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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Dalcanale, Enrico , Arena, Carmela , Catellani, Marta and Chiusoli, Gian Paolo(1992) 'Mesogenic aromatic esters with sulphur containing alkyl chains', *Liquid Crystals*, 12: 6, 905 – 912

To link to this Article: DOI: 10.1080/02678299208032806

URL: <http://dx.doi.org/10.1080/02678299208032806>

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Mesogenic aromatic esters with sulphur containing alkyl chains

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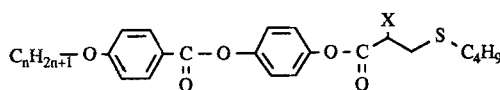
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(Received 16 March 1992; accepted 7 July 1992)

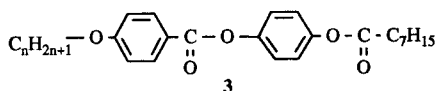
A new series of aromatic esters, **1** and **2** with a sulphur atom in one of the side chains, is described. They exhibit nematic and/or smectic A/C mesophases as a function of the length of the alkyloxy chain. The presence of sulphur in the 4-position of the alkanoyloxy chain depresses both the clearing and the melting points with respect to the corresponding carbon analogues **3**, resulting from the higher conformational mobility of the thiaalkyl chain. In **2**, the presence of a methyl group in the 2-position of the alkanoyloxy chain induces a S_A phase below room temperature.

1. Introduction

Structure-mesogenicity relationships in liquid crystals are of fundamental importance for the elucidation of the molecular factors responsible for mesomorphic self-assembly [1,2]. In this regard, the introduction of heteroatoms provides a useful way to modify the properties of liquid crystal materials. Sulphur in particular offers some advantages such as the possibility to introduce chirality into the molecule [3]. Here we report the synthesis, characterization and mesomorphic properties of new rod-like mesogens of general formula **1** and **2**, containing a sulphur atom in one of the side chains. Furthermore we analyse the mesomorphic properties of mesogens **1c, e** in comparison with those of the corresponding carbon analogues **3a, b**.



1: X=H; 2: X=CH₃



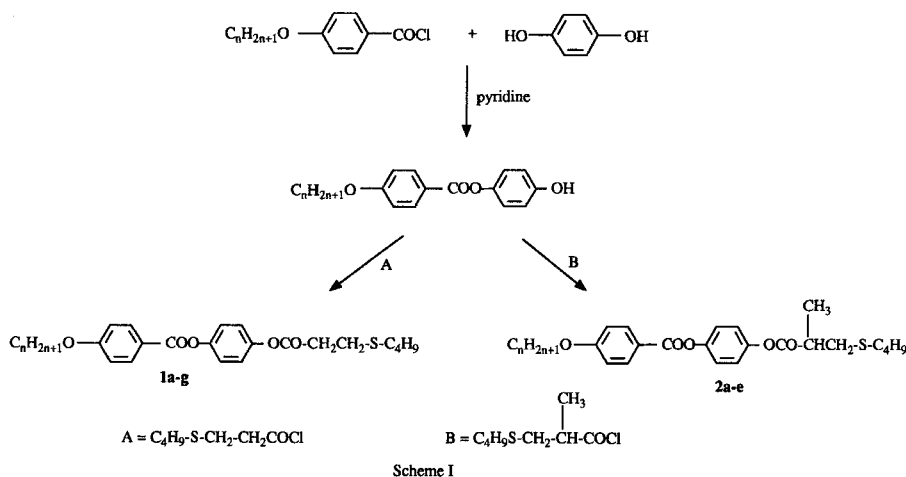
1a: n = 6	2a: n = 4	3a: n = 8
1b: n = 7	2b: n = 6	3b: n = 10
1c: n = 8	2c: n = 7	
1d: n = 9	2d: n = 8	
1e: n = 10	2e: n = 10	
1f: n = 12		
1g: n = 16		

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While this work was near completion a study appeared on the effect of heteroatoms like oxygen and sulphur in the side chains on the thermal phase behaviour of discotic liquid crystals [4]. This paper provides further information on this effect.

2. Synthesis and characterization

Compounds **1a–g** and **2a–e** were prepared according to the reaction scheme.



Condensation of hydroquinone with the appropriate 4-*n*-alkoxybenzoyl chloride in dry pyridine gave the precursors 4-hydroxyphenyl-4'-alkoxybenzoates in good yield (70–75 per cent) [5]. Their condensation with the corresponding acyl chlorides A and B (no solvent used) afforded the ester derivatives **1a–g** and **2a–e**, respectively (65–85 per cent). Compounds **3a–b** were prepared by condensation of the appropriate 4-hydroxyphenyl-4'-alkoxybenzoates with octanoyl chloride (76–78 per cent). Spectral (¹H NMR and EI-MS spectra) and microanalytical data are in agreement with the assigned structure (see the Experimental section). The thermal properties of the homologous series were studied using differential scanning calorimetry and optical microscopy. Reproducible transition temperatures were obtained for all of the compounds during the second and subsequent heating–cooling cycles (see tables 1, 2 and 3).

The S_A phases of derivative **1c–g** and **3a–b** were identified through miscibility studies with known S_A compounds (4-*n*-alkyloxy)-4'-cyanobiphenyls K36 and M30 by Merck, Poole). The S_C phase of **1e** was identified by its schlieren texture together with the continuous changes in texture on cooling which are typical for a S_C phase occurring below a S_A phase. The S_A phase of **2d** was identified by the observation of the focal conic texture typical of this phase (see figure 1) [6].

3. Results and discussion

3.1. Mesomorphic properties of derivatives **1a–g**

The thermal phase behaviour of compounds **1a–g** is shown in figure 2. Three of the seven derivatives studied exhibit enantiotropic nematic mesophases (**1a**, **1c**, **1e**), while only one forms a smectic A enantiotropic mesophase (**1e**). The overall mesophase temperature range is reduced on increasing the number of carbon atoms in the alkyloxy chain: 27°C for **1a**, 15°C for **1c** and 9°C for **1e**. This is caused by the increase of the

Table 1. Transition temperatures and enthalpy changes for **1a–g(a)**.

Compound	Transition (b)	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	Transition (c)	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
1a ($n=6$)	I–N	74	0.8	C–N	58	21.2
	N–C	47	20.6	N–I	74	0.7
1b ($n=7$)	I–N	64	0.8	C–I	66	38.3
	N–C	53	35.3			
1c ($n=8$)	I–N	70	1.3	C–N	64	24.2
	N–S _A	57	0.1	N–I	71	1.3
	S _A –C	55	9.8			
1d ($n=9$)	I–N	60	1.2	C–I	73	38.0
	N–C	57	26.6			
1e ($n=10$)	I–N	72	1.8	C–S _A	66	23.8
	N–S _A	68	1.2	S _A –N	69	1.2
	S _A –S _C	66	0.1	N–I	73	1.5
	S _C –C	63	11.5			
1f ($n=12$)	I–S _A	73	1.5	C–I (d)	72	32.4
	S _A –C	68	7.0			
1g ($n=16$)	I–S _A	81	8.1	C–I	83	59.6
	S _A –C	76	11.6			

(a) These results refer to DSC measurements, 3°C min^{-1} .

(b) Cooling run.

(c) Second heating run.

(d) Transient enantiotropic S_A mesophase observed only under the polarizing microscope.

Table 2. Transition temperatures and enthalpy changes for **2a–e(a)**.

Compound	Transition (b)	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	Transition (c)	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
2a ($n=4$)	I–C	8	21.4	C–I	33	24.3
2b ($n=6$)	I–C	11	20.6	C–I	27	21.8
2c ($n=7$)	I–C	6	26.7	C–I	30	32.8
2d ($n=8$)	I–S _A	16	3.5	C–I	26	27.8
	S _A –C (d)	9	22.2			
2e ($n=10$)	I–C (e)	13	25.5	C–I	33	28.4

(a) These results refer to DSC measurements, 3°C min^{-1} .

(b) Cooling run.

(c) Second heating run.

(d) The S_A phase crystallizes if kept in the lower mesophase temperature range (10 – 12°C) for more than 5 min.

(e) Transient monotropic S_A mesophase observed only under the polarizing microscope.

Table 3. Transition temperatures and enthalpy changes for **3a–b(a)**.

Compound	Transition (b)	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	Transition (c)	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
3a	I–N	95	1.4	C–N	72	24.9
	N–S _A	71	0.9	N–I	95	1.3
	S _A –C	54	21.7			
3b	I–N	91	2.2	C–S _A	72	28.9
	N–S _A	78	0.9	S _A –N	79	1.0
	S _A –C ₁ (d)	60	9.6	N–I	91	2.3
	C ₁ –C ₂	44	14.8			

(a) These results refer to DSC measurements, 3°C min^{-1} .

(b) Cooling run.

(c) Second heating run.

(d) Transient enantiotropic S_C mesophase observed only under the polarizing microscope.

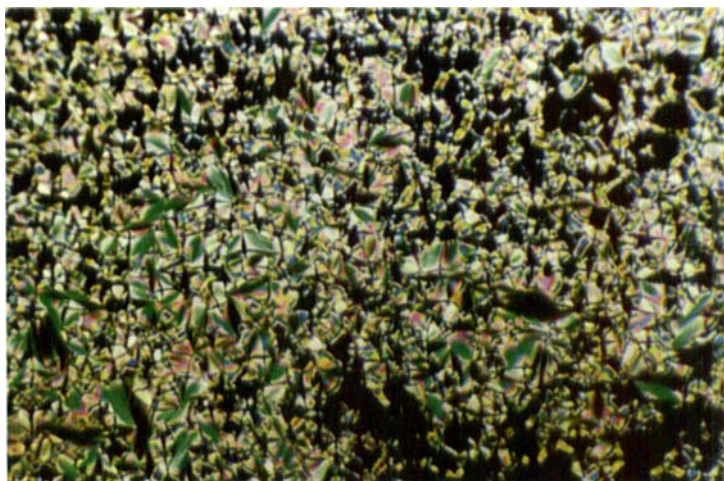


Figure 1. The focal conic texture of the S_A mesophase of **2d** obtained from the isotropic liquid at 15°C.

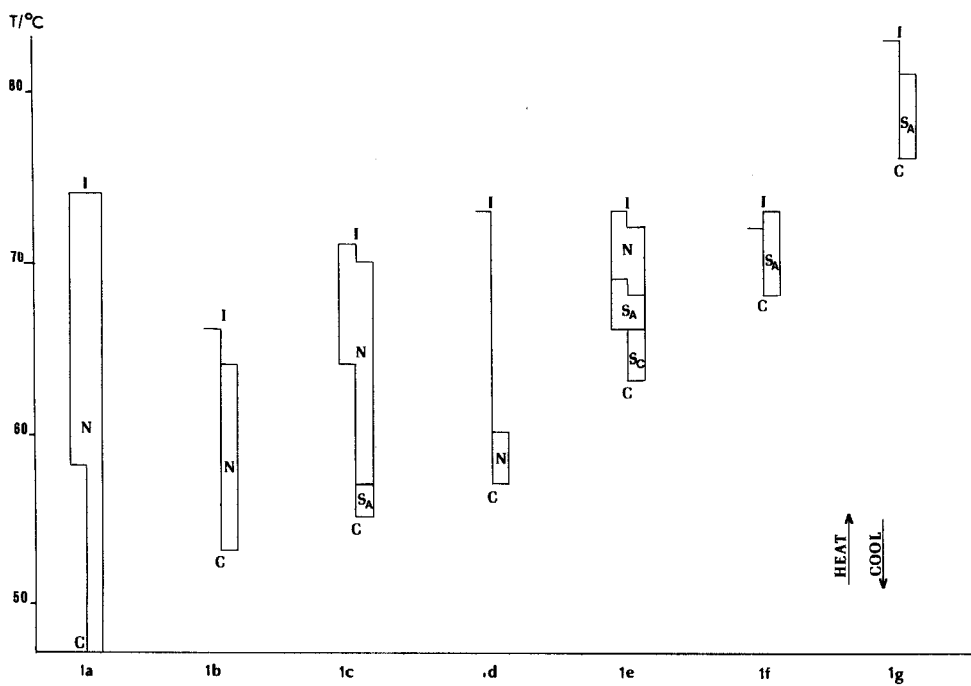


Figure 2. Mesomorphic properties for derivatives **1a–g**.

crystal to mesophase transition which is not sufficiently compensated in the mesophase to isotropic transition (see figure 2). This effect is especially evident for derivatives **1b** and **1d**, for which in the heating cycle the mesophase is totally suppressed.

The number of carbon atoms in the alkyloxy chain affects also the polymorphism of the mesogens. The N phase is dominant for $n=6-9$ (**1a-d**), while the S_A phase is only present as a monotropic mesophase in the longer chain derivatives **1f** and **1g**. To this trend is superimposed an odd-even effect for the nematic phase, clearly seen in derivatives **1a-e** (the numbering includes the oxygen atom of the alkyloxy chain). A monotropic S_C phase is exhibited by **1e**. Solid-solid transitions were not observed in this class of mesogens.

3.2. Mesomorphic properties of derivatives **2a-e**

The methyl group α to the carbonyl of the alkanoyloxy chain was introduced because it is known that chain branching favours the formation of S_C phases [7]. In our case the effect is drastically different. Out of five derivatives studied (**2a-e**) only one

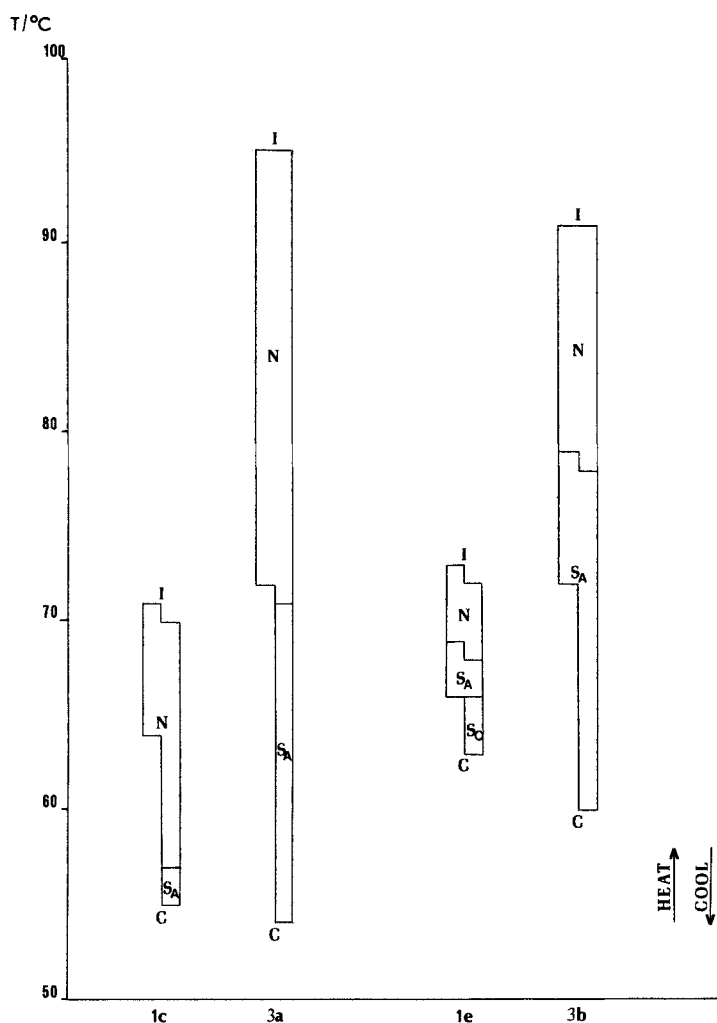


Figure 3. Comparison of the mesomorphic properties of **1c, e** with those of **3a, b**.

exhibits a monotropic S_A phase (**2d**, see figure 1), while another (**2e**) gives a transient, monotropic S_A mesophase observable only by optical microscopy. No S_C phases were detected at all. An unusually large melting point depression is observed for branched chain derivatives **2a–e** with respect to the corresponding linear chain analogues **1a–e**. In our case the presence of a methyl group close to the core appears to destabilize both mesophase and crystal formation, interfering sterically with the packing of the cores [7, 8].

3.3. Sulphur effect on mesophase formation

The influence of the sulphur atom in the 4-position of the alkanoyloxy chain on the mesomorphic properties of this class of liquid crystal has been evaluated by comparing the thermal behaviour of compounds **1c** and **1e** with that of the corresponding carbon analogues **3a–b**.

The introduction of sulphur produces a consistent reduction of the overall mesophase temperature range. This results from the depression of the clearing points of **1c** and **1e** with respect to those of **3a** and **3b** (see figure 3). In the heating cycle the melting points are also depressed.

The depression in both transitions can be explained considering the different conformational mobility of the thiaalkyl chains with respect to that of the alkyl chains. The lower rotation barrier around the carbon–sulphur bond relative to the carbon–carbon bond [9] facilitates the formation of the sterically demanding *trans–gauche* (*tg*) conformers [10], which in turn increase the disorder of the system. A reduction of the clearing transition associated with the introduction of oxygen in the terminal chain has been reported for other rod-like mesogens [11]. In particular comparison between alkyloxy and alkyloxymethylene phenyl cyclohexanecarboxylates has shown the effect of the higher conformational mobility associated with the presence of oxygen in the terminal chains [12]. This behaviour is fully consistent with our present findings.

4. Conclusions

A new class of sulphur containing mesogens has been synthesized and characterized. They exhibit nematic and/or smectic phases depending on the length of the alkyloxy chain. Branching in the 2-position of the alkanoyloxy chain (**2a–e**) produces an unusually large melting point depression coupled with the suppression of the nematic phase and the narrowing of the thermal range of the residual S_A phase.

The influence of sulphur in the 4-position of the alkanoyloxy chain on mesophase formation has been evaluated by comparison with the carbon analogues. The depression of both clearing and melting transition temperatures has been attributed to the higher conformational mobility of the thiaalkanoyloxy side chain relative to the alkanoyloxy one. This effect, already observed for oxygen in rod-like mesogens [11, 12] and both for oxygen and sulphur in discotic mesogens [4, 13], seems to be common in liquid crystals independent of their mesomorphic organization.

5. Experimental

ACS Grade reagents were used without further purification. Flash chromatography was carried out using silica gel 60 (Merck, 400–230 mesh ASTM). Analytical TLC was conducted on precoated silica gel 60 plates. NMR spectra were recorded on a Bruker AMX-400 spectrometer, chemical shifts are given in parts per million ($\delta_{TMS} = 0$) using as an internal reference the solvent peak referred to TMS. Mass spectra were

recorded on a Finnigan MAT SSQ 710 spectrometer, using the electron impact technique (EI). Elemental analyses were carried out with a Carlo Erba Mod. 1106 elemental analyser. All products were identified through their elemental analyses, NMR and mass spectra. DSC measurements were performed with a Perkin-Elmer DSC 7 thermal analyser. The textures were studied using a polarizing microscope (Leitz-Wetzlar) equipped with a Leitz-Wetzlar hot stage. Thin samples were observed between two untreated cover slips of ordinary glass.

4-Hydroxyphenyl-4'-alkyloxybenzoates were obtained following a published procedure [5] and purified by flash chromatography. Acyl chlorides A and B were obtained from the corresponding mercaptopropionitriles [14] through hydrolysis and subsequent treatment with thionyl chloride. They were distilled prior to use.

Compound 1c. A stirred mixture of 0.514 mg (1.5 mmol) of 4-hydroxyphenyl-4'-octyloxybenzoate and 7 g (38.7 mmol) of 3-butylthiopropionyl chloride (A) was heated at 80°C for 2 h. The excess acyl chloride was removed by vacuum distillation (55°C/0.4 mmHg) to give a solid which was dissolved in dichloromethane. The organic phase was extracted with 0.1 N sodium hydroxide, washed with water to neutrality and dried over sulphate. After filtration and evaporation of the solvent 620 mg of a white solid were obtained (85 per cent). The solid was recrystallized from *n*-hexane to give white crystals.

¹H NMR (CDCl₃): δ0.87 (t, 3 H, O-(CH₂)₇-CH₃, *J*=6.8 Hz), 0.92 (t, 3 H, S-(CH₂)₃-CH₃, *J*=7.3 Hz), 1.25–1.52 (m, 12 H, CH₂), 1.58 (m, 2 H, S-CH₂-CH₂), 1.81 (m, 2 H, O-CH₂-CH₂), 2.58 (t, 2 H, S-CH₂, *J*=7.4 Hz), 2.87 (m, 4 H, CO-CH₂-CH₂-S), 4.03 (t, 2 H, O-CH₂, *J*=6.5 Hz), 6.95 (AA' part of an AA'BB'm, 2 H, ArH), 7.18 (AA'BB'm, 4 H, ArH), 8.11 (BB' part of an AA'BB'm, 2 H, ArH).

MS (EI, 70 eV): 486 (M⁺, 5 per cent); 233(100 per cent); 121(60 per cent).

C₂₈H₃₈O₅S. Calculated C, 69.10 per cent; H, 7.87 per cent; S, 6.59 per cent. Found C, 68.88 per cent; H, 7.69 per cent; S, 6.47 per cent.

Compounds **1a–g** were obtained following this procedure, using in each case the corresponding phenol.

Compound 2d. A stirred mixture of 343 mg (1.0 mmol) of 4-hydroxyphenyl-4-octyloxybenzoate and 5.63 g (28.9 mmol) of 3-butylthio-2-methylpropanoyl chloride (B) was heated at 100°C for 3 h. The excess acyl chloride was removed by vacuum distillation (43°C/0.03 mmHg) to give an oil which was dissolved in dichloromethane. The organic phase was extracted with 0.1 N sodium hydroxide, washed with water to neutrality and dried over sodium sulphate. After filtration and evaporation of the solvent the oil residue was purified by flash chromatography on silica gel with hexane/ethyl acetate (9 : 1) as eluant yielding 365 mg (73 per cent) of a colourless oil. It crystallized on standing after a few hours.

¹H NMR (CDCl₃): δ0.89 (t, 3 H, O-(CH₂)₇-CH₃, *J*=7.1 Hz), 0.92 (t, 3 H, S-(CH₂)₃-CH₃, *J*=7.2 Hz), 1.25–1.52 (m, 12 H, CH₂), 1.32 (d, 3 H, CH-CH₃, *J*=6.5 Hz), 1.59 (m, 2 H, S-CH₂-CH₂), 1.81 (m, 2 H, O-CH₂-CH₂), 2.58 (t, 2 H, S-CH₂, *J*=7.5 Hz), 2.71 (q, 1 H, CH, *J*=6.5 Hz), 2.93 (m, 2 H, CO-CH(CH₃)-CH₂-S), 4.03 (t, 2 H, O-CH₂, *J*=6.6 Hz), 6.95 (AA' part of an AA'BB'm, 2 H, ArH), 7.18 (AA'BB'm, 4 H, ArH), 8.12 (BB' part of an AA'BB'm, 2 H, ArH).

MS (EI, 70 eV): 500(10 per cent); 234(100 per cent); 121(80 per cent).

C₂₉H₄₀O₅S. Calculated C, 69.57 per cent; H, 8.05 per cent; S, 6.40 per cent. Found C, 69.50 per cent; H, 8.13 per cent; S, 6.28 per cent.

Compounds **2a–e** were obtained following this procedure, using in each case the corresponding phenol.

Compound **3a**. A stirred mixture of 520 mg (1.5 mmol) of 4-hydroxyphenyl-4-octyloxybenzoate and 5 ml (30 mmol) of octanoyl chloride was heated at 80°C for 2 h. The excess acyl chloride was removed by vacuum distillation (50°C/0.4 mmHg) to give a solid which was dissolved in dichloromethane. The organic phase was extracted with 0.1 N sodium hydroxide, washed with water to neutrality and dried over sodium sulphate. After filtration and evaporation of the solvent 538 mg of a pale yellow solid were obtained (76 per cent). The solid was recrystallized from *n*-hexane to give white crystals.

¹H NMR (CDCl₃): δ0.89 (m, 6 H, CH₃), 1.25–1.50 (m, 18 H, CH₂), 1.75 (m, 2 H, CO–CH₂–CH₂), 1.82 (m, 2 H, O–CH₂–CH₂), 2.56 (t, 2 H, CO–CH₂, *J* = 7.5 Hz), 4.04 (t, 2 H, O–CH₂, *J* = 6.6 Hz), 6.96 (AA' part of an AA'BB'm, 2 H, ArH), 7.17 (AA'BB'm, 4 H, ArH), 8.12 (BB' part of an AA'BB'm, 2 H, ArH).

MS (EI, 70 eV): 468 (M⁺, 5 per cent); 233(100 per cent); 121(40 per cent).

C₂₉H₄₀O₅. Calculated C, 74.32 per cent, H, 8.60 per cent. Found C, 73.98 per cent; H, 8.73 per cent.

Compound **3b** was prepared in 78 per cent yield following the same procedure as for **3a** using octanoyl chloride and 4-hydroxy-4-decyloxybenzoate.

This work was supported by ENICHEM and by Ministero Università e Ricerca Scientifica MURST. C. Arena was recipient of a grant from ENICHEM. We thank Professor M. P. Fontana (University of Parma), Professor N. Kirov (University of Sofia), Professor M. G. Rossi (University of Ancona) and Dr P. Gherardi (Camattini S.p.A.) for some physical determinations. Centro Interfacoltà di Misure of the University of Parma provided the facilities for NMR and mass spectroscopy.

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