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Influence of the structure of the mesogenic core on the thermotropic properties of ω-unsaturated fluorinated liquid crystals

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Three series of calamitic liquid crystals have been prepared, consisting of a mesogenic core attached to which is a perfluorinated chain via a thioester linkage, and a hydrocarbon chain containing a terminal double bond. The rigid core is either a monophenyl, biphenyl or phenyl benzoate group. The mesomorphic properties were characterized by polarizing optical microscopy and differential scanning calorimetry. The influence of the structure of the mesogenic core and of the hydrocarbon chain length on mesomorphic behaviour was studied. Increasing the length of the alkyl chain strongly reduces the mesomorphic behaviour while increasing the number of aromatic rings in the core increases the transition temperatures, with the widest LC range observed for derivatives with the phenyl benzoate core. The introduction of a single ring as the mesogenic core is considered of great interest in the development of low cost liquid crystal materials.

1. Introduction

Growth in the theoretical and practical interest in side chain liquid crystalline polymers (LCPs) is closely correlated to the development of new LC monomers [1–4]. These substances not only have potential use for display applications in electro-optical devices, but also as coatings [5–8] which can induce specific anchoring on the surface [9]. The presence of perfluorinated tails allows the synergetic use of their surface and anisotropic properties often required within liquid crystal displays. Thus, the synthesis of molecular rod-like mesogens that exhibit conventional calamitic mesophases and which contain an unsaturated moiety is required. The majority of rod-like liquid crystalline structures contain at least two aromatic, cycloaliphatic or a combination of one aromatic and one cycloaliphatic groups interconnected either directly or through a suitable linking unit. This unit is often an ester, Schiff's base or an azo linkage. In this work, we describe compounds with only a single aromatic ring substituted in the 1,4 positions with a perfluorinated chain and a hydrocarbon chain containing a terminal double bond (coded Ph_m). It is worth noting that the development of liquid crystals having a single benzene ring as the mesogenic core is of importance and of current interest. In order to determine the impact of the core structure on mesomorphic properties we have prepared two other series, namely, the corresponding biphenyl (B_m) and phenylbenzoate (PhB_m) compounds. The rather unusual feature in these three series is the nature of the linking group, which is a thioester. This choice is based on previous studies of biphenyl derivatives showing the considerable potential of the thioester link on mesomorphic properties [10, 11]. On the other hand, in a LCP a spacer between the polymer backbone and the mesogenic unit must be present and must satisfy one basic requirement. Specifically it must allow us relatively undisturbed organization of the aligned mesogenic units. Thus in our work, the design of new precursors, includes in each series two lengths of spacer between the rigid core and the terminal double bond, i.e. one or nine methylene units. The chemical structures of the monomers are shown in figure 1.

The mesomorphic behaviour of all the compounds has been studied by differential thermal analysis (DSC) and polarizing optical microscopy (POM). The influence of the structure of the core and hydrocarbon spacer will be discussed.

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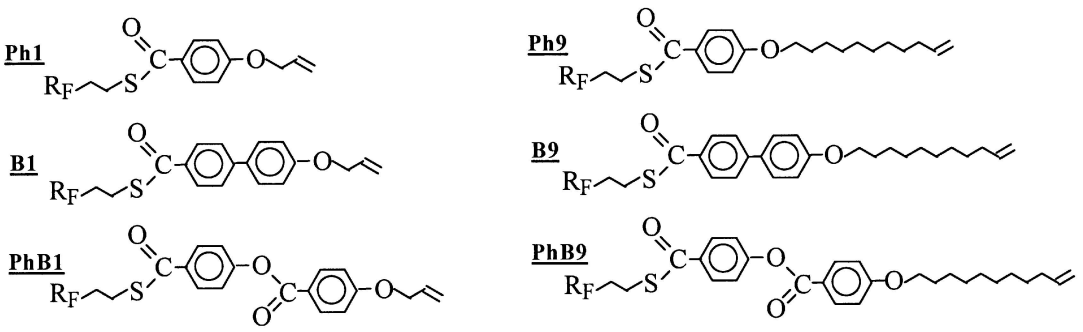

Figure 1. Structures of the series **Ph*m***, **B*m***, **PhB*m*** ($m = 1, 9$, $R_F = C_6F_{13}$).

2. Experimental

2.1. *Materials*

4-Hydroxybenzoic acid (99%), 4′-hydroxybiphenyl-4-carboxylic acid (99%), 3-bromopropene (99%), 11-bromoundec-1-ene (99%), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 99%) and methylchloroformate (99%) were purchased from Aldrich and used as received. 2-(Perfluorohexyl)-ethane-1-thiol was donated by Atofina. Unless otherwise specified the solvents were unpurified reagent grade.

2.2. *Characterization*

Confirmation of the proposed structures of the intermediates and products was obtained using nuclear magnetic resonance (NMR) and mass spectrometry (MS). NMR spectroscopy was carried out using a Brucker AC 200 MHz spectrometer. All spectra were recorded using deuterated solvents with TMS as internal reference for ^{1}H NMR and $CFCl_3$ for ^{19}F NMR. MS was carried out using a Finnigan Matt INCOS 500E mass spectrometer coupled with a gas chromatograph (Varian 3400). The purity of the compounds was determined by thin layer chromatography (TLC) and gas chromatography (GC). Thermal transitions were measured on a Mettler Toledo DSC 821 instrument. Samples of between 5 and 10 mg were placed in aluminium pans and heated in a static nitrogen atmosphere. The heating and cooling rate was $10^\circ C\,min^{-1}$. In all cases, transition temperatures were reported as peak maxima. An Olympus BX 60 polarizing optical microscope, equipped with a Linkam Scientific Instruments LTS 350 heating unit and a TMS 94 temperature control unit, was used to verify thermal transitions and characterize the optical textures.

2.3. *Synthesis*

2.3.1. *4-Allyloxybenzoic acid (**2a-1**)*

To a solution of 4-hydroxybenzoic acid (10 mmol) in water/ethanol (4 ml/11 ml) was added a solution of potassium hydroxide (20 mmol) in water (5 mL). The reaction mixture was stirred at 50°C until the suspension disappeared and then 3-bromopropene (11 mmol) was added slowly and stirred for 12 h. To the resulting precipitate was added a solution of potassium hydroxide (5 mmol) in water (1 mL) and the mixture stirred for 2 h. The reaction mixture was dried under vacuum, and the solid residue acidified with HCl (10%) until pH 3; it was then washed 3 times with water and finally with light petroleum (40–60°C) to yield compound **2a-1** as a white solid (yield 54%). The same procedure was used for the preparation of **2a-9**, **2b-1** and **2b-9** using 11-bromoundec-1-ene or/and 4′-hydroxybiphenyl-4-carboxylic acid as appropriate.

2a-1. ^{1}H NMR (CD_3OD/TMS, δ ppm J Hz): 4.60 (2H, OCH_2CH, dt, $J = 5.3$, $J = 1.5$); 5.25 (1H, $CH = cis$, dd, $J_{cis} = 10.5$, $J = 1.5$); 5.35 (1H, $CH = trans$, dd, $J_{trans} = 17.3$, $J = 1.5$); 6.05 (1H, $CH = gem$, m, $J_{cis} = 10.5$, $J_{trans} = 17.3$, $J = 5.3$); 6.95 ($2H_{ar}$, d, $J = 9.1$), 7.92 ($2H_{ar}$, d, $J = 9.1$), (carboxylic acid H not detected).

2.3.2. *2-(Perfluorohexyl)ethyl-4-allyloxythiobenzoate (**Ph1**)*

To a solution of 4-allyloxybenzoic acid, **2a-1**, (10 mmol), DCC (11 mmol) and DMAP (1 mmol) in freshly distilled dichloromethane (50 mL), 2-(perfluorohexyl)ethane-1-thiol (9 mmol) was added. The reaction mixture was stirred at room temperature for 6 h after which the dicyclohexylurea was filtered off. The solvent was removed under vacuum from the resulting solution and the crude product purified by column chromatography over silica gel using dichloromethane/hexane (3/2) as eluent to give compound **Ph1** as a white solid (yield 80%). The same procedure was used for the preparation of **Ph9**, **B1** and **B9** using **2a-9**, **2b-1** or **2b-9** as appropriate.

Ph1. ^{1}H NMR ($CDCl_3$/TMS, δ ppm J Hz): 2.50 (2H, CF_2CH_2, tt, $J_{HH} = 7.9$, $J_{HF} = 18.6$); 3.28 (2H, CH_2S, t, $J = 7.9$); 4.60 (2H, OCH_2, dt, $J = 5.3$, $J = 1.5$); 5.25 (1H, $CH = cis$, m, $J_{cis} = 10.5$, $J = 1.5$); 5.35 (1H, $CH = trans$, m, $J_{trans} = 17.3$, $J = 1.5$); 6.05 (1H, $CH = gem$, m,

$J_{cis} = 10.5$, $J_{trans} = 17.3$, $J = 5.3$); 6.95 ($2H_{ar}$, d, $J = 9.1$), 7.92 ($2H_{ar}$, d, $J = 9.1$). ^{19}F NMR ($CDCl_3/CFCl_3$, δ ppm), -81.2 (CF_3, m), -115.0 [$(CF_2)_\alpha$, m], -122.3 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.8 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m]. MS (70 eV) *m/z* (%), 521 (0.5); 161 (100); 121 (27.4); 69 (7.7); 41 (51.4). Elemental analysis: calc. for $C_{18}H_{13}F_{13}O_2S$ (540.35) C 40.01, H 2.42, F 45.71, S 5.93; found C 39.98, H 2.46, F 45.68, S 5.87%.

Ph9. ^1H NMR ($CDCl_3$/TMS, δ ppm *J* Hz): 1.31 (12H, $(CH_2)_6CH_2CH_2O$, m); 1.67 (2H, OCH_2CH_2, m); 2.06 (2H, $=CHCH_2$, m); 2.48 (2H, CF_2CH_2, tt, $J_{HH} = 7.9$, $J_{HF} = 18.6$); 3.22 (2H, CH_2S, t, $J = 7.9$); 4.02 (2H, OCH_2, t, $J = 5.8$); 4.92 (1H, $CH = cis$, m, $J_{cis} = 10.5$, $J = 1.5$); 5.03 (1H, $CH = trans$, m, $J_{trans} = 17.3$, $J = 1.5$); 5.83 (1H, $CH = gem$, m, $J_{cis} = 10.5$, $J_{trans} = 17.3$, $J = 5.3$); 6.95 ($2H_{ar}$, d, $J = 9.1$), 7.92 ($2H_{ar}$, d, $J = 9.1$). ^{19}F NMR ($CDCl_3/CFCl_3$, δ ppm), -81.2 (CF_3, m), -115.1 [$(CF_2)_\alpha$, m], -122.3 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.8 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m]. MS (70 eV) *m/z* (%), 633 (0.6); 273 (100); 121 (15.7); 69 (12.0); 41 (42.1). Elemental analysis: calc. for $C_{26}H_{29}F_{13}O_2S$ (652.56) C 47.86, H 4.48, F 37.85, S 4.91; found C 47.91, H 4.46, F 37.79, S 4.84%.

B1. ^1H NMR ($CDCl_3$/TMS, δ ppm *J* Hz): 2.50 (2H, CF_2CH_2, tt, $J_{HH} = 7.9$, $J_{HF} = 18.6$); 3.28 (2H, CH_2S, t, $J = 7.9$); 4.60 (2H, OCH_2, dt, $J = 5.3$, $J = 1.5$); 5.25 (1H, $CH = cis$, m, $J_{cis} = 10.5$, $J = 1.5$); 5.35 (1H, $CH = trans$, m, $J_{trans} = 17.3$, $J = 1.5$); 6.05 (1H, $CH = gem$, m, $J_{cis} = 10.5$, $J_{trans} = 17.3$, $J = 5.3$); 7.02 ($2H_{ar}$, d, $J = 9.0$), 7.57 ($2H_{ar}$, d, $J = 9.0$); 7.64 ($2H_{ar}$, d, $J = 8.8$); 8.00 ($2H_{ar}$, d, $J = 8.8$). ^{19}F NMR ($CDCl_3/CFCl_3$, δ ppm), -81.3 (CF_3, m), -115.1 [$(CF_2)_\alpha$, m], -122.3 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.8 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m]. MS (70 eV) *m/z* (%), 616 (5.1); 575 (1.2); 237 (100); 209 (5.8); 196 (68.1); 119 (2.8); 69 (16.9). Elemental analysis: calc. for $C_{24}H_{17}F_{13}O_2S$ (616.45) C 46.76, H 2.78, F 40.06, S 5.20; found C 46.82, H 2.73, F 40.13, S 5.16%.

B9. ^1H NMR ($CDCl_3$/TMS, δ ppm *J* Hz): 1.32 (12H, $(CH_2)_6CH_2CH_2O$, m); 1.63 (2H, OCH_2CH_2, m); 2.03 (2H, $=CHCH_2$, m); 2.52 (2H, CF_2CH_2, tt, $J_{HH} = 7.9$, $J_{HF} = 18.6$); 3.31 (2H, CH_2S, t, $J = 7.9$); 4.05 (2H, OCH_2, t, $J = 5.8$); 4.93 (1H, $CH = cis$, m, $J_{cis} = 10.5$, $J = 1.5$); 5.03 (1H, $CH = trans$, m, $J_{trans} = 17.3$, $J = 1.5$); 5.81 (1H, $CH = gem$, m, $J_{cis} = 10.5$, $J_{trans} = 17.3$, $J = 5.3$); 7.01 ($2H_{ar}$, d, $J = 9.0$), 7.58 ($2H_{ar}$, d, $J = 9.0$); 7.68 ($2H_{ar}$, d, $J = 8.8$); 8.02 ($2H_{ar}$, d, $J = 8.8$). ^{19}F NMR ($CDCl_3/CFCl_3$, δ ppm), -81.2 (CF_3, m), -115.0 [$(CF_2)_\alpha$, m], -122.4 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.8 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m]. MS (70 eV) *m/z* (%), 728 (4.0); 575 (0.2); 349 (100); 321 (2.1); 196 (21.3); 119 (4.1); 69 (9.2). Elemental analysis: calc. for $C_{32}H_{33}F_{13}O_2S$ (728.66) C 52.75, H 4.56, F 33.89, S 4.40; found C 52.69, H 4.51, F 33.90, S 4.37%.

2.3.3. *4-Methoxycarbonyloxybenzoic acid (**3a**)*

To a slurry of sodium hydroxide (60 mmol) in water (60 mL) which was maintained at $-10°C$, 4-hydroxybenzoic acid (**1a**) (20 mmol) was added with vigorous stirring. Methylchloroformate (40 mmol) was added dropwise maintaining the suspension at a temperature lower than $-5°C$. The reaction mixture was allowed to warm to room temperature and then stirred overnight. The resulting solution was acidified with HCl (10%) to pH 5 with the formation of a thick precipitate. The solid was filtered off, washed with water and dried to yield compound **3a** as a white solid (yield 85%).

3a. ^1H NMR (CD_3OD/TMS, δ ppm *J* Hz): 3.91 (3H, CH_3O, s); 7.31 ($2H_{ar}$, d, $J = 9.0$), 8.09 ($2H_{ar}$, d, $J = 9.0$); the acidic proton was not observed.

2.3.4. *2-(Perfluorohexyl)ethyl-4-methoxycarbonyloxythiobenzoate (**4a**)*

To a solution 4-methoxycarbonyloxybenzoic acid (**3a**) (17 mmol), DCC (19 mmol) and DMAP (0.24 g, 2 mmol) in freshly distilled dichloromethane (85 mL), 2-(perfluorohexyl)ethane-1-thiol (15 mmol) was added. The reaction mixture was stirred at room temperature for 6 h after which the dicyclohexylurea was filtered off. The solvent was removed under vacuum and the crude product purified by column chromatography over silica gel using dichloromethane/*n*-hexane (3/2) as eluent to give **4a** as a white solid (yield 88%).

2.3.5. *2-(Perfluorohexyl)ethyl-4-hydroxythiobenzoate (**5a**)*

Compound **4a** (17 mmol) was dissolved in 10 mL of CH_2Cl_2. The solution was stirred in a mixture of ethanol (10 mL) and ammonia 30% (20 mL) at room temperature for 2 h. The solvent was removed under reduced pressure, and traces of water removed by azeotropic distillation with absolute ethanol to give compound **5a** as white solid (yield 80%).

5a. ^1H NMR (CD_3OD/TMS, δ ppm *J* Hz): 2.48 (2H, $CF_2CH_2CH_2$, tt, $J_{HH} = 8.1$, $J_{HF} = 18.6$); 3.26 (2H, $CF_2CH_2CH_2$, t, $J = 8.1$); 6.90 ($2H_{ar}$, d, $J = 9.0$), 7.90 ($2H_{ar}$, d, $J = 9.0$); the phenolic proton was not observed. ^{19}F NMR ($CDCl_3/CFCl_3$, δ ppm): -81.2 (CF_3, m), -114.9 [$(CF_2)_\alpha$, m], -122.3 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.9 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m].

2.3.6. *2-(Perfluorohexyl)ethyl-4-[4-(allyloxy)-benzoyloxy]thiobenzoate (**PhB1**)*

A solution of 4-allyloxybenzoic acid (**2a-1**) (13 mmol), 2-(perfluorohexyl)ethyl-4-hydroxythiobenzoate (**5a**) (12 mmol), DCC (13 mmol) and DMAP (1 mmol) in freshly distilled dichloromethane (85 mL) was stirred at room temperature for 6 h and the precipitated dicyclohexylurea filtered off. The solvent was removed under

vacuum from the filtrate and the crude product purified by column chromatography over silica gel using dichloromethane/*n*-hexane (3/2) as eluent to give compound **PhB1** as a white solid (yield 80%). The same procedure was used for the preparation of **PhB9** using **2a-9**.

PhB1. ^{1}H NMR ($CDCl_3$/TMS, δ ppm J Hz): 2.50 (2H, CF_2CH_2, tt, $J_{HH} = 8.0$, $J_{HF} = 18.3$); 3.30 (2H, CH_2S, t, $J = 8.0$); 4.60 (2H, OCH_2, dt, $J = 5.3$, $J = 1.5$); 5.35 (1H, $CH = cis$, m, $J_{cis} = 10.5$, $J = 1.5$); 5.45 (1H, $CH = trans$, m, $J_{trans} = 17.3$, $J = 1.5$); 6.07 (1H, $CH = gem$, m, $J_{cis} = 10.5$, $J_{trans} = 17.3$, $J = 5.3$); 7.00 (2H$_{ar}$, d, $J = 9.0$); 7.33 (2H$_{ar}$, d, $J = 8.9$); 8.03 (2H$_{ar}$, d, $J = 8.9$); 8.14 (2H$_{ar}$, d, $J = 9.0$). ^{19}F NMR ($CDCl_3$/$CFCl_3$, δ ppm): -81.2 (CF_3, m), -114.9 [$(CF_2)_\alpha$, m], 122.3 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.8 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m]. MS (70 eV) m/z (%), 660 (0.2); 281 (9.2); 161 (100); 121 (63.1); 77 (15.0); 69 (10.7). Elemental analysis: calc. for $C_{25}H_{17}F_{13}O_4S$ (660.45) C 45.47, H 2.59, F 37.40, S 4.85; found C 45.50, H 2.53, F 37.36, S 4.89%.

PhB9. ^{1}H NMR ($CDCl_3$/TMS, δ ppm J Hz): 1.30 (12H, $(CH_2)_6CH_2CH_2O$, m); 1.64 (2H, OCH_2CH_2, m); 2.04 (2H, $=CHCH_2$, m); 2.52 (2H, CF_2CH_2, tt, $J_{HH} = 8.0$, $J_{HF} = 18.3$); 3.31 (2H, CH_2S, t, $J = 8.0$); 4.07 (2H, OCH_2, t, $J = 5.3$); 4.94 (1H, $CH = cis$, m, $J_{cis} = 10.5$, $J = 1.5$); 5.01 (1H, $CH = trans$, m, $J_{trans} = 17.3$, $J = 1.5$); 5.81 (1H, $CH = gem$, m, $J_{cis} = 10.5$, $J_{trans} = 17.3$, $J = 5.7$); 7.00 (2H$_{ar}$, d, $J = 9.0$); 7.33 (2H$_{ar}$, d, $J = 8.9$); 8.03 (2H$_{ar}$, d, $J = 8.9$); 8.14 (2H$_{ar}$, d, $J = 9.0$). ^{19}F NMR ($CDCl_3$/$CFCl_3$, δ ppm): -81.2 (CF_3, m), -114.9 [$(CF_2)_\alpha$, m], -122.3 [$(CF_2)_\beta$, m], -123.3 [$(CF_2)_\gamma$, m], -123.8 [$(CF_2)_\delta$, m], -126.6 [$(CF_2)_\omega$, m]. MS (70 eV) m/z (%), 772 (0.1); 393 (4.3); 273 (100); 121 (42.1); 77 (2.6); 69 (10.7). Elemental analysis: calc. for $C_{33}H_{33}F_{13}O_4S$ (772.67) C 51.30, H 4.30, F 31.96, S 4.15; found C 51.26, H 4.32, F 32.00, S 4.21%.

3. Results and discussion

3.1. *Synthesis*

The synthesis of the monophenyl and biphenyl compounds (series **Ph** and **B**, respectively) was carried out in two steps (figure 2). The preparation of the carboxylic acid intermediates (**2a**, **2b**) consisted of the reaction of the hydroxy group with the appropriate ω-bromoalk-1-ene in the presence of potassium hydroxide. Thioesterification of **2a** and **2b** with 2-(perfluorohexyl)-ethane-1-thiol was accomplished by the condensation of the carboxylic group with the fluorinated thiol in the presence of *N*,*N*′-dicyclohexylcarbodiimide catalysed by 4-(*N*,*N*-dimethylamino)pyridine.

Preparation of the derivatives with the phenyl benzoate core (series **PhB**) was realized according to the pathway shown in figure 3. The synthesis consisted of

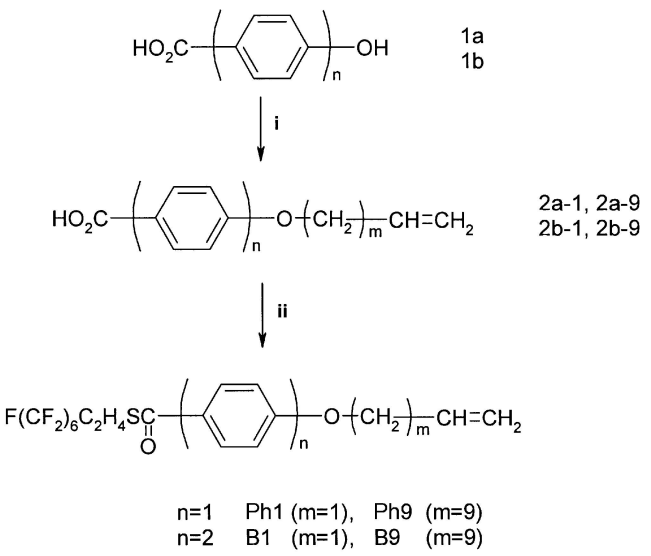

Figure 2. Synthetic route to monophenyl, **Ph1** and **Ph9**, and biphenyl derivatives, **B1** and **B9** (for intermediates: 'a' for $n = 1$, 'b' for $n = 2$). Reagents and conditions: (i) $Br(CH_2)_mCH{=}CH_2$ $m = 1, 9$; KOH, EtOH/H_2O, reflux; (ii) $F(CF_2)_6C_2H_4SH$, DCC, DMAP, CH_2Cl_2, room temperature.

the preparation of the partially fluorinated 4-hydroxy thiobenzoate (**5a**) which was then esterified using DCC and DMAP with the **2a** derivative to give the final product. The thioesterification of 4-hydroxybenzoic acid was accomplished by the protection of the hydroxy substituent of the benzoic acid (**1a**), followed by the thioesterification of the acidic function with a fluorinated thiol, and finally deprotection of the hydroxy group in basic media. The first protecting step used methyl chloroformate. The carbonate group was selected as a suitable protecting function because deprotection occurs under mild conditions tolerated by the thioester linkage [12]. The thioesterification was accomplished using standard methods in the presence of DCC and DMAP. The deprotection with aqueous ammonia (30%) was carried out in ethanol which solvates the different reactants. This proceeded quickly (two hours) and the hydroxy derivative was recovered in good yield. The overall yields of these compounds, are given in the table.

3.2. *Mesomorphic behaviour*

Transitions temperatures (°C) of the target compounds are reported in the table. The mesophases of all members of these series appear as bâtonnets on cooling from the isotropic melt which coalesce to form a well developed fan-shaped texture with focal-conic domains when viewed under the microscope. This texture characteristic of the layered structure of smectic mesophases (figure 4). Miscibility studies carried out using standard materials [13] showed that the phases are mainly of the smectic

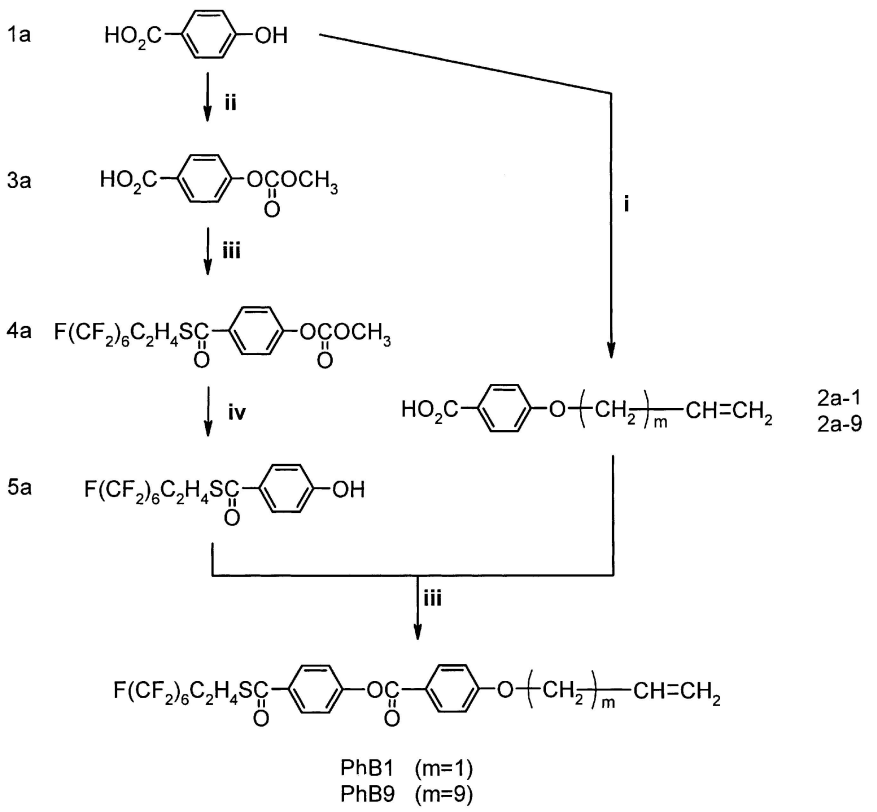

Figure 3. Synthetic route to the phenyl benzoate derivatives (**PhB1**, **PhB9**). Reagents and conditions: (i) $Br(CH_2)_mCH{=}CH_2$ $m = 1, 9$; KOH, $EtOH/H_2O$, reflux; (ii) $CH_3OC(O)Cl$, NaOH $-5°C$ to rt; (iii) $F(CF_2)_6C_2H_4SH$, DCC, DMAP, CH_2Cl_2, rt; (iv) NH_3aq, EtOH, rt.

Table 1. Overall yields and transition temperatures measured on heating for the ω-unsaturated derivatives; enthalpies of transitions ($J\,g^{-1}$) are given in square brackets. Cr, SmX, SmA and I indicate crystal, smectic X, smectic A, and isotropic phases, respectively. Parentheses indicate a monotropic transition (cooling).

		Transition temperatures/°C						
Compound	Yield/%	Cr		SmX		SmA		I
Ph1	43	•	29.3 [39.5]			•	97.8 [14.0]	•
Ph9	49	•	50.3 [19.6]			(•	51.7 [8.0])	•
B1	49	•	138.5 [8.9]			•	226.6 [16.8]	•
B9	35	•	111.7 [8.4]	•	152.8 [1.9]	•	158.8 [7.9]	•
PhB1	26	•	36.3 [11.5]			•	217.6 [14.2]	•
PhB9	30	•	62.8 [26.0]	•	138.0 [2.1]	•	148.8 [12.7]	•

A type. The nature of the mesogenic core strongly influences the liquid crystal behaviour of molecules (figure 5).

Within the allyloxy series (**Ph1**, **B1**, **PhB1**) the monophenyl group gives mesomorphic transitions at lower temperatures in comparison with the homologues containing two aromatic rings. The comparison of the mesomorphic properties of these compounds with previous single-ring structures described in the literature [14–19] is of great interest. In fact the incompatibility of the fluorocarbon chains with both saturated and aromatic hydrocarbons leads to a microsegregation which favours the observation of LC behaviour [20, 21] even in monocyclic derivatives, which would not be expected for the corresponding hydrocarbon series. The presence of two non-miscible segments should induce mesomorphism [22, 23]. Many molecular designs have been explored in order to determine the molecular parameter which promotes enantiotropic behaviour. The compounds described in the literature [14–17] are mainly monotropic in nature, with only few showing enantiotropic phases. The temperature range of the

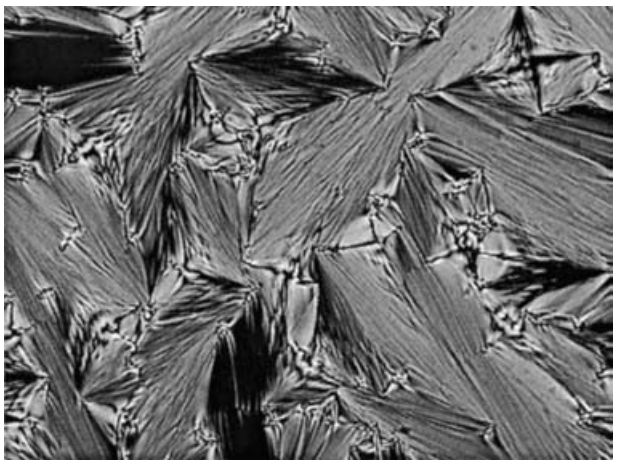

Figure 4. Optical polarizing micrograph of 2-(perfluorohexyl)-ethyl-4-allyloxythiobenzoate (**Ph1**). (×66): $T = 54^{\circ}C$, I → SmA.

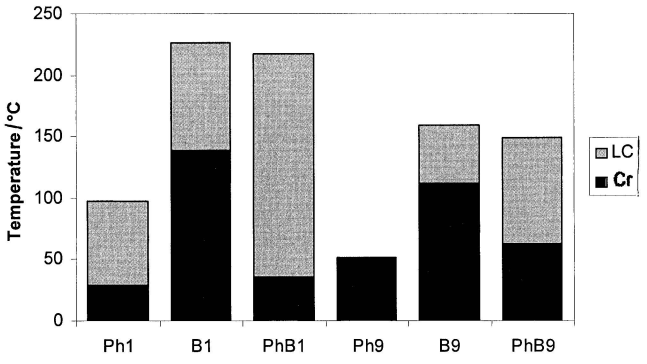

Figure 5. Comparison of the temperature ranges of the mesophases for the compounds **Ph*m***, **B*m***, **PhB*m***.

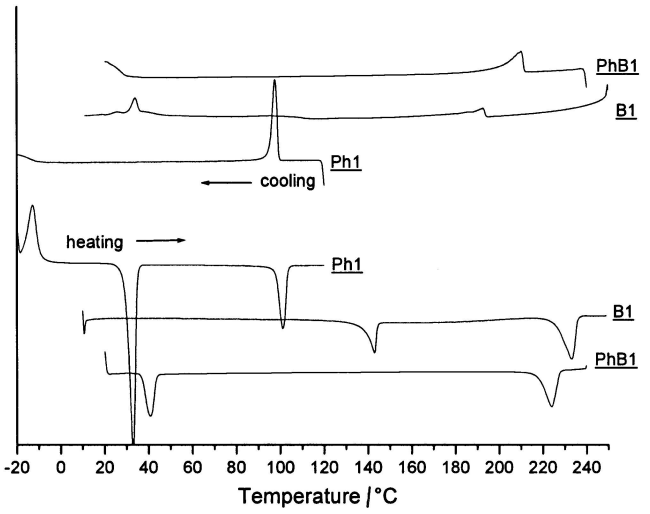

Figure 6. DSC curves for allyloxy compounds **B1** (heating and cooling rate: $10^{\circ}C\ min^{-1}$) and **PhB1** first heating.

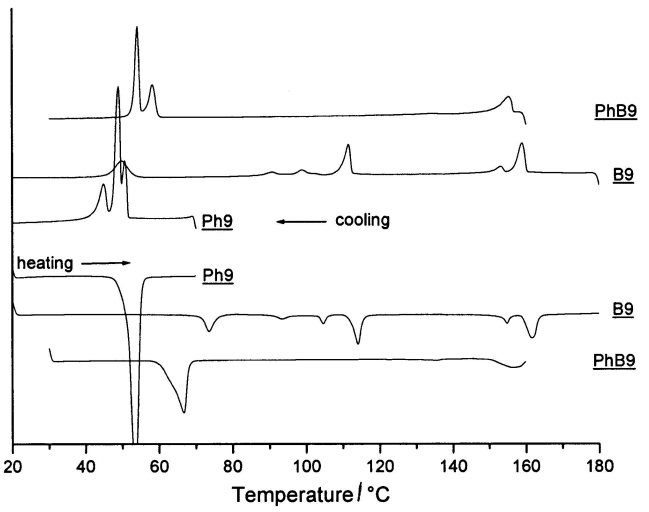

Figure 7. DSC curves for undec-10-enyloxy compounds **B9**, **Ph9** and **PhB9** (heating and cooling rate: $10^{\circ}C\ min^{-1}$).

mesophase is less than 30°C [18, 19]. By comparison, **Ph1** exhibits a mesophase spanning approximately 68°C on heating and more than 100°C on cooling. Indeed the compound requires strong supercooling to crystallize (figure 6) and it remains for at least twelve hours in the mesophase at room temperature. The key to obtaining these impressive physical properties is the presence of the thioester functionality [24]. The biphenyl core (**B1**) leads to the shift of the mesophase to higher temperatures but with the temperature range essentially unchanged; the phenyl benzoate group actually stabilizes the mesophase over a wider range (181°C). **B1** and **PhB1** exhibit high clearing temperatures accompanied by structure modifications and thus is irreversible. Observations using POM seems to show a slow degradation at these temperatures; this has been confirmed by thermogravimetric measurements. The introduction of the spacer containing nine methylene units between the core and the double bond greatly decreases the liquid crystalline character (figure 7); this is evident in the case of the monophenyl derivative (**Ph9**) which is monotropic nature (the mesophase appears for 1–2°C on cooling). The compounds with two aromatic rings do not show the thermal instability of the allyloxy derivatives. These structures show an enantiotropic polymorphism which is evident in calorimetry and microscopic observations. This phenomenon is particularly interesting for the **B9** which shows several transitions, some below the melting point. POM confirmed the existence of mesomorphic transitions; for example from SmA to SmX at 152°C; see figures 8(*a*) and 8(*b*).

4. Conclusion

Three series of ω-unsaturated compounds containing a linear perfluorinated chain and differing rigid cores were synthesized. For all the compounds, increasing the

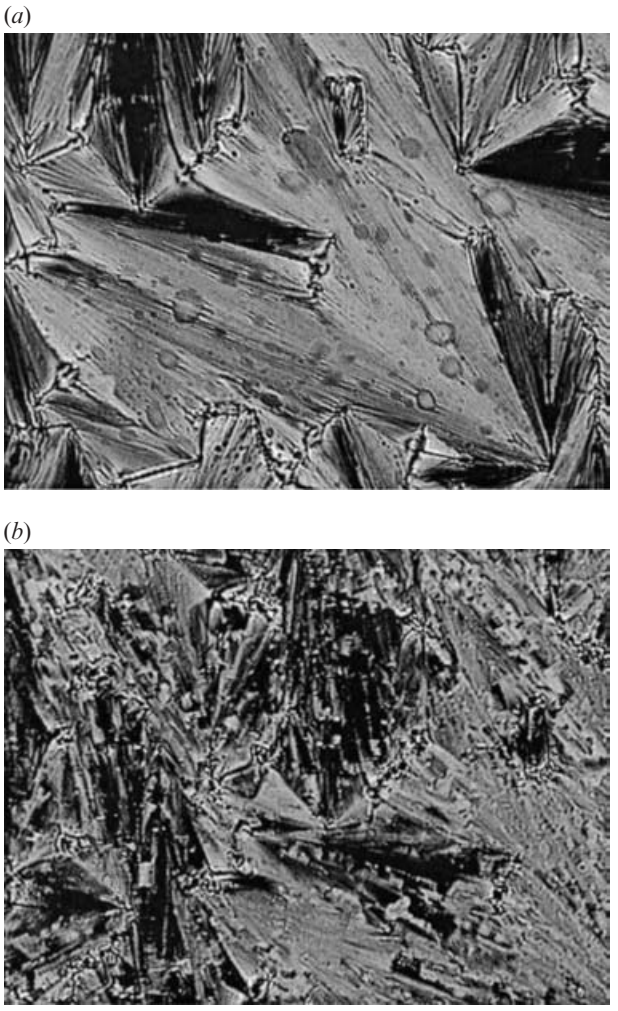

Figure 8. Optical polarizing micrograph of 2-(perfluorohexyl) ethyl-4-[4-(undec-10-enyloxy)phenyl]thiobenzoate (**B9**). (×66), (*a*) $T = 156^{\circ}$C, I → SmA; (*b*) $T = 151^{\circ}$C, SmA → SmX.

length of the hydrocarbon chain reduces the mesomorphic character. The monophenyl allyloxy derivative shows interesting smectogenic enantiotropic character near room temperature. The compounds with two rings have higher temperature transitions, and the presence of a long hydrocarbon chain introduces polymorphism. These wide mesomorphic temperature ranges highlight the significant influence of the thioester link within this class of compound. Furthermore, this supports the fundamental interest in the use of fluorinated chains for the easy access to less expensive mesogenic cores. The enantiotropic behaviour showed by all the molecules, and how this is modified by polymerization, now provides intriguing reasons for obtaining the corresponding side chain liquid crystalline polymers.

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