Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 11 November 2010

To cite this Article Da Cruz, C. , Rouillon, J. C. , Marcerou, J. P. and Nguyen, H. T.(2003) 'Synthesis and mesomorphic properties of a new chiral series with a heterocycle in the molecular core', Liquid Crystals, 30: 10, 1175 — 1179
To link to this Article: DOI: 10.1080/0267829031000136075
URL: http://dx.doi.org/10.1080/0267829031000136075

LIQUID CRYSTALS, VOL. 30, NO. 10, OCTOBER, 2003, 1175–1180

Synthesis and mesomorphic properties of a new chiral series with a heterocycle in the molecular core

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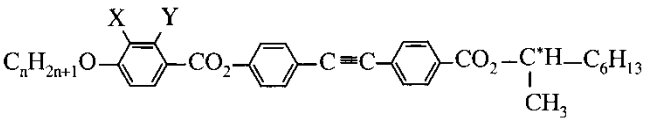
(*Received 6 January 2003; in final form 28 February 2003; accepted 27 March 2003*)

We report a number of different homologous series with a heterocycle incorporated in the molecular core near the chiral chain. Two of these series differ in the type of chiral chain, –CH*(CH_3)C_6H_{13} or –CH*(CH_3)–CO_2–C_4H_9. Their properties are compared and found to show completely different polymorphism. The first series exhibits only SmC* and SmA phases whereas the second possesses TGB, N* and BP phases. The mesomorphic properties were studied by optical microscopy, DSC and electro-optical measurements. The effect of substitution of the phenyl ring near the chiral chain by a heterocycle is discussed.

1. Introduction

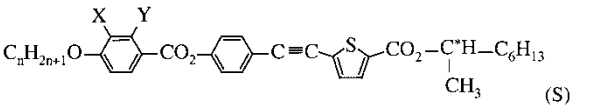
Several years ago, chiral liquid crystals were the focus of much attention as a result of the experimental discovery of the twist grain boundary phase (TGB) by Goodby *et al.* [1, 2] in 1989. The TGBA phase structure can be described as slabs of SmA material stacked regularly in a helical fashion along an axis parallel to the smectic layers. A grain boundary (grid of parallel equispaced screw dislocation lines) connects adjacent slabs and allows helical twisting. TGBC and TGBC* phases composed of, respectively, SmC and SmC* slabs were also predicted [3–6], and the existence of the TGBC phase was demonstrated by the Bordeaux group [7]. Recently, a novel TGB phase, the TGB antiferroelectric phase, was discovered [8].

Various molecular parameters have already been studied concerning the formation of the TGB phase [9, 10]. The local dipolar moment is of fundamental importance. Keeping this in mind, we tried to analyse what the influence of a heterocycle would be on the polymorphism of a 'TGB series'. The Bordeaux group have already reported the tolane series [11]



for which a TGBA phase exists for the longer chain members ($n = 16$, 18, 20).

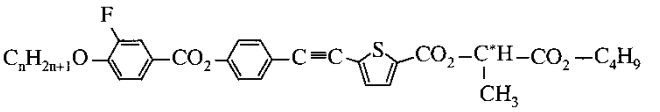
In this paper, we focus on the influence on phase behaviour of substituting the phenyl group near the chiral centre by a heterocycle, specifically, the thiophene group. We synthesized and studied the series:



(S)

Series I (HH) when XY = HH
Series I (FH) when XY = FH
Series I (FF) when XY = FF.

A further structural modification was made in order to study the influence of the chiral chain on phase behaviour, specifically a different chiral group was introduced into the molecule,



Series II

The properties of series II are compared to those of series I. Thus, the work reported here represents an investigation of how the formation of the TGB phase is affected by the structural nature of the core.

2. Synthesis and mesomorphic properties

The materials studied in this paper were synthesized according to the scheme. The fluoro-substituted 4-alkyloxybenzoic acids and the 1-tetrahydropyranyloxy-phenylacetylene were prepared using well known methods [9, 12, 13]. The phase sequence was determined from texture observations made on conventional thin samples under the polarizing microscope (Leitz Orthoplux microscope equipped with a Mettler FP5 hot stage).

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000136075

Table 1. Transition temperatures (°C) determined on heating, and associated enthalpies in brackets (kJ mol^{-1}) of series I (HH) measured at 3°C min^{-1} ([] denotes monotropic).

n	Cr	SmC*	SmA	I
8	• 47.9 *(30.63)*		• 96.3 *(5.411)*	•
9	• 55.0 *(37.67)*		• 92.6 *(5.038)*	•
10	• 65.5 *(32.42)*		• 93.1 *(5.459)*	•
11	• 68.2 *(32.81)*	• [67.1] *(0.075)*	• 90.2 *(4.972)*	•
12	• 62.9 *(53.32)*	• 75.1 *(0.104)*	• 89.3 *(5.227)*	•
13	• 55.1 *(35.47)*	• 74.8 *(0.147)*	• 86.6 *(4.274)*	•
14	• 52.8 *(41.50)*	• 78.8 *(0.240)*	• 86.0 *(5.200)*	•
15	• 64.0 *(51.72)*	• 79.9 *(0.367)*	• 84.7 *(5.336)*	•
16	• 59.8 *(46.31)*	• 79.9 *(0.298)*	• 83.8 *(5.522)*	•
18	• 46.1 *(35.22)*	• 78.0 *(0.219)*	• 81.5 *(4.426)*	•

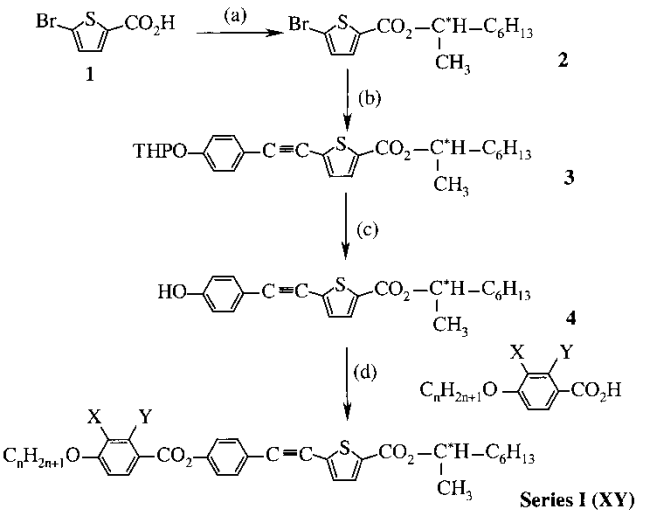
Table 2. Transition temperatures (°C) determined on heating, and associated enthalpies in brackets (kJ mol^{-1}) of series I (FH) measured at 3°C min^{-1} ([] denotes monotropic).

n	Cr	SmC*	SmA	I
12	• 59.2 *(35.55)*	• [59.2] *(0.046)*	• 74.1 *(4.823)*	•
14	• 42.5 *(27.10)*	• 65.2 *(0.160)*	• 71.2 *(4.600)*	•
16	• 39.8 *(39.20)*	• 64.1	• *(5.256)*[a] 69.1	•

[a] Sum of SmC*–SmA and SmA–I transition enthalpies.

Table 3. Transition temperatures (°C) determined on heating, and associated enthalpies in brackets (kJ mol^{-1}) of series I (FF) measured at 3°C min^{-1} ([] denotes monotropic).

n	Cr	SmC*	SmA	I
12	• 59.9 *(41.19)*	• [59.3] *(0.017)*	• 82.4 *(4.523)*	•
14	• 61.1 *(62.00)*	• 69.8 *(0.120)*	• 78.9 *(4.000)*	•
16	• 59.4 *(44.42)*	• 73.6 *(0.167)*	• 77.8 *(4.279)*	•



Scheme. Synthetic route. (a) HO–C*H(CH_3)–C_6H_{13} (*S*), DCC, DMAP, CH_2Cl_2. (b) THPO–Ph–C≡C–H, (*i*Pr)$_2$NH, TPP, $PdCl_2$, $Cu(AcO)_2$ H_2O. (c) CH_2Cl_2, MeOH, PTSA. (d) DCC, DMAP; CH_2Cl_2.

The phase transition temperatures and the associated enthalpies were evaluated from DSC studies (Perkin-Elmer DSC7).

The mesomorphic properties of all the newly synthesized compounds are collected in tables 1–4. The phase transition temperatures and associated enthalpies were determined on heating for the enantiotropic phases and on cooling for the monotropic phases. All the compounds of the series are mesogenic. The series I (HH), I (FH) and I (FF) exhibit only two phases, SmA and SmC*, whereas for series II the phase sequence is more complex, Cr–SmA–TGBA–N*–BP–I for the short chain members and Cr–SmC*–TGBA–N*–BP–I for the longer homologues.

Table 4. Transition temperatures (°C) determined on heating and associated enthalpies in brackets (kJ mol^{-1}) of series II measured at 3°C min^{-1} ([] denotes monotropic).

n	Cr	SmC*	SmA	TGBA	N*	BP	I
7	• 78.0 *(40.24)*		• [76.6] *(2.25)*		• 83.2	• *(0.53)*[b] 84.8	•
8	• 67.7 *(31.33)*		• 81.5 *(2.33)*		• 85.2	• *(0.66)*[b] 86.6	•
9	• 65.5 *(36.13)*		• 75.0 *(1.35)*		• 79.8	• *(0.62)*[b] 81.6	•
10	• 61.4 *(35.90)*		• 75.6 *(1.16)*		• 80.2	• *(0.77)*[b] 81.9	•
11	• 69.2 *(40.70)*		• 72.2 *(0.80)*		• 76.8	• *(0.69)*[b] 78.6	•
12	• 75.9 *(42.22)*	• [50.0]		• [71.4] *(0.59)*	• 77.7	• *(0.56)*[b] 79.0	•
13	• 74.2 *(41.73)*	• [53.6] *(0.02)*		• [69.5] *(0.42)*	• 75.5	• *(0.43)*[b] 76.4	•
14	• 70.7 *(38.60)*	• [58.5] *(0.02)*		• [75.5] *(0.38)*	• 75.2	• *(0.80)*[b] 76.8	•
16	• 68.9 *(38.35)*	• [61.1] *(0.09)*		• 72.2 *(0.27)*	• 73.1	• *(1.18)*[b] 75.1	•
18	• 68.9 *(43.00)*	• [66.1] *(0.07)*		• 72.5	• *(2.61)*[a] 73.0	• 73.9	•
20	• 68.6 *(52.00)*	• [66.2] *(0.05)*		• 73.4	• *(3.85)*[a] 73.8		•

[a] Sum of TGBA–N*, N*–BP and BP–I transition enthalpies.

2.1. *Series I*

We can see that in series I (HH) the SmC* phase is initially monotropic for $n=11$ and then becomes enantiotropic for $n=12$ to 18. Figure 1 shows the regular decrease of the SmA phase range as the chain length grows and by contrast the concurrent increase of the SmC* phase range. Two discontinuities can be observed in this trend; for $n=15$ and 16 their higher melting points result in a decreased SmC* temperature range (figure 1).

No regular variation is observed in the SmA–I transition enthalpies as a function of chain length. We do note an increase in these enthalpies for $n=13$–16. Thus the SmA–I transition becomes stronger, suggesting that the smectic layer order increases which is in agreement with the decrease in tendency to form TGB phases [14]. To form a twisted SmA phase, the I–SmA transition must tend towards being second order in nature, as the chain length n increases. According to De gennes [3] and Renn and Lubensky [4], a second order phase transition with strong fluctuations associated with adjacent phases must occur to stabilize the TGB phase.

Substituting the hydrogen atom in the rigid molecular core by a small electronegative atom such as fluorine decreases the SmC*–SmA and SmA–I transition temperatures as well as destabilizing the mesophases (figure 2). The steric effect resulting from this substitution reduces the SmC* phase range. The decrease in the temperatures is greater when the phenyl ring near the aliphatic chain is monosubstituted rather than disubstituted.

Compared with the corresponding tolane series, the general trend is observed that the transition temperatures are decreased because of the substitution of one phenyl ring by a heterocycle. In series I the range of the SmA phase does not decrease sufficiently to obtain TGB phases when the chain length increases, whereas in the tolane series TGBA phases are observed.

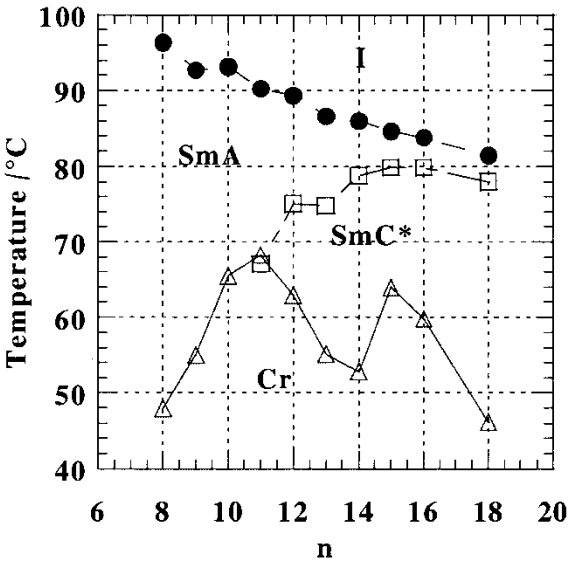


Figure 1. Transition temperatures as a function of the number of carbon atoms n in the aliphatic chain for series I (HH).

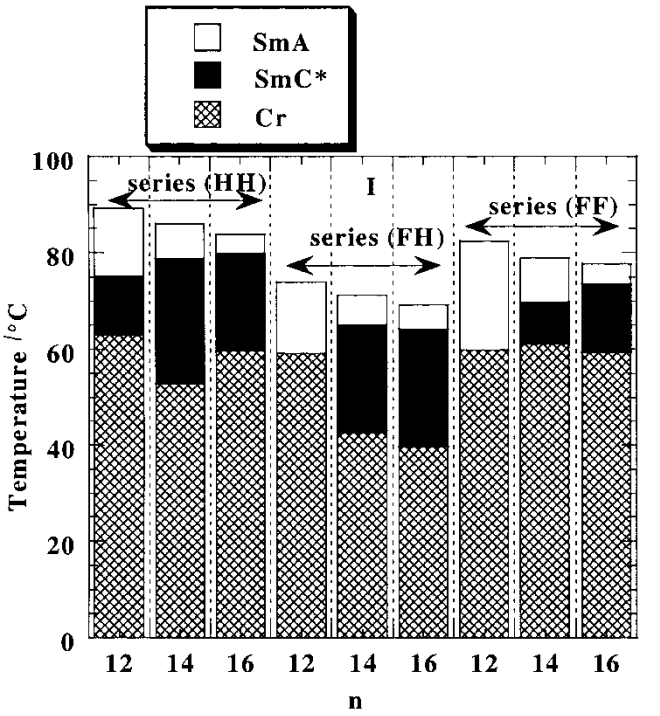


Figure 2. Histogram representing the meso phase temperature ranges as a function of the number of carbon atoms n in the aliphatic chain for the series I (HH), I (FH) and I (FF).

2.2. *Series II*

The experimental method for the synthesis of series II is identical to that for series I, using (-) L-butyl lactate instead of (S)-octan-2-ol in the first synthetic step.

If we compare series I (FH) with series II, only one structural difference exists, which is the replacement of the chiral chain $-C_6H_{13}$ with $-CO_2-C_4H_9$. The overall chain length is similar. However, a notable change in polymorphism occurs in the series II compounds. For the short chain compounds ($n\leq 11$), N* and classical blue phases exist whereas for the longer chain members ($n\geq 12$), a TGBA phase below the cholesteric phase is found. For $n=12$, 13 and 14, the TGBA phase is monotropic. With regard to smectic phases, a SmA phase exists for the short chain members and a SmC* phase for the longer ones. To distinguish between these two phases for the compound with $n=16$, the electro-optic method was used. This compound exhibits a small polarization before crystallization. The problem with

these compounds was their high crystallization temperatures which prevented any electro-optical studies.

3. Electro-optical studies

Electro-optical properties were studied using the SSFLC configuration in order to evaluate polarization, response time, and tilt angle in a single set-up.

Commercial cells (EHC from Japan) coated with ITO (indium tin oxide) and rubbed polyimide were used. The thickness of the cells was around 15 μm, and the active area was 0.25 cm^2. Slow cooling from the isotropic phase through the SmA phase (0.1°C min^{-1}) into the SmC* phase leads to planar alignment. The compounds 14 HH, 14FH, and 14 FF of series I were studied. The field used was a rectangular a.c. field of 2 V μm^{-1}, with frequency 41 Hz for the measurements of polarization and electric response time and 0.1 Hz for the tilt angle. The polarization was calculated by integration of the switching current under a rectangular a.c. field; the apparent tilt angle θ of the molecules from the smectic layer normal was calculated from the difference in the extinction positions between crossed polarizers under opposite unwinding fields. Well aligned samples were needed for θ measurements.

For the three compounds, the polarization curves are very similar (figure 3). The polarization behaviour versus temperature is conventional and, polarization decreases with increasing temperature. The maximum value for polarization is around 76 nC cm^{-2} and then tends to zero at the transition to the SmA phase. The three compounds were synthesized using the same phenol, so the difference in electric properties can be assigned to the fluorine atom effect.

The apparent tilt angle decreases from 26°C to 5°C on heating, in the normal manner, and θ is more or less proportional to P (figure 4). The electric response time

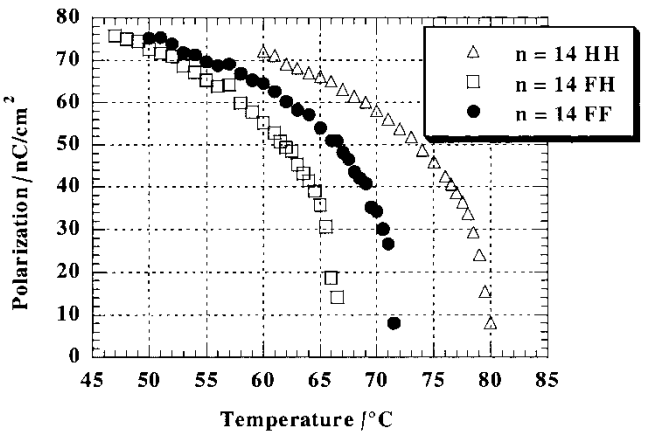


Figure 3. Temperature dependence of the polarization at saturation compared for the three compounds 14 HH, 14 FH and 14 FF ($E = 2V\mu m^{-1}$, $v = 41$ Hz) of series I.

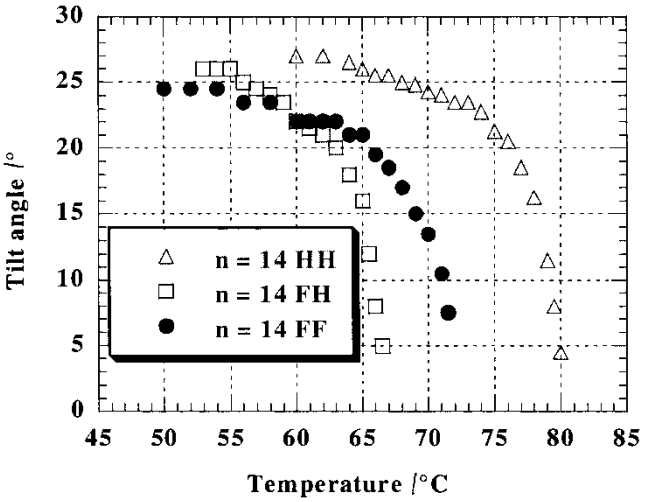


Figure 4. Temperature dependence of the tilt angle compared for the three compounds 14 HH, 14 FH and 14 FF ($E = 2V\mu m^{-1}$, $v = 0.1$ Hz) of series I.

curves (figure 5) show no anomalies, they decrease with increasing temperature due to the classical thermal behaviour of the viscosity of the compounds. In the temperature range 56–80°C, the electric response time is more significant for the compound 14 HH compared with those for 14 FH and 14 FF.

4. Discussion and conclusion

We report here the influence of replacing the phenyl ring near the chiral centre by a thiophene 2,5-disubstituted group. In contrast to the corresponding tolane series, no TGB phases were found, only SmC* and SmA phases. The curving introduced by the presence of the heterocycle seems to destabilize the phases

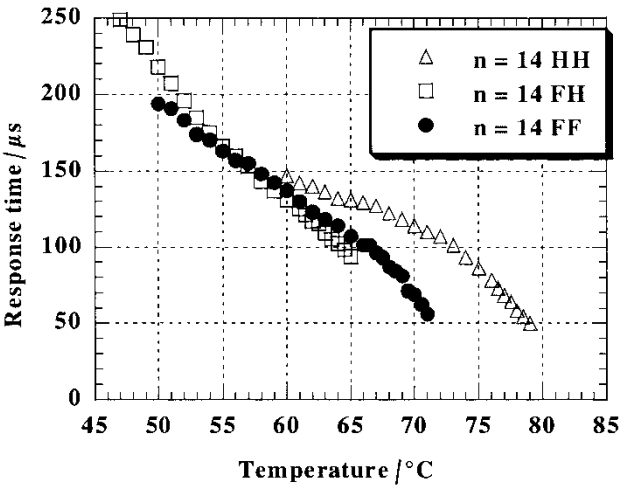
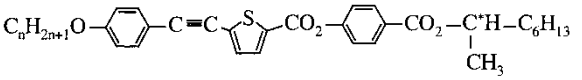


Figure 5. Temperature dependence of the electric response times compared for the three compounds 14 HH, 14 FH and 14 FF ($E = 2V\mu m^{-1}$, $v = 41$ Hz) of series I.

considerably. However, we can obtain a TGBA phase for $n=16$ by introducing the complementary phenyl group –Ph–CO_2– near the alkyl chain. The molecule appears to be sufficiently long not to be perturbed by the curving due to the heterocycle.

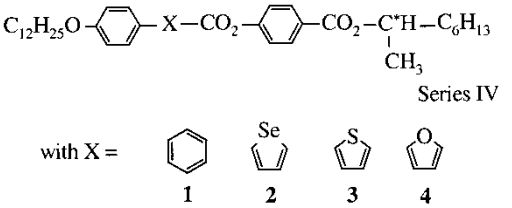
In our series I, the phases existing for the phenyl series were completely destabilized and only the SmA and SmC* phases were present. But series II, which differs from series I (FH) by a different chiral group, exhibited the same phases as the series containing only phenyl rings and the group –CH*(CH_3)–CO_2–C_2H_5 [15] instead of –CH*(CH_3)–CO_2–C_4H_9. This chiral group seems to favour the formation of N* and TGB phases. The phases are less destabilized in series II.

Two compounds ($n=10$ and 14) of the series:



(*R*) Series III

were also synthesized for comparison with series I (HH). The same phases were found, i.e. SmC* and SmA phases with the phase sequence Cr–SmC*–SmA–I. However, the corresponding series containing three phenyl rings exhibits anticlinic and ferrielectric phases [16]. Various series containing the thiophene group have been reported [17–20]. The effect of a heterocycle was already reported by Seed *et al.*, in a comparison of the properties of three-ring compounds containing a 2,5-disubstituted selenophene, thiophene and furan [21]:



Series IV

with X =

1 2 3 4

Only a destabilization of the smectic phases was observed but the same phases exist, except for the furan compound which is not mesomorphic (table 5). A comparison with the analogous parent phenyl material would show how a bent core structure effects the tendency towards the generation of the anticlinic phase. The molecular structures of series III and IV differ from one another in that the heterocycle is linked to the phenyl ring near the alkyloxy chain by a –C≡C– group in series III, whereas it is linked by a single bond in series IV. It seems that the alkyl chain compensated for the bend in the molecules of series IV while it does not in series III because of the presence of the –C≡C– group.

Thus the effect of introducing a heterocycle such as thiophene is not as obvious as it may seem. Sometimes the mesophases are so destabilized that they disappear, while sometimes another molecular parameter (such as a different chiral chain) can stabilize the existence of the same phases. The curvature introduced by the thiophene is certainly compensated by the chiral chain in series II whereas it is not in series I. This curvature effect is obvious following the synthesis of the furan homologues. Thus, these compounds are not mesomorphic, even though their melting temperatures are low. The heterocycle modifies the linearity of the molecular core so that the polymorphism can be totally changed because of the destabilization in phase structure accompanying this change.

5. Experimental

The NMR spectra were recorded on a Bruker HW 300 MHz spectrometer. The following examples are typical of the synthetic methods used to obtain the compounds given in tables 1–4.

5.1. *(S)-1-methylheptyl 5-bromothiophene-2-carboxylate* **2**

To a solution of (*S*)-2-octanol (5.2 g, 40 mmol) in CH_2Cl_2 (45 ml) was added DCC (9.1 g, 40 mmol), DMAP (0.4 g) and 5-bromothiophene-2-carboxylic acid (9.1 g, 40 mmol). The resulting solution was stirred at room temperature overnight; it was then filtered, and the solvent evaporated. The residue was chromatographed on silica gel with CH_2Cl_2 as eluant. The desired compound was used without further purification; yield 9.8 g (77%). ^{1}H NMR ($CDCl_3$, ppm): 0.9 (t, 3H, CH_3 of C_6H_{13}), 1.2–1.5 (m, 11H, $4CH_2$ and CH_3–CHO), 1.6–1.8 (m, 2H, $CH_2\beta$), 5.15 (m, 1H, O–CH–CH_2), 7.05 (d, 1H of the heterocycle in position 4), 7.5 (d, 1H of the heterocycle in position 3).

Table 5. Transition temperatures (°C) determined on heating of series IV.

Compound	Cr		SmC^*_A		SmC^*_{FI}		SmC*		SmA		I
1 (Ph)[a]	•	72.9	•	99.9	•	103.5	•	122.2	•	132.7	•
2 (Se)[b]	•	67.7	•	97.8	•	99.0	•	109.4	•	116.6	•
3 (S)	•	64.2	•	80.2	•	82.8	•	92.6	•	97.6	•
4 (O)	•	61.2									•

[a] The compound exhibits a SmC_α^* phase at 117°C.
[b] The compound possesses monotropic auticlinic phases termed Sm*I and Sm^*I_A [16].

5.2. *(S)-1-methylheptyl 5-[(1-tetrahydropyranyloxyphenyl)ethynyl]thiophene-2-carboxylate* ***3***

To a solution of compound **2** (8.93 g, 28 mmol) in 85 ml of diisopropylamine was added 0.69 g of triphenylphosphine; the mixture was stirred until complete dissolution was achieved. Catalysts (76.9 mg of palladium chloride and 84 mg of monohydrated copper acetate) were then added, followed by 1- tetrahydropyranyloxyphenylacetylene (5.67 g, 28 mmol) under nitrogen atmosphere. The solution was heated for 2 h between 75 and 80°C, then cooled to room temperature, the mixture was filtered off, washed with heptane, evaporated and extracted with heptane. The organic phase was dried over Na_2SO_4 and chromatographed on silica gel using toluene as eluant; yield 8.6 g (70%). ^{1}H NMR ($CDCl_3$, ppm): 0.9 (t, 3H, CH_3 of C_6H_{13}), 1.2–1.5 (m, 11H, $4CH_2$ and CH_3–CHO), 1.6–1.8 (m, 2H, $CH_2\beta$ and $3CH_2$ (THP)), 3.6–4 (m, 2H, CH_2–CH_2–O (THP)), 5.15 (m, 1H, O–CH–CH_2), 5.5 (m, 1H, O–CH–O (THP)), 7.05 (m, 2H arom. in position 3 and 5), 7.2 (d, 1H of the heterocycle in position 4), 7.45 (m, 2H arom. in position 2 and 6), 7.7 (d, 1H of the heterocycle in position 3).

5.3. *(S)-1-Methylheptyl 5-[(4-hydroxyphenyl)ethynyl]thiopene-2-carboxylate* ***4***

To a solution of compound **3** (5.4 g, 12.3 mmol) in mixture of CH_2Cl_2 (32 ml) and MeOH (54 ml) was added para-toluenesulphonic acid (0.14 g). After 1 h at room temperature, the resulting mixture was evaporated and chromatographed on silica gel using CH_2Cl_2 as eluant. The product (yellow powder) was recrystallized from heptane; yield 3.7 g (86%). ^{1}H NMR ($CDCl_3$, ppm): 0.9 (t, 3H, CH_3 of C_6H_{13}), 1.2–1.5 (m, 11H, 4 CH_2 of C_6H_{13} and CH_3–CHO), 1.6–1.8 (m, 2H, $CH_2\beta$), 5 (s, 1H, O–H), 5.15 (m, 1H, O–<u>CH</u>–CH_2–), 6.9 (m, 2H arom. in position 3 and 5), 7.2 (d, 1H of the heterocycle in position 4). 7.45 (m, 2H arom. in position 2 and 6), 7.7 (d, 1H of the heterocycle in position 3).

5.4. *(S)-1-Methylheptyl 5-[(4-tetradecyloxybenzoyloxyphenyl)ethynyl]thiophene-2-carboxylate (n=14):* ***5***

4-Tetradecyloxybenzoic acid (0.17 g, 0.5 mmol) was added to a solution of compound **4** (0.18 g, 0.5 mmol), DCC (0.11 g, 0.5 mmol) and DMAP (0.005 g) dissolved in CH_2Cl_2 (5 ml). The mixture was stirred overnight at room temperature; it was then filtered and the solvent evaporated. The residue was purified by chromatography on silica gel using dichloromethane as eluant. The product was crystallized from absolute ethanol; yield 0.2 g (59.5%). ^{1}H NMR ($CDCl_3$, ppm): 0.9 (m, 6H, CH_3 of C_6H_{13}, CH_3 of $C_{14}H_{29}$), 1.2–1.5 (m, 33H, $11CH_2$ of $C_{14}H_{29}$, $4CH_2$ of C_6H_{13} and CH_3–CHO), 1.6–1.8 (m, 4H, $2CH_2\beta$), 4 (m, 2H, –CH_2–O of $C_{14}H_{29}$), 5.1 (m, 1H, O–CH–CH_2–), 7 (t, 1H arom. in position 3 and 5 for the phenyl ring near the aliphatic chain), 7.25 (m, 3H, 1H of the heterocycle in position 4 and 2H arom. in position 3 and 5), 7.6 (m, 2H arom. in position 2 and 6), 7.7 (d, 1H of the heterocycle in position 3), 8.2 (m, 2H arom. in position 2 and 6 for the phenyl ring near the aliphatic chain). Elemental analysis: calculated C 74.03, H 8.7, S 4.94; found C 74.55, H 8.85, S. 5.07%.

C. Da Cruz wishes to thank Praxis XXI for financial support.

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