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Giulia Fornasieri[a]; Frédéric Guittard Corresponding author[a]; Serge Géribaldi[a]
[a] Laboratoire de Chimie des Matériaux Organiques et Métalliques, Faculté des Sciences, Université de Nice-Sophia Antipolis, 06108 Nice Cedex 2, France

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Nitro and bromo derivatives of a highly fluorinated thiobenzoate

GIULIA FORNASIERI, FRÉDÉRIC GUITTARD* and SERGE GÉRIBALDI

Laboratoire de Chimie des Matériaux Organiques et Métalliques, Faculté des Sciences, Université de Nice-Sophia Antipolis, Parc Valrose, 06108 Nice Cedex 2, France

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Several compounds derived from monosubstituted thiobenzoates, with substituents in the *meta*- or *para*-position, have been prepared; these contain a thioester spacer between a semifluorinated chain and the rigid core unit. The substituent is either a bromo or a nitro group. Their mesomorphic properties were evaluated using polarizing optical microscopy and differential scanning calorimetry. The influence of the different substituents on the phenyl core was considered. No mesomorphic behaviour was seen except for one nitro derivative. The introduction of the nitro group in the *para*-position of the thiobenzoate core leads to a LC transition on heating. As with previous studies, these results show that substitution at the 4 position on a monophenyl core can lead to liquid crystallinity, whereas substitution in the *meta*-position does not; this supports the view that meta-substitution is not a necessary condition for obtaining a LC phase.

1. Introduction

In the development of liquid crystal materials [1], the introduction of fluorine [2] either in the core [3] or in the chains [e.g. 4] attracts considerable research effort. The introduction of a highly fluorinated chain on conventional calamitic liquid crystals [5] often gives unexpected properties when compared with the hydrocarbon analogue; for example, the development of monophenyl structures which show LC character without hydrogen bonding [6–13]. This behaviour can be explained by strong amphiphilic character [14] (in our case the strong incompatibility between the fluorocarbon and the hydrocarbon moiety) leading to microphasic separation favourable for the appearance of a liquid crystalline phase from lyotropic [15] or thermotropic behaviour [16]. However, it is worth noting that introducing a perfluorinated chain does not lead systematically to mesomorphic properties. The careful choice of the connector binding the fluorinated chain to the rigid core can affect the thermal range of the mesophase.

The present work is focused on monophenyl derivatives with nitro or bromo substituents in the 3- or 4-positions of a semifluoroalkylthiobenzoate moiety. The introduction of a single ring as the mesogenic core is of great interest for the development of low cost LC materials due to the fluorophobic effect. In fact, the choice of spacer binding the fluorinated chain to the mesogenic core can govern the LC character; the liquid crystal character can therefore be tuned by appropriate molecular design. This can be illustrated from reports on a series of partially fluorinated 4-biphenyl derivatives [17–20] showing that the introduction of an incompatible fragment, such as a perfluorinated chain and aromatic moiety, does not lead systematically to mesomorphic behaviour. The presence of a highly fluorinated chain in a calamitic structure, for example, can produce segregation into distinct microdomains favourable for the formation of a well organized phase. In our case, the compounds synthesized are of the thiobenzoate type. The choice of connector is related to previous studies showing that ester, imine and thioester induce mesomorphic behaviour over a wide range of temperatures. In particular the thioester derivative shows the widest smectic range (100°C) [21]. Therefore in this work we focus on a series of monophenyl compounds linked by a thioester connector to the aromatic core which has a nitro or bromo substituent in the 3- or 4-position. The mesomorphic behaviour of all the compounds has been studied by a combination of differential thermal analysis and polarized light microscopy experiments. The influence of the nature of substituents and their position in the rigid core on the LC properties will be discussed.

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*Author for correspondence; e-mail: guittard@unice.fr

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2. Experimental

2.1. *Characterization*

Confirmation of product structures was obtained by nuclear magnetic resonance (NMR) and mass spectrometry (MS). NMR spectroscopy was carried out using a Bruker AC 200 MHz spectrometer. All spectra were recorded using $CDCl_3$ as solvent, with Me_4Si as internal reference for ^1H 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-phase chromatography (GPC). Melting points were determined using a Büchi Tottoli apparatus.

Initial phase assignments and corresponding transition temperatures were determined using an Olympus BX60 polarizing microscope equipped with crossed polarizers and a Linkam TMS 94 – LTS 350 hot stage. Smectic to isotropic phase transition temperatures (clearing temperature) and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Perkin-Elmer PC series DSC7 calorimeter equipped with a TAC 7/DX thermal analysis controller from 25 to 190°C. Heating and cooling curves were obtained at a rate of $10^{\circ}C\,min^{-1}$; Zn and In were used as calibration standards. In all cases, transition temperatures are reported at the maxima and minima of the endothermic and exothermic peaks.

2.2. *Materials*

3-Nitrobenzoic acid (99%), 4-nitrobenzoic acid (98%), 3-bromobenzoic acid (98%), 4-bromobenzoic acid (98%), *N,N′*-dicyclohexylcarbodiimide (DCC, 99%) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 99%) were purchased from Aldrich and used as received. 2-(Perfluorohexyl)ethane-1-thiol, obtained from Atofina, was used as received. Unless specified the solvents were of unpurified reagent grade.

2.3. *Synthesis*

2.3.1. *2-(Perfluorohexyl)ethyl 3-nitrothiobenzoate (**A**) and 2-(perfluorohexyl)ethyl 4-nitrothiobenzoate (**B**)*

To a solution of 3-nitrobenzoic acid or 4-nitrobenzoic acid (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, and 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/hexane (3/2) as eluant to give a white solid (yields: **A** 93%; **B** 90%). For **A**: ^1H NMR ($CDCl_3/Me_4Si$ δ ppm, J Hz): 2.54 (2H, CF_2CH_2, tt, $J_{HH}=7.40$, $J_{HF}=18.30$); 3.38 (2H, CH_2S, t, $J=7.40$); 7.70 ($1H_{ar}$, t, $^3J=8.00$); 8.27 ($1H_{ar}$, ddd, $^3J=8.00$, $^4J=1.85$, $^4J=1.10$); 8.46 ($1H_{ar}$, ddd, $^3J=8.00$, $^4J=1.85$, $^4J=1.10$); 8.78 ($1H_{ar}$, t, $^4J=1.85$). ^{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* (%): 529 $[M]^+$ (0.1), 150 $[O_2NC_6H_4CO]^+$ (57), 119 $[CF_3CF_2]^+$ (10.3), 104 $[C_6H_4CO]^+$ (100), 69 $[CF_3]^+$ (19.8). For **B**: ^1H NMR ($CDCl_3/Me_4Si$ δ ppm, J Hz): 2.54 (2H, CF_2CH_2, tt, $J_{HH}=7.40$, $J_{HF}=18.30$); 3.38 (2H, CH_2S, t, $J=7.40$); 8.12 ($2H_{ar}$, d, $^3J=8.20$); 8.32 ($2H_{ar}$, d, $^3J=8.20$). ^{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* (%): 529 $[M]^+$ (0.5), 150 $[O_2NC_6H_4CO]^+$ (100), 119 $[CF_3CF_2]^+$ (4.1), 104 $[C_6H_4CO]^+$ (90.5), 69 $[CF_3]^+$ (14.5).

2.3.2. *2-(Perfluorohexyl)ethyl 3-bromothiobenzoate (**C**) and 2-(perfluorohexyl)ethyl 4-bromothiobenzoate (**D**)*

To a solution of 3-bromobenzoic acid or 4-bromobenzoic acid (15 mmol), DCC (16 mmol) and DMAP (1.5 mmol) in freshly distilled dichloromethane (70 ml), 2-(perfluorohexyl)ethane-1-thiol (14 mmol) was added. The reaction mixture was stirred at room temperature for 5 h and 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/hexane (3/2) as eluant to give a white solid (yields: **C** 96%; **D** 95%). For **C**: ^1H NMR ($CDCl_3/Me_4Si$ δ ppm, J Hz), 2.53 (2H, CF_2CH_2, tt, $J_{HH}=7.40$, $J_{HF}=18.30$); 3.30 (2H, CH_2S, t, $J=7.40$); 7.35 ($1H_{ar}$, t, $^3J=7.90$); 7.73 ($1H_{ar}$, ddd, $^3J=7.90$, $^4J=1.70$, $^4J=1.05$); 7.89 ($1H_{ar}$, ddd, $^3J=7.90$, $^4J=1.70$, $^4J=1.05$); 8.08 ($1H_{ar}$, t, $^4J=1.70$). ^{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* (%): 562 564 $[M]^+$ (0.2 0.2); 183 185 $[BrC_6H_4CO]^+$ (58.0 57.2), 155 157 $[BrC_6H_4]^+$ (34.0 34.7), 119 $[CF_3CF_2]^+$ (10.3), 104 $[C_6H_4CO]^+$ (100), 69 $[CF_3]^+$ (29.3). For **D**, ^1H NMR ($CDCl_3/Me_4Si$ δ ppm, J Hz), 2.53 (2H, CF_2CH_2, tt, $J_{HH}=7.40$, $J_{HF}=18.30$); 3.30 (2H, CH_2S, t, $J=7.40$); 7.61 ($2H_{ar}$, d, $^3J=7.80$); 7.81 ($2H_{ar}$, d, $^3J=7.80$). ^{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* (%): 562 564 $[M]^+$ (0.5 0.5), 183 185 $[BrC_6H_4CO]^+$ (100

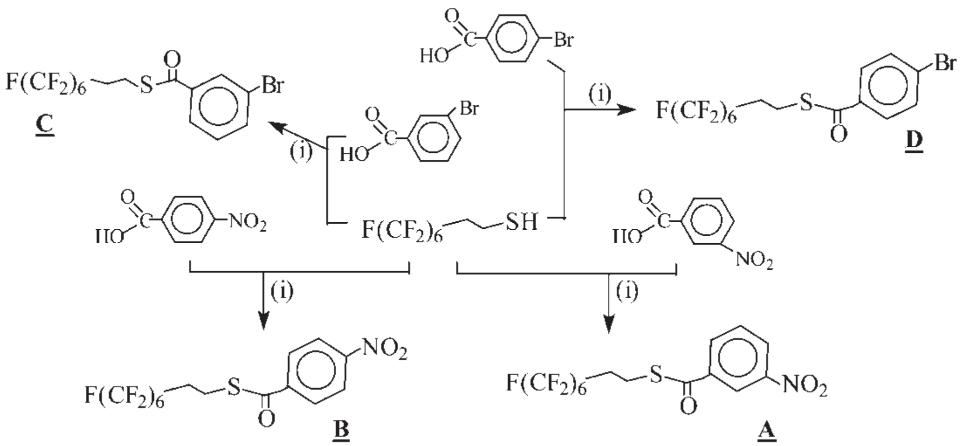


Figure 1. Synthetic route to 2-(perfluorohexyl)ethyl 3- or 4-nitro(bromo)thiobenzoates (**A**–**D**). Reagents and conditions: (i) $F(CF_2)_6C_2H_4SH$, DCC, DMAP, CH_2Cl_2, room temperature.

98.0), 155 157 $[BrC_6H_4]^+$ (44.0, 44.7), 119 $[CF_3CF_2]^+$ (6.7); 104 $[C_6H_4CO]^+$ (23.5), 69 $[CF_3]^+$ (25.1).

3. Results and discussion

3.1. *Synthesis*

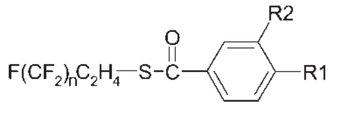
All the compounds were prepared from 2-(perfluorohexyl)ethane-1-thiol. Preparation of the target compounds was carried out in one step from 3- or 4-nitro(bromo)benzoic acid starting materials. The thioester function was formed through the reaction of the substituted benzoic acid with 2-(perfluorohexyl)-ethane-1-thiol in the presence of DCC and DMAP. The synthetic pathway is represented in figure 1. All the compounds are colourless and chemically stable. Yields are collected in table 1.

3.2. *Thermal and optical characterization*

All the derivatives prepared (**A**–**D**) were studied by polarizing optical microscopy and differential (DSC). The bromo derivatives **C** and **D** did not exhibit mesomorphic behaviour. The introduction of a nitro substituent induced a different behaviour according to its position (3 or 4) on the aromatic ring. This differing behaviour can be correlated with previous reports [6–13]. In fact observation by microscopy of the 2-(perfluorohexyl)ethyl 4-nitrothiobenzoate **B** showed the appearance of a mesophase. We should note that there is no indication of thermal instability during the experiments. Traces of solvent, which can contribute to a lyotropic behaviour, are not present. This behaviour is reproducible after further heating–cooling cycles.

The DSC curve for **B** is shown in figure 2 and confirms this mesomorphic behaviour by the observation of the splitting of the peak on heating. The

Table 1. Yields of the monophenyl derivatives **A**–**D**.



Compound	*n*	*R*1	*R*2	m.p./°C[a]	Yield/%
A	6	H	NO_2	68	93
B	6	NO_2	H	88	90
C	6	H	Br	33	96
D	6	Br	H	63	95

[a]From a Büchi Tottoli apparatus (±1°C).

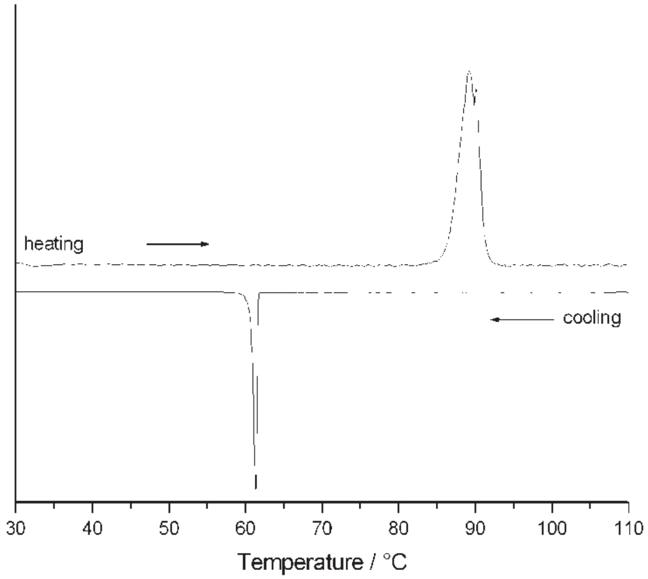
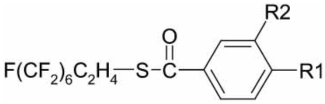


Figure 2. DSC curves for 2-(perfluorohexyl)ethyl 4-nitrothiobenzoate **B** on heating and cooling (scanning rate: $10°C\,min^{-1}$).

Table 2. Transition temperatures observed for the nitro and bromo derivatives **A**–**D**; enthalpies of transition ($J\,g^{-1}$) in square brackets.



			Transition temperatures/°C				
Compound	*R*1	*R*2	Cr		SmX		I
A	H	NO_2	•	67.1 [58.3]			•
B	NO_2	H	•	87.6 [62.2][b]	•	89.9[a]	•
C	H	Br	•	32.9[a]			•
D	Br	H	•	62.3 [45.4]			•

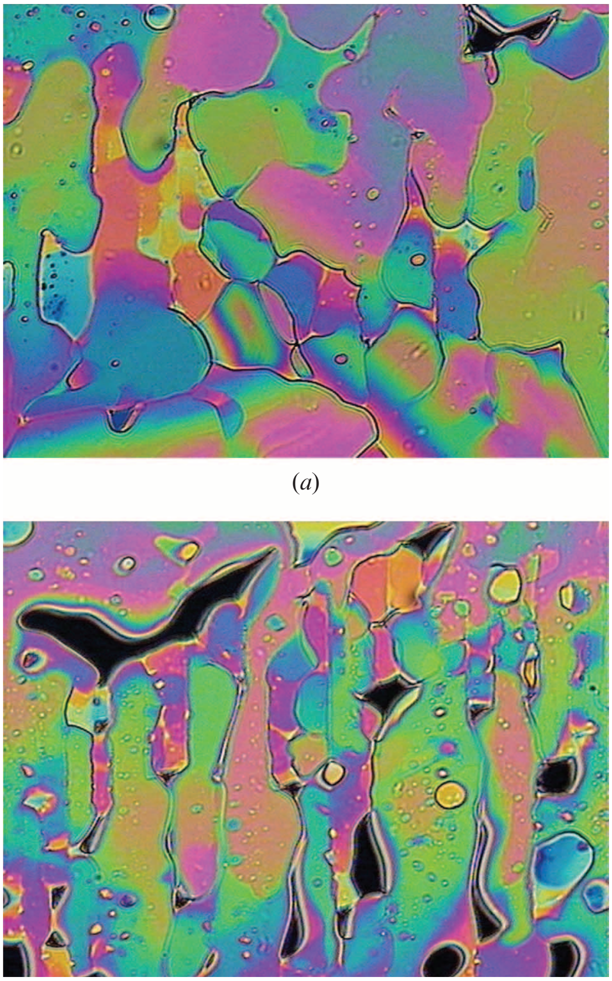
Cr, SmX and I indicate crystal, smectic X and isotropic phases, respectively.

[a] Transitions observed from optical microscopy.

[b] Corresponds to the sum of melting and clearing transition enthalpies.

transition temperatures are reported in table 2. However, DSC traces measured on different thermal cycles starting from a temperature of 25°C with different scanning rates (1–10°C min^{-1}) do not lead to the total splitting of melting and clearing peaks. As a consequence the recorded enthalpy corresponds to the sum of these two transitions. We observe also that changing the substituent position in the nitro and bromo series, leads to a decrease of the melting temperatures which can be used in further developments to obtain room temperature LC transitions. In fact, the literature reports many examples of monophenyl derivatives with a long perfluoroalkyl group, and one or two substituents (including the nitro group) in *ortho*-, *meta*- or *para*-positions [6–13]. Nevertheless all these compounds are only slightly enantiotropic in nature and essentially monotropic. It appears that substitution in the *meta*-position, or a ratio between hydro- and fluoro-methylene units less than unity, seems to be important for the appearance of a LC phase. This present work also confirms [7, 9] that 3-substitution in a phenyl core is not a necessary condition [6, 11] for the appearance of liquid crystal character within monophenyl series.

By optical observation, the mesophase of **B** seems to be a smectic phase but does not appear as bâtonnets on cooling from the normal isotropic liquid and does not coalesce to form a well developed fan-shaped texture. The miscibility studies carried out using standard materials [22] developed in this laboratory show that the phase described is not of the smectic A or crystal E type. The characteristic textures of phases observed are illustrated in figure 3.



(*a*)

(*b*)

Figure 3. Optical polarizing micrograph displayed by 2-(perfluorohexyl)ethyl 4-nitrothiobenzoate **B** (66×): (*a*) $T=89^\circ C$, Cr→SmX; (*b*) $T=89.9^\circ C$ SmX→I (clearing temperature).

4. Conclusion

In this paper we describe the synthesis and evaluation of mesomorphic properties of a new class of semifluorinated thiobenzoate derivatives bearing a nitro or bromo substituent in the 3- or 4-position on the aromatic core. From optical microscopy and differential scanning calorimetry, only the 4-nitro compound exhibits a smectic LC phase. As with previous studies [6–13], this work shows that liquid crystalline behaviour can be obtained from substitution in the *para*-position and also that substitution in the *meta*-position is not a necessary condition for obtaining a LC phase. Thus, the development of liquid crystals having a single benzene ring core represents an interesting challenge and could be useful because it shows the potential to access low cost materials and leads to products with liquid crystalline transitions at lower temperatures [23].

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