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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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### Study of the influence of ester orientation on the thermal stability of the smectic C phase: experimental investigation

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**To cite this Article** Vadnais, Richard , Beaudoin, Marc-André , Beaudoin, Alexandre , Heinrich, Benoît and Soldera, Armand(2008) 'Study of the influence of ester orientation on the thermal stability of the smectic C phase: experimental investigation', *Liquid Crystals*, 35: 3, 357 – 364

**To link to this Article:** DOI: 10.1080/02678290701851689

**URL:** <http://dx.doi.org/10.1080/02678290701851689>

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## Study of the influence of ester orientation on the thermal stability of the smectic C phase: experimental investigation

Richard Vadnais<sup>a</sup>, Marc-André Beaudoin<sup>a</sup>, Alexandre Beaudoin<sup>a</sup>, Benoît Heinrich<sup>b</sup> and Armand Soldera<sup>a\*</sup>

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(Received 16 October 2007; final form 7 December 2007)

Two series of mesogenic molecules of variable terminal chain lengths have been synthesised and characterised. The molecules feature a tolane-based rigid core surrounded by two esters groups. The two series differ from each other only by the orientation of an ester linker. Their mesogenic properties have been characterised and are reported. It is found that the orientation of the ester linker and the length of the terminal chain greatly influence their polymorphism. Binary mixtures of the two series have been prepared and their phase diagrams are also reported. They offer some insight at the role of the side chains in the formation of the S<sub>C</sub> phase.

**Keywords:** ester orientation; binary mixture; phase diagram; polymorphism

### 1. Introduction

Relationships among ester orientation inside the rigid core, the terminal chain length and the temperature range of smectic phases have been studied on molecules with rigid cores containing one (1) and two (2–5) ester groups. Seto et al. (6) studied the influence of the direction of the ester group inside the rigid core, compared with the direction of the ester group at the boundary of the core, the two esters being separated by a tolane moiety. In all of the aforementioned cases, the S<sub>A</sub> phase is always exhibited whatever the direction of each ester group, while the S<sub>C</sub> phase appears when the central ester is in the opposite direction to the terminal ester (anti-parallel arrangement). However, other molecules bearing two esters groups separated by a tolane moiety actually exhibit the opposite behaviour. That is, these molecules exhibit the S<sub>C</sub> phase when the two esters are in a parallel arrangement (7, 8).

In this article we further investigate the influence of the ester arrangement on the thermal stability of the mesophase (mainly S<sub>C</sub> and S<sub>A</sub>). Two new series of molecules have been synthesised. Each series differs by the orientation of an ester group inside the rigid core. The great importance of the orientation of the ester group in the S<sub>C</sub> phase formation was found in our compounds.

The molecules presented in this paper bear a benzoate and tolane rigid core with alkoxy side chains (Figure 1). For ease of reading, the molecules are referred to as the *p*-CooT-*n* and the *p*-ooCT-*n* series, the former having a parallel ester arrangement and the latter having an anti-parallel ester arrangement. The liquid crystal behaviour of the benzoate

compounds is determined from the direction of the rigid core ester group and the length of lateral chains. The polymorphism of each pure compound has been determined as well as the binary mixture phase diagram for the homologues of the two series with equal terminal chain length.

### 2. Experimental

#### 2.1. Synthesis

Triethylamine was distilled and dried with sodium hydroxide. DCM was dried with calcium hydride and distilled. Nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were obtained with a Bruker AC-300 NMR spectrometer in deuterated chloroform. The mass of each liquid crystal used for the preparation of binary mixtures was determined with a Mettler AE240 ± 0.01 mg precision scale.

The general procedure for the synthesis of the mesogens *p*-CooT-*n* and *p*-ooCT-*n* is schematised in Figure 2. The synthesis of the molecule **3** is controlled to prevent the formation of dialkoxybenzene. The synthesis of *p*-alkyloxybenzoic acid proposed by Heinrich (9) was used. It differs from other procedures reported in the literature. The synthesis of *p*-alkyloxyphenol, **3**, was carried out using the procedure given by Neubert et al. (10). The ester condensation reactions were made via the well-known DCC/DMAP protocol (11). The Sonogashira coupling reaction (12) used in the synthesis of the intermediate **6** and the final molecules is frequently used for the preparation of liquid crystals with a tolane moiety in the rigid core.

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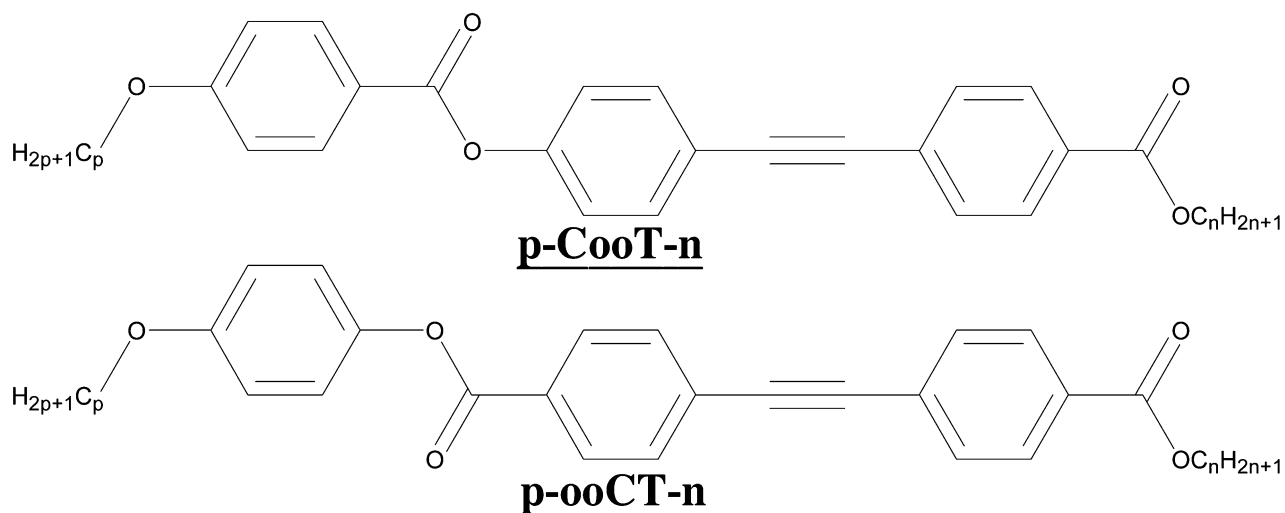


Figure 1. Molecule series *p-CooT-n* and *p-ooCT-n* with  $p=6, 8, 10$  and  $12$ ,  $n=6, 8, 10$  and  $12$ . For symmetric *p-CooT-n* and *p-ooCT-n*,  $p, n=6, p, n=8, p, n=10, p, n=12$ . For asymmetric *p-CooT-n* and *p-ooCT-n*,  $p=8, n=12$  and  $p=12, n=8$ .

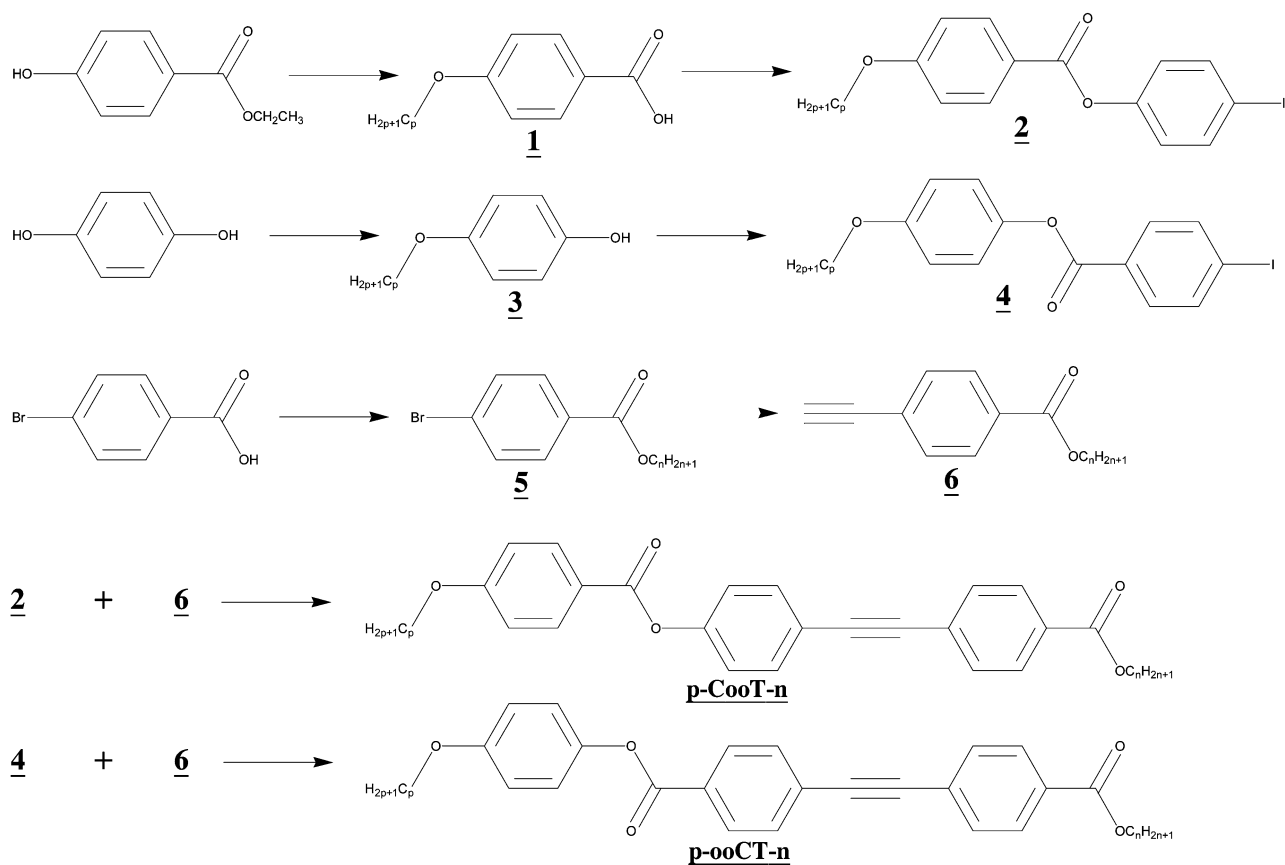


Figure 2. Synthesis scheme of the *p-CooT-n* and *p-ooCT-n* series of mesogens. For molecules 1 to 6,  $p=6, 8, 10$  and  $12$ ,  $n=6, 8, 10$  and  $12$ . For symmetric *p-CooT-n* and *p-ooCT-n*,  $p, n=6, p, n=8, p, n=10, p, n=12$ . For asymmetric *p-CooT-n* and *p-ooCT-n*,  $p=8, n=12$  and  $p=12, n=8$ .

### 2.1.1. Synthesis of *p*-alkyloxybenzoic acid (**1**)

A typical procedure for the synthesis of *p*-hexyloxybenzoic acid, **1a**, is presented first. To a 250 ml single-neck flask equipped with a condenser we added 5.91 g (36.0 mmol) of *n*-1-bromohexane, 6.58 g (39.6 mmol) of *p*-bromobenzoic acid ethyl ester, 1.73 g (43.2 mmol) of sodium hydroxide and 100 ml of ethanol. This mixture was stirred with a magnetic stirrer and refluxed for 24 h. The solution was cooled and a solution of 5 g of sodium hydroxide in 75 ml of water was added for the hydrolysis of the ester. The solution was stirred for 30 min and was acidified with concentrated HCl. The precipitate was filtered out, dissolved in ethyl acetate and filtered again to remove the sodium salts. The organic solution was washed with three parts of water, dried with anhydrous magnesium sulphate and evaporated under reduced pressure. Recrystallisation from a 5:1 solution of ethanol and water yielded 5.76 g of needle-like white crystals (72% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.90 (t, 3H, *J*=6.4 Hz), 1.25–1.75 (m, 6H), 1.81 (q, 2H, *J*=6.9 Hz), 4.02 (t, 2H, *J*=6.5 Hz), 6.93 (d, 2H, *J*=8.9 Hz), 8.05 (d, 2H, *J*=8.9 Hz). The other homologues, **1b** (*p*-octyloxybenzoic acid), **1c** (*p*-decyloxybenzoic acid) and **1d** (*p*-dodecyloxybenzoic acid), were prepared using the same method with respective yields of 96%, 85% and 89%. The <sup>1</sup>H NMR spectra of these molecules are similar, except for the aliphatic peak at  $\delta$ =1.25–1.75 ppm, depending on the number of aliphatic protons.

### 2.1.2. Synthesis of *p*-alkyloxybenzoic acid *p*-iodophenyl ester (**2**)

A typical procedure for the synthesis of *p*-hexyloxybenzoic acid *p*-iodophenyl ester, **2a**, is presented first. To a dry 250 ml flask we added 4.16 g (20.2 mmol) of DCC, 0.21 g (1.7 mmol) of DMAP, 3.89 g of the acid **1a** (17.5 mmol) and 75 ml of distilled DCM. The system was flushed with nitrogen and a solution of 4.05 g (18.4 mmol) of *p*-iodophenol in 25 ml of DCM was added slowly under magnetic stirring. After 4 h, the solution was filtered to eliminate the 1,3-dicyclohexyl urea. The solution was washed with water and brine and then dried with anhydrous magnesium sulphate. The solvent was evaporated and the purification was made by recrystallisation from ethanol. A mass of 6.93 g of fine white crystals was obtained (87% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.88 (t, 3H, *J*=6.6 Hz), 1.25–1.75 (m, 6H), 1.82 (q, 2H, *J*=8.0 Hz), 4.04 (t, 2H, *J*=6.6 Hz), 6.95 (d, 2H, *J*=8.5 Hz), 6.98 (d, 2H, *J*=8.5 Hz), 7.71 (d, 2H, *J*=9.1 Hz), 8.11 (d, 2H, *J*=9.1 Hz). The other homologues, **2b** (*p*-octyloxybenzoic acid *p*-iodophenyl ester), **2c** (*p*-decyloxybenzoic acid *p*-iodophenyl

ester) and **2d** (*p*-dodecyloxybenzoic acid *p*-iodophenyl ester), were prepared using the same method with respective yields of 91%, 76% and 87%. The <sup>1</sup>H NMR spectra of these molecules are similar, except for the aliphatic peak at  $\delta$ =1.25–1.75 ppm, depending on the number of aliphatic protons.

### 2.1.3. Synthesis of *p*-iodobenzoic acid *p*-alkyloxyphenyl ester (**4**)

A typical procedure for the synthesis of *p*-iodobenzoic acid *p*-hexyloxyphenyl ester, **4a**, is presented first. To a dry 250 ml flask we added 5.62 g (27.2 mmol) of DCC, 0.29 g (2.4 mmol) of DMAP, 4.60 g of product **3a** (23.7 mmol) and 75 ml of distilled DCM. The system was flushed with nitrogen and a solution of 6.17 g (24.9 mmol) of *p*-iodobenzoic acid in 25 ml of DCM was added slowly under magnetic stirring. The rest of the synthesis proceeded as for the *p*-alkyloxybenzoic acid *p*-iodophenyl esters, **2**. The yield was 74%, giving 5.53 g of white needle-like crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.88 (t, 3H, *J*=6.3 Hz), 1.25–1.60 (m, 4H), 1.79 (q, 2H, *J*=7.6 Hz), 3.95 (t, 2H, *J*=6.6 Hz), 6.92 (d, 2H, *J*=8.8 Hz), 7.09 (d, 2H, *J*=8.8 Hz), 7.87 (d, 2H, *J*=10.7 Hz), 7.90 (d, 2H, *J*=10.7 Hz). The other homologues, **4b** (*p*-iodobenzoic acid *p*-octyloxyphenyl ester), **4c** (*p*-iodobenzoic acid *p*-decyloxyphenyl ester) and **4d** (*p*-iodobenzoic acid *p*-dodecyloxyphenyl ester), were prepared using the same method with respective yields of 91%, 76% and 87%. The <sup>1</sup>H NMR spectra of these molecules are similar, except for the aliphatic peak at  $\delta$ =1.25–1.60 ppm, depending on the total number of aliphatic protons.

### 2.1.4. Synthesis of *p*-iodobenzoic acid alkyl ester (**5**)

A typical procedure for the synthesis of *p*-iodobenzoic acid hexyl ester, **5a**, is presented first. To a dry 250 ml flask we added 5.21 g (25.3 mmol) of DCC, 0.26 g (2.1 mmol) of DMAP, 4.44 g of *p*-iodobenzoic acid and 75 ml of distilled DCM. The system was flushed with nitrogen and a solution of 2.15 g (21.0 mmol) of *n*-1-hexanol in 25 ml of DCM was added slowly under magnetic stirring. The rest of the synthesis proceeded as for the *p*-alkyloxybenzoic acid *p*-iodophenyl esters, **2**, except for the purification that was made by flash chromatography using a 10% ethyl acetate in hexane eluent. A total of 4.84 g (81% yield) of yellowish liquid was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.87 (t, 3H, *J*=7.2 Hz), 1.25–1.65 (m, 4H), 1.75 (q, 2H, *J*=7.0 Hz), 4.30 (t, 2H, *J*=6.7 Hz), 7.58 (d, 2H, *J*=8.5 Hz), 7.90 (d, 2H, *J*=8.5 Hz). The other homologues, **5b** (*p*-iodobenzoic acid octyl ester), **5c** (*p*-iodobenzoic acid decyl ester) and **5d**

(*p*-iodobenzoic acid dodecyl ester), were prepared using the same method with respective yields of 75%, 87% and 88%. The  $^1\text{H}$  NMR spectra of these molecules are similar, except for the aliphatic peak at  $\delta=1.25\text{--}1.65$  ppm which depends on the total number of aliphatic protons.

### 2.1.5. Synthesis of *p*-acetylenylbenzoic acid alkyl ester (**6**)

A typical procedure for the synthesis of *p*-acetylenylbenzoic acid hexyl ester, **6a**, is presented first. To a dry 50 ml flask we added 1.79 g (6.29 mmol) of **5a**, 15 ml of distilled triethylamine, 24 mg (0.13 mmol) of copper (I) iodide and 145 mg of tetrakis(triphenylphosphine)palladium(0). The flask was closed with a rubber septum. The system was flushed with nitrogen and 0.93 g (9.4 mmol) of trimethylsilylacetylene was added under magnetic stirring. The mixture was stirred for 24 h at 40°C. After the first reaction was over, 2.6 ml of a 75% (w/w) tetrabutylammonium fluoride solution in water was added to unprotect the product from the silane moiety. After 30 minutes, the solvent was evaporated under reduced pressure and the resulting mixture was dissolved in DCM and filtered. The organic phase was washed with a 0.5 N HCl aqueous solution, dried over anhydrous magnesium sulphate and evaporated. The acetylenic compound was purified by flash chromatography using a 30% DCM in hexane eluent. A clear liquid was obtained (78% yield).  $^1\text{H}$  NMR (CDCl<sub>3</sub>): 0.88 (t, 3H,  $J=7.0$  Hz), 1.25–1.70 (m, 4H), 1.76 (q, 2H,  $J=7.1$  Hz), 3.22 (s, 1H), 4.31 (t, 2H,  $J=6.9$  Hz), 7.55 (d, 2H,  $J=8.6$  Hz), 7.99 (d, 2H,  $J=8.6$  Hz). The other homologues, **6b** (*p*-acetylenylbenzoic acid octyl ester), **6c** (*p*-acetylenylbenzoic acid decyl ester) and **6d** (*p*-acetylenylbenzoic acid dodecyl ester), were prepared using the same method with respective yields of 86%, 78% and 82%. The  $^1\text{H}$  NMR spectra of these molecules are similar, except for the aliphatic peak at  $\delta=1.25\text{--}1.70$  ppm, depending on the number of aliphatic protons.

### 2.1.6. Synthesis of mesogens *p*-CooT-*n* and *p*-ooCT-*n*

A typical procedure for the synthesis of **6-CooT-6** is presented first. To a dry 50 ml flask we added 1.73 g (4.07 mmol) of **2a**, 1.59 g (4.48 mmol) of **6a**, 15 ml of distilled triethylamine, 24 mg (0.13 mmol) of copper(I) iodide and 145 mg of tetrakis(triphenylphosphine)palladium(0). The flask was closed with a rubber septum and flushed with nitrogen and placed under magnetic stirring. The mixture was stirred for 24 h at 45°C. The solvent was evaporated under reduced pressure and the resulting mixture was

dissolved in DCM and filtered. The organic phase was washed with a 0.5 N HCl aqueous solution, dried over anhydrous magnesium sulphate and evaporated. The final compound was purified by flash chromatography using a 25% DCM in hexane eluent. White crystals were obtained (73% yield).  $^1\text{H}$  NMR (CDCl<sub>3</sub>): 0.91 (t, 3H,  $J=6.5$  Hz), 0.92 (t, 3H,  $J=6.9$  Hz), 1.20–1.75 (m, 8H), 1.78 (q, 2H,  $J=7.0$  Hz), 1.80 (q, 2H,  $J=7.1$  Hz), 4.05 (t, 2H,  $J=6.7$  Hz), 4.32 (t, 2H,  $J=6.6$  Hz), 6.98 (d, 2H,  $J=8.7$  Hz), 7.23 (d, 2H,  $J=8.6$  Hz), 7.58 (d, 2H,  $J=8.6$  Hz), 7.60 (d, 2H,  $J=8.4$  Hz), 8.03 (d, 2H,  $J=8.4$  Hz), 8.14 (d, 2H,  $J=8.7$  Hz). The other *p*-CooT-*n* compounds, **8-CooT-8** (from **2b** and **6b**), **10-CooT-10** (from **2c** and **6c**), **12-CooT-12** (from **2d** and **6d**), **8-CooT-12** (from **2b** and **6d**) and **12-CooT-8** (from **2d** and **6b**), were prepared using the same method with respective yields of 59%, 54%, 56%, 71% and 60%. The *p*-ooCT-*n* molecules, **6-ooCT-6** (from **4a** and **6a**, 55% yield), **8-ooCT-8** (from **4b** and **6b**, 57% yield), **12-ooCT-12** (from **4c** and **6c**, 54% yield), **12-ooCT-12** (from **4d** and **6d**, 48% yield), **8-ooCT-12** (from **4b** and **6d**, 76% yield) and **12-ooCT-8** (from **4d** and **6b**, 82% yield), were synthesised in the same way.  $^1\text{H}$  NMR (CDCl<sub>3</sub>) of **6-ooCT-6**: 0.90 (t, 3H,  $J=6.8$  Hz), 0.92 (t, 3H,  $J=6.8$  Hz), 1.20–1.75 (m, 8H), 1.77 (q, 2H,  $J=7.0$  Hz), 1.79 (q, 2H,  $J=7.0$  Hz), 3.95 (t, 2H,  $J=6.6$  Hz), 4.35 (t, 2H,  $J=6.8$  Hz), 6.93 (d, 2H,  $J=9.5$  Hz), 7.12 (d, 2H,  $J=9.5$  Hz), 7.60 (d, 2H,  $J=8.4$  Hz), 7.67 (d, 2H,  $J=8.4$  Hz), 8.05 (d, 2H,  $J=8.6$  Hz), 8.18 (d, 2H,  $J=8.6$  Hz).

## 2.2. Preparation of the binary mixtures

Six binary mixtures were prepared. Each sample was prepared by weighing a total of 25 mg in a 1 ml vial of the two types of mesogens, *p*-CooT-*n* and *p*-ooCT-*n*. The mixture was then heated above the clearing point and mixed for 5–10 s. The vial was then cooled and the operation was repeated twice. Aluminium caps with around 12 mg of product were used for differential scanning calorimetry (DSC).

## 2.3. Characterisation

Investigations of the transition temperatures of the pure compounds and the binary mixtures of liquid crystals were carried out using DSC and polarising optical microscopy (POM).

The DSC measurements were performed using a TA instruments Q10 differential scanning calorimeter apparatus. Onset transition temperature ( $T_0$ ) and transition enthalpy ( $\Delta H$ ) for the mixtures were obtained at a scanning rate of 10°C min<sup>-1</sup>. Textural observations and phase nature were observed under a

Leica polarising microscope equipped with a FP 82 hot stage. The polarising microscope was used to determine the second-order  $S_A$ - $S_C$  phase transition temperature which could not be seen clearly with the DSC. The experimental results for the transition temperatures and the enthalpies are shown in Table 1.

### 3. Results and discussion

#### 3.1. Polymorphism of pure compound

At first glance, it is obvious that the  $p$ -**ooCT**- $n$  series has a greater tendency to form the  $S_C$  phase: all of the  $p$ -**ooCT**- $n$  series displays this phase while only two members of the  $p$ -**CooT**- $n$  series show the  $S_C$  phase. Two members of the  $p$ -**CooT**- $n$  series exhibit an ordered smectic phase that has not been identified successfully and is not observed in any of the other compounds investigated. Globally, the properties of the  $p$ -**ooCT**- $n$  series show much less variation than the  $p$ -**CooT**- $n$  series in terms of phases displayed and trends in the change of transition temperature (Figure 3). This is particularly obvious when we examine the six compounds with equal total terminal chain length ( $n+p=20$ ). The three **ooCT** compounds have very similar phase ranges and transition enthalpies while the **CooT** compounds differ in most aspects (phases exhibited, thermal stability, etc.) with one exception: the upper transition temperature for the  $S_A$  phase is very similar.

The general trend in the presently studied compounds is that as the terminal chains are

lengthened and the overall mesophase temperature range is decreased, as are the nematic and  $S_A$  ranges. However, the  $S_C$  phase range is increased (it only appears for the 12-8 and 12-12 molecules of the  $p$ -**CooT**- $n$  series).

When homologues of both series are compared, in all pairs of same terminal chain length, the lower temperature limit for the  $S_A$  phase is always lower for the **CooT** compound. In all cases, the overall mesophase and the  $S_A$  phase temperature ranges are always greater for the **CooT** compound. Furthermore, the crystallisation temperature is always lower for the **CooT** compound. Finally, as the length of the terminal chains is increased, the differences between two homologues are diminished. In the case of the 12-12 pair, only the upper temperature limit of the  $S_A$  phase differs.

#### 3.2. Binary phase diagram

In order to estimate the propensity of molecules in the **CooT** series to exhibit the  $S_C$  phase as well as the effect of terminal chain length and the central ester inversion, binary mixtures of  $p$ -**CooT**- $n$  and  $p$ -**ooCT**- $n$  with the same terminal  $p$  and  $n$  aliphatic chains were prepared. Figures 4 and 5 show the phase diagrams for the compounds with symmetrical and unsymmetrical terminal chains. The mixtures give both the focal-conic fan and the homeotropic textures in the  $S_A$  phase. The determination of the  $S_A$ - $S_C$  transition temperature was performed in the same way as

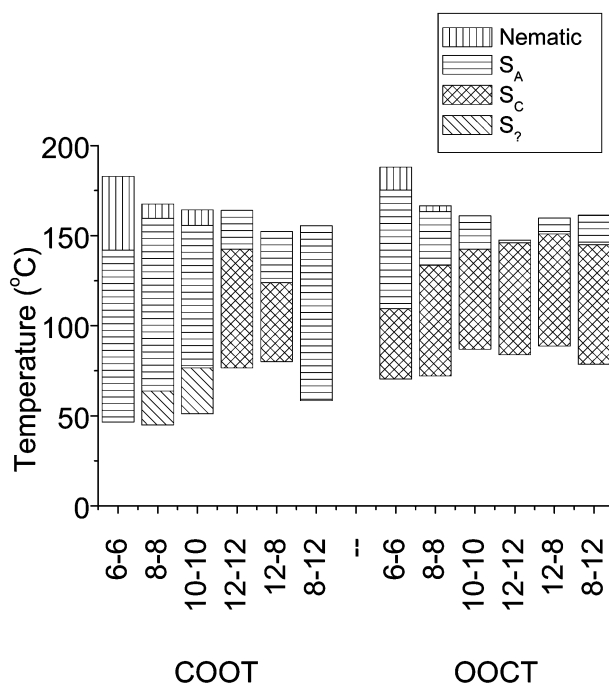


Figure 3. Temperature ranges of liquid crystalline phases for the  $p$ -**CooT**- $n$  and  $p$ -**ooCT**- $n$  homologous series.

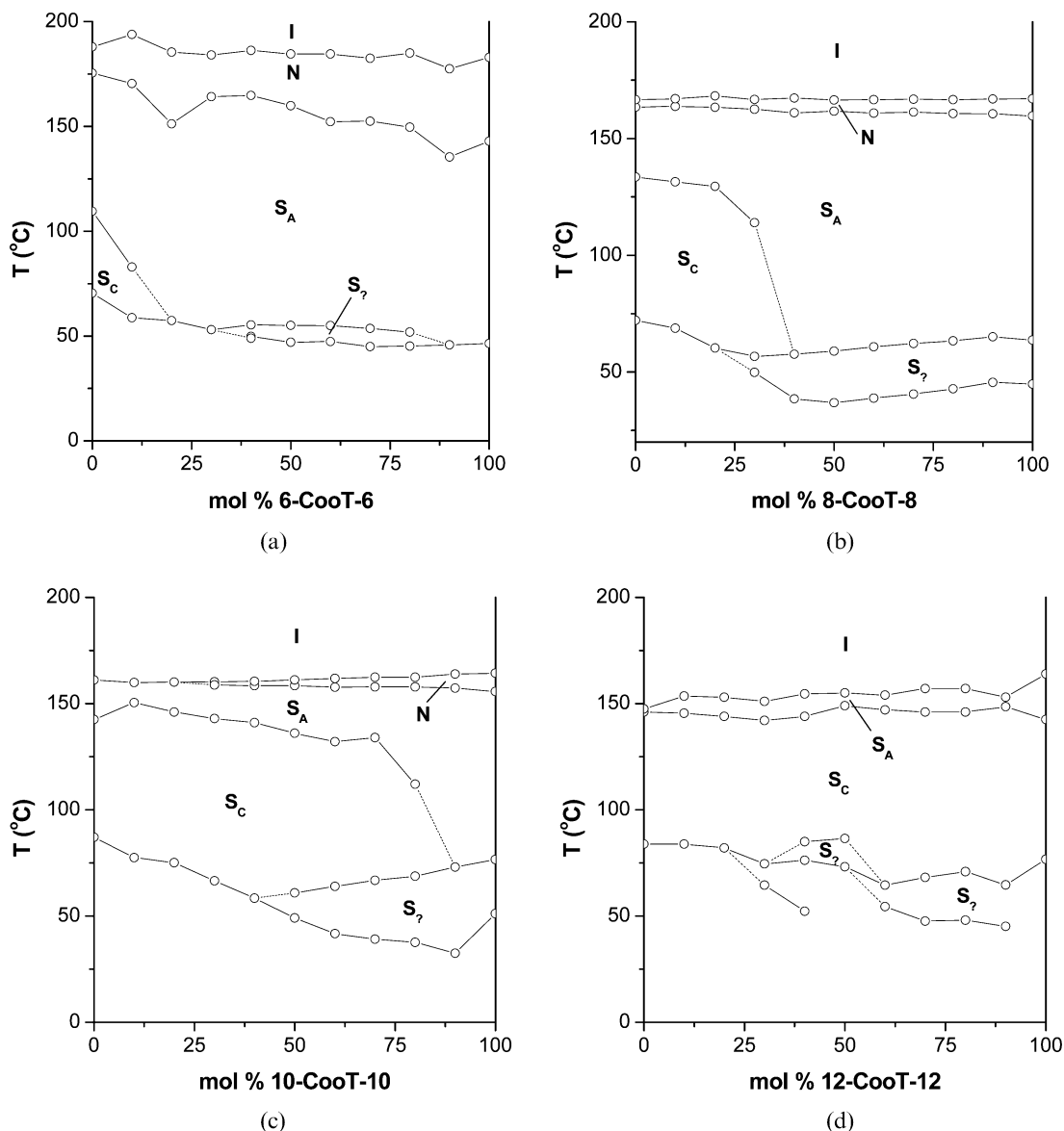


Figure 4. Phase diagrams for binary mixtures of liquid crystals with symmetric terminal chains: (a) **6-CooT-6** and **6-ooCT-6**; (b) **8-CooT-8** and **8-ooCT-8**; (c) **10-CooT-10** and **10-ooCT-10**; (d) **12-CooT-12** and **12-ooCT-12**.  $S_?$  is an unidentified ordered smectic phase and I is the isotropic liquid phase.

described for pure compounds. It has to be pointed out that the two discontinuities present at around 20% and 90% on the N- $S_A$  transition line are considered to a result of experimental error and are not considered to be deviations from ideality.

Beyond the specifics of each phase diagram some trends can be identified. First, there is no phase separation of the components within the liquid crystal regions. This means that both compounds of the mixture take on the same phase configuration instead of separating.

Concerning specifically the  $S_A$ - $S_C$  transition, Figure 4 shows an interesting trend. It can be seen

that the  $S_C$  region of stability grows wider as the terminal chain lengths of both components increase until they measure 12 carbon atoms each (Figure 4d) where it is present across all concentrations. This growth in stability range corresponds with the same trend in the  $p$ -ooCT- $n$  series: an increase in terminal chain lengths favours the  $S_C$  phase. One can therefore conclude that this trend is also present in the  $p$ -CooT- $n$  series but cannot normally be observed.

Comparing Figures 4 and 5, an interesting observation can be made. The **8-12** binary mixture phase diagram (Figure 5a) is qualitatively very similar to the **8-8** mixture (Figure 4b). Conversely, the **12-8** mixture

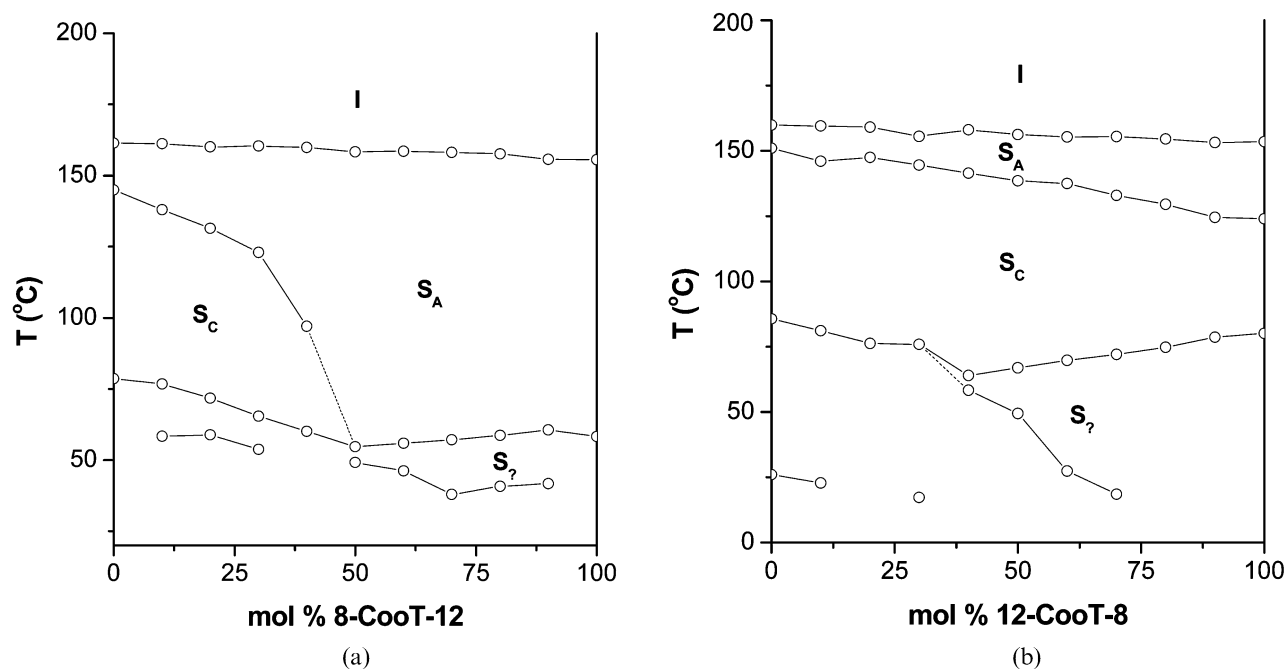


Figure 5. Phase diagrams for binary mixtures of liquid crystals with dissymmetric terminal chains: (a) **8-CooT-12** and **8-ooCT-12**; (b) **12-CooT-8** and **12-ooCT-8**.  $S_7$  is an unidentified ordered smectic phase, Cr is the crystalline phase and I is the isotropic liquid phase.

Table 1. Transition temperatures (in °C) and enthalpies (in  $\text{J g}^{-1}$ , shown in *italics*) for the cooling of the pure liquid crystals **p-CooT-n** and **p-ooCT-n**. Cr is the crystalline phase, I is the isotropic phase and  $S_7$  is an unidentified smectic phase.

Rigid core	<i>p</i>	<i>n</i>	Cr	$S_7$	$S_C$	$S_A$	N	I				
<b>CooT</b>	6	6	•	46.5 <i>-34</i>	–	–	•	142.9 <i>-1</i>	•	183.0 <i>-2</i>	•	
	8	8	•	44.9 <i>-37</i>	•	63.7 <i>-5.7</i>	–	•	159.7 <i>-3</i>	•	167.5 <i>-2</i>	•
	10	10	•	51.1 <i>-70</i>	•	76.6 <i>-6.9</i>	–	•	155.7 <i>-2</i>	•	164.3 <i>-2</i>	•
	12	12	•	76.6 <i>-91</i>	–	–	•	142.5 <i>&lt;-0.1</i>	•	164.0 <i>-6</i>	–	•
	12	8	•	80.1 <i>-85</i>	–	–	•	124.0 <i>&lt;-0.1</i>	•	153.4 <i>-10</i>	–	•
	8	12	•	58.3 <i>-84</i>	–	–	–	•	155.6 <i>-7</i>	–	–	•
	<b>ooCT</b>	6	6	•	70.4 <i>-51</i>	–	•	109.5 <i>&lt;-0.1</i>	•	175.4 <i>-2</i>	•	188.0 <i>-1</i>
8		8	•	72.2 <i>-76</i>	–	•	133.5 <i>&lt;-0.1</i>	•	163.5 <i>-6</i>	•	166.7 <i>-0.4</i>	•
10		10	•	87.0 <i>-83</i>	–	•	142.5 <i>&lt;-0.1</i>	•	161.1 <i>-6</i>	–	–	•
12		12	•	83.9 <i>-92</i>	–	•	146.0 <i>&lt;-0.1</i>	•	147.5 <i>-6</i>	–	–	•
12		8	•	88.7 <i>-83</i>	–	•	151.0 <i>&lt;-0.1</i>	•	159.9 <i>-7</i>	–	–	•
8		12	•	78.6 <i>-91</i>	–	•	145.0 <i>&lt;-0.1</i>	•	161.4 <i>-10</i>	–	–	•



(Figure 5b) shows a great similarity to the 12–12 mixture (Figure 4d). This would suggest that the left chain has a certain predominance over the right chain in determining the polymorphism of the mixture and also the pure compounds by themselves.

#### 4. Conclusion

The experimental data clearly show that both the orientation of the ester group within the rigid core and the length of the terminal chains influence the thermal stability of the mesophases. One particular trend observed is that molecules with the two esters in anti-parallel arrangements (the *p-ooCT-n* series) form the  $S_C$  phase more readily. Another was that within that series, with the terminal chain lengths available, longer terminal chains increase the stability range of the  $S_C$  phase.

The progressive increase of the  $S_C$  phase range with lengthening of the terminal chains (Figure 4) shows that even though the pure **6-CooT-6**, **8-CooT-8** and **10-CooT-10** compounds do not exhibit the  $S_C$  phase, they have an increasingly greater potential for it, just like their *p-ooCT-n* counterparts. As the terminal chains are lengthened it takes progressively less of the corresponding *p-ooCT-n* compound to allow the mixture to have the  $S_C$  phase.

The apparent dominance of the left chain over the right chain, hinted at by the comparison of Figures 4 and 5, should be considered carefully and the importance of the right-most ester group should not be dismissed. Indeed, as mentioned in the introduction, the substitution of a sulphur atom for the carbon atom leads to a reversal of behaviour concerning the arrangement of the two ester groups in the molecule (7, 8).

The synthesis and characterisation of the molecules in this paper is actually part of a larger endeavour in the search for additional clues regarding the molecular origins of the  $S_C$  phase. Indeed, molecular modelling of these molecules has already been completed and an upcoming article will present

an analysis integrating the experimental as well as simulation data into a comprehensive framework. We chose to present the experimental data in a separate article because we found those results to be very interesting on their own.

#### Acknowledgement

The present work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada and Université de Sherbrooke. Computations have been made available thanks to the Canadian Fund Innovation (CFI) and the Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT).

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