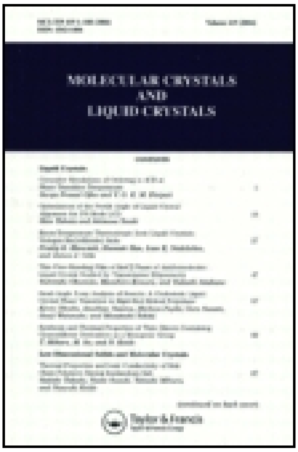

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The Influence of Lateral Fluoro-Substituents on TGB Phases in Chiral Propiolates

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THE INFLUENCE OF LATERAL FLUORO-SUBSTITUENTS ON TGB PHASES IN CHIRAL PROPIOLATES

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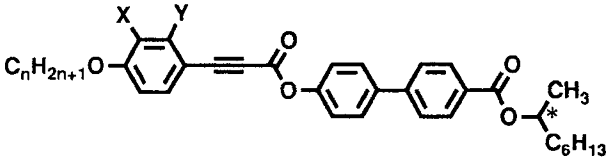
Abstract The transition temperatures and associated enthalpies of chiral and racemic 1-methylheptyl 4'-[(2- or 3-fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates are reported along with phase diagrams for binary mixtures of *(R)*- and *(S)*-isomers. The position of the fluoro substituent was found to influence the formation of twist grain boundary phases both in the enantiomers and in binary mixtures of enantiomers. DSC studies revealed that the enantiomeric 3-fluoro compounds possessed a diffuse liquid-liquid transition above the clearing point, which did not arise for the racemates or for the 2-fluoro analogues. Circular dichroism and optical rotation studies carried out over the temperature range of the diffuse liquid phase, confirm that a form of cybotactic, chiral organisation in the isotropic liquid is responsible for this phenomenon.

INTRODUCTION

Recent investigations into the occurrence of the Twist Grain Boundary A* phase (TGB A*) in a variety of optically active alkyl 4'-[(4-alkoxyphenyl)propioloyloxy]-biphenyl-4-carboxylates have now been well documented and it is clear that certain structural relationships must be fulfilled for this novel twisted state to occur [1-3]. TGB A* phases have only been observed in propiolates which have (i) a high degree of form chirality which has been imparted by certain chiral ester moieties (*e.g.*, 1-methylheptyl); (ii) long terminal alkyl chains which appear to induce 'second order' clearing behaviour; (iii) a short range S_A* phase and S_A*-S_C* transition close to the clearing point. To date, little work has been performed on the influence of lateral fluoro-substituents attached to the molecular core on the stability and occurrence (if any) of TGB A* mesophases; it should be noted however, that some work has been performed in this area on the structurally isomeric tolane materials [4-6]. The fluoro-substituent is favoured as a lateral group in liquid-crystal research for a variety of reasons, namely its small van der Waals radius [7] and its high polarity [8]; these properties frequently having well established effects on thermal stability [9] and other related properties [10].

Two structurally isomeric series of mono fluoro-substituted propiolate esters have been synthesized and evaluated in this work; these are the *(R)*- and *(S)*-1-methylheptyl 4'-[(2- or 3- fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates, as shown in general structure **1**, which allow direct comparison of their mesogenic properties with the unfluorinated parent series [1,2].



1; **n** = 12 to 16; **X** , **Y** = **H**, **F** or **F**, **H**.

SYNTHESIS OF THE MATERIALS

Both series of enantiomeric materials were prepared as shown in scheme I; the precise experimental details have been covered thoroughly in a previous publication [12]. The racemic samples were prepared by accurately weighing equal quantities of the *(R)*- and *(S)*-enantiomers into a clean glass vial and thoroughly mixing them in the isotropic state. The chemical structures of all intermediates and final products were confirmed using a combination of analytical techniques; infra red spectroscopy, proton nuclear magnetic resonance spectroscopy and mass spectrometry. The purities of all final compounds were determined to be in excess of 99% pure using a Merck-Hitachi gradient HPLC system using both normal and reverse phase columns employing acetonitrile as the mobile phase. Initial phase assignments and transition temperatures were determined using a Zeiss Universal polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 controller (data recorded at a cooling rate of 2 deg. min^{-1}). The enthalpies associated with certain transitions were determined using a Perkin-Elmer DSC7 calorimeter previously calibrated using an indium standard (all enthalpies are quoted in kJ mol^{-1}).

RESULTS

(a) *(R)*- and *(S)*-1-Methylheptyl 4'-[(2-fluoro-4-alkoxyphenyl)propioloyloxy]-biphenyl-4-carboxylates

The phase assignments, transition temperatures and associated enthalpy changes for the *(R)*- and *(R,S)*-modifications are listed in table 1; it should be noted that the *(S)*- and *(R)*-

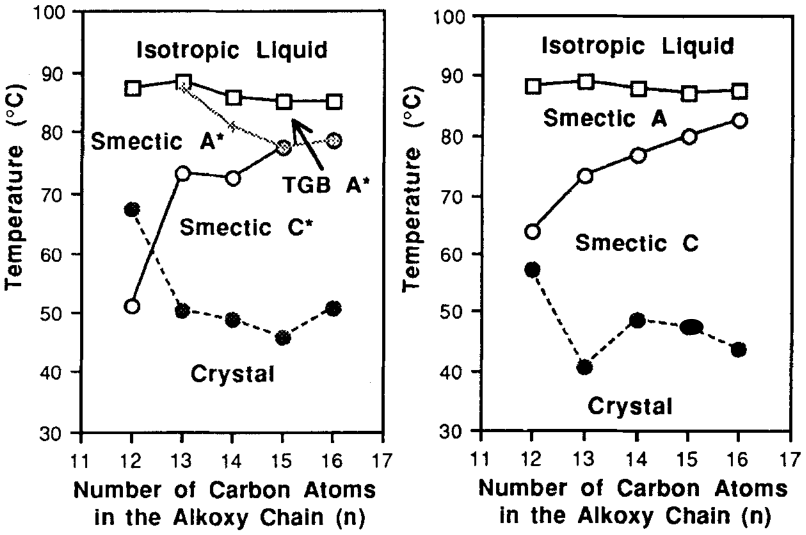
pentadecyloxy and hexadecyloxy homologues (**8** and **10**), and on cooling, the TGB A* phase transforms *via* a series of filaments which merge into an iridescent planar S_C* texture. The general mesogenic trends of the *(R)*-enantiomers have been plotted as a function of temperature *versus* the length of the terminal alkoxy chain in figure 1(a).

Compound	Chain	Abs.	Transition Temperatures (°C) [a]				
Number	Length, n	Config.	Iso. Liq.	TGB A*	S_A*/A	S_C*/C	m.p.
2	12	*(R)*-	. 87.1 [4.64] [b]		. 50.9 [c]	.	67.3
3	12	*(R,S)*-	. 88.2 [5.49]		. 63.9 [d]	.	57.5
4	13	*(R)*-	. 88.4 [4.96]	. 87.3 [d]	. 73.4 [0.11]	.	50.3
5	13	*(R,S)*-	. 88.8 [5.55]		. 73.3 [0.06]	.	40.7
6	14	*(R)*-	. 85.8 [5.41]	. 80.8 [d]	. 72.6 [0.17]	.	48.9
7	14	*(R,S)*-	. 87.7 [5.92]		. 76.8 [0.06]	.	48.6
8	15	*(R)*-	. 85.0	. 77.7 [5.49]	[0.20]	.	45.6
9	15	*(R,S)*-	. 87.0 [5.96]		. 79.7 [0.09]	.	47.4
10	16	*(R)*-	. 84.9 [5.45]	. 78.8 [0.24]		.	50.6
11	16	*(R,S)*-	. 87.5 [6.11]		. 82.4 [0.20]	.	43.6

[a].. determined by optical microscopy at a cooling rate of 2 deg. min^{-1}; [b].. figures in square brackets denote enthalpy (kJ mol^{-1}), recorded at a cooling rate of 5 deg. min^{-1}; [c].. enthalpy of transition could not be accurately determined due to proximity of Iso-S_A* peak; [d].. enthalpy change too small to record.

Table 1 : The Transition Temperatures and Associated Enthalpies of *(R)*- and *(R,S)*-1-Methylheptyl 4'-[(2-fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates

The racemic forms displayed conventional focal-conic S_A and *schlieren* S_C textures (with s = ±1 singularities). The general mesogenic trends are shown in figure 1(b) as a function of temperature *versus* length of the terminal alkoxy chain. It is of note that the enantiomers all display lower clearing temperatures than their respective racemates.



(a) (b)

Figure 1 : The Transition Temperatures and Phase Assignments of the *(R)*-and *(R,S)*-1-Methylheptyl 4'-[(2-fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates Plotted as a Function of the Length of the Terminal Alkyl Chain

(b) *(R)*- and *(R,S)*-1-Methylheptyl 4'-[(3-fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates

The phase assignments, transition temperatures and associated enthalpies of the *(R)*-enantiomers and the *(R,S)*-modifications are listed in table 2. The phase behaviour of the *(R)*-enantiomers is relatively straight forward for all homologues; cooling from the isotropic liquid, through the liquid phase, results in the appearance of an iridescent planar S_C* texture; there is a slight increase in the Iso.-S_C* transition as the homologous series is ascended, whilst the S_C* phase range simultaneously increases. This is shown in figure 2(a), which shows the mesogenic trends as a function of temperature *versus* terminal alkoxy chain length. No ferrielectric, antiferroelectric or twist inversion phenomena were observed on further cooling of the S_C* phases of these *(R)*-enantiomers.

Turning to the homologous series of racemic compounds, on cooling from the isotropic liquid all compounds (**13**, **15**, **17**, **19** and **21**) show S_A and underlying S_C phases before crystallization; the phase behaviour is shown in figure 2(b) as a function of temperature *versus* terminal alkoxy chain length. The presence of this orthogonal smectic phase is somewhat surprising since the enantiomeric materials only formed a tilted smectic phase (S_C*), and this is presumably attributable to the lowering of space symmetry due to the presence of the chiral centre. Once again it is noticeable that the clearing points of the racemates are some 5 °C higher than those of the respective *(R)*-enantiomers.

Compound	Chain	Abs.	Transition Temperatures (°C) [a]				
Number	Length, n	Config.	Iso. Liq.	Liq.-Liq.[b]	S_A	$S_C{}^*/C$	m.p.
12	12	*(R)*-	• 78.9 [1.13] [c]	• 75.1 [0.93]		•	81.5
13	12	*(R,S)*-		• 81.3 [3.24]	• 77.4 [0.44]	•	78.4
14	13	*(R)*-	• 78.3 [1.32]	• 75.6 [0.98]		•	80.6
15	13	*(R,S)*-		• 80.3 [3.14]	• 77.8 [0.48]	•	77.4
16	14	*(R)*-	• 79.7 [1.40]	• 75.3 [1.12]		•	80.3
17	14	*(R,S)*-		• 81.5 [3.52]	• 79.3 [0.46]	•	77.4
18	15	*(R)*-	• 79.8 [1.58]	• 76.6 [1.34]		•	77.7
19	15	*(R,S)*-		• 83.7 [3.83]	• 81.7 [0.56]	•	74.9
20	16	*(R)*-	• 79.6 [1.79]	• 77.3 [1.28]		•	74.3
21	16	*(R,S)*-		• 82.4 [3.99]	• 80.3 [0.24]	•	72.4

[a]..determined by optical microscopy at a cooling rate of 2 deg. min^{-1}; [b]..temperature obtained from peak minima (not onset) from DSC thermograms recorded at a cooling rate of 5 deg. min^{-1}; [c]..figures in square brackets denote enthalpy (kJ mol^{-1}) as determined by DSC.

Table 2 : The Transition Temperatures and Associated Enthalpies of *(R)*- and *(R,S)*-1-Methylheptyl 4'-[(3-fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates

It is important to stress that these diffuse transitions are not visible by optical microscopy and the sample simply appears as a black isotropic field under crossed polarizers; however, on close inspection, the presence of small 'bubble-like' nuclei are just visible. However, DSC analysis of the pure enantiomers revealed the presence of a diffuse 'transition' or heat capacity anomaly which occurs above the sharply first order

Iso-S_C* transition during cooling cycles. This behaviour is highlighted in the superimposed DSC thermograms of the *(S)*-enantiomers in figure 3

DSC analysis of the racemic materials, showed that the diffuse heat capacity anomaly observed for the *(R)*- and *(S)*-enantiomers is absent, and a normal Iso-S_A and S_A-S_C phase transition sequence is observed instead. However, by overlaying the thermograms of a particular enantiomer and its racemate, the Iso-S_A transition for the racemates occurs at approximately the same temperature as the diffuse 'transition' does in the pure enantiomers; this is shown for the tetradecyloxy compounds **16** and **17** in the inset of figure 3.

Interestingly, summation of the enthalpies of the diffuse peak and the Iso-S_C* peak in a particular optically active material gives a value which is slightly lower than the enthalpy associated with the Iso-S_A transition in the relevant racemic compound; a similar relationship has been observed previously ^{13}. The enthalpy of the diffuse 'transition' increases slowly as the homologous series is ascended.

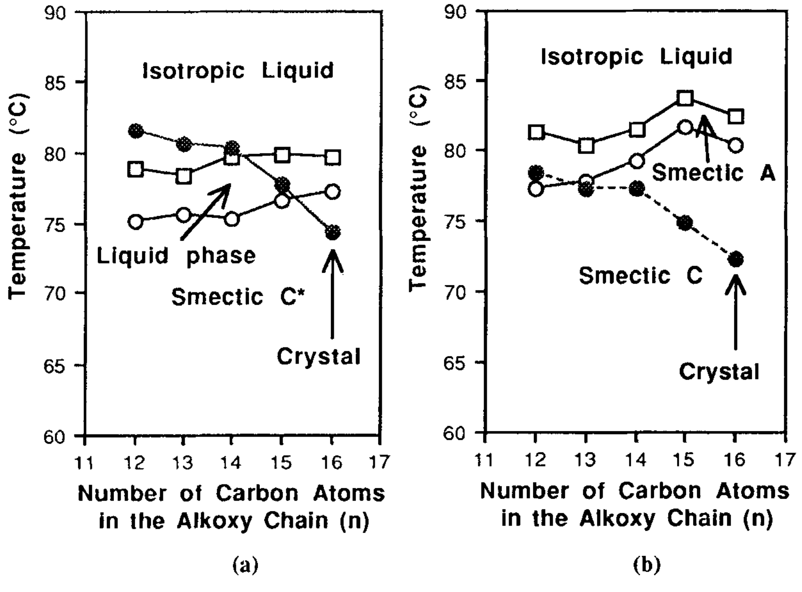


Figure 2 : The Transition Temperatures and Phase Assignment of the *(R)*- and *(R,S)*-1-Methylheptyl 4'-[(3-fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates Plotted as a Function of the Length of the Terminal Alkyl Chain

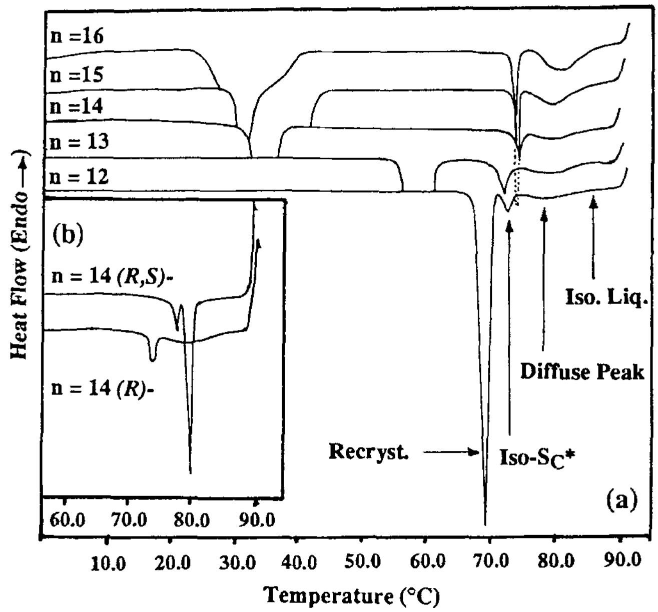


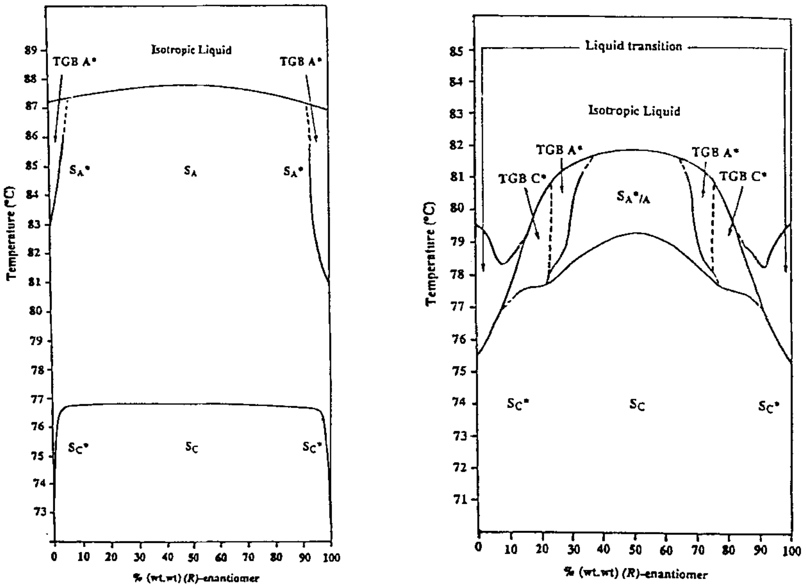
Figure 3: The Superimposed DSC Thermograms of (a) the *(S)*-1-Methylheptyl 4'-[(3-fluoro-4-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates and (b) the Clearing Point Detail for an *(R)*- and an *(R,S)*-Homologue

Optical Purity Studies

The influence of optical purity on phase behaviour was studied by construction of complete phase diagrams for a variety of homologues. This was carried out by accurately weighing the required amounts of *(R)*- and *(S)*-enantiomers and thoroughly mixing them in their isotropic state; the binary mixtures were then analyzed by thermal optical microscopy and DSC.

The phase diagram for 1-methylheptyl 4'-[(2-fluoro-4-tetradecyloxyphenyl)-propioloyloxy]biphenyl-4-carboxylate is shown in figure 4(a). The diagram is characterized by the presence of two "wing-like" regions of TGB A* which appear at compositions of between 0 and 5 % (wt.wt) of either enantiomer; at lower enantiomeric excess compositions a region of normal $S_{A^*/A}$ was observed. Further cooling of the $S_{A^*/A}$ saw the formation of a broad region of $S_{C^*/C}$ before crystallization occurred.

The phase diagram for the 3-fluoro analogues is very different in appearance, as is shown in figure 4(b). One of the most striking features is the dramatic and steep increase in the magnitude of the clearing point (*ca.*, 7 °C) as the optical purity decreases. Furthermore, although neither of the enantiomers displays TGB phases, two regions of induced TGB phases are observed at compositions between 10-25 % (wt.wt) of either enantiomer. The TGB A* phase was identified on cooling from the isotropic liquid by the presence of the usual filament texture ^{2}. More intriguing is the presence of another TGB phase, the proposed TGB C* phase, which appears as a grey, shimmering *schlieren* texture, in which pitch bands may be observed in certain domains; other domains of the texture appeared be highly selectively reflecting and planar in nature, possibly indicating the presence of two different helical axes which are thought to be associated with the TGB C* structure. Finally, DSC studies performed on high enantiomeric purity samples (0 - 20 % (wt.wt) showed that the diffuse, liquid transition temperatures decreases and eventually disappear as optical purity decreases.



(a) **(b)**

Figure 4: The Phase Diagrams for Mixtures of (a) *(R)*- and *(S)*-1-Methylheptyl 4'-[(2-fluoro-4-tetradecyloxyphenyl)propioloyloxy]-4-carboxylates and (b) *(R)*- and *(S)*-1-Methylheptyl 4'-[(3-fluoro-4-tetradecyloxyphenyl)propioloyloxy]-4-carboxylates

The presence of a transition within the isotropic liquid was noted previously for the parent propiolates which displayed TGB A* phases; furthermore diffuse scattering of X-rays appears to suggest the presence of some form of "fog-like" structure analogous to the Blue fog phase [2]. However, as the 3-fluoro enantiomers described earlier do not show TGB A* phase and therefore the presence of a fog phase appears anomalous.

Optical Properties of the Isotropic Liquid Close to the Diffuse Peak

A series of studies to measure the optical rotatory power and circular dichroism behaviour were carried out in order to further probe the subtle structural detail of the liquid transition. The optical rotatory power of the *(S)*-enantiomer of compound **16** was found to increase dramatically on cooling and this behaviour is shown in figure 5(a); the onset of this behaviour coincides with the temperature of the diffuse transiton detected by

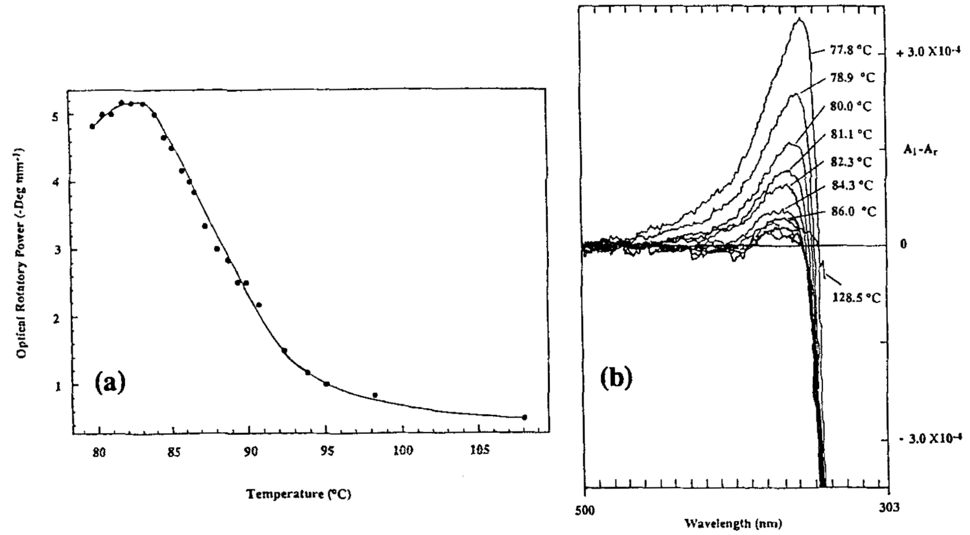


Figure 5 : (a) The Optical Rotatory Power of the *(S)*-Enantiomer of Compound 16 Plotted as a Function of Temperature and (b)CD-Wavelength Curves for the *(S)*-Enantiomer of Compound 16 Plotted at Different Temperatures

DSC. Similarly, a strong enhancement of the CD signal (attributable to the absorption of the biphenyl-CO_2-alkyl ester group) was observed on cooling form the isotropic liquid in the 355-370 nm region of the CD spectra; this is illustrated in figure 5(b). The results from this CD study correlate well with both the optical rotatory power experiment and the data obtained by DSC, and appear to indicate that the diffuse peak phenomena is related to the presence of a degree of cybotactic chiral order within an isotropic medium [12].

Ferroelectric Properties

The position of the fluoro-substituent was found to markedly influence the magnitude of both the spontaneous polarization and the switched tilt angle of the S_C* phase; the results for compound **6** and **16** are listed in table 3.

Comp. Number	Position of F-Substituent	Spontaneous Polarization (nC cm^{-2}) [a]	Switched Tilt Angle (Degrees) [b]
16	3	90	15
6	2	40	30

[a]..value taken at 4 °C below the Iso-S_C* or S_A*-S_C* transition, measured at 15 V ac. and 60 Hz; [b]..saturation values.

Table 3 : Comparison of Spontaneous Polarization and Switched Tilt Angles of the *(R)*-1-Methylheptyl 4'-[(2- and 3-fluoro-4-tetradecyloxyphenyl)propioloyloxy]-4-carboxylates

The differences in both the spontaneous polarization and tilt angle between the 2- and 3-fluoro-substituted compounds is remarkable considering that the only change in the molecular structure occurs at the opposite end of the molecules to the chiral moiety which undoubted influences both symmetry breaking operations and the polarization. It has been postulated that a combination of influences may be responsible, including hindered rotation of the terminal 4-alkoxy substituent, subsequent biaxial ordering and compensation of electric and steric dipoles by different packing [12].

DISCUSSION

The authenticity of the diffuse liquid 'transition' observed for the optically active compounds has been confirmed, and the optical rotatory power and circular dichroism studies both clearly indicate that some form of chiral organization close to the clearing point is responsible. A tentative explanation for the phenomenon may be that the S_C* phase possesses some latent TGB nature (such as a chirality induced frustration), given that that a TGB phase is thought to be stabilized by the presence of a network (or lattice) of screw dislocations. The possibility may then arise in which either the screw dislocations or smectic block regions melt leaving either a cybotactic network of smectic blocks or screw dislocations in an isotropic liquid. Further isotropisation of such a system would result in the formation of a macroscopically disordered liquid. The optical studies appear to suggest that the situation in which a network of screw dislocations is formed in a macroscopically disordered background is more probable. Alternatively, if the S_C* phase has no TGB character, the diffuse transition may not constitute a real phase change, but represent some cooperative change in conformational or molecular packing.

CONCLUSIONS

The position of the fluoro-substituents in a propiolate ester core is crucial to both the formation of S_C* and TGB phases in the pure compounds as well as strongly influencing the nature of the ferroelectric properties, such as spontaneous polarization and tilt angle. The origin of the diffuse transition observed in the 3-fluoro-substituted enantiomers appears to be due to the existence of cybotactic chiral ordering close to the clearing point.

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References

1 J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak and J.S. Patel, Nature (London), **337**, 449, (1987).
2 J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak and J.S. Patel, J. Am. Chem. Soc., **111**, 8119, (1989).
3 M.A. Waugh, S.M. Stein, E. Chin and J.W. Goodby, Liquid Crystals, **11**, 135, (1992).
4 A. Bouchta, H.T. Nguyen, M.F. Achard, F. Hardouin, C. Destrade, R.J. Twieg, A. Maaroufi and N. Isaert, Liquid Crystals, **12**, 575, (1992).

5 H.T. Nguyen, A. Bouchta, L. Navailles, P, Barois, N. Isaert, R.J. Twieg, A. Maaroufi, and C. Destrade, J. Phys II (France), **2**, 1889, (1992).

6 L. Navailles, H.T. Nguyen, P. Barois, C. Destrade and N. Isaert, Liquid Crystals, **15**, 479, (1993).

7 P. Balkwill, D. Bishop, A. Pearson and I. Sage, Mol. Cryst. Liq. Cryst., **123**, 1, (1985).

8 V. Reiffenrath, J. Krause, H.J. Plach and G. Weber, Liquid Crystals, **5**, 159, (1989).

9 M.A. Osman, Mol. Cryst. Liq. Cryst., **128**, 45, (1985).

10 C. Viney, R.J. Twieg, T.P. Russell and L.E. Depero, Liquid Crystals, **5**, 1793, (1989).

11 C, Viney, T.P. Russell, L.E. Depero and R.J. Twieg, Mol. Cryst. Liq. Cryst., **168**, 63, (1989).

12 C.J. Booth, D.A. Dunmur, J.W. Goodby, J.S. Kang and K.J. Toyne, J. Mater. Chem., **4**, 747, (1994).

13 J.W. Goodby, A.J. Slaney, C.J. Booth, I. Nishiyama, J.D. Vuijk, P. Styring and K.J. Toyne, Mol. Cryst. Liq. Cryst., **243**, 231, (1994).