Electroclinic and antiferroelectric properties of (R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate

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The synthesis of the novel chiral mesogen (R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate and a discussion of its various liquid-crystalline properties are reported. Initial optical microscopy studies revealed the presence of a smectic A* phase and what was at first thought to be a smectic C* phase; further examination of this compound as thin film preparations revealed the presence of $s \pm 1/2$ disclinations suggesting that the phase is an antiferroelectric subphase. Furthermore, these observations were supported by results from both differential scanning calorimetry and contact miscibility studies using known smectic C*_A standards. The antiferroelectric nature of the phase was confirmed by obtaining sharp threshold characteristic curves during electrical switching studies from the antiferroelectric to an induced ferroelectric phase. Additionally, the chirality of the compound results in a reduction in the environmental symmetry for the smectic C*_A transition to take place under suitable conditions.

The discovery of the antiferroelectric subphase of the chiral smectic C* phase has led to many investigations of its physical properties¹⁻¹¹ and offers the potential for applications in liquid crystal display devices.^{10,11} The structural changes associated with the transition from a ferroelectric to an antiferroelectric phase are believed to be due, in part, to the competition of the pairing energy of the ferroelectric dipoles and the packing entropy.⁸ Structurally, the S_{C*A} phase is a modification of the S_{C*} phase in which the 'layers' adopt an energetically more stable zig-zag like structure, and the dipoles associated with the molecules in one 'layer' oppose the dipoles of the molecules in a neighbouring 'layer'; thus the S_{C*A} phase has no net spontaneous polarization, unlike the ferroelectric S_{C*} phase. These differences in the structures are shown in Fig. 1, which depicts unwound ferroelectric and antiferroelectric structures.

In summary, it may be said that on cooling, as the $S_{C^{*-}}$ S_{C*A} transition is traversed, the magnitude of the spontaneous polarization first rises and saturates in the ferroelectric phase, and then decays and falls to zero in the antiferroelectric phase. By the application of a dc field to an antiferroelectric smectic C* phase, it is possible to destroy the 'zig-zag' orientational order between 'layers' and to induce a poled ferroelectric state. This switching process occurs at a sharply defined field strength (threshold field, $E_{\rm th}$) and as a consequence this threshold behaviour may be followed by observing changes in tilt angle during switching studies.¹² The physical characteristics of this state can also be examined by a combination of optical microscopy, differential thermal analysis and spontaneous polarization. In addition other optical techniques such as conoscopy, ellipsometry and Raman spectroscopy, can be used to cast further light on this subtle molecular organization.8,9,13,14

Antiferroelectric phases generally require an alternating, zigzag ordering of the layers and many of the materials which display this property of forming alternating structures possess unique molecular geometries, indeed they may largely be classified in the following categories; (i) materials which possess a chiral centre close to a rigid molecular core, $^{4-6,8,9}$ (ii) materials which have swallow-tailed terminal moieties,⁷ (such moieties need not necessarily be chiral,⁴), (iii) materials which possess a zig-zag or *trans* packing orientation (especially in polymers) which is capable of inducing alternating ordering of the layers within a phase.^{15,16} Although achiral compounds are capable of giving alternating layer tilt phases, only the study of chiral materials offers scope for the examination of the influence of molecular chirality/geometry on the chiral macroscopic properties of the antiferroelectric phase and related phase structures.

The material investigated [(R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1)] may be classified as belonging to categories (i) and (ii), in that it has a chiral centre close to a rigid liquid-crystalline core and it has some swallow-tailed character in the terminal chiral aliphatic moiety.



Experimental

Compound 1 was prepared as shown in Scheme 1. The first step involved the benzylation of 4-bromo-2-fluorophenol (2) to give 1-benzyloxy-4-bromo-2-fluorobenzene (3) in good yield. This was then treated with butyllithium in dry tetrahydrofuran (THF) at -78 °C to generate a lithium salt in situ, and subsequent treatment of this salt with solid carbon dioxide, followed by acidification gave 3-fluoro-4-benzyloxybenzoic acid (4).¹⁷ Compound 4 was then esterified with (S)-nonan-3ol using diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) to give the (R)-nonan-3-yl ester (5) as a colourless liquid.⁴⁻⁷ The benzyl protecting group was then removed by mild hydrogenolysis using palladium-on-charcoal in ethanol to give compound 6.18 The final step involved the esterification of compound 6 with 4'-dodecyloxybiphenyl-4-carboxylic acid (7)^{\ddagger} using dicyclohexylcarbodiimide (DCC) and 4-(N,Ndimethylamino)pyridine (DMAP) in dry dichloromethane.¹⁹

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[‡] Compound 7 was prepared by alkylation of 4-cyano-4'-hydroxybiphenyl with 1-bromododecane to give 4-cyano-4'-dodecyloxybiphenyl which was subsequently hydrolysed to give 7.



Scheme 1 Synthetic route to (R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1). Reagents and conditions: i, PhCH₂Br, K₂CO₃, butanone, reflux; ii, (a) BuLi, THF, N₂, -78 °C; (b) CO₂(s), THF, -78 °C—room temp.; (c) H⁺, H₂O, room temp.; iii, (S)-C₆H₁₃CH(OH)C₂H₅, DEAD, TPP, THF, N₂, room temp.; iv, H₂, 10% palladium-on-charcoal, ethanol, room temp.; v, DCC, DMAP, CH₂Cl₂ or THF, room temp.



Antiferroelectric Smectic C* Phase

Fig. 1 Structures of the ferroelectric and antiferroelectric variants of the smectic \mathbf{C}^* mesophase

The crude product (1) was rigorously purified by flash chromatography²⁰ and repeated recrystallization.

The chemical structures of all intermediates and final products were confirmed by a combination of the following techniques; ¹H nuclear magnetic resonance spectroscopy [JEOL GX NM270 FT-NMR spectrometer using tetramethylsilane (TMS) as the internal standard], infrared spectroscopy (Perkin Elmer 783 spectrometer) and mass spectrometry (Finnigan 1020 GC-MS spectrometer). Specific optical rotations were performed using an Optical Activity Ltd AA-10 Automatic Polarimeter using chloroform (Spectrosol) as the solvent and are given in units of 10^{-1} degree cm² g⁻¹.

At each stage of preparation the materials were purified by flash chromatography (May & Baker Sorbsil C60 40-60H micron silica gel) as described by Clark Still et al.20 The purities of all intermediates and final compounds were checked by thin layer chromatography (using Merck 60 F254 preformed aluminium backed plates) and by normal- and reversed-phase HPLC (Merck etc) using Microsorb C18 or Si columns and acetonitrile (May & Baker Chromanorm) as the mobile phase. Each of the final products was found to have chemical purities in excess of 99.5%. All solvents used in reactions were dried, distilled and stored as described in Perrin and Amarego.²¹ The initial phase assignments and transition temperatures were determined by thermal polarized light microscopy using a polarizing microscope (Zeiss Universal) in conjunction with a hot stage and controller (Mettler FP82 microfurnace and FP80 control unit). Differential scanning calorimetry (Perkin Elmer DSC7 calorimeter, TAC7/PC controller and IBM system /2model 50Z computer) was used to determine both the transition temperatures and the heats of transitions. The instrument was calibrated against an indium standard (measured $\Delta H = 28.35 \text{ J g}^{-1}$, literature value 28.45 J g⁻¹)²² and all enthalpies are quoted in kJ mol⁻¹. Tilt angle and ferroelectric polarization measurements were performed in planar aligned 1.4-5.8 µm thick cells (Electronics Chemicals High Technology Group, Japan) with an active area of 0.25 cm² indium-tin oxide electrodes, previously treated with undirectionally buffed polyimide (PI) alignment layers and electrical contacts were made directly to the internal surfaces. The cells were filled by capillary action while the materials were in their isotropic liquid states. Good alignment for switched tilt angle and polarization studies was achieved by slowly cooling from the isotropic liquid into the respective smectic states. Cooling rates were of the order of $0.2 \,^{\circ}C \,^{-1}$. Once filled the cell was connected to an ac frequency generator, a dual trace oscilloscope and a Diamant bridge.²³ Tilt angles (θ) in the smectic C* phase were obtained by measuring the angle (2θ) between the optical extinction positions for the ferroelectrically switched states observed in the polarizing microscope.²⁴

1-Benzyloxy-4-bromo-2-fluorobenzene (3)

Benzyl bromide (23.3 g, 136 mmol) in butanone (20 ml) was added dropwise to a refluxing, stirred suspension of 4-bromo-2-fluorophenol (2) (24.9 g, 131 mmol), potassium carbonate (19.0 g, 138 mmol) and butanone (150 ml). Once the addition was complete the reaction was heated under reflux for a further 20 h; TLC analysis showed completion of the reaction. The cooled mixture was filtered and the filtrate washed with brine (50 ml), dried (MgSO₄), refiltered and evaporated under reduced pressure to give a colourless liquid. This was purified by column chromatography (silica gel-dichloromethane) to give a white solid, which was recrystallized (cyclohexane) and dried in vacuo (P_2O_5 , 0.1 mmHg, 40 °C, 5 h) to give the title compound (31.5 g, 86%); mp 67–70 °C; $\delta_{\rm H}$ (270 MHz; CDCl₃; TMS) 5.10 (2 H, s), 6.85 (1 H, t), 7.14 (1 H, m), 7.24 (1 H, m), 7.38 (5 H, m); ν (KBr disc)/cm⁻¹ 3030, 2960, 2880, 1490, 1385, 1300, 1265, 1200, 1130, 1005, 860, 805; m/z (70 eV) (%) 282 $(M^+, 2\%), 280 (M^+, 2), 91 (100), 81 (8).$

3-Fluoro-4-benzyloxybenzoic acid (4)

Butyllithium (3.6 ml, 10.0 mol dm^{-3} in hexanes) was added dropwise to a cooled (-78 °C), stirred solution of compound 3 (10.0 g, 35.7 mmol) in dry tetrahydrofuran (150 ml) under a positive nitrogen pressure. The reaction was maintained at -78 °C for 3 h, before being poured onto a mixture of crushed 'Cardice' and dry tetrahydrofuran (25 ml) with vigorous stirring and subsequently allowed to warm to room temperature. The mixture was then acidified with conc. hydrochloric acid and then diluted with water (200 ml). After separation of the organic phase, the aqueous phase was washed with diethyl ether $(3 \times 100 \text{ ml})$ the combined organic extracts were washed with brine (50 ml), dried (MgSO₄), filtered and evaporated to give a pale brown solid. The solid was recrystallized (cyclohexane-ethyl acetate) and dried in vacuo (P2O5, 0.20 mmHg, 25 °C, 72 h) to give the title compound as a colourless powder (4.18 g, 47%); mp 188–190 °C; $\delta_{\rm H}$ (270 MHz; CDCl₃; TMS) 5.40 (2 H, s), 7.05 (1 H, t), 7.35 (5 H, m), 7.75 (2 H, m), no carboxylic acid proton detected; $v(KBr \text{ disc})/\text{cm}^{-1}$ 2930, 2870, 1675, 1610, 1515, 1445, 1280, 1210, 990, 765, 690, 645; m/z (70 eV) (%) 246 $(M^+, 4\%), 91 (100), 65 (12).$

(R)-(-)-Nonan-3-yl 3-fluoro-4-benzyloxybenzoate (5)

Triphenylphosphine (1.23 g, 4.69 mmol), (S)-nonan-3-ol (1.00 g, 6.94 mmol) and dry tetrahydrofuran (10 ml) were added dropwise to a stirred solution of compound **4** (1.16 g, 4.71 mmol), diethyl azodicarboxylate (0.82 g, 4.71 mmol) and dry tetrahydrofuran (10 ml) under nitrogen at room temperature. The reaction was then stirred for a further 20 h before being diluted with diethyl ether (50 ml) and filtered through a pad of 'Hyflosupercel'. The filtrate was washed with brine (50 ml), dried (MgSO₄), filtered and evaporated to give a colourless solid which was purified by flash chromatography [fine mesh silica gel; 5% (v/v) ethyl acetate in petrol (bp 40–60 °C)] to give a colourless liquid which was dried *in vacuo* (P₂O₅, 0.20 mmHg, RT, 72 h) to give the title compound (1.09 g, 62%); $[\alpha]_D^{BT} - 5.5$ (c = 0.0366 g ml⁻¹; CHCl₃); $\delta_{\rm H}(270$ MHz; CDCl₃; TMS) 0.87 (3 H, t), 0.93 (3 H, t), 1.28 (10 H, m), 1.68 (2 H, m), 5.03 (1 H, sextet), 5.20 (2 H, s), 7.01 (1 H, t), 7.39 (5 H, m), 7.76 (1 H, m), 7.79 (1 H, t); v(film)/cm⁻¹ 2955, 2930, 2860, 1720, 1612, 1510, 1280, 1200, 1130, 1090, 950, 760, 700; *m/z* (70 eV) (%) 372 (M⁺, 5%), 247 (7), 229 (9), 91 (100).

(R)-(-)-Nonan-3-yl 3-fluoro-4-hydroxybenzoate (6)

Compound 5 (0.75 g, 2.0 mmol), 10% palladium-on-charcoal (0.15 g) and ethanol (50 ml) were degassed under vacuum and then stirred under an atmosphere of hydrogen for 72 h at room temperature. The mixture was degassed under vacuum and filtered through a pad of 'Hyflo-supercel' moistened with ethanol and the filtrate was then evaporated under reduced pressure to give a liquid residue which was purified by flash chromatography (fine mesh silica gel; dichloromethane) to give a colourless liquid which was then dried in vacuo (P_2O_5 , 0.2 mmHg, RT, 20 h) to give the title compound (0.44 g, 79%); $[\alpha]_D^{RT} - 17.8 \ (c = 0.0224 \ \text{g ml}^{-1}; \text{CHCl}_3); \ \delta_H(270 \ \text{MHz}; \text{CDCl}_3;$ TMS) 0.90 (3 H, t), 0.95 (3 H, t), 1.30 (8 H, m), 1.65 (4 H, m), 5.05 (1 H, sextet), 5.85 (1 H, br s), 7.05 (1 H, t), 7.75 (2 H, m); v(film)/cm⁻¹ 3340, 2950, 2930, 2860, 1685, 1615, 1595, 1515, 1440, 1300, 1215, 1110, 1090, 950, 765; m/z (70 eV) (%) 282 (M⁺, trace), 156 (43%), 139 (100), 126 (32).

(*R*)-(-)-Nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1)

Dicyclohexylcarbodiimide (0.41 g, 1.9 mmol) was added to a stirred suspension of compound 6 (0.39 g, 1.4 mmol), 4'dodecyloxybiphenyl-4-carboxylic acid (7) (0.57 g, 1.5 mmol), 4-(N,N-dimethylamino)pyridine (0.05 g, 0.4 mmol) and dry dichloromethane (15 ml) at room temperature. The reaction was stirred for a further 18 h, before being diluted with dichloromethane (50 ml) and filtered through a pad of 'Hyflosupercel'. The filtrate was washed with water (50 ml), 5% (v/v) acetic acid (2×50 ml) and water, before being dried (MgSO₄), filtered and evaporated to give a colourless solid. The solid was purified by flash chromatography [fine mesh silica gel; 4% (v/v) ethyl acetate in petrol (bp 40–60 °C)] to give a white solid on standing which was recrystallized (ethanol; then diethyl ether-cyclohexane) and dried in vacuo (P_2O_5 , 0.30 mmHg, 40 $^{\circ}$ C, 6 h) to give the title compound (0.55 g, 61%); mp 44 °C; transition temperatures: I 73.6 S_{A*} 59.9 S_{C*A} <23.6 Recryst. (°C); $[\alpha]_D^{RT}$ -4.0 (c=0.0250 g ml⁻¹; CHCl₃); δ_H(270 MHz; CDCl₃; TMS) 0.90 (9 H, m), 1.30 (26 H, m), 1.80 (6 H, m), 4.02 (2 H, t), 5.08 (1 H, sextet), 7.01 (2 H, d), 7.37 (1 H, m), 7.60 (2 H, d), 7.76 (2 H, d), 7.92 (2 H, d), 8.24 (2 H, d); v(KBr disc)/cm⁻¹ 2920, 2850, 1745, 1725, 1600, 1505, 1295, 1260, 1185, 1110, 1080, 835, 765; m/z (70 eV) (%) 646 (M⁺, 8%), 365 (100).

Results

Optical microscopy and thermal studies

The phase assignments and the transition temperatures of compound 1 were determined by optical microscopy using clean, untreated glass microscope slides and coverslips; the transition temperatures were recorded on cooling from the isotropic liquid at a cooling rate of $2 \,^{\circ}C \min^{-1}$ and are as



Fig. 2 Photomicrograph showing the mosaic texture of the S_{C^*A} phase just below the S_{A^*} to S_{C^*A} transition (×100)

follows: I 73.6 S_{A*} 59.9 $S_{C*A} < 23.6$ Recryst. (°C). The smectic A* (S_{A*}) phase manifests itself as small regions of broken focal-conic fans amongst larger regions of a dark homeotropically aligned phase. Dispersion of white light was not obtained on rotation of the microscope's upper polarizer, indicating that this phase is not helical in nature (the asterisk simply denotes a reduced space symmetry as a consequence of the phase containing chiral molecules). Further cooling of this S_{A*} phase resulted in the sudden appearance of a very paleblue 'mosaic'-like texture in the homeotropic regions and this texture is shown in Fig. 2; closer inspection of the texture in the regions outside the area covered by the coverslip revealed the presence of small domains of schlieren texture containing 4-brush ($s = \pm 1$) singularities.

By mechanically disturbing the cover slip, it is possible to make the phase adopt a blue-green planar texture. If the sample is removed from the hot stage and viewed against a dark background, the sample selectively reflects the blue-green components of white incident light, indicating a pitch length of ca. 0.4 µm, hence it is helical (i.e. chiral). With these facts, a tentative phase assignment may be made as smectic C^* (S_{C*}); however, further clues as to its true identity may be obtained on examining thin films of the compound. In such films, larger regions of schlieren texture were observed, but most revealing was the presence of two forms of singularities; 4-brush (s = ± 1) and a smaller number of 2-brush singularities ($s = \pm 1/2$). The presence of the latter form of dispiration is direct evidence that this is an antiferroelectric phase.¹⁶ The final confirmation that this smectic C* phase is an antiferroelectric phase was provided by a contact microscope slide preparation performed at 50.3 °C using the known antiferroelectric compound (S)-1-4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3methylheptyl fluorobenzoate (8) (often referred to by the acronym $12F1M7)^6$ (see Fig. 3). The contact region was a narrow band of compensated schlieren $S_{C^* \infty A}$ texture bordered by long pitch regions of the antiferroelectric phase; the selectively reflected colours which change from red to green to blue away from the centre of the contact clearly indicate the shortening of pitch length in the preparation. Further cooling of the S_{C^*A} phase resulted only in the crystallization of the sample.



8; Iso 101.0 S_A^* 80.2 S_C^* 67.9 $S_C^*_{\gamma}$ 61.2 $S_C^*_A$ (°C)

DSC analysis of compound 1 revealed that it shows enantiotropic phase behaviour, and the observed transition temperatures and associated enthalpies are given Table 1. Interestingly,



Fig. 3 Photomicrograph showing contact preparation between compound 1 and compound 8 (12F1M7) in their antiferroelectric phases at a temperature of 50.3 °C (×100)

Table 1 Transition temperatures and enthalpimetric results for (R)-
(-)-nonan-3-yl 4-(4'-dodecyloxybipenyl-4-yl carboxyloxy)-3-fluoro-
benzoate (1) as determined by DSC^a

transition	T/°C	enthalpy kJ mol ⁻¹	
K-S _{C*A}	44.2	32.11	
S _{C*A} -S _A *	61.0	0.29	
S₄∗−I	75.0	1.94	
I-S _A *	74.6	1.92	
SA*-SC*A	61.3	0.35	
$S_{C*A} - K$	15.5	22.63	

^a Recorded at heating and cooling rates of $5 \,^{\circ}C \, min^{-1}$.



Fig. 4 DSC cooling thermogram of (R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1) (recorded at 5 deg min⁻¹)

the transition from the $S_{A*}-S_{C*A}$ in compound 1 is weakly first order in nature and is shown in Fig. 4. This contrasts very sharply with the $S_{A*}-S_{C*}$ transitions in other 2- or 3-substituted alkyl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoates, which are second order in nature and have markedly lower associated enthalpies (0.18–0.07 kJ mol⁻¹).²⁵

Electrical switching studies

On cooling a 5.8 μ m spaced polyimide (PI) rubbed cell containing compound 1 towards the S_A*-S_{C*A} phase transition, it was found possible to switch the sample in an applied dc field (3.45 MV m⁻¹). A change in the birefringence of the sample, which was oriented with its rubbing direction parallel to the polariser, was clearly noticeable, *i.e.* switching from black to



Fig. 5 Electroclinic response of (R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1) in the smectic A* phase as a function of temperature (recorded in a 5.8 µm spaced cell at 20 V dc)

grey. Fig. 5 shows the electroclinic response of compound 1 as the temperature is slowly lowered towards the $S_{A*}-S_{C*A}$ transition. As the sample is cooled through the S_{A*} phase, the switched tilt angle is at first very difficult to measure, and has values which are typically of the order of 2°. However, as the $S_{A*}-S_{C*A}$ transition is approached the magnitude of the switched tilt angle angles become bigger, as shown in Fig. 5. Here the switched tilt angles rise to values of *ca*. 7° before difficulty is encountered in obtaining switching at this field strength and cell thickness. The behaviour shown in Fig. 5 could indicate a pretransitional electroclinic response to an S_{C*} phase which has been induced by the applied field and has a higher $S_{A*}-S_{C*}$ transition temperature than the $S_{A*} S_{C*A}$ value shown in the figure. This issue is being investigated further and will be reported in greater detail in a future paper.

The antiferroelectric phase of compound 1 was found to exhibit classical dependency of the tilt angle on the applied field as the phase is electrically switched. For these measurements, a 1.4 μ m spaced PI-coated cell was used at a variety of temperatures within the S_{C*A} phase (57.9, 55.9, 53.9 and 51.9 °C), and the results are plotted in Fig. 6. At a given



Fig. 6 Field dependence of the switched tilt angle at various temperatures in the antiferroelectric phase of compound 1 [recorded in a 1.4 μ m spaced cell at 57.9 °C (\bigcirc), 55.9 °C (\bigcirc), 53.9 °C (\blacksquare) and 51.9 °C (\Box)]

Table 2 Comparison of the variation of threshold electric fields, E_{th} , as a function of reduced temperature for (R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1)

reduced temperature /°C	threshold electric field $E_{\rm th}/\rm MV~m^{-1}$
2	8.4
4	9.0
6	11.0
8	18.2

temperature e.g. 57.9 °C, under applied field strengths of approximately 8.4 MV m⁻¹ the antiferroelectric phase becomes fully poled into a ferroelectric state, which when switched gives a measurable tilt angle (in this case $ca. 22^{\circ}$). As the applied field is gradually lowered, a point is reached where the field can no longer oppose the energetically preferred antiferroelectric structure, and the electrically induced ferroelectric phase therefore collapses back to the more stable antiferroelectric subphase; this process is accompanied by a fall in the measured switched tilt angle to 0° , *i.e.* P_s becomes 0. Thus a sharp threshold characteristic is obtained; the magnitude of the field strength at this threshold is termed the threshold field value $(E_{\rm th})$ and is a direct measure of the stability of the antiferroelectric phase. Similarly, the increased stability of the antiferroelectric phase was recognised from the changing nature of the double hysteresis loop formed by use of the Diamant bridge. As the temperature was lowered, the double hysteresis loop became more stable. Further experiments were performed at progressively lower temperatures to observe the effect of temperature on the threshold field value $(E_{\rm th})$. As is evident in Fig. 6, the stability of the antiferroelectric phase increases as the temperature is lowered from the $S_{A*}-S_{C*A}$ transition, *i.e.* higher applied field strengths are required to form a poled ferroelectric phase and overcome the opposing torque in the antiferroelectric phase. The individual results for the dependence of threshold field strength on temperature are given in Table 2. Another feature clearly visible in Fig. 6, is the small, yet noticeable decrease in magnitude of the switched tilt angle of the electrically induced ferroelectric phase as both the temperature is lowered and the applied external field strength is increased. For an ideal ferroelectric phase, the tilt angle (θ) increases with decreasing temperature (T), as described by the relationship, $\theta_{\rm T} = \theta_0 (T_{\rm c} - T)^{\alpha}$, clearly the experimental data for the switched induced ferroelectric phase does not obey this relationship. Needless to say this behaviour is not at all clearly understood yet.

When compound 1 was constrained in a cell and under the influence of the polyimide alignment layers, the S_{C*A} mesophase gave a distinctive, striped domain texture, with the resultant extinction direction parallel to the striped domain structures,⁴ this is shown in Fig. 7. During the field dependence investigations, compound 1 was also found to display a double hysteresis loop at a temperature of 58.8 °C with an applied electric field of 5.4 MV m⁻¹ (at 22 Hz). This result indicates that the stability of the antiferroelectric phase of compound 1 is greatly enhanced by the presence of the lateral ethyl moiety attached to the chiral point;⁵ this point is discussed in more detail later.

Discussion

It is clear from these results that the high degree of molecular chirality of compound 1 influences both the electroclinic switching observed in the S_{A*} phase and the switching characteristics of the S_{C*A} phase. The reasons for the formation of the S_{C*A} phase for compound 1 may be twofold, *i.e.* arising from dipolar and/or steric effects. It was originally believed that large lateral dipole moments were required to stabilize



Fig. 7 Photomicrograph of the striped domain texture of the antiferroelectric phase of (*R*)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1) contained within a 1.4 μ m spaced PIcoated cell (× 100; *T*=57.2 °C)

antiferroelectric phases by virtue of the molecules being able to form pairs in which the lateral dipoles, acting along the C_2 symmetry axis, directly oppose one another. This is shown schematically in Fig. 8. However, this view can be discounted as being the primary reason for the stabilization of such phases because studies of the spontaneous polarization of novel mesogens containing lateral methyl and ethyl groups at the chiral point show that the magnitudes of spontaneous polarizations for these compounds are similar, possibly indicating that the differences in the dipole moments are minimal.⁵ A more plausible explanation for the primary cause for the stabilization of the S_{C^*A} phase is based on steric reasoning. It is well known that ferroelectric and ferrielectric phases occur predominantly in materials where the lateral branch is rotationally trapped for the chiral moieties.⁵ Rotational trapment would produce a structure that would have limited packing arrangements with its nearest neighbours. One such efficient packing arrangement is believed to be a bilayer-like structure consisting of associated molecular pairs. Bilaver and monolaver structures could possibly coexist and it has been suggested that the combination of such a series of monolayers and bilayers in a macroscopic phase assembly would result in a structure with a net residual polarization, i.e. a ferrielectric phase.⁴ By increasing the steric bulk of this lateral branch (e.g. to an ethyl or propyl), the ability to pack in such a manner should be somewhat reduced. Evidence so far for materials containing large lateral moieties appears to show that ferroelectric and ferrielectric phases are destabilized and disfavoured over antiferroelectric structures.⁵ This reasoning is applicable to compound 1 since comparison of its phase behaviour with that of the related homologue, compound 8 (12F1M7),⁶ shows that lengthening the lateral



Fig. 8 Molecular pairing of opposing lateral dipoles in an antiferroelectric phase⁴



Fig. 9 Antiferroelectric packing of molecular pairs of swallow tailed molecules $\!\!\!^4$



Fig. 10 Torsion energies plotted as a function of torsion angle, θ , for compound 1, along with the Newman projections of conformers (a), (b) and (c)

methyl group to an ethyl group results in the ferroelectric and ferrielectric phases seen in compound 8 being eclipsed by an antiferroelectric phase.

It has previously been postulated that 'swallow-tailed' compounds appear to aid mesophase formation by the so-called process of parallel association of molecules as dimeric pairs,^{26,27} and this is also believed to play a part in the formation of antiferroelectric phase structures.⁴ In the case of compound 1, the 'swallow-tailed' terminal moiety cannot adopt a co-planar relationship with the liquid-crystalline core, and allows a zigzag pairing of molecules to occur, as shown schematically in Fig. 9. Molecular modelling of compound 1 suggests that the ethyl group attached to the chiral centre protrudes markedly from the molecular axis.§ A conformational search around the varying dihedral angles of $C_2C_3^*$ —OCO was performed on the geometrically optimized structure of compound 1. As seen in Fig. 10, this search gives the variation of the relative torsional energy as a function of torsion angle for the rotation around

[§] The results published were generated using the programs CHARMm and QUANTA. These programs have been developed by Molecular Simulations, Inc.

the C_3^*-O bond; three energy minima corresponding to the three energetically preferred conformers (a, b and c) of compound 1 are observed; the computer generated models of conformers a, b and c are shown in Fig. 10. The methine proton in conformers **a** and **b** adopts a gauche relationship with respect to the carbonyl group. These conformers have similar relative energies [ca. 4 kcal mol⁻¹ (1 cal=4.134 J) as determined by molecular modelling using CHARMm and QUANTA] and the energy barrier for conversion between the two forms is small and interconversion between the conformers a and b could be easily achieved. The higher energy conformer c occurs at an energy minimum which is reached only after surmounting a torsional energy barrier of some 9 kcal mol⁻¹; here the methine proton adopts a trans relationship with respect to the carbonyl bond. This conformer's higher energy is presumably due to the increased steric forces experienced between the carbonyl oxygen atom and the ethyl and hexyl chains attached to the chiral centre. As this state has a substantially higher energy it might be expected that it will be less populated than a or b. In a broader sense, Fig. 10 shows that compound 1 will probably adopt one of the two possible conformations, either conformer **a** or **b** or a mixture of both. If this conformational argument is correct, then it suggests that the ethyl substituent at the chiral centre points off-axis. Recent X-ray diffraction studies on similar systems by Ouchi et al. tend to agree with this interpretation.²⁸ Ouchi's studies indicate that the substituents at the chiral centre are projected onto the planes of the layers in such a way that they give the impression of a tripod. This organisation is important when considering the interlayer interactions which ultimately lead to the formation of an alternating tilt structure. For instance, as the ethyl substituent allows for the possibility of a more pronounced tripod structure (i.e. over that produced by the equivalent 1-methylheptyl system), then it is also possible that the terminal tripod structures pack in the layers to almost form dimeric pairs where the tripod structures of facing feet pack together across the layer divide. Thus while the occurrence of molecular pairs or dimers has not been proved, it may be considered as being a distinct possibility, given the geometrical relationship between the liquid-crystalline core and the 'swallow-tail', for the formation of an alternating smectic C phase. Similar arguments for the packing of bent molecules leading to the formation of an antiferroelectric phase have been postulated by Nishiyama and Goodby.⁴

The switching studies performed in the antiferroelectric state demonstrate that the threshold field (E_{th}) at which electrically induced ferroelectric-antiferroelectric switching occurs is strongly temperature dependent, as shown Fig. 12. The threshold field (E_{th}) required to effect switching between the antiferroelectric and induced ferroelectric phase increases steadily at first and then more rapidly as the sample temperature is

Fig. 11 Computer generated models of the three lowest energy conformers (a), (b) and (c)

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Fig. 12 Plot of the magnitude of threshold field (E_{th}) as a function of reduced temperature for the electrically induced ferroelectric-antiferroelectric switching process in (R)-(-)-nonan-3-yl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1) (recorded in a 1.4 µm PI-coated cell)

reduced into the S_{C^*A} phase. This behaviour is believed to be a measure of the increased rotational viscosity experienced by the molecules during the poling process of the experiment as the temperature is lowered; *i.e.* it would reasonably be expected that the switching process would become more difficult at lower temperatures as the viscosity of the S_{C^*} or S_{C^*A} phase increases. There is also a marked increase in this threshold field (E_{th}) as the lateral alkyl moiety is increased from methyl [compound 8 (12F1M7)]; $E_{\rm th}$ ca. 2 MV m⁻¹, 7 °C below the S_{C^*A} transition)⁶ to ethyl (compound 1; E_{th} ca. 13.5 MV m⁻¹, $7\,^\circ\!C$ below the S_{C^*A} transition) and this clearly indicates that a more stable antiferroelectric structure is obtained for the longer lateral substituent. Finally, it is worth noting that no 'pre-transitional' effect was observed in the switched tilt angle versus applied field strength curves (Fig. 6), as is usually observed for compounds with a small lateral moiety (i.e. methyl⁷) and this is presumably related to the greater stabilization provided by the lateral ethyl group, and supports the earlier discussion relating molecular structure to stabilization of antiferroelectric phases.

Conclusions

In summary, the results reported show that (R)-(-)-nonan-3vl 4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-3-fluorobenzoate (1) displays both smectic A* and antiferroelectric smectic C* mesophases. These phases have been identified by optical microscopy, miscibility and electrical switching studies. Compound 1 also appears to mark the boundary for the 3fluorobenzoate series between both ferroelectric and antiferroelectric smectic C* structures [as in compound 8 (12F1M7)] and its purely antiferroelectric chiral smectic C* properties; this change in behaviour is characterized by the relative stabilities of the antiferroelectric phase towards an applied electric field (threshold field, E_{th}) and through its double hysteresis loop. The stability of the antiferroelectric phase (E_{th}) of compound 1 is demonstrated to be temperature dependent, with higher thresholds for switching being required at lower temperatures.

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