 cm^{-1}

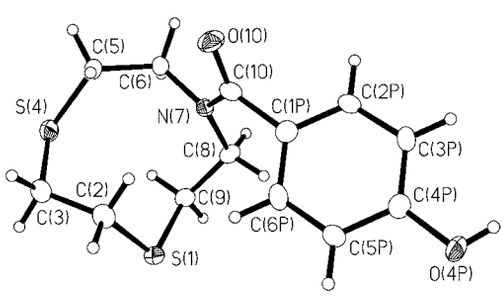


Fig. 1 The structure of **7** showing atom numbering scheme for one of the two independent molecules in the asymmetric unit. Displacement ellipsoids represent the 50% electron probability level.

Table 1 Macrocyclic ring torsion angles and hydrogen-bonding parameters for **7**

Torsion angles/° for **7**

Molecule 1		Molecule 2	
S1–C2–C3–S4	−67.5(7)	S1A–C2A–C3A–S4A	69.2(8)
C2–C3–S4–C5	−54.8(6)	C2A–C3A–S4A–C5A	53.6(7)
C3–S4–C5–C6	101.9(6)	C3A–S4A–C5A–C6A	−104.1(6)
S4–C5–C6–N7	−79.0(8)	S4A–C5A–C6A–NA7	83.2(8)
C5–C6–N7–C8	112.8(7)	C5A–C6A–N7A–C8A	−114.9(8)
C6–N7–C8–C9	−66.4(8)	C6A–N7A–C8A–C9A	66.9(8)
N7–C8–C9–S1	−69.9(8)	N7A–C8A–C9A–S1A	69.3(8)
C8–C9–S1–C2	67.6(7)	C8A–C9A–S1A–C2A	−69.5(6)
C9–S1–C2–C3	74.1(7)	C9A–S1A–C2A–C3A	−72.0(7)

Hydrogen-bonding parameters (Å,°) for **7**

D	H	A	H···A/Å	D···A/Å	D–H···A/°	Symmetry operation for A
O(4P)	H(4P)	O(10)	1.89	2.708(7)	166	$5/2-x, 2-y, 1/2+z$
O(4PA)	H(4PA)	O(10A)	1.81	2.650(7)	176	$1/2-x, 1-y, -1/2+z$

corresponding to the carbonyl stretching vibrations of an ester and amide group, respectively. However, the ^{1}H NMR spectrum of the reaction product only shows two AA′XX′ spin systems. This is not consistent with the desired reaction product, which should reveal three different AA′XX′ spin systems as a result of three aromatic units in the benzoate tail group. Instead, the ^{1}H NMR spectrum of the pure reaction product indicates the formation of the transesterification product, **10**. The presence of only two aromatic units in **10** was confirmed by the ^{13}C{^{1}H} NMR spectrum which shows only four tertiary carbon resonances at 132.38, 128.32, 122.11 and 114.47 ppm. Three resonances at 57.57, 49.81 and 31.83 ppm corresponding to the macrocyclic carbon atoms are observed.

The formation of **10** can be rationalised by nucleophilic attack of the *N*,*N*′-dicyclohexylcarbodiimide or 4-pyrrolidinopyridine on the ester carbonyl linkage of 4′-(4-octyloxybenzoyloxy)benzoic acid. Alternatively, attack of a phenolate centre on the ester carbonyl linkage of 4′-(4-octyloxybenzoyloxy)benzoic acid or once the latter is attached to [9]aneNS$_2$ is also possible. No transesterification products are apparent from the reactions of **7**, which only bears one hydroxy group, to give **4a**–**c** and **5**. We therefore suggest that inter- or intramolecular nucleophilic attack of a phenolate in **9** takes place at the pendant ester groups formed as the reaction proceeds to give a range of transesterification products.

As for the synthesis of **10**, reaction of **9** with 4′-[3,4,5-tris(dodecyloxybenzoyloxy)]benzoic acid affords **11** *via* transesterification reactions as confirmed by infra-red and NMR spectroscopy and mass spectrometry.

Mesomorphism

All the compounds were studied using optical microscopy and DSC. The mono-substituted derivative **1b**, based on a single 4-octyloxybenzoate group, simply melts at 68 °C to give an isotropic phase and, likewise, the analogous material **2** with a 4′-(4-octyloxybenzoyloxy)benzoate group also melts directly to the isotropic phase at 108 °C. Clearly then, with such a large terminal group as [9]aneNS$_2$, a more anisotropically functionalised system was required to achieve mesomorphic behaviour. Thus, a macrocycle functionalised with three phenyl rings, **3**, was synthesised.

On first heating **3**, one melting event is observed at 117 °C in which part of the sample becomes isotropic, with the rest remaining crystalline until 127 °C when it too melts. These events are observed by DSC as a rather broad transition with a combined enthalpy of 28.3 kJ mol^{-1} and suggests the presence of two crystal polymorphs. Then, on cooling, a monotropic nematic phase is observed at 113.5 °C which persists to below 100 °C, after which crystallisation is observed. Depending upon the cooling conditions, a monotropic S_A phase can be seen just ahead of crystallisation, with the S_A–N transition temperature at 96 °C. On re-heating the now crystalline solid, only a single melting event is seen at 118 °C ($\Delta H = 23.7$ kJ mol^{-1}), giving way to the isotropic phase. We believe that following cooling from the melt, only one crystal polymorph forms, and that this is the lower-melting of the two formed from solution. A remarkable aspect of **3** is its rather low transition temperatures for such an extended structure. This confirms that the [9]aneNS$_2$ ring can act as a terminal group to an anisotropic system to generate relatively low-melting materials, although

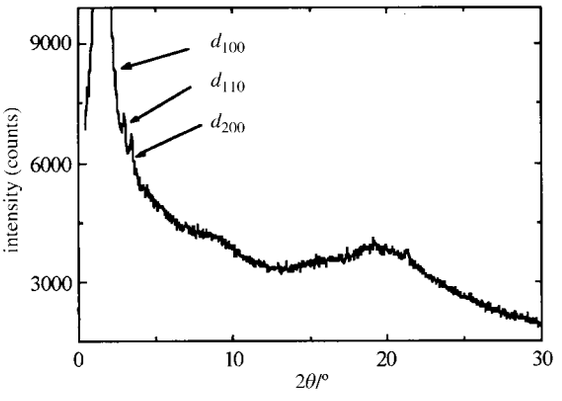


Fig. 2 X-Ray diffraction pattern of **5** measured at 40 °C in the columnar mesophase.

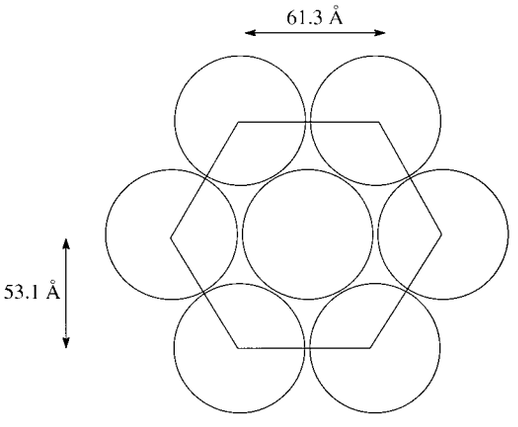


Fig. 3 Schematic of hexagonal columnar mesophase of **5**.

there is an interesting comparison with $C_8H_{17}O$-C_6H_4-4-CO_2-C_6H_4-4-CO_2-C_6H_4-4-$CONBu_2$,[10] which melts at 111 °C (Crys→I) and shows a monotropic nematic phase at 102 °C (I→N).[11] However, replacement of the terminal $CONBu_2$ group with, for example, a cyano function, raises the mesophase stability considerably (Crys•123•N•233•I).[12]

The related dioctyloxyoxy derivative, **4b**, melts at 90 °C and shows what appears to be a weakly birefringent texture by optical microscopy, although X-ray diffraction failed to confirm the presence of a mesophase. On cooling, the material did not crystallise, rather forming a glassy state. Compounds **4a** and **4c** were similarly non-mesomorphic, melting at 68 and 82 °C, respectively.

However, the tri-substituted derivative **5** was observed to melt at 37 °C to give a weakly birefringent phase which appeared columnar, and cleared at 48 °C. X-Ray scattering experiments were carried out to identify the mesophase unequivocally. The pattern recorded (Fig. 2) is typical of a disordered hexagonal columnar mesophase with three Bragg diffraction peaks in the low angle region in the squared ratio 1 : 3 : 4 and with a diffuse signal in the wide angle region at *ca.* 4.5 Å due to the liquid-like state of the terminal aliphatic chains. The two-dimensional hexagonal parameter (d_{10}) was evaluated as 53.1 Å corresponding to a distance of 61.3 Å between neighbouring columns (Fig. 3).

The current compound **5** may be compared with more conventional polycatenar molecules with aliphatic chains at both ends of a long rigid core, which also generally exhibit columnar mesophases. In polycatenar systems,[13] the cross-section of the columnar core is regarded as being constituted by a certain number of rigid cores (this number depends upon the number of aliphatic chains and upon the rigid core length of each individual molecule) all surrounded by molten aliphatic end chains.[5a] In the present case, the macrocyclic molecule is of lower symmetry with three aliphatic chains at only one end of the long rigid core, and so such a packing arrangement is not so readily achievable. There is then an interesting comparison with DOBOB-based [DOBOB = 3,4,5-tris(dodecyloxy)benzyloxybenzoyl] materials described by Percec and co-workers which are observed to form columnar hexagonal phases on complexation with Li^+ or Na^+.[14] Finally, to our knowledge this is a rare example of a hemiphasmidic material. One other example of which we are aware is that of a Mo(VI) complex reported by Serrette and Swager,[15] in which columnar organisation is suggested to result from intermolecular Mo···O interactions.

For **5**, the X-ray diffraction patterns registered between room temperature and 37 °C are typical of well ordered, three-dimensional crystalline structures with a large number of sharp diffraction peaks in the low- and wide-angle regions. Above 37 °C, the patterns are typical of a columnar mesophase until isotropisation. The observed column diameter for **5** from X-ray analysis is 61.3 Å, significantly greater than the molecular length of **5** with chains extended, which is calculated as 38 Å by molecular modelling. Therefore, in order to understand the arrangement in the mesophase in more detail, dilatometry[5a,15–17] experiments were carried out. In these experiments, the absolute molar volume is established, as is the variation in this volume as a function of temperature. Such experiments are of great value in the study of columnar mesophases, particularly those derived from polycatenar mesogens, and have been used to great effect.[5a,17]

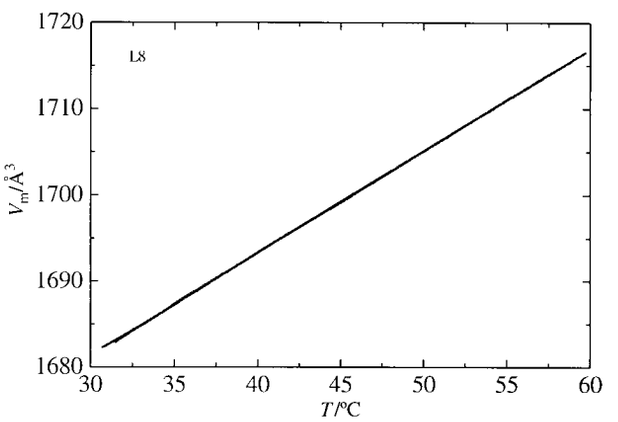


Fig. 4 Plot of molar volume, V_m, as a function of temperature for **5**, including data from both heating and cooling runs.

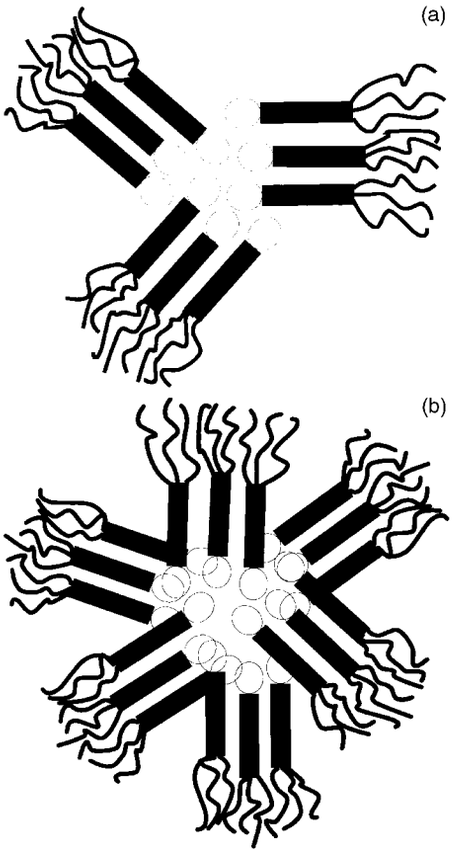


Fig. 5 (a) Schematic of packing of one layer in **5** showing nine molecules per layer. (b) Schematic of packing of two layers in **5** showing relation between 18 molecules.

Thus, it was found that the molecular volume increased linearly as a function of temperature within the whole stability domain of the columnar mesophase (Fig. 4). The value of the dilatation coefficient, $\alpha = (1/V)(dV/dT) = 7 \times 10^{-4}\ K^{-1}$ agrees quite well with earlier values found for other columnar systems,[18] and also reasonably well with those measured for smectic mesophases.[19] It is important to note the perfect reversibilty of the data obtained on increasing and decreasing the temperature, and it is also worth pointing out that the transition between the columnar mesophase and the isotropic phase occurs without an apparent step change in the volume, and without even a change in the thermal expansion coefficient (*i.e.* the slope of $V_m = f(T)$ is the same in both phases), in contrast to that observed with most liquid crystals. This would tend to suggest some sort of continuous transition between the columnar mesophase and the isotropic phase.

As stated above, from X-ray diffraction at 40 °C, d_{10} was found to be 53.1 Å, from which the intercolumnar distance, *a*, of 61.3 Å is obtained. Dilatometry gave a molar volume, $V_m = 1693$ Å^3 at the same temperature and it is known that the number of molecules, *n*, found in a columnar repeat can be

expressed by eqn. (1):

$$n = \frac{\sqrt{3}/2 \times a^2 \times h}{V_m} \quad (1)$$

where h = the columnar repeat (4.7 Å from the X-ray data). Evaluation of this function gives $n = 9$, suggesting a model for the packing motif illustrated in Fig. 5a, and, if it is assumed that two successive repeat units are superposed on one another in a staggered conformation (Fig. 5b), then it is also possible to explain the rather diffuse signal at 9–10 Å observed in the X-ray pattern (Fig. 2).

Optical microscopy of compounds **10** and **11** confirmed that these materials melted at 81 and 71 °C, respectively, forming glasses on cooling.

Conclusions

We have confirmed that increasing the number of peripheral aliphatic groups has a fundamental effect on mesophase behaviour, with a switch occurring on going from mono-functionalised species **3**, which show calamitic phases, to tri-functionalised species **5**, which show columnar phases. These results are consistent with the expected molecular topology of these materials.

Experimental

Optical microscopy was carried out using an Olympus BH-40 polarising microscope equipped with a Link-Am HFS91 hot stage, TMS92 controller, and LNP2 cooling unit. Differential scanning calorimetry was carried out using a Perkin Elmer DSC7 system running the thermal analysis software on a Unix platform; the system was calibrated to the enthalpy and temperature of melting of ultrapure indium metal. Samples were hermetically sealed in Al pans, and heating and cooling rates of 10 K min^{-1} were routinely employed. Dilatometric measurements were performed with a high-precision, home-built apparatus with automatic computer-controlled operation, including data acquisition and temperature control to within ±0.03 °C. Relative variations of the specific volume could be detected with a resolution of 0.1%, and its absolute value determined with an accuracy of 0.01%.

Powder X-ray diffraction patterns were recorded at 40 °C using a Guinier-type camera with bent quartz monochromator (CuKα radiation, $\lambda = 1.5406$ Å), an Instec hot-stage (±0.01 °C) and an Inel CP120 curved position-sensitive gas detector. Samples were housed in sealed Lindemann glass capillaries. Patterns were also recorded on film using a Philips PW1009 generator as the source.

Solvents were dried over sodium wire (THF) or P_2O_5 (toluene, CH_2Cl_2) under oxygen-free N_2 prior to use. Infra-red spectra were recorded on Perkin Elmer 598 or FT-1600 spectrometers. FAB and EI mass spectra were obtained on a MS 50TS (Kratos) or a VG Ortho-Spec spectrometer (Kratos) while ES mass spectra were obtained on a VG Quattro II (Fisons, VG Biotech). Elemental analyses were obtained from the Microanalytical Service at the School of Chemistry, University of Nottingham. ^{1}H and ^{13}C NMR spectra were acquired using Bruker AC250 and DPX300 spectrometers. Methyl chloroformate, 4-hydroxybenzoic acid, *N*,*N*′-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine were purchased from Aldrich and stored under anhydrous conditions. [9]aneNS$_2$ and [9]aneN$_2$S were synthesised following literature procedures.[8]

Synthesis of 4-methoxycarbonyloxybenzoic acid

Methyl chloroformate (6.89 g, 69.8 mmol) was added slowly to a stirred solution of 4-hydroxybenzoic acid (6.89 g, 49.9 mmol) dissolved in NaOH (0.5 mol dm^{-3}, 200 cm^3) at 0 °C resulting in the immediate formation of a colourless precipitate. The reaction mixture was stirred for 4 h at 0 °C and allowed to warm up to room temperature. The precipitate was filtered and crystallised from EtOH to afford a colourless, crystalline solid (yield 3.73 g, 40%). Found C% 55.24, H% 3.92; calculated for $C_9H_8O_5$ C% 55.11, H% 4.11. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.18$ (d, 2 H, CH_{ar}), 7.39 (d, 2 H, CH_{ar}), 3.96 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 161.29$, 155.90, 153.32, 126.49 (C_q), 132.33, 121.54 (CH), 55.68 (CH_3); IR(KBr): $\nu = 1769$, 1750, 1727 (C=O), 1263, 1219 (C–O) cm^{-1}; EI-MS (70 eV): *m*/*z*(%): 196 (8) [M]$^+$, 179 (100) [M−H$_2$O]$^+$, 135 (82) [M−H$_2$CO$_3$]$^+$.

Synthesis of 4-methoxycarbonyloxybenzoyl chloride

$SOCl_2$ (0.274 g, 2.306 mmol) was added to 4-methoxycarbonyloxybenzoic acid (0.302 g, 1.537 mmol) and the reaction mixture stirred for 10 h. Residual $SOCl_2$ was removed *in vacuo* and the remaining crude solid sublimed (60 °C, 10^{-1} Torr) to give a colourless solid (yield 0.214 g, 65%). Found C% 49.82, H% 3.25; calculated for $C_9H_7ClO_4$ C% 50.37, H% 3.29. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.20$ (d, 2 H, CH_{ar}), 7.38 (d, 2 H, CH_{ar}), 3.98 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 155.43$, 153.14, 130.91, 109.67 (C_q), 133.15, 121.49 (CH), 55.75 (CH_3); IR(KBr): $\nu = 1771$ (C=O), 1275, 1224, 1202 (C–O) cm^{-1}; EI-MS: *m*/*z*(%): 179 (100) [M−Cl]$^+$, 135 (79) [M−CO$_2$Cl]$^+$.

Synthesis of 1a

4-Propyloxybenzoic acid (0.50 g, 0.0028 mol) was dissolved in CH_2Cl_2 (10 cm^3) with oxalyl chloride (0.706 g, 0.0055 mol) and DMF (1 drop). The reaction was stirred under N_2 until evolution of gas had ceased, and the solvent removed *in vacuo*. A second portion of CH_2Cl_2 (10 cm^3) was added and then evaporated *in vacuo* in order to ensure that all of the excess oxalyl chloride had been removed. The 4-propyloxybenzoyl chloride was then redissolved in CH_2Cl_2 (10 cm^3) along with [9]aneNS$_2$ (0.150 g, 0.00092 mol) and pyridine (0.30 g, 0.0038 mol), and this mixture was stirred overnight under N_2. This solution was then diluted to 30 cm^3 and washed successively with 20 cm^3 solutions of HCl (1 mol dm^{-3}), $NaHCO_3$ (1 mol dm^{-3}) and water. After drying over $MgSO_4$ the solvent was removed *in vacuo*. Column chromataography on silica (1 : 25 acetone–CH_2Cl_2) afforded the pure product **1a** as a viscous oil (0.243 g, 81%). ^{1}H NMR (250.13 MHz, $CDCl_3$) $\delta = 0.99$ (3H, t, CH_3), 1.77 (2H, m, $CH_2CH_2CH_3$), 2.60, 2.88, 2.96, 3.08, 3.31, 3.66 (2H, br s, CH_2, ring), 3.90 (2H, t, OCH_2), 6.87 and 7.43 ppm (2H, m, AA′XX′, Ar*H*); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 10.28$ (CH_3), 22.26 (CH_2CH_3), 32.13, 32.23, 32.61, 37.48, 50.78, 52.95 (CH_2, ring), 69.31 (OCH_2), 113.99 (aromatic CH), 128.30 (aromatic quaternary), 128.72 (aromatic *C*H), 159.94 (aromatic quaternary) and 172.28 ppm (NCO); IR: $\nu_{CO} = 1629$ cm^{-1}; EI-MS: *m*/*z*(%): 325 (M$^+$).

Synthesis of 1b

4-Octyloxybenzoic acid was converted into its acid anhydride by reaction with bis(2-oxooxazolidin-3-yl)phosphinic chloride (BOP-Cl). A typical procedure involved reaction of 0.00275 mol of acid with 0.00275 mol of BOP-Cl and 0.00138 mol of Et_3N in a small volume (3–5 cm^3) of freshly distilled THF for 30 min. This solution was filtered (or centrifuged) and concentrated *in vacuo* to afford the crude anhydride, which could then be reacted with [9]aneNS$_2$ without further purification. [9]aneNS$_2$ (0.10 g, 0.00061 mol) was stirred overnight with the anhydride (0.442 g, 0.00092 mol) with pyridine (5 drops) in freshly distilled CH_2Cl_2 (10 cm^3). The solution was concentrated *in vacuo* and the residue was purified

by column chromatography on silica (1 : 10 acetone–CH_2Cl_2) to afford the product as a pale oil which crystallised upon standing for several days (0.190 g, 79%). Found C% 63.9, H% 8.03, N% 3.63%; calculated for $C_{21}H_{33}NO_2S_2$ C% 63.8, H% 8.36, N% 3.54. ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 0.86$ (3H, t, CH_3), 1.27 (8H, m, $CH_2CH_2CH_2CH_2CH_3$), 1.42 (2H, m, $OCH_2CH_2CH_2$), 1.76 (2H, tt, OCH_2CH_2), 2.89, 2.98, 3.09, 3.33, 3.68, 3.91 (2H, br s, CH_2 ring), 3.94 (2H, t, OCH_2), 6.87 and 7.44 ppm (2H, AA′XX′, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 13.94$ (CH_3), 22.47, 25.83, 28.97, 29.04, 29.15, 31.61, ($OCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 32.03, 32.13, 32.64, 37.54, 50.82, 53.00 (CH_2, ring), 67.90 (OCH_2), 114.04 (aromatic CH), 128.32 (aromatic quaternary), 128.77 (aromatic CH), 160.01 (aromatic quaternary) and 172.35 ppm (NCO); IR (KBr disc): $\nu_{CO} = 1631$ cm^{-1}; EI-MS: *m*/*z*(%): 395 (M^+), 233 [$C(O)C_6H_4OC_8H_{17}$].

Synthesis of 2

4′-(4-Octyloxybenzoyloxy)benzoic acid was converted to its acid chloride following the method described for the synthesis of **1a**. The acid chloride (0.272 g, 0.0007 mol) was reacted with [9]aneNS$_2$ (0.120 g, 0.00074 mol) and dimethylaminopyridine (DMAP) (0.098 g, 0.0008 mol) in CH_2Cl_2 (10 cm^3) overnight. The solution was then diluted to 30 cm^3, washed with hydrochloric acid (1 mol dm^{-3}) and water, then dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica (1 : 10 acetone–CH_2Cl_2) to afford the product as a white solid (0.190 g, 51%). The product could be further purified by recrystallisation from hot MeOH–water. Found: C% 65.2, H% 7.18, N% 2.72%, calculated for $C_{28}H_{37}NO_4S_2$ C% 65.9, H% 7.16, N% 2.68. ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 0.87$ (3H, t, CH_3), 1.30 (8H, m, $CH_2CH_2CH_2CH_2CH_3$), 1.37 (2H, m, $OCH_2CH_2CH_2$), 1.77 (2H, tt, OCH_2CH_2), 2.90, 3.00, 3.12, 3.38, 3.65, 3.93 (2H, br s, CH_2 ring), 4.01 (2H, t, OCH_2), 6.94, 7.26, 7.59 and 8.01 (2H, m, AA′XX′, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 13.97$ (CH_3), 22.49, 25.82, 28.91, 29.06, 29.16, 31.64 ($OCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 32.09, 32.22, 32.76, 37.76, 50.89, 52.84 (CH_2, ring), 68.19 (OCH_2), 114.19 (aromatic CH), 120.97 (aromatic quaternary), 121.79, 128.39, 132.18 (aromatic CH), 133.80, 151.76, 163.53 (aromatic quaternary), 164.45 and 171.76 ppm (CO quaternary); IR (KBr disc): $\nu = 1735$ (CO-ester) and 1630 cm^{-1} (CO-amide); EI-MS: *m*/*z*(%): 515 (M^+), 233 [$C(O)C_6H_4OC_8H_{17}$].

Synthesis of 3

4″-[4′-(4-Octyloxybenzoyloxy)benzoyloxy]benzoic acid anhydride (0.145 g, 0.151 mmol), prepared from the parent acid, was added to a solution of [9]aneNS$_2$ (0.016 g, 0.098 mmol) and pyridine (7.9 μl, 0.1 mmol) in freshly distilled CH_2Cl_2 (10 cm^3) and the reaction mixture stirred for 12 h. The resulting reaction mixture was filtered, the solvent removed *in vacuo* and the crude solid was purified by column chromatography (silica, 15 × 1 cm, CH_2Cl_2–acetone, 10 : 1) to give a colourless solid which was crystallised from toluene–*n*-hexane (yield 53 mg, 85%). Found C% 66.04, H% 6.62, N% 2.20; calculated for $C_{35}H_{41}NO_6S_2$ C% 66.11, H% 6.50, N% 2.20). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.29$ (d, 2 H, ^3J(H,H) = 8.63 Hz, CH_{ar}), 8.17 (d, 2 H, ^3J(H,H) = 8.80 Hz, CH_{ar}), 7.63 (d, 2 H, ^3J(H,H) = 8.45 Hz, CH_{ar}), 7.39 (d, 2 H, ^3J(H,H) = 8.64 Hz, CH_{ar}), 7.31 (d, 2 H, ^3J(H,H) = 8.49 Hz, CH_{ar}), 7.01 (d, 2 H, ^3J(H,H) = 8.87 Hz, CH_{ar}), 4.07 (t, 2 H, ^3J(H,H) = 6.54 Hz, OCH_2), 3.98 (m, 2 H, CH_2), 3.71 (m, 2 H, CH_2), 3.43 (m, 2 H, CH_2), 3.42 (m, 2 H, CH_2), 3.18 (m, 2 H, CH_2), 3.06 (m, 2 H, CH_2), 2.95 (m, 2 H, CH_2), 1.85 (quintet, 2 H, OCH_2CH_2), 1.53–1.27 (m, 10 H, CH_2), 0.92 (pseudo-triplet, 3 H, CH_3); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 171.53$, 163.99, 163.85, 163.56, 155.25, 151.41, 133.99, 126.24, 120.57 (C_q), 132.16, 131.58, 128.38, 121.94, 121.60, 114.15 (CH), 68.12, 52.73, 50.81, 37.63, 32.60, 32.07, 31.94, 31.53, 29.06, 28.95, 28.81, 25.71, 22.40 (CH_2), 13.88 (CH_3); IR(KBr): $\nu = 1733$ (C=O), 1630 (O=CN), 1603 (C=C_{ar}), 1260, 1200, 1160 (C–O) cm^{-1}; ES-MS: *m*/*z*(%): 636 (43) $[M]^+$, 284 (100).

Synthesis of 4a

Compound **7** (0.049 g, 0.185 mmol), 4′-[3,4-bis(butyloxybenzoyloxy)]benzoic acid (0.058 g, 0.185 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.038 g, 0.185 mmol) and 4-pyrrolidinopyridine (2 mg) were dissolved in freshly distilled CH_2Cl_2 (10 cm^3) and the reaction mixture stirred for 16 h. The solvent was removed *in vacuo* and the resulting colourless solid purified by column chromatography (silica, 10 × 1 cm, CH_2Cl_2–MeOH, 100 : 1) to give a colourless solid which was recrystallised several times from toluene–*n*-hexane (yield 73 mg, 61%). Found C% 63.02, H% 6.21, N% 1.91; calculated for $C_{35}H_{41}NO_7S_2$ C% 64.49, H% 6.34, N% 2.15. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.29$ (d, 2 H, ^3J(H,H) = 8.81 Hz, CH_{ar}), 7.85 (dd, 1 H, ^3J(H,H) = 8.44 Hz, ^4J(H,H) = 2.06 Hz, CH_{ar}), 7.69 (d, 1 H, ^4J(H,H) = 2.07 Hz, CH_{ar}), 7.63 (d, 2 H, ^3J(H,H) = 8.69 Hz, CH_{ar}), 7.39 (d, 2 H, ^3J(H,H) = 8.88 Hz, CH_{ar}), 7.31 (d, 2 H, ^3J(H,H) = 8.64 Hz, CH_{ar}), 6.96 (d, 1 H, ^3J(H,H) = 8.56 Hz, CH_{ar}), 4.11 (two overlapping triplets, 4 H, OCH_2), 3.98 (m, 2 H, CH_2), 3.71 (m, 2 H, CH_2), 3.42 (m, 2 H, CH_2), 3.18 (m, 2 H, CH_2), 3.06 (m, 2 H, CH_2), 2.95 (m, 2 H, CH_2), 1.85 (two overlapping quintets, 4 H, OCH_2CH_2), 1.56 (two overlapping quintets, 4 H, $OCH_2CH_2CH_2CH_3$), 1.02 (two overlapping triplets, 6 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.88$, 164.45, 164.18, 155.69, 154.38, 151.82, 148.95, 134.39, 126.68, 121.00 (C_q), 131.88, 128.68, 124.68, 122.24, 121.88, 115.01, 112.24 (CH), 69.28, 68.94, 32.46, 31.31, 31.17, 19.27, 19.24 (CH_2), 13.87, 13.85 (CH_3); IR(KBr): $\nu = 1734$ (C=O), 1635 (O=CN), 1599 (C=C_{ar}), 1272, 1187 (C–O) cm^{-1}; FAB-MS: *m*/*z*(%): 652 (15) $[M]^+$, 249 (100) $[OCC_6H_3$-$(OC_4H_9)_2]^+$.

Synthesis of 4b

This compound was synthesised according to the same general procedure described for **4a**. Amounts used: **7** (0.050 g, 0.189 mmol), 4′-[3,4-bis(octyloxybenzoyloxy)benzoic acid (0.097 g, 0.189 mmol) *N*,*N*′-dicyclohexylcarbodiimide (0.039 g, 0.189 mmol) and 4-pyrrolidinopyridine (2 mg). The crude reaction product was purified by column chromatography (silica, 12 × 2 cm, CH_2Cl_2–acetone, 20 : 1) to give a colourless solid which was recrystallised several times from toluene–*n*-hexane (yield 79 mg, 55%). Found C% 68.80, H% 7.76, N% 1.91; calculated for $C_{43}H_{57}NO_7S_2$ C% 67.60, H% 7.52, N% 1.83. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.30$ (d, 2 H, ^3J(H,H) = 8.86 Hz, CH_{ar}), 7.85 (dd, 1 H, ^3J(H,H) = 8.46 Hz, ^4J(H,H) = 2.06 Hz, CH_{ar}), 7.68 (d, 1 H, ^4J(H,H) = 2.04 Hz, CH_{ar}), 7.63 (d, 2 H, ^3J(H,H) = 8.70 Hz, CH_{ar}), 7.39 (d, 2 H, ^3J(H,H) = 8.84 Hz, CH_{ar}), 7.31 (d, 2 H, ^3J(H,H) = 8.68 Hz, CH_{ar}), 6.96 (d, 1 H, ^3J(H,H) = 8.58 Hz, CH_{ar}), 4.09 (two overlapping triplets, 4 H, OCH_2), 3.98 (m, 2 H, CH_2), 3.71 (m, 2 H, CH_2), 3.42 (m, 2 H, CH_2), 3.18 (m, 2 H, CH_2), 3.06 (m, 2 H, CH_2), 2.95 (m, 2 H, CH_2), 1.88 (two overlapping quintets, 4 H, OCH_2CH_2), 1.52 (pseudo-quintet, 4 H, $OCH_2CH_2CH_2$), 1.42–1.27 (m, 16 H, CH_2), 0.91 (two overlapping triplets, 6 H, CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 171.61$, 169.74, 164.21, 155.41, 151.66, 148.52, 134.06, 133.16, 126.25, 120.64 (C_q), 131.65, 128.17, 124.37, 122.03, 121.84, 114.37, 111.71 (CH), 69.16, 68.87, 52.78, 50.87, 37.71, 32.70, 32.13, 32.04, 31.60, 29.11, 28.90, 27.61, 25.77, 22.46 (CH_2), 13.91 (CH_3); IR(KBr): $\nu = 1734$ (C=O), 1631 (O=CN) cm^{-1}. ES-MS: *m*/*z*(%): 764 (22) $[M]^+$, 658 (20) $[OCC_6H_3$-$(OC_8H_{17})_2]^+$.

Synthesis of 4c

This compound was synthesised according to the same general procedure described for **4a**. Amounts used: **7** (0.050 g, 0.188 mmol), 4′-[3,4-bis(dodecyloxybenzoyloxy)]benzoic acid (0.094 g, 0.188 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.039 g, 0.188 mmol) and 4-pyrrolidinopyridine (2 mg). The crude product was purified by column chromatography (silica, 15×2 cm, CH_2Cl_2–MeOH, 200 : 1) to give a colourless solid which was recrystallised several times from toluene–*n*-hexane (yield 44 mg, 31%). Found C% 70.10, H% 8.75, N% 1.85; calculated for $C_{51}H_{73}NO_7S_2$ C% 69.91, H% 8.40, N% 1.60. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.30$ (d, 2 H, $^3J(H,H) = 8.79$ Hz, CH_{ar}), 7.85 (dd, 1 H, $^3J(H,H) = 8.49$ Hz, $^4J(H,H) = 2.02$ Hz, CH_{ar}), 7.68 (d, 1 H, $^4J(H,H) = 2.04$ Hz, CH_{ar}), 7.64 (d, 2 H, $^3J(H,H) = 8.63$ Hz, CH_{ar}), 7.39 (d, 2 H, $^3J(H,H) = 8.78$ Hz, CH_{ar}), 7.31 (d, 2 H, $^3J(H,H) = 8.62$ Hz, CH_{ar}), 6.96 (d, 1 H, $^3J(H,H) = 8.59$ Hz, CH_{ar}), 4.09 (two overlapping triplets, 4 H, OCH_2), 3.98 (m, 2 H, CH_2), 3.71 (m, 2 H, CH_2), 3.42 (m, 2 H, CH_2), 3.18 (m, 2 H, CH_2), 3.06 (m, 2 H, CH_2), 2.95 (m, 2 H, CH_2), 1.88 (two overlapping quintets, 4 H, OCH_2CH_2), 1.52 (pseudo-quintet, 4 H, $OCH_2CH_2CH_2$), 1.35–1.28 (m, 32 H, CH_2), 0.90 (two overlapping triplets, 6 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.89$, 165.46, 164.18, 155.69, 151.82, 148.93, 134.39, 126.67, 124.67, 121.07 (C_q), 131.89, 128.69, 122.24, 121.89, 114.96, 112.20, 109.67 (CH), 69.56, 69.23, 37.48, 32.47, 31.97, 29.73, 29.70, 29.66, 29.65, 29.45, 29.42, 29.40, 29.26, 29.13, 26.03, 22.72 (CH_2), 14.13 (CH_3); IR(KBr): $\nu = 1734$, 1715 (C=O), 1634 (O=CN), 1601 (C=C_{ar}), 1272, 1204 (C–N), 1163 (C–O) cm^{-1}; EI-MS: *m*/*z*(%): 876 (0.5) $[M]^+$, 473 (100) $[OCC_6H_3\text{-}(OC_{12}H_{25})_2]^+$.

Synthesis of 5

This compound was synthesised according to the same general procedure described for **4**. Amounts used: **7** (0.267 g, 0.942 mmol), 4′-[3,4,5-tris(dodecyloxybenzoyloxy)]benzoic acid (0.749 g, 0.942 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.194 g, 0.942 mmol) and 4-pyrrolidinopyridine (3 mg). The crude product was purified by column chromatography (silica, 15×2 cm, CH_2Cl_2–MeOH, 100 : 1) to give a colourless solid (yield 0.62 g, 62%). Found C% 72.00, H% 9.16, N% 1.23; calculated for $C_{63}H_{97}NO_8S_2$ C% 71.35, H% 9.22, N% 1.32. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.29$ (d, 2 H, $^3J(H,H) = 8.67$ Hz, CH_{ar}), 7.63 (d, 2 H, $^3J(H,H) = 8.48$ Hz, CH_{ar}), 7.43 (s, 2 H, CH_{ar}), 7.38 (d, 2 H, $^3J(H,H) = 8.73$ Hz, CH_{ar}), 7.31 (d, 2 H, CH_{ar}), 4.03 (two obscured triplets, 6 H, OCH_2), 3.97 (m, br, 2 H, CH_2), 3.70 (m, br, 2 H, CH_2), 3.42 (m, br, 2 H, CH_2), 3.17 (m, br, 2 H, CH_2), 3.05 (m, br, 2 H, CH_2), 1.86 (m, br, 2 H, CH_2), 1.82 (two obscured quintets, 6 H, OCH_2CH_2), 1.51 (unresolved quintets, 6 H, $OCH_2CH_2CH_2$), 1.25 (m, 48 H, CH_2), 0.86 (m, 9 H, CH_3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 171.66$, 169.80, 164.29, 155.31, 152.52, 143.18, 134.14, 126.54, 123.06 (C_q), 131.73, 128.49, 122.07, 121.69, 108.48 (CH), 73.45, 69.13, 52.83, 50.93, 37.78, 32.75, 32.20, 32.09, 31.76, 29.57, 29.54, 29.49, 29.47, 29.41, 29.22, 29.13, 25.92, 22.54 (CH_2), 13.96 (CH_3); IR(KBr): $\nu = 1738$ (C=O), 1631 (O=CN) cm^{-1}; FAB-MS: *m*/*z*(%): 1061 (8) $[M]^+$, 658 (100) $[OCC_6H_2\text{-}(OC_{12}H_{25})_3]^+$.

Synthesis of 6

4-Methoxycarbonyloxybenzoic acid chloride (0.053 g, 0.248 mmol) was added to a solution of [9]aneNS_2, (0.027 g, 0.165 mmol) in freshly distilled CH_2Cl_2 (20 cm^3) and Et_3N (35 μl, 0.25 mmol). The reaction mixture was stirred for 12 h, filtered and washed twice with HCl (1 mol dm^{-3}, 20 cm^3), sat. $NaHCO_3$ solution (20 cm^3) and water (20 cm^3). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to afford a colourless solid. The crude product was purified by column chromatography (silica, 15×1 cm, CH_2Cl_2–MeOH, 20 : 1) to afford a colourless solid (yield 36 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.57$ (d, 2 H, $^3J(H,H) = 8.77$ Hz, CH_{ar}), 7.25 (d, 2 H, CH_{ar}), 3.96 (m, 2 H, CH_2), 3.93 (s, 3 H CH_3), 3.66 (m, 2 H, CH_2), 3.40 (m, 2 H, CH_2), 3.16 (m, 2 H, CH_2), 3.04 (m, 2 H, CH_2), 2.93 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.68$, 153.84, 151.95, 134.53 (C_q), 128.65, 121.08 (CH), 52.99, 51.17, 37.87, 33.09, 32.43 (CH_2), 55.47 (CH_3).

Synthesis of 7

Compound **6** (0.032 g, 0.094 mmol) was dissolved in EtOH (3 cm^3). NH_3(aq) (32% v/v, 68.6 μl) was added and the resulting reaction mixture stirred for 10 h and EtOH removed *in vacuo*. Recrystallisation from EtOH afforded a colourless crystalline solid (yield 14 mg, 52%). Found C% 54.62, H% 6.01, N% 4.83; calculated for $C_{13}H_{17}NO_2S_2$ C% 55.09, H% 6.05, N% 4.94. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.38$ (d, 2 H, CH_{ar}), 6.80 (d, 2 H, CH_{ar}), 6.41 (s, br, 1 H, OH), 3.96 (m, br, 2 H, CH_2), 3.70 (m, br, 2 H, CH_2), 3.38 (m, br, 2 H, CH_2), 3.14 (m, br, 2 H, CH_2), 3.02 (m, br, 2 H, CH_2), 2.91 (m, br, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 172.80$, 157.21, 99.67 (C_q), 129.14, 115.42 (CH), 32.52 (CH_2); IR(KBr): $\nu = 3165$ (O–H), 1601 (OC–N) cm^{-1}; EI-MS (70 eV): *m*/*z*(%): 283 (6) $[M]^+$, 121 (100) $[OCPhOH]^+$.

Synthesis of 8

This compound was synthesised according to the same general procedure described for **1**. Amounts used: 4-methoxycarbonyloxybenzoic acid chloride (0.270 g, 1.256 mmol), [9]aneN$_2$S (0.088 g, 0.598 mmol) and pyridine (0.101 cm^3, 1.256 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2–MeOH, 20 : 1, 15×2 cm) to give a colourless solid (yield 0.180 g, 60%). Found C% 57.13, H% 5.41, N% 5.37; calculated for $C_{24}H_{26}N_2O_8S$ C% 57.36, H% 5.22, N% 5.57. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.62$ (d, 4 H, $^3J(H,H) = 8.43$ Hz, CH_{ar}), 7.28 (d, 4 H, CH_{ar}), 3.93 (s, 6 H, OCH_3), 3.93 (m, br, 4 H, NCH_2), 3.80 (m, br, 4 H, SCH_2), 2.88 (m, br, 4 H, SCH_2CH_2S); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.36$, 153.83, 152.02, 133.99 (C_q), 128.76, 121.24 (CH), 53.42, 47.04 28.39 (CH_2), 55.53 (CH_3); IR(KBr): $\nu = 1766$ (C=O), 1628 (O=CN), 1264, 1219 (C–N) cm^{-1}; EI-MS (70 eV): *m*/*z*(%): 502 (0.5) $[M]^+$.

Synthesis of 9

This compound was synthesised according to the same general procedure described for **7**. Amounts used: **8** (0.180 g, 0.598 mmol) and NH_3(aq) (0.7 cm^3, 32% v/v). Crystallisation from EtOH afforded a colourless crystalline solid (yield 0.10 g, 45%). Found C% 61.54, H% 5.77, N% 6.75; calculated for $C_{23}H_{22}N_2O_4S{\cdot}H_2O$ C% 62.71, H% 5.49, N% 6.36. IR(KBr): $\nu = 3273$ (O–H), 1610 (O=CN), 1595, 1577 (C=C_{ar}) cm^{-1}; EI-MS (70 eV): *m*/*z*(%): 386 (3) $[M]^+$. No NMR data could be obtained due to the insolubility of the sample in all common organic solvents.

Synthesis of 10

This compound was synthesised according to the same general procedure described for **3**. Amounts used: **9** (0.030 g, 0.078 mmol), 4′-(4-octyloxybenzoyloxy)benzoic acid (0.057 g, 0.155 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.032, 0.155 mmol) and 4-pyrrolidinopyridine (0.5 mg). The crude product was purified by column chromatography (silica, 16×1 cm, CH_2Cl_2–acetone 30 : 1) to give a colourless solid (yield 0.019 g, 23%). Found C% 71.57, H% 8.86, N% 4.41; calculated for $C_{28}H_{37}N_2O_4S$ C% 67.58, H% 7.49, N% 5.63. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.14$ (d, 4 H, $^3J(H,H) = 8.97$ Hz, CH_{ar}), 7.65 (d, 4 H, $^3J(H,H) = 8.75$ Hz, CH_{ar}), 7.27 (d, 4 H, $^3J(H,H) = 8.73$ Hz, CH_{ar}), 6.99 (d, 4 H, $^3J(H,H) = 9.01$ Hz, CH_{ar}), 4.20–4.10 (m, 2 H, NCH_2), 4.06 (t, 4 H,

^3J(H,H) = 6.54 Hz, OCH_2), 3.58–3.48 (m, 2 H, SCH_2), 2.19–2.00 (m, 4 H, SCH_2), 1.84 (m, 4 H, OCH_2CH_2), 1.80–1.36 (m, 20 H, CH_2), 0.91 (m, 6 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 170.49, 164.39, 163.82, 154.38, 153.18, 143.33, 121.24 (C_q), 132.38, 128.32, 122.11, 114.47 (CH), 68.46, 57.57, 49.81, 32.41, 31.83, 30.85, 29.73, 29.35, 29.24, 29.15, 26.29, 26.03, 25.45, 25.33, 24.58, 22.68 (CH_2), 14.09 (CH_3); IR(KBr): ν = 1733 (C=O), 1673, 1648 (O=CN), 1261, 1207, 1167 (C–O) cm^{-1}. FAB-MS: *m*/*z*(%): 577(5), 452 (11), 233 (21). The product could not be obtained in high purity even after repeated column chromatography and successive recrystallisations from toluene–*n*-hexane.

Synthesis of 11

This compound was synthesised according to the same general procedure described for **4c**. Amounts used: **9** (0.020 g, 0.052 mmol), 4′-[3,4,5-tris(dodecyloxybenzoyloxy)]benzoic acid (0.165 g, 0.207 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.043, 0.207 mmol) and 4-pyrrolidinopyridine (3 mg). The crude product was purified by column chromatography (silica, 15 × 2 cm, CH_2Cl_2–*n*-hexane 4 : 1) to give a colourless solid. (yield 59 mg, 58%). Found C% 75.60, H% 10.75, N% 3.02; calculated for $C_{106}H_{174}N_2O_{12}S$ C% 74.86, H% 10.31, N% 1.65. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, 4 H, ^3J(H,H) = 8.69 Hz, CH_{ar}), 7.41 (s, 4 H, CH_{ar}), 7.25 (d, 4 H, CH_{ar}), 4.15 (dt, 2 H, NCH_2), 4.06 (two overlapping triplets, 12 H, OCH_2), 3.53 (m, 2 H, SCH_2), 2.05 (m, 4 H, SCH_2), 1.85 (two overlapping quintets, 12H, OCH_2CH_2), 1.73–1.48 (two overlapping multiplets, 12 H, $OCH_2CH_2CH_2$), 1.70–1.28 (m, 96 H, CH_2), 0.90 (t, 18 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.48, 154.37, 153.10, 147.48, 134.49, 123.52, 108.85 (C_q), 128.33, 122.13, 109.67 (CH), 73.67, 69.45, 57.61, 49.79, 32.42, 31.98, 31.97, 30.86, 30.41, 29.79, 29.77, 29.74, 29.70, 29.67, 29.61, 29.44, 29.40, 26.30, 26.15, 26.11, 24.58, 22.73 (CH_2), 14.13 (CH_3); IR(KBr): ν = 1736 (C=O), 1648 (O=CN), 1198 (C–O)cm^{-1}; FAB-MS: *m*/*z*(%): 1001 (5), 877 (30), 657 (100). The product could not be obtained in high purity even after repeated column chromatography and successive recrystallisations from toluene–*n*-hexane.

Single crystal structure determination of 7†

Crystals of **7** were grown from EtOH at −15 °C. A crystal was encapsulated in a film of RS3000 perfluoropolyether oil and mounted on a glass fibre before transfer into the cold stream of the diffractometer's cryostat.

Crystal data. $C_{13}H_{17}NO_2S_2$, M = 283.40, orthorhombic, a = 13.167(2), b = 13.969(6), c = 14.443(3) Å, U = 2656.5(13) Å^3, T = 150(2) K, space group $P2_12_12_1$ (No. 19), Z = 8, D_c = 1.417 g cm^{-3}, μ(Mo-Kα) = 0.394 mm^{-1}, 2537 unique absorption-corrected reflections measured and used in all calculations. Final R_1 [2196 $F \geqslant 4\sigma(F)$] = 0.0498 and wR (all F^2) was 0.114. The Flack parameter[20] refined to 0.1(2).

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†CCDC reference number 1145/262. See http://www.rsc.org/suppdata/jm/bo/b006753i/ for crystallographic files in .cif format.

References

1 For example: P. Weber, D. Gullion and A. Skoulios, *J. Phys. Chem.*, 1987, **91**, 2242; Z. Berlabi, C. Sirlin, J. Simon and J.-J. André, *J. Phys. Chem.*, 1989, **93**, 8105.
2 Y. Shimizu, A. Ishikawa, S. Kusabayashi, M. Miya and A. Nagata, *J. Chem. Soc., Chem. Commun.*, 1993, 656; Y. Shimizu, J-Y. Nakao, K. Ohta, M. Miya and A. Nagata, *Mol. Cryst., Liq. Cryst.*, 1995, **260**, 491.
3 Q. M. Wang and D. W. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 150; Q. M. Wang and D. W. Bruce, *J. Chem. Soc., Chem. Commun.*, 1996, 2505.
4 J. Malthête, A.-M. Levelut and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1985, 1794; J. Malthête, A.-M. Levelut and J.-M. Lehn, *J. Chem. Soc., Chem.Commun.*, 1992, 1434; C. Mertesdorf and H. Ringsdorf, *Liq. Cryst.*, 1989, **5**, 1757; G. Lattermann, *Liq. Cryst.*, 1989, **6**, 619; G. Lattermann, *Mol. Cryst., Liq. Cryst.*, 1990, **B182**, 299; S. Schmidt, G. Latterman, R. Kleppinger and J. H. Wendorff, *Liq. Cryst.*, 1994, **16**, 693; U. Stebani, G. Latterman, M. Wittenberg, R. Festag and J. H. Wendorff, *Adv. Mater.*, 1994, **6**, 572; H. Fisher, S. S. Ghosh, P. A. Heiney, N. C. Maliszewskyj, T. Plesnivy, H. Ringsdorf and M. Seitz, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 795.
5 (*a*) D. Guillon, A. Skoulios and J. Malthête, *Europhys. Lett.*, 1987, **3**, 67; (*b*) R. P. Tuffin, K. J. Toyne and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 2093; (*c*) R. P. Tuffin, K. J. Toyne and J. W. Goodby, *J. Mater. Chem.*, 1996, **6**, 1271; (*d*) R. P. Tuffin, G. H. Mehl, K. J. Toyne and J. W. Goodby, *Mol. Cryst., Liq. Cryst.*, 1997, **304**, 223.
6 G. X. He, F. Wada, K. Kikukawa, S. Shinkai and T. Matsuda, *J. Org. Chem.*, 1990, **55**, 541.
7 A. J. Blake, D. W. Bruce, I. A. Fallis, S. Parsons and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1994, 2471; A. J. Blake, D. W. Bruce, I. A. Fallis, S. Parsons, H. Richtzenhain, S. A. Ross and M. Schröder, *Phil. Trans. R. Soc. Lond. A*, 1996, **35**, 1.
8 A. J. Blake, J. P. Danks, A. Harrison, S. Parsons, P. Schooler, G. Whittaker and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 2335; A. J. Blake, J. P. Danks, I. A. Fallis, A. Harrison, W-S. Li, S. Parsons, S. A. Ross, G. Whittaker and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 3969.
9 (*a*) A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1; (*b*) J. P. Danks, N. R. Champness and M. Schröder, *Coord. Chem. Rev.*, 1998, **174**, 417.
10 W. Weissflog, PhD Thesis, Universität Halle, 1989.
11 V. Vill, LiqCryst 3.1, LCI Publishers, Hamburg, 1998.
12 B. K. Sadashiva, *Mol. Cryst., Liq. Cryst.*, 1986, **132**, 143.
13 H. T. Ngyuen, C. Destrade and J. Malthête, *Adv. Mater.*, 1997, **9**, 375; D. Guillon, *Struct. Bonding*, 1999, **25**, 41.
14 V. Percec, D. Tomaczos, J. Heck, H. Blackwell and G. Ungar, *J. Chem. Soc., Perkin Trans. 2*, 1994, 31; G. Johannsson, V. Percec, G. Ungar and D. Abramic, *J. Chem. Soc., Perkin Trans. 1*, 1994, 447.
15 A. G. Serrette and T. M. Swager, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2342.
16 See for example: C. Cruz, J. L. Figueirinhas, P. J. Sebastião, A. C. Ribeiro, F. Noack, H. T. Nguyen, B. Heinrich and D. Guillon, *Z. Naturforsch., A: Phys. Sci.*, 1996, **51A**, 155.
17 B. Donnio, D. W. Bruce, B. Heinrich, D. Guillon, H. Delacroix and T. Gulik-Krzywicki, *Chem. Mater.*, 1997, **9**, 2951; D. Guillon, B. Heinrich, A. C. Ribeiro, C. Cruz and H. T. Nguyen, *Mol. Cryst., Liq. Cryst.*, 1998, **317**, 51.
18 H. Abied, D. Guillon, A. Skoulios, A. M. Giroud-Godquin, P. Maldivi and J. C. Marchon, *Colloid Polym. Sci.*, 1988, **266**, 579.
19 P. Seurin, D. Guillon and A. Skoulios, *Mol. Cryst., Liq. Cryst.*, 1981, **65**, 85; G. Poeti, E. Fanelli, G. Torquati and D. Guillon, *Nuovo Cimento Soc. Ital. Fis., D*, 1983, **2D**, 1335.
20 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.