Achiral swallow-tailed materials with 'antiferroelectric-like' structure and their potential use in antiferroelectric mixtures

Christopher J. Booth[ab]; David A. Dunmur[bc]; John W. Goodby[ab]; Julie Haley[ab]; Kenneth J. Toyne[ab]

[a] School of Chemistry, The University of Hull, Hull, UK [b] Sharp Laboratories of Europe Ltd, Oxford, UK [c] Centre for Molecular Materials, The Department of Chemistry, University of Sheffield, Sheffield, UK

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Achiral swallow-tailed materials with 'antiferroelectric-like' structure and their potential use in antiferroelectric mixtures

by CHRISTOPHER J. BOOTH*†, DAVID A. DUNMUR‡,
JOHN W. GOODBY†, JULIE HALEY† and KENNETH J. TOYNE†

†School of Chemistry, The University of Hull, Hull HU6 7RX, UK
‡Centre for Molecular Materials, The Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

Achiral 'swallow-tailed' liquid crystalline materials are known to give alternating-tilt smectic C phases ($S_{C_{alt}}$) which have structural similarities to the chiral antiferroelectric phases denoted as $S_{C_A}^*$. This paper describes the synthesis and characterization of three achiral branched-alkyl 4-(4'-dodecyloxybiphenyl-4-carbonyloxy)-3-fluorobenzoates. Optical microscopy and differential scanning calorimetry confirm that these materials show $S_{C_{alt}}$ and overlying S_A phases. The compounds were investigated as potential hosts which could be doped with a chiral ferroelectric liquid crystal so as to provide a viable antiferroelectric mixture. These studies (microscopy and differential scanning calorimetry), to characterize the properties of the mixtures, show that antiferroelectric phases are induced. However, switching studies show that the antiferroelectric phases are extremely stable, a property which is almost certainly a consequence of the length of the lateral branching groups (ethyl, propyl and butyl).

1. Introduction

Recently it has been shown that the length of the lateral substituent at the asymmetric centre of optically active liquid crystalline materials is critical in influencing the type of chiral mesophase observed. For instance, in certain classes of chiral phenyl propiolates and benzoates, lengthening the lateral substituent from methyl to propyl results in the complete eclipse of ferroelectric and ferrielectric smectic C* phases and leads to the preferred formation of inherently stable antiferroelectric smectic C* phases ($S_{C_A}^*$) [1, 2]. It has also been demonstrated subsequently that certain achiral swallow-tailed materials may display 'antiferroelectric-like' or 'zig-zag' smectic C phases, which are hereafter denoted as $S_{C_{alt}}$ [3, 4].

The aim of this work was to synthesize and evaluate a series of achiral swallow-tailed compounds which could possibly be used as host components of antiferroelectric eutectic mixtures. This approach to producing antiferroelectric systems is particularly advantageous as it avoids the use of costly chiral alcohols in producing the main component of the mixture, since only small quantities of the appropriate chiral dopants would need to be added to an achiral host. In addition, the host

system could be tuned to have a low viscosity and a wide operating temperature range.

As the ferro-, ferri- and antiferroelectric properties of several chiral 4-(4'-dodecyloxybiphenyl-4-carbonyloxy)-3-fluorobenzoates are known [5, 6], it was decided that this class of materials would offer a suitable starting point for such an investigation. The materials to be synthesized and evaluated as mixtures are represented by the general structure 1.

1a,n=2; 1b,n=3 and 1c,n=4.
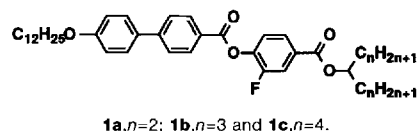
2. Synthesis of materials

The synthesis of the series 1a–c is outlined in the scheme; the individual synthetic steps have been described in some detail previously [7]. All the intermediates and target materials were rigorously purified by flash chromatography [8] and/or repeated recrystallizations. The structures of the intermediates and products were confirmed by a combination of ^{1}H NMR spectroscopy (JEOL GX NM270 FT-NMR), IR spectroscopy (Perkin Elmer 783 spectrometer) and mass spectrometry (Finnigan 1020 GC-MS spectrometer).

* Author for correspondence.
Current address: Sharp Laboratories of Europe Ltd, Edmund Halley Road, Oxford Science Park, Oxford OX4 4GA, UK.

Satisfactory elemental analyses were obtained for all products (performed on a Fisons Instruments EA 1108 CHN analyzer). Purities of the products **1a–c** and intermediates **3, 4, 5a–c, 6a–c** were checked by thin layer chromatography (Merck 60 F254 preformed plates) and by normal- and reverse-phase HPLC using Microsorb C18 or Si columns and acetonitrile (May & Baker Chromanorm) as the mobile phase. The initial phase assignments and transition temperatures were determined by thermal polarizing light microscopy (Zeiss Universal microscope) in conjunction with a hot stage and controller (Mettler FP82 microfurnace and FP80 control unit). Differential scanning calorimetry (Perkin Elmer DSC7) was used to determine the enthalpies of the transitions; the instrument was previously calibrated against an indium standard (measured $\Delta H = 28\cdot35\,\mathrm{J\,g^{-1}}$, literature $28\cdot45\,\mathrm{J\,g^{-1}}$ [9]) and all values are quoted in $\mathrm{kJ\,mol^{-1}}$. Electro-optic measurements were carried out with planar-aligned, polyimide-coated, $4\cdot7\,\mu\mathrm{m}$ spaced cells (Electronics Chemicals High Technology Group, Japan) with an active area of $0\cdot25\,\mathrm{cm^2}$ for the indium–tin oxide electrodes; electrical contacts were made directly to the electrode surface using conductive epoxy resin cement (Radio Spares). The analytical data for materials **1a–c** are given below.

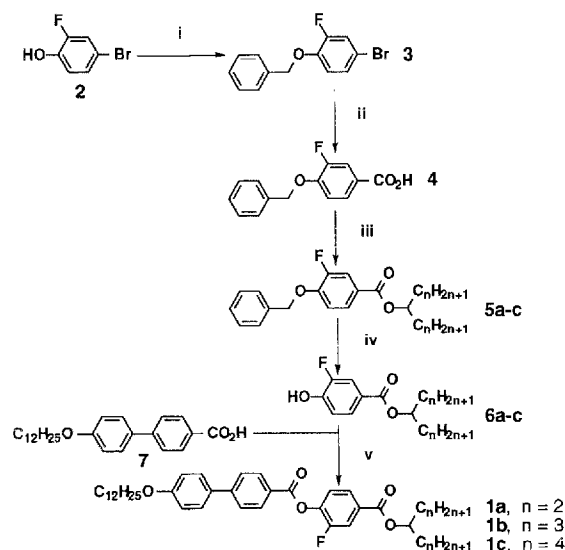*1-Ethylpropyl 4-(4'-dodecyloxybiphenyl-4-carbonyl-oxy)-3-fluorobenzoate **1a***

I $108\cdot6$ S_A $82\cdot2$ $S_{C_{alt}}$ $\leqslant32\cdot0$ recryst. (°C); ^{1}H NMR ($270\,\mathrm{MHz}$; solvent CDCl$_3$) δ: $0\cdot79$ (3H, t), $0\cdot87$ (6H, t), $1\cdot19$ (18H, m), $1\cdot57$–$1\cdot77$ (6H, m), $3\cdot93$ (2H, t), $4\cdot94$ (1H, quintet), $6\cdot92$ (2H, d), $7\cdot28$ (1H, dd), $7\cdot51$ (2H, d), $7\cdot62$ (2H, d), $7\cdot83$ (2H, m), $8\cdot16$ (2H, d). IR ν_{max} (KBr): 2920, 2850, 1740, 1715, 1600, 1270, 1180, 1050, 830, $760\,\mathrm{cm^{-1}}$. M.s.: m/z (70 eV): 590 (M^+, 5 per cent), 366 (100 per cent), 198 (51 per cent). Found: C $75\cdot09$; H $8\cdot17$. $C_{37}H_{47}FO_5$ requires C $75\cdot22$; H $8\cdot02$ per cent.

*1-Propylbutyl 4-(4'-dodecyloxybiphenyl-4-carbonyl-oxy)-3-fluorobenzoate **1b***

I $72\cdot9$ S_A $56\cdot8$ $S_{C_{alt}}$ $39\cdot7$ recryst. (°C); ^{1}H NMR ($270\,\mathrm{MHz}$; solvent CDCl$_3$) δ: $0\cdot92$ (3H, t), $0\cdot94$ (6H, t), $1\cdot25$–$1\cdot50$ (20H, m), $1\cdot66$ (4H, sextet), $1\cdot82$ (4H, quartet), $4\cdot02$ (2H, t), $5\cdot17$ (1H, m), $7\cdot01$ (2H, d), $7\cdot37$ (1H, dd), $7\cdot60$ (2H, d), $7\cdot71$ (2H, d), $7\cdot91$ (2H, m), $8\cdot25$ (2H, d). IR ν_{max} (KBr): 2950, 2920, 2840, 1745, 1730, 1600, 1295, 1260, 1185, 1105, 1065, 830, $760\,\mathrm{cm^{-1}}$. M.s.: m/z (70 eV): 365 (100 per cent), 197 (38 per cent), 169 (12 per cent), 139 (23 per cent). Found: C $75\cdot79$; H $8\cdot57$. $C_{39}H_{51}FO_5$ requires C $75\cdot69$; H $8\cdot31$ per cent.

*1-Butylpentyl 4-(4'-dodecyloxybiphenyl-4-carbonyl-oxy)-3-fluorobenzoate **1c***

I $58\cdot1$ S_A $45\cdot7$ $S_{C_{alt}}$ $40\cdot5$ recryst. (°C); ^{1}H NMR ($270\,\mathrm{MHz}$; solvent CDCl$_3$) δ: $0\cdot89$ (9H, m), $1\cdot20$–$1\cdot40$ (24H, m), $1\cdot67$ (4H, m), $1\cdot82$ (4H, quartet), $4\cdot02$ (2H, t), $5\cdot14$ (1H, quintet), $7\cdot01$ (2H, d), $7\cdot37$ (1H, dd), $7\cdot60$ (2H, d), $7\cdot71$


Scheme 1. Synthetic route to the branched-alkyl 4-(4'-dodecyloxybiphenyl-4-carbonyloxy)-3-fluorobenzoates, **1a–c**.

(2H, d), $7\cdot91$ (2H, m), $8\cdot25$ (2H, d). IR ν_{max} (KBr): 2950, 2920, 2840, 1740, 1710, 1600, 1290, 1260, 1185, 1105, 1065, 830, $760\,\mathrm{cm^{-1}}$. M.s.: m/z (70 eV): 646 (M^+,trace), 366 (100 per cent), 196 (20 per cent), 139 (20 per cent), 91 (32 per cent). Found C $75\cdot93$; H $8\cdot67$. $C_{41}H_{55}FO_5$ requires C $76\cdot12$; H $8\cdot57$.

3. Optical microscopy and differential thermal analysis studies

The phase assignments and transition temperatures for compounds **1a–c** were initially made by optical microscopy using clean, untreated microscope slides and coverslips; all transition temperatures were recorded on cooling from the isotropic liquid at a cooling rate of $2°\mathrm{C\,min^{-1}}$ and are given in table 1.

On cooling from the isotropic liquid, compounds **1a–c** show broken focal-conic fans of a smectic A phase, but this texture rapidly becomes homeotropic (i.e. appears black between crossed polarizers). Further cooling of the smectic A phases of all three compounds results in the formation of a grey, shimmering *schlieren* texture characterized by the presence of many 4-brush

Table 1. Transition temperatures and associated enthalpy data for the 4-(4'-dodecyloxybiphenyl-4-carbonyloxy)-3-fluorobenzoate esters (compounds 1 a–c).

$$C_{12}H_{25}O - \text{biphenyl} - C(=O)O - \text{benzene}(F) - C(=O)O - CH(C_nH_{2n+1})(C_nH_{2n+1})$$
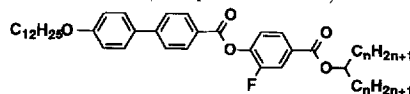
Compound number	n	Transition temperatures (°C)[a]				
		m.p.[b]	I	S_A	$S_{C_{alt}}$	Recryst.
1a	2	46·4 • [31·16][d]	108·6 • [3·91]	82·2 • [0·18]	32[c] •	•
1b	3	65·9 • [37·06]	72·9 • [2·12]	56·8 • [0·28]	40 •	•
1c	4	49·2 • [33·16]	58·1 • [1·36]	45·7 • [0·39]	40 •	•

[a] Recorded by optical microscopy at cooling rates of 2°C min^{-1}.
[b] Taken from DSC thermograms recorded at heating rates of 5°C min^{-1}.
[c] Recrystallization values included only to give an indication of the approximate phase range.
[d] Figures in square parenthesis denote enthalpies quoted in kJ mol^{-1}.

singularities, indicating a smectic C phase, see figures 1 (a), (b) and (c).

Closer examination of thin films of compounds 1 b and 1 c revealed the presence of a small number of 2-brush singularities. This type of brush disclination has been previously observed in other antiferroelectric compounds [10] and indicates that these achiral smectic C phases possess some degree of antiferroelectric-like order (i.e. have an alternating 'zig-zag' layer structure); the phases have consequently been denoted as $S_{C_{alt}}$ (alt = alternating) in table 1 [3, 4]. Further cooling of compounds 1 a–c results in the crystallization of each sample.

Differential scanning calorimetry of compounds 1 a–c, revealed that the $S_{C_{alt}}$ phases of compounds 1 b and 1 c

Table 2. Transition temperatures, phase assignments and associated enthalpies of antiferroelectric binary mixtures.

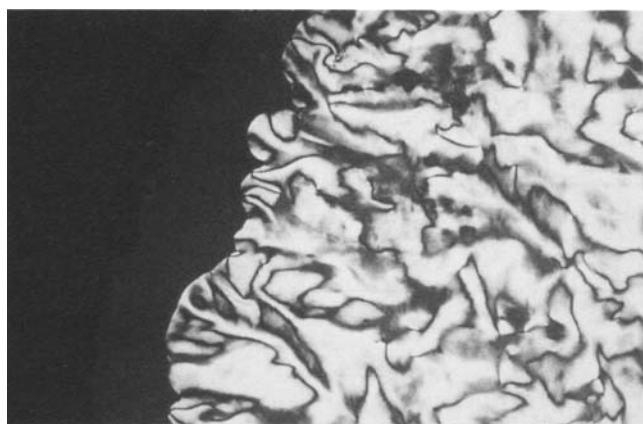| Compound number (host)	wt % dopant 8[a]	Transition temperatures (°C)[b]
1a	11·8	I 107·4S_A^* 81·5S_C^* 81·1$S_{C_A}^*$ 27[c] recryst. [6·55][d][0·03] [0·32]
1b	9·5	I 76·6S_A^* 59·6$S_{C_A}^*$ 33 recryst. [3·77] [0·47]
1c	9·2	I 63·0S_A^* 47·9$S_{C_A}^*$ 26 recryst. [2·52] [0·56]

[a] (S)-1-Fluoro-oct-2-yl 4-(4'-dodecyloxybiphenyl-4-carbonyloxy)-3-fluorobenzoate (8), I 94·4 S_A^* 76·3 S_C^* 44·9 recryst. (°C).
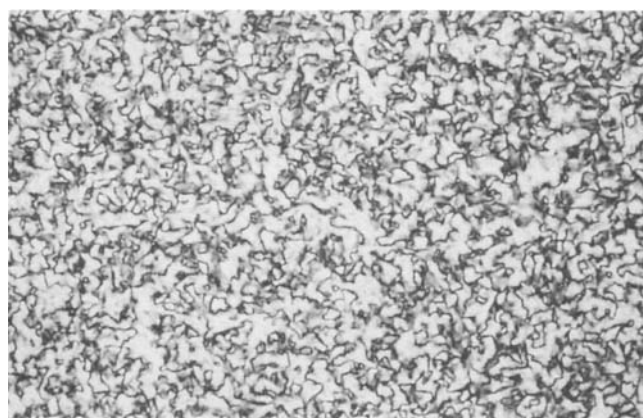[b] As determined by optical microscopy, at a cooling rate of 2°C min^{-1}.
[c] Recrystallization values included only to give an indication of the approximate phase range.
[d] Figures in parenthesis denote enthalpies in kJ mol^{-1}.

are in fact monotropic. Also the enthalpies associated with the I–S_A and S_A–$S_{C_{alt}}$ transitions decrease and increase, respectively, as the terminal alkyl chain lengths increase. The S_A–$S_{C_{alt}}$ transitions all have strong first order characteristics, as is observed for other chiral and achiral swallow-tail compounds which display antiferro-electric or 'antiferroelectric-like' tendencies [4, 7]. Similarly, the enthalpies associated with the S_A–$S_{C_{alt}}$ transitions are of approximately the same magnitude as the enthalpies of the S_A/S_A^*–$S_{C_{alt}}/S_{C_A}^*$ transitions of the materials cited in [4, 7], i.e. c. 0·2–0·4 kJ mol^{-1}.

4. Mixture studies

A series of three test mixtures was then formulated by accurately weighing a quantity of chiral ferroelectric dopant (S)-1-fluoro-oct-2-yl 4-(4'-dodecyloxybiphenyl-4-carbonyloxy)-3-fluorobenzoate 8 [11] into a known weight of the host compounds 1 a–c contained in a clean glass vial. The mixtures were then intimately mixed in their isotropic states. The transition temperatures and phase assignments were then made by optical microscopy; these assignments are given in table 2, along with the weight percentage of dopant 8 used.

The mixture containing host compound 1 a shows S_A^*, S_C^* and what is believed to be a $S_{C_A}^*$ phase. Cooling of the S_A^* phase into the S_C^* phase is accompanied by the appearance of dechiralization lines on the broken focal-conic fans. Rotation of the microscope's upper polarizer reveals that the resulting dispersion of white light from the S_C^* phase of the mixture of 1 a occurs in a clockwise manner, i.e. this ferroelectric S_C^* phase has a right-handed helix. Cooling the S_C^* phase results in the sudden disappearance of the dechiralization lines on the focal-conic fans and the appearance of *schlieren* domains in the
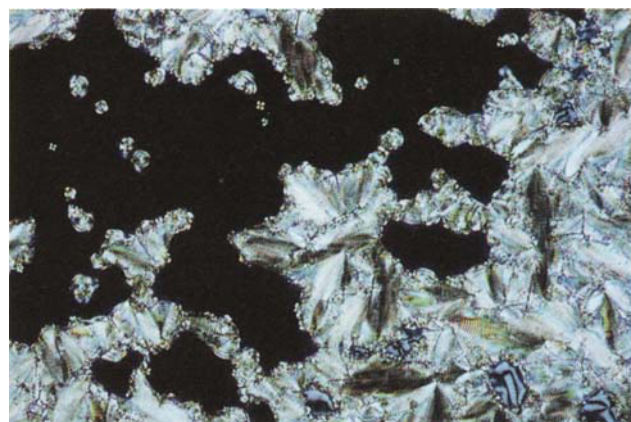
(a)

(b)
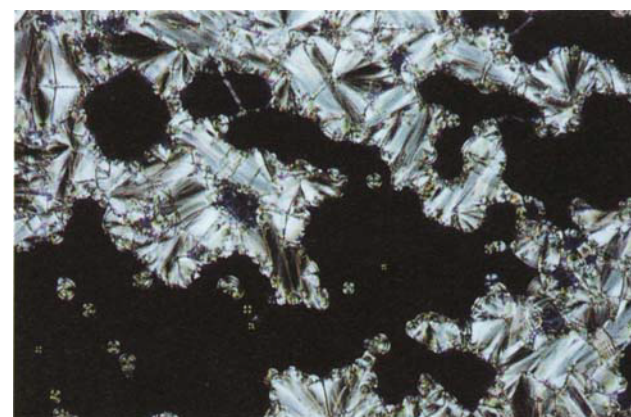

(c)

Figure 1. (a) and (b) Schlieren texture of $S_{C_{alt}}$ phases of compound **1a** and **1b** respectively (magnification × 100). (c) Schlieren texture of the $S_{C_{alt}}$ phase of compound **1c** (magnification × 100).

(a)

(b)

Figure 2. (a) The ferroelectric S_C^* phase of the 11·8 wt % mixture of dopant **8** in host **1c** showing dechiralization lines; (b) the antiferroelectric phase (magnification × 100).
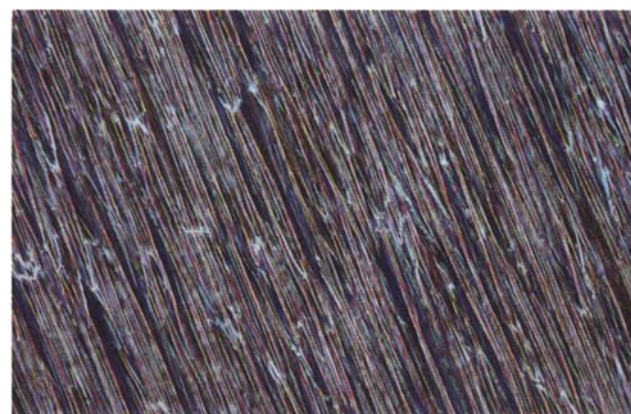

Figure 4. The striped domain texture of an induced antiferro-electric phase constrained in a rubbed PI cell (4·7 μm) (magnification × 100).

pseudo-homeotropically aligned zones of the sample; this marks the phase transition between the S_C^* and what is believed to be an $S_{C_A}^*$ phase (presumably the pitch

length decreases suddenly at this transition). Again the dispersion of white light occurs in a clockwise manner, indicating that the antiferroelectric phase has a right-handed helix and a twist inversion phenomenon has not taken place at this transition. The difference between the S_C^* and $S_{C_A}^*$ phases is shown in figures 2(a) and (b), which depict the transition in a mixture with host 1a; here the dechiralization lines are clearly visible on the focal-conic fans in figure 2(a), but not on the focal-conic fans in the antiferroelectric phase in figure 2(b).

By contrast, the 9·5 and 9·2 wt % mixtures of dopant 8 with hosts 1b and 1c, respectively, show only antiferroelectric phases on cooling from the S_A^* phase; these appear as a mosaic grey background with small *schlieren* zones amongst regions of focal-conic fans. Once again the phases in both mixtures were found to have a right-handed helix, using the method described previously.

All three mixtures were analysed by differential scanning calorimetry which supported the S_A^*–S_C^*–$S_{C_A}^*$ sequence found for the 11·8 wt % mixture of compound 1a. The S_A^*–S_C^* and S_C^*–$S_{C_A}^*$ were clearly resolved as second and first order events as shown in figures 3(a) and (b).

The shapes of the S_A^*–$S_{C_A}^*$ transition peaks for mixtures involving hosts 1b and 1c, were clearly, consistent with their first order nature, supporting the assignment of the $S_{C_A}^*$ phases.

5. Switching studies

The mixtures of the doped hosts 1a-c were constrained within 4·7 μm thick cells (with rubbed polyimide alignment layers) and the 'antiferroelectric' phases all gave the distinctive, striped domain texture which has been commonly observed before for other antiferroelectric compounds [4, 7]. The resultant extinction direction is always parallel to the direction of the striped domain structures. Figure 4 shows the striped domain texture of the $S_{C_A}^*$ phase of the 11·8 wt % dopant 8 in host 1a.

However, it was found impossible to effect antiferroelectric–ferroelectric switching at the maximum voltage of our power supply (30 V, 6·38 MV m^{-1}). It was noticed for all three mixtures based on hosts 1a-c that during the attempted switching, the transmitted light was attenuated but the extinction angle proved to be too small to measure. This tends to suggest that it should be possible to switch the materials at much higher applied field strengths than were available in this laboratory.

Interestingly, it was found possible to effect ferroelectric switching in host mixture 1a; here the tilt angle, although small, was measurable and reached a saturation value of aproximately 10° before falling to zero at the S_C^*–$S_{C_A}^*$ transition. The switched tilt angle–temperature characteristic is shown in figure 5, and was recorded at 25 V in a 4·7 μm thick cell (5·32 MV m^{-1}).
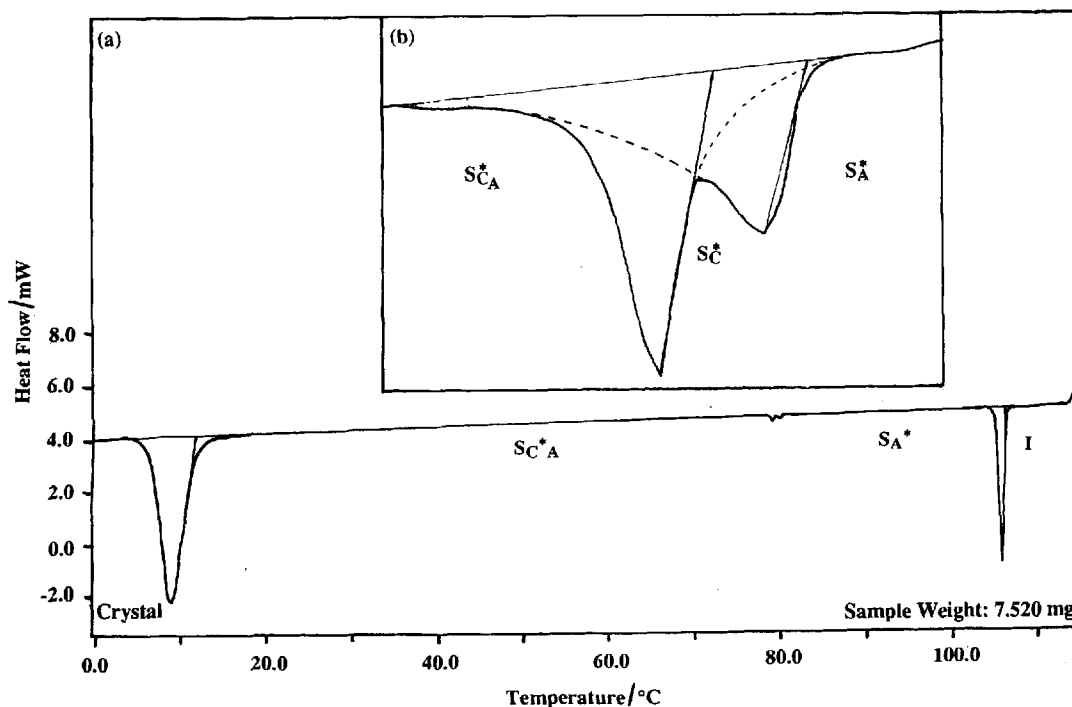

Figure 3. (a) DSC thermogram of 11·8 wt % of dopant 8 in host 1a; (b) expanded area of the S_A^*–S_C^*–$S_{C_A}^*$ phase sequence region.
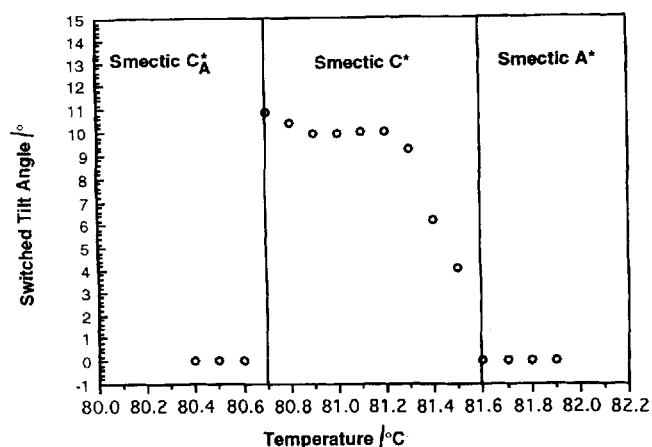
Figure 5. A plot of switched tilt angle as a function of temperature for a 11·8 wt % mixture of dopant **8** in host **1a** (recorded at 25 V, in a 4·7 μm cell).

6. Discussion

It is clear from these results that doping an $S_{C_{alt}}$ phase of a host liquid crystal with a chiral compound or liquid crystal material can induce antiferroelectric phase behaviour in the resultant binary mixture. It is reasonable to suggest that the $S_{C_{alt}}$ and $S^*_{C_A}$ phases are indeed structurally similar; in the case of the $S_{C_{alt}}$ phase, the structure may be represented by an arrangement of alternately tilted S_C 'layers', so as to give a zig-zag type situation. This contrasts slightly with the $S^*_{C_A}$ phase, where the 'zig-zag' nature is further influenced by the inclusion of chiral molecules and results in a macroscopic alternating tilt orientational order throughout the bulk of the sample.

Practically speaking, the mixtures employed here resulted in very stable induced antiferroelectric phases, and the threshold fields necessary to achieve switching from the antiferroelectric to the induced ferroelectric state were in excess of 6·38 MV m^{-1} under the cell conditions employed. This is largely a result of the structure of the host's terminal ester group; compounds **1 a–c** essentially having ethyl, propyl and butyl lateral branch points, respectively. It should be recalled that the stability of antiferroelectric phases is known to be increased by lengthening the lateral branching group; in certain antiferroelectric systems (e.g. (*R*)- or (*S*)-1-alkylheptyl 4'-[(4-nonyloxyphenyl)propioloyloxy]biphenyl-4-carboxylates) the threshold stability is recorded as having been increased from *c*. 3·5 MV m^{-1} for the ethylbranched compound, to *c*. 11·5 MV m^{-1} for the propylbranched homologue [1]. Indeed a cross-over point from ferroelectric and antiferroelectric properties to solely antiferroelectric properties for such a system has

been characterized as occurring for the propyl-branched compound. Similarly, high threshold fields have also been reported for other chiral systems, notably the 2- or 3-alkylheptyl 4'-[(4-nonyloxyphenyl)propenyloyloxy]-biphenyl-4-carboxylates, which require threshold switching voltages in excess of 400 V peak-to-peak for samples contained in 4·0 μm spaced test cells [3].

7. Conclusions

Although ferroelectric-to-antiferroelectric switching was not achieved in any of the three mixtures discussed in this paper, the results obtained from the optical microscopy, differential scanning calorimetry and electro-optic experiments show that it is possible to formulate stable 'induced' antiferroelectric mixtures using a chiral ferroelectric dopant and an achiral swallow-tail host which displays an $S_{C_{alt}}$ mesophase. The ramifications of this result are that such an approach may provide a practical route to antiferroelectric eutectic mixtures for use in display device applications. A similar approach is used for obtaining ferroelectric liquid crystalline mixtures from smectic C material and a chiral dopant.

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