# V-Shaped switching and interlayer interactions in ferroelectric liquid crystals

Alexey Petrenko† and John W. Goodby\*

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Linear electrooptic responses in ferroelectric liquid crystals can be achieved *via* thresholdless switching. The molecular parameters for the design of ferroelectric liquid crystals that may yield a thresholdless response have not been delineated so far. In this article we explore some of the chemical design features that may be utilised in controlling switching processes, and we develop property–structure correlations in order to achieve materials that exhibit thresholdless behaviour.

## 1. Introduction

Ferroelectric liquid crystals (FLCs) have recently been commercialised in small area displays, which are typically used in near eye applications such as in the eyepieces of digital cameras. The fast electrooptic responses of ferroelectric liquid crystals mean that they are also compatible with direct drive on silicon devices (LCOS), and various device configurations employed in projection displays. However, there are various drawbacks to using FLCs, most notably the need to utilise temporal dither to create grey-scale, their weak resistance to mechanical distortion, and their common inability to form aligned samples without the formation of defects.

Crossland<sup>1</sup> recently reported, without heating or applying high voltages, that the CDRR family, the (S,S)-4-[4-[ $\omega$ -(1,1,3,3,3-pentamethyldisiloxanyl)alkyloxy]benzoyloxy]phenyl 2-fluoro-3-methylpentanoates, can be aligned into monodomains, where the monodomains are electro-optically bistable (*i.e.* the buffing alignment direction bisects the two optical bistable states). Such stable bistable states, that do not relax into chevron structures, are ideal for device applications. If the states are destroyed, for example by thermal or mechanical shock, then the bistable monodomain structure can be restored using only conventional drive voltages, thus the bistability is robust and secure. If these properties can be better understood and reproduced in ferroelectric liquid crystal device mixtures it would remove possibly the main impediment to the wider commercial exploitation of FLC devices.

Grey-scale operation can be achieved through the utilisation of 'V-shaped' electrooptic switching techniques where the transmission through the devices varies linearly as a function of the applied electric field. The 'V-shaped electrooptic response' was first observed in 1996<sup>2</sup> through the study of the so-called 'Tokyo Mixture' (Fig. 1), which is a formulation of three different smectic liquid crystals. Under the application of an electric field the optical response observed, over a broad temperature range, was found to be hysteresis-free with a sharp, but linear, change in transmission. The switching which produced such a 'V-shaped' response was, at the time of the discovery, designated as a thresholdless antiferroelectric liquid crystal response.

The 'V-shaped descriptor' subsequently became one of the more controversial terms used in liquid crystals, with debate being centred on the very nature of what is '*ferroelectric or antiferroelectric*' and the type of mesophase that is involved in 'V-shaped switching'. The main characteristics of the 'V-shaped switching response' to note are as follows:

1. The presence of a third state during the dynamic switching in a planar oriented thin cell. The state occurs at zero field and, when the cell is placed between crossed polarizers with the lower polarizer being parallel to the layer normal, almost complete extinction of light can be achieved.

2. The absence or collapse of a 'ferroelectric or antiferroelectric' hysteresis loop, resulting in a narrow shape of the tip of the 'V' of the electrooptic response (see Fig. 1), indicating that switching between the third zero-voltage state and the uniform ferroelectric switched states has no threshold.

Thus the 'V-shaped switching response' appears to be an extremely attractive effect, which can produce an electrooptic response with grey-scale and high contrast. A device based on such an electrooptic was produced<sup>3</sup> even though there was no complete understanding of the molecular processes at the heart of the phenomenon. Nevertheless, if one accepts the current view<sup>4</sup> that the SmX\* phase in the Tokyo mixture is a ferroelectric smectic C\* phase, a V-shaped form of the transmittance–voltage dependence at certain frequencies can



Fig. 1 Chemical structures and concentration (in weight percent) of the components in the Tokyo mixture, which exhibits a 'V-shaped electrooptic response'.

Department of Chemistry, The University of York, York, UK YO10 5DD † Current address: Department of Chemistry, The University of Hull, Hull, UK HU6 7RX.

be explained by the formation of twisted states during dynamic switching in the surface-stabilised geometry. In order to explain almost complete light extinction when the system transforms into the twisted state, a model using a polarized-stabilised kink (PSK) structure was introduced by Clark *et al.*<sup>4</sup>

Omitting the details of the phenomenological description of the polarization stabilised states provided by Clark et al, the theoretical models explicitly demonstrate that a high magnitude of the spontaneous polarization appears to play a crucial role in the stabilisation and uniformity of the zero field state which a material adopts in the surface stabilised cell. However, subsequent studies have shown that this is not necessarily the case, and most materials can exhibit 'V-shaped switching' at defined frequencies of the applied electric field and at certain temperatures. Thus we reasoned that details of the molecular structures and interactions of the materials employed in such devices are of particular importance. For example, consider the structure of the surface stabilised ferroelectric device with bookshelf geometry associated with the layers, which are shown as dotted lines in Fig. 2. The molecules are shown by cylinders (aromatic cores) and wiggly lines (aliphatic chains). The chains overlap at the interfaces between layers, and so there will be interactions and transmittance of structural information between the molecules across the layers. Thus, in addition to interfacial interactions, there will also be interactions and associated correlation lengths between the molecules and the surfaces (polar interactions), penetration distances of the surface ordering, and lateral interactions between the molecules in the bulk.

We reasoned that by using microphase segregating techniques we could affect the interfacial interactions, and thereby also the switching behaviour of a ferroelectric phase in an applied electric field.

Materials that exhibit SmC mesophases usually have molecular structures where there are two aliphatic chains attached by polar groups to a central aromatic or heteroaromatic core, as shown in Fig. 1. Our work, <sup>5–8</sup> and that of Coles *et al.*, <sup>9–12</sup> has shown when the terminal positions in the aliphatic chains of the molecules are substituted with chemically and/or sterically different groups to the chains, the type and nature of the physical properties of the mesophase can be controlled and melting points can be *substantially* lowered.



Fig. 2 A ferroelectric smectic liquid crystal device with surface stabilised geometry and bookshelf alignment of the layers.

This technique for controlling mesophase formation and physical properties has been termed *microphase segregation*. The chemically and/or sterically different end groups are thought to directly affect the interactions between the molecules at the interfaces of the layers in smectic phases, which in turn affects the way in which the molecules as a whole pack together and transfer structural information between layers. Thus, the phase transitions, the smectic polymorphism and physical properties exhibited by a smectogen are also affected.

Consequently, the chemical nature of the moiety associated with the terminal position can, in effect, be used to determine the structure and phase classification of the mesophase produced. A judicious choice of the terminal moiety, coupled with a suitable asymmetric centre, can be employed (almost at will) to create systems that exhibit ferroelectric or antiferroelectric mesophases. In addition, as the process of microphase segregation has the effect of suppressing melting points and introducing glassy phases, wide temperature ranges for the existence of the liquid crystal state can be induced. This molecular design technique is relatively unexplored in either commercial or research liquid crystals. However, it is a new and powerful design technique that will have many important implications for the field in years to come.

In this report we describe the mesomorphic properties of a family of materials where the molecular structure has been varied systematically to give six family sub-groups A to F (Fig. 3). The groups have been modified with respect to the terminal microphase segregating units and lateral polar groups associated with the central core. We also examine the electrooptic behaviour of the materials under various frequencies of the applied electric field in order to examine their 'V-shaped' responses.

# 2. Experimental

#### 2.1 Syntheses of materials

Full details of the synthetic procedures and spectral and purity analyses were reported elsewhere.<sup>13</sup> However, it should noted that the materials were purified to a very high level (>99%), in particular the silyloxy products were purified by preparative chromatography techniques due to the fact that the starting materials were often found to be impure with various isomers. Attachment of the chiral substrates (2-octanol) was achieved through the use of the Mitsunobu reaction using diethylazodicarboxylate (DEAD) and triphenyl phosphine, which typically produces products of varying optical purity due to inversion at the stereogenic centre. Enantiomeric excesses were determined by chiral HPLC.

Families A, C and E were prepared using essentially the same synthetic pathway up until the penultimate steps, see Scheme 1. Thus commercially available 4'-hydroxy-4-cyanobiphenyl, 1, was subjected to hydrolysis using concentrated sulfuric acid in glacial acetic acid to give 4'-hydroxybiphenyl-4-carboxylic acid 2. The hydroxy group was protected as the methyl carbonate through reaction with methyl chloroformate to give 3. Compound 3 was then subjected to esterification with (R or S)-2-octanol in the presence of DEAD and triphenyl phosphine to give 4. The Mitsunobu reaction was favoured over the standard esterification method using



Fig. 3 Target materials studied.

dicyclohexylazodicarboxylate (DCC) and 4-dimethylaminopyridine (DMAP) because little deprotection was found to occur. Compound **4** was then deprotected under mild conditions by using ammonia in ethanol to give **5**, which was a common substrate to the preparations of the three families of materials. However, the Mitsunobu reaction induces partial



Scheme 1

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racemisation, preparation of diastereoisomers of compound 5, and separation by chromatography (chiral HPLC) gave enantiomeric excesses of the (S)-enantiomers as 0.9 and the (R)-enantiomers as  $0.86 \pm 0.2$ .

The acids to be used in the esterifications of 5 were prepared in similar ways. Ethyl 4-hydroxybenzoate, 6, was etherified with either an alkyl bromide or a terminally unsaturated bromide in the presence of potassium carbonate with dry acetone or butanone as the solvent. After pouring the reaction mixture into water the various esters (7) were recovered and purified by recrystallization. The esters were saponified under acidic conditions to give the acids 8.

The individual acids 8 were esterified with compound 5 to give families A1-3 and C1-3. The unsaturated materials C1-3 were subjected to hydrosilylation with various hydrosiloxanes in the presence of Karstedt's catalyst to give products E1-5.

Compounds **B1-5**, **D1-3** and **F1-3** were prepared by the synthetic pathway shown in Scheme 2. The basic difference in the synthesis with respect to Scheme 1 is the preparation of the acids (16) used in the final esterification to yield the liquid-crystalline products. The preparation of 16 utilizes the lithiation of 1,2-difluorobenzene with butyllithium followed by treatment with trimethyl borate to give the boronic acid 10. Oxidation of the boronic acid with hydrogen peroxide

afforded phenol **11**. The phenol was benzyl protected to give **12**, which was then subjected to lithiation, carbonylation and deprotection to give 4-hydroxy-3,2-difluorobenzoic acid. The acid was then esterified with ethanol to give the ethyl ester **15**, which was etherified and saponified to give the alkyl or alkenyl substituted acids **16**. Then as in Scheme 1, esterification with **5** led ultimately to products **B1-5**, **D1-3** and **F1-3**.

#### 2.2 Phase identification by optical and thermal methods

Phase identifications and determination of phase transition temperatures were carried out by thermal polarized light microscopy using an Olympus BH-2 polarizing light microscope equipped with a Mettler FP82HT microfurnace in conjunction with an FP90 Central Processor. Homeotropic sample preparations suitable for phase characterization were prepared simply by using very clean glass microscope slides (washed with acetone). Differential scanning calorimetry was used to determine enthalpies of transition and to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms (scan rate 10 °C min<sup>-1</sup>) were obtained using a Perkin Elmer DSC 7 PC system operating on Pyris software. The results obtained were standardized to indium (measured onset 156.68 °C,  $\Delta H$  28.47 J g<sup>-1</sup>, lit. value 156.60 °C,  $\Delta H$  28.45 J g<sup>-1</sup>).



Scheme 2

#### 2.3 Electrooptical measurements

The cells for the electrical field tests were contained within a Mettler FP82HT hot-stage oven in conjunction with a Mettler FP90 temperature controller. The applied waveform was supplied by a Hewlett Packard 33120A Arbitrary Waveform Generator into a linear  $\times 20$  amplifier (custom-built by QinetiQ). The electrical response from the cell was fed into a nano-current detector (20 k $\Omega$  or 100 k $\Omega$  impedance) and to a Hewlett Packard 54600B oscilloscope, which was connected to a PC.

The cells used in the electrical field studies were constructed from ITO coated glass which had various separations depending on the experiment performed (i.e. either 2 or 5 µm cell spacings), with the internal surfaces coated with a polyimide aligning agent. For the 2 µm cell separations the materials in their smectic C\* phases would be expected to have their helical structures unwound due to the strengths of the surface interactions. The cells were filled by capillary action. Alignment of the materials was achieved by differing procedures depending on the cell thickness. For the thinner cells, alignment was achieved by slowly cooling the sample from the isotropic liquid into the smectic mesophase, at a rate of 0.1  $^{\circ}$ C min<sup>-1</sup> and in the absence of an electric field. However, in the cases where the materials exhibited both smectic A and smectic C phases, for thicker cells alignment was achieved by slowly cooling into the smectic A mesophase from the isotropic state, and applying a high electric field in the form of a square wave (typically 16–20 V  $\mu m^{-1}$ ) at a frequency of 50 Hz to 1 kHz depending on the material. Once the material was aligned in the cell, the voltage was removed and the cell cooled into the smectic C\* or CA\* mesophases. For comparison of results, measurements were determined as a function of the reduced temperature,  $T_c - T$ , where  $T_c$  is the Curie point.

Upon alignment of the liquid crystal, the spontaneous polarization in the tilted phases was determined, on cooling, using a triangular waveform current reversal technique. An AC field in a triangular waveform (typically 10 V  $\mu m^{-1}$  at 30 Hz) was applied to the cell. As the polarization is inverted by the field, a current pulse was observed. The magnitude of the spontaneous polarization was determined from the area under the current-reversal peak.

The light transmission through any specimen cell was determined using a photodiode in conjunction with a voltmeter. Initially, an empty cell was placed in a microscope hot-stage oven and the transmittance values between crossed polarizers (extinction) and with parallel polarizers (maximum transmittance) were determined. The cell when filled was then placed again into the hot-stage oven at a set reduced temperature (typically  $T_c - T = 10$  °C), the cell was poled with a DC voltage and aligned so that the poled state was set to extinction and the transmittance value was recorded. The material was then switched, by applying a DC field of opposite polarity, and the value of transmittance of the poled bright state was recorded. Comparing the values for the filled cell with those for the empty cell gave the percentage of transmission.

The determination of tilt angle was achieved by measuring the optical transmission of the switched states using a photodiode (RS303-674; 1 cm<sup>2</sup> active area, high speed >50 ns) in an apparatus custom built by QinetiQ. The equipment was fitted with a green-eye response filter (Coherent-Ealing, 26-7617-000, 1 in diameter, transmittance 400–700 nm, maximum transmittance 539.5 nm). The transmission values were determined using a Thurlby Thandar Instruments 1604 Digital Multimeter.

## 3. Results

#### 3.1 Transition temperatures and mesophase characterization

**3.1.1 (R)-1-Methylheptyl 4'-(4-n-alkoxybenzoyloxy)biphenyl-4-carboxylates, A1–3.** All of the members of the parent series **A** were found to be purely smectogenic with nematic and frustrated blue and TGB phases being completely suppressed from their phase sequences. The transition temperatures, along with their associated enthalpies, are given in Table 1.

The smectic polymorphism was found to be similar to that of MHPOBC,<sup>3</sup> *i.e.* including SmA\*, SmC\*, SmC<sub>FI1</sub>\*, SmC<sub>FI2</sub>\*, SmC<sub>A</sub>\* and SmI\* phases. The ferroelectric smectic C\* phase was found to dominate the phase sequences over broad temperature ranges. It remained enantiotropic regardless of the length of the non-chiral alkyl chain and, generally, the phase stability increased with elongation of the chain at the expense of the high temperature smectic A\* phase. In contrast, the antiferroelectric smectic C\* phase was less pronounced, and in most cases it remained monotropic. Even when the antiferroelectric phase appeared on heating, its temperature range was significantly shorter than during the cooling cycle. The hysteresis in the phase transition temperatures of the antiferroelectric phases (on heating and cooling) indicated that

**Table 1** Transition temperatures (°C) and associated enthalpy values ( $\Delta H/J \mod^{-1}$ ) for the (*R*)-1-methylheptyl 4'-(4-n-alkoxybenzoyloxy)biphenyl-4-carboxylates, A1 to A3

	$C_nH_{2n+1}O$																
No.	п	Mp		SmI*		$\mathrm{SmC}_{\mathrm{A}}^{*}$		$\text{SmC}_{\rm FI1}*$		$\text{SmC}_{\rm FI2}{}^{*}$		SmC*		SmA*		Iso Liq	Cr
A1	10	•	64.5 [24.9]	(•	47.1 [3.7]	•)	73.0 [—]	•	73.6 [—]	•	78.7 [0.02]	•	105.4 [0.18]	•	123.6 [5.1]	•	38.1 [0.1]
A2	12	•	77.3		[]	(•	69.8 [—]	•)	71.2 [—]	•)	77.2 [0.02]	•	108.7 [0.28]	•	118.9 [5.0]	•	63.4 [43.9]
A3	14	•	55.5 [40.0]	(•	37.5 [3.5]	•	54.8 [—]	•)	56.2 [—]	•	64 [—]	•	109.3 [0.3]	•	115.4 [4.5]	•	29.9 [17.6]



Fig. 4 DSC cooling trace for compound A1. Scanning rate  $10 \,^{\circ}\text{C min}^{-1}$ .

the phase transitions are not conventional liquid crystal phase changes, which are driven by a change in 'lattice-type' of structure, but rather due to changes in the frustration of the molecular packing. The  $SmC_A$ \* phase was also found to be preceded by two modifications of the ferrielectric phase, which emerge over narrow temperature intervals, thereby preventing direct  $SmC^*-SmC_A$ \* phase transitions. Their appearance is a direct consequence of the competition between synclinic and anticlinic ordering.

First order phase transitions between the isotropic liquid and the smectic A\* phase, as well as the melting and recrystallisation transitions, were detected by differential scanning calorimetry (see Fig. 4 for compound A1). The SmA\*-SmC\* and SmC<sub>A</sub>\*-SmI\* transitions were also "visible" in the DSC thermograms due to their weak first-order characteristics. The enthalpy values for the SmA\*-SmC\* transitions were approximately ten times smaller than the typical values of the first-order Iso Lig-SmA phase transition. For compound A1, it was found that a minor discontinuity was also obtained at the transitions from the SmC\* to the ferrielectric (FI1) phase, which was classified from the thermodynamic sequencing of the phases, and the subsequent  $SmC_A^*$  phase gave rise to small peaks in the DSC curve. However, in most cases the enthalpies of the second-order transitions between the smectic C modifications were too small to measure, and therefore the phase identification was carried out using polarizing microscopy.

In the microscopy preparations the types of liquid-crystalline phases were assigned by comparing their textures to reference sources. Thus, for compound A3, the smectic A\* phase was characterised *via* its clear focal-conic domains which exhibited elliptical and hyperbolic lines of optical discontinuity and the extinct homeotropic region when the material was observed between crossed polarizers (see Fig. 5a). At the transition to the smectic C\* phase, the focal-conic fans appeared broken and in some areas banded as a result of stabilisation of the molecular tilt and helix formation. At the same time, the homeotropic region became dark blue (Fig. 5b) indicating the formation of the helical structure. Small domains of the *schlieren* texture were also observed in uncovered droplets of the material. In the vicinity of the SmC<sub>F12</sub>\* phase, the homeotropically aligned region exhibited *schlieren* domains which became very mobile with disordered fluctuations observed throughout the sample.

On cooling the characteristic *schlieren* pattern gradually developed over all of the homeotropic region and the fluctuations diminished (Fig. 5c). At the transition to the  $SmC_{F12}^*$  phase another wave of fluctuations reconstructed the sample's appearance, and with a further temperature decrease the green coloured domain of the antiferroelectric phase started growing in the homeotropically aligned region of the specimen (Fig. 5d). The focal-conic fans cleared as a result of the formation of the alternating molecular tilt in smectic layers. The direction of the helix that was formed in the smectic C\* phase changed its sign to the opposite hand in the antiferroelectric phase.

The antiferroelectric properties of the  $SmC_A^*$  phase were studied in detail through electric field measurements using the triangular wave method. In the ferroelectric smectic C\* phase, molecular reorientation from one uniform state to another produced an electric current, which flows between the surfaces when the external electric field passes a zero point. As a result, one sharp peak is usually observed in the current–time trace and the value of the spontaneous polarization was calculated from the area under this peak in voltage–time coordinates. In turn, tristate switching in the antiferroelectric phase involves two independent molecular reorientations giving rise to two electric currents (Fig. 6b).

Thus for compound A2 two switching peaks were clearly observed in the temperature range of the antiferroelectric phase (Fig. 6b), thereby confirming that the switching in this phase proceeds *via* three states. Thus the switching responses provide confirmatory evidence for mesophase identification, which is particularly useful for complex mesophase behaviour exhibited by some of the materials under investigation.

In general, all three compounds of general structure **A** possess quite a high value of the "saturated" spontaneous polarization, *ca.* 100 nC cm<sup>-2</sup> (see results for compound **A2**) in the temperature region of the antiferroelectric phase. It can be seen from Fig. 7 that the magnitude of the spontaneous polarization grows continuously with decreasing temperature from the Curie point (SmA\*–SmC\* transition) and disappears in the SmI\* phase because the electric field was too small to switch the higher ordered phase. The optical tilt angle has a different temperature dependence, at the Curie temperature it has a zero value and it reaches 25° in the antiferroelectric phase (Fig. 7).

**3.1.2** (*R*)-1-Methylheptyl 4'-(4-alkoxy-2,3-difluorobenzoyloxy)biphenyl-4-carboxylates, B1–5. The general structure for compounds **B** includes two *ortho*-fluorine substituents attached to the outer ring of the 4-benzoyloxybiphenyl core, which was used in series **A** as the parent system for comparative studies (see Fig. 3). This structural modification greatly affected the magnitude of the transverse molecular dipole as a consequence of the introduction of the fluorine atoms. As predicted in McMillan's model of the smectic C phase,<sup>14</sup> strengthening the lateral dipole should improve the stability of the molecular tilt in smectic layers. However, in series **B** the stability of the tilted smectic phases was found to be almost unchanged when the transition temperatures were



**Fig. 5** Textures of compound **A3**. a) SmA\*, 111 °C; b) SmC\* phase, 104 °C; c) SmC<sub>F12</sub>\* phase, 56.5 °C; d) SmC<sub>A</sub>\* phase, 52.2 °C; e) SmI\* phase, 34 °C (×100).

compared to those of the type A materials. For instance, the temperature interval of the SmC\* phase for C14 homologues A3 and B5 is roughly the same and extends over 50  $^{\circ}$ C (Table 2).

Lateral fluorine substituents, however, promote formation of the TGBA phase, which was observed over a narrow temperature interval (less than a half of a degree) for all of the homologues synthesised. At the low temperature end of the phase sequences, enantiotropic ferrielectric and antiferroelectric SmC\* phases were exhibited by the C12 and C14 homologues (compounds **B3** and **B5**). There is an odd-even effect that suppresses the antiferroelectric and frustrated ferrielectric sub-phases for odd members of the homologue series. For even numbers the optimal chain length, which favours the  $SmC_A^*$  phase, is the C12 homologue. Conversely, the C10 homologue, which exhibits the broadest antiferroelectric phase in series **A**, does not possess smectic sub-phases at all.

The microscopy studies were carried out as described for compounds of structure **A**. It was difficult to observe the transition from the SmA\* to the SmC\* phase in the homeotropic region because the pitch length in the smectic



Fig. 6 The current-time traces recorded for compound A2: a) SmC\* phase, 78 °C, electric field 10 Hz, 20 volts peak-to-peak (VPP). b) SmC<sub>A</sub>\* phase, 68 °C, electric field 10 Hz, 20 VPP.



Fig. 7 The spontaneous polarization and optical tilt angle as a function of reduced temperature recorded for compound A2. Applied electric field 20 Hz, 20 VPP.

C\* phase was very short, and therefore both phases appeared optically extinct between crossed polarizers. In free-standing preparations it was possible to distinguish between textures of the SmC\* and SmA\* phases (Fig. 8), as white fingers associated with the *schlieren* texture were clearly seen on the edge of the film in the SmC\* phase.

The textures of the ferrielectric and antiferroelectric phases are shown in Fig. 9 for compound **B3**. The regions associated with homeotropic alignment of the smectic  $A^*$  phase were

covered with fluctuating *schlieren* domains in the  $SmC_{FI2}^*$  phase, which became more fluid and colourful in the  $SmC_{FII}^*$  phase. In the  $SmC_A^*$  phase the *schlieren* texture was replaced with a network of blue domains.

The compounds were found to possess a large values of the spontaneous polarization, which in the antiferroelectric phase reached an apparent value of *ca*. 160 nC cm<sup>-2</sup> (compound **B2**). This is approximately 30% higher than the corresponding value determined for the members of series **A**. The magnitude of the apparent tilt angle also grew with the reduced temperature and varied between 32° and 33° for the longer chain homologues.

3.1.3 (S)-1-Methylheptyl 4'-(4-alk- $\omega$ -enyloxybenzoyloxy)biphenyl-4-carboxylates C1–3 and the (S)-1-methylheptyl 4'-(4-alk- $\omega$ -enyloxy-2,3-difluorobenzoyloxy)biphenyl-4-carboxylates D1–3. In order to attach silyloxy bulky end groups to systems such as compounds of structure A and B, first the equivalent terminal olefins had to be prepared. Thus the (S)-1-methylheptyl 4'-(4-alk- $\omega$ -enyloxybenzoyloxy)biphenyl-4-carboxylates C1 to C3 and the (S)-1-methylheptyl 4'-(4-alk- $\omega$ -enyloxybenzoyloxy)biphenyl-4-carboxylates C1 to C3 and the (S)-1-methylheptyl 4'-(4-alk- $\omega$ -enyloxy-2,3-difluorobenzoyloxy)biphenyl-4-carboxylates D1 to D3 were synthesised. However, these intermediates also exhibited interesting mesomorphic behaviour. The transition temperatures and enthalpies are given together in Tables 3 and 4 respectively.

In both series of alkenes **C** and **D** the phase sequences appeared less diverse in comparison to the wide variety of the smectic phases exhibited by the alkyl analogues. Interestingly,

**Table 2** Transition temperatures (°C) and associated enthalpy values ( $\Delta H/kJ \text{ mol}^{-1}$ ) for the (*R*)-1-methylheptyl 4'-(4-alkoxy-2,3-difluoroben-zoyloxy)biphenyl-4-carboxylates, **B1** to **B5** 

No.	n	Мр		$\mathrm{SmC}_{\mathrm{A}}^{*}$		Sm <sub>FI1</sub> *		Sm <sub>FI2</sub> *		SmC*		SmA*	TGBA		Iso	Cr
B1	10	•	75.5					_		•	92.9	•	•	111.1	•	58.2
B2	11	•	[31.3] 68.4					_		•	97.7	•	•	108.3	•	51.5
<b>B3</b>	12	•	[29.4] 52.5	•	65.8	•	66.4	•	72.2	•	[0.27] 99.8	•	•	[3.9] 107.3	•	44.3
B4	13	•	[38.1] 67.2		[0.01]		[—]	_	[—]	•	99.71	•	•	105.6	•	56.3
B5	14	•	46.7 [42.6]	•	47.1 [—]	_		•	49.7 [—]	•	[0.29] 98.4 [0.38]	•	•	103.9 [4.0]	•	[ <del>1</del> 3.5] 33.6 [31.1]



Fig. 8 Photomicrographs of the free-standing films made for compound B3: a) SmA\*, 104.0 °C; b) SmC\*, 90.0 °C (×100).



Fig. 9 Textures for compound B3: a) SmC<sub>F12</sub>\*, 70 °C; b) SmC<sub>F11</sub>\*, 66 °C; c) SmC<sub>A</sub>\*, 64 °C (×100).

the presence of the terminal double bond did not appear to favour formation of the TGB, unlike the saturated analogues, also, the SmI\* phases were not exhibited by these two homologous series. The SmA\* and SmC\* phases followed similar trends to those in series **A** and **B**. Namely, the SmA\* phase thermal stability deteriorated with increase of the alkyl chain length while the SmC\* phase gradually became more stable.

In most cases, the antiferroelectric  $SmC_A^*$  phase was observed only during cooling cycles. The phase was preceded with the  $SmC_{FII}$  phase in the **C** series, which prevented a direct  $SmC^*-SmC_A^*$  phase transition. For the difluorobenzoate compound **D2** the  $SmC^*$  phase was replaced with a noncommensurate  $SmC_{\alpha}^*$  phase, which underwent a direct transition to a  $SmC_A^*$  phase without mediation of ferri phases. This phase appears to exhibit ferroelectric properties at the higher temperatures in its thermal range and becomes antiferroelectric near the phase transition to the  $SmC_A^*$  phase, its structure, however, still needs to be clarified.

When observed in the polarizing microscope, the  $\text{SmC}_{\alpha}^*$  phase showed a characteristic pattern of the focal-conic fans, which was easily distinguished from the focal-conics of the SmC\* phase (Fig. 10a) through an unusual bright-orange colour of the edges of the fans. In the SmC<sub>A</sub>\* phase the colour disappeared giving rise to a focal-conic pattern which was similar to the texture of the antiferroelectric phase observed for compounds of structure **A**, see Fig. 10b. In free-standing film preparations the *schlieren* texture of the SmC<sub>A</sub>\* phase exhibited several two-brush defects that were clearly visible in the central parts of the film. The appearance of two-brush dispirations signifies the presence of alternating molecular tilt direction in the smectic layers and is regarded as a classical defect characteristically found in *schlieren* textures of the SmC<sub>A</sub>\* phase.

**Table 3** Transition temperatures (°C) and associated enthalpy values ( $\Delta H/kJ \text{ mol}^{-1}$ ) for the (S)-1-methylheptyl 4'-(4-alk- $\omega$ -enyloxybenzoyl-oxy)biphenyl-4-carboxylates, C1–C3

$CH_3$	$CH_2 = CH - C_n H_{2n}O $	С
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No.	п	Мр		$\mathrm{SmC}_{\mathrm{A}}^{*}$		$\mathrm{Sm}_{\mathrm{FI1}}^{*}$		SmC*		SmA*		Iso	Cr
C1	4	•	61.4 [16.2]	_		_		(•	55.7 [0.13]	•)	123.0 [4_6]	•	42.6
C2	6	•	61.5 [19.4]	•	64.8 [—]	•	67.6	•	77.9	•	119.6 [4 4]	•	23.7
C3	8	•	54.1 [33.1]	(•	47.7 [0.014]	•)	51.8 [—]	•	93.2 [0.28]	•	113.4 [4.8]	•	32.2 [4.74]

**Table 4** Transition temperatures (°C) and associated enthalpy values ( $\Delta H/J \mod^{-1}$ ) for the (S)-1-methylheptyl 4'-(4-alk- $\omega$ -enyloxy-2,3-difluorobenzoyloxy)biphenyl-4-carboxylates, **D1–D3** 

$CH_2 = CH - C_n H_{2n} O $	)
— — — — — — — — — — — — — — — — — — —	

No.	п	Мр		$\mathrm{SmC}_{\mathrm{A}}^{*}$		SmC*		$SmC_{\alpha}{}^{\ast}$		SmA*		Iso Liq	Cr
D1	4	•	64.1 [21.0]	_		(•	58.0 [0.14]	_		•)	107 [4.04]	•	37 [16.4]
D2	8	•	72.6 [35.5]	(•	64.6 [—]	•)			75.9 [0.08]	•	104.1 [4.40]	•	48.7 [32.6]
D3	9	•	73.4 [31.6]			•	84.6 [0.19]	_	[]	•	103.5 [4.42]	•	54.1 [28.9]



Fig. 10 Textures of the smectic phases observed for compound D2: a)  $\text{SmC}_{\alpha}$  67 °C; b)  $\text{SmC}_{A}$ \*, 62.7 °C, and for compound C3: c)  $\text{SmC}_{FI1}$ \*, 47.9 °C; d)  $\text{SmC}_{A}$ \*, 45.2 °C (×100).

The texture of the ferrielectric  $\text{SmC}_{\text{FII}}^*$  phase for compound **C3** was also composed of focal-conic domains. As shown in Fig. 10c, the broken fans of the smectic C\* phase became covered with narrow lines indicating a transition to the  $\text{SmC}_{\text{FII}}^*$ . At the transition to the antiferroelectric phase the focal-conic defects appeared clearer due to the alternating layer structure giving an apparent director perpendicular to the layers (Fig. 10d).

Additional evidence for the properties of the ferroelectric and antiferroelectric SmC\* and SmC<sub>A</sub>\* phases was obtained through the studies of the electrooptical response of compound **C2**. In the smectic C\* phase the transmittance as a function of voltage had the shape of a hysteresis loop. The loop split into two smaller hystereses in the antiferroelectric smectic  $C_A$ \* phase indicating the appearance of the third state during the field-induced switching. The antiferroelectric double hysteresis could be converted back into the single loop when the frequency of the applied field became too high and there was not enough time for relaxation to occur back to the antiferroelectric state (see Fig. 11).

The spontaneous polarizations for compounds D1 to D3 were determined, and the values as a function of the reduced temperature from the Curie point are shown together in Fig. 12. Interestingly the values of the spontaneous polarizations for the alkenes C and D were found to be slightly lower than those determined for compounds A and B.

3.1.4 (S)-1-Methylheptyl 4'-{4- $[\omega$ -(1,1,3,3,3-pentamethyldisiloxanyl)alkoxy-2,3-difluoro]benzoyloxy}biphenyl-4-carboxylates E1-5 and the (S)-1-methylheptyl 4'-{4- $[\omega$ -(1,1,3,3,3pentamethyldisiloxanyl)alkoxy-2,3-difluoro]benzoyloxy}biphenyl-4-carboxylates F1-3. In substituting parent systems C and D with di- and tri-siloxane units two new series E and F were prepared respectively. There were two major consequences of this structural modification, see Tables 5 and 6. Firstly a significant depression in phase transition temperatures was observed for all of the silyloxy homologues synthesised. The decrease in the isotropization temperature observed for the siloxane materials was as much as 40 °C to 50 °C when compared to the alkenes and alkyl analogues respectively (compare for example **E3**, **C3** and **A1**). This large drop in transition temperatures is driven by the siloxane fragments that group together in the mesomorphic state and, thereby, increase the relative stability of a layered smectic C\* structure at low temperatures. It also facilitates supercooling, which in the case of the 2,3-difluorobenzoate compound **E1** extends over 52 °C reaching almost -10 °C before crystallisation/ glassification sets in.

The second consequence of the inclusion of the siloxane chain in the molecular structure was that the phase sequences were reduced to one liquid crystalline phase, which in all cases was the smectic  $C^*$  phase. Its stability remained unaffected by the length of either siloxane or alkyl chain unless the total number of atoms exceeded 14. In this case, an increase in both the clearing and melting points ws observed.

The antiferroelectric phase was not found for any of the homologues in series **E** or **F**. The odd–even stability effect of the siloxane chain observed for bimesogen materials<sup>15–18</sup> seemed not to be applicable for the mono-substituted siloxane compounds, synclinic smectic C\* ordering was preferred for both odd and even numbers of the siloxane units in the terminal chain.

The smectic C\* phase was identified with the help of a freestanding preparation. Only four-brush defects were found in the *schlieren* texture (in Fig. 13 compare plate a: anticlinic



Fig. 11 The voltage–optical transmittance (*y*-axis) curves recorded for compound C2. a) SmC\* phase, 88 °C, 2 Hz, 2 VPP; b) SmC<sub>A</sub>\* phase, 44 °C, 20 mHz, 2 VPP; d) SmC<sub>A</sub>\* phase, 44 °C, 2 Hz, 2 VPP. The orientation of the cell was set such that the layer normal of the smectic C\* phase was parallel to the top polarizer. As a result both ferroelectric states had a similar level of transmittance and the hysteresis loops appeared folded into 'W-shaped' curves.



Fig. 12 The spontaneous polarization of the ferroelectric phase plotted as a function of the reduced temperature from the Curie point for compounds of structure **D**, at 20 Hz, 2 VPP.

phase for compound C2, and plate b: synclinic phase for compound E2. Comparison shows that the *schlieren* texture (Fig. 13b) possesses only s = 1 singularities, whereas for parent system (Fig. 13b) s = 1/2 dispirations are also found. These textures are diagnostic for the formation of synclinic and anticlinic phases. Broken focal-conic domains were also observed in the samples prepared in thin electro-optical cells.

In switching studies rather high magnitudes of the optical tilt angles with respect to the smectic layers were measured. The experimental measurements found that for all of the siloxane materials synthesised the tilt angle was *ca.*  $45^{\circ}$ .

The spontaneous polarization was found to be almost two times higher than the corresponding value in the alkene

**Table 5** Transition temperatures (°C) and associated enthalpy values  $(\Delta H/kJ \text{ mol}^{-1})$  for the (*S*)-1-methylheptyl 4'-{4-[ $\omega$ -(1,1,3,3,3)-pentamethyl)disiloxanyl- and 4'-{4-[ $\omega$ -(1,1,3,3,5,5)-heptamethyl)trisiloxanyl- alkoxy]benzoyloxy}biphenyl-4-carboxylates, **E1** to **E5** 

H₃C-	Сн₃ –Si- <del>(</del> О СН₃	сн -Si <del>)</del> , СН	3 C <sub>n</sub> H <sub>2</sub>  3	.,O-			→ CH	H <sub>13</sub> E 3
No.	п	т	Мр		SmC*		Iso Liq	Cr
E1	4	2	•	32.7	•	50.9 [3.1]	•	-4 [7.3]
E2	6	2	•	28.2 [14.4]	•	69.3 [3.2]	•	6.3 [11.6]
E3	4	1	•	32.3 [20.9]	•	70.3 [5.8]	•	7.7
E4	6	1	•	36.4 [17.8]	•	83.3 [4.2]	•	12.2
E5	9	1	•	52.7 [41.8]	•	91.1 [4.48]	•	9.9 [18.9]

analogues, reaching values of over 200 nC cm<sup>-2</sup>. The magnitude of spontaneous polarization undergoes a smooth growth with decrease in temperature, see Fig. 14.

### 3.2 Electrooptic studies

In order to investigate voltage–transmittance characteristics as a function of chemical structure, a set of electrooptical experiments were performed for several of the materials. The measurements were taken in thin (*ca.* 2 or 5  $\mu$ m) planar aligned cells by applying a triangular electric field and varying the orientation of the cell between crossed polarizers in transmission. The transmittance as a function of the electric field was recorded at different frequencies, voltages and temperatures for each of the compounds.

**Table 6** Transition temperatures (°C) and associated enthalpy values  $(\Delta H/J \text{ mol}^{-1})$  for the (S)-1-methylheptyl 4'-{4-[ $\omega$ -(1,1,3,3,3-pentamethyldisiloxanyl)alkoxy-2,3-difluoro]benzoyloxy}biphenyl-4-carboxylates, F1–3

H <sub>3</sub> C–	CH₃ I -Si–(0 CH₃	сн Si-Si-) Сн	₃ ⊢−−C <sub>n</sub> H₂ m I₃		۶ ۲ ۲ ۲	<u>}</u>	→ CH	H <sub>13</sub> F
No.	п	т	Мр		SmC*		Iso Liq	Cr
F1	1	4	•	43.4 [33.2]	•	63.2 [3.38]	•	-8.9 [9.13]
F2	1	8	•	60.3 [23.5]	•	88.7 [3.37]	•	42.6 [20.7]
F3	1	9	•	63.5 [23.4]	•	90.4 [2.45]	•	49.4 [21.3]

Firstly, a V-shaped response was simulated for compound A2, because its rich mesomorphic behaviour is reminiscent of the phase morphology of the Tokyo mixture, *ie* the phase sequence includes SmA\*, SmC\*, SmC<sub>ferri</sub>\* and SmC<sub>A</sub>\* phases. The spontaneous polarization gradually increases from 30 nC cm<sup>-2</sup> at the SmA\*–SmC\* transition and reaches a value of above 140 nC cm<sup>-2</sup> near to the transition to the antiferroelectric phase. This value is fairly similar to the estimated spontaneous polarization for the phase exhibited by the Tokyo mixture.<sup>2</sup>

The electrooptical response showed a normal ferroelectric hysteresis at the frequencies above 5 Hz (Fig. 15a). Decreasing the frequency resulted in the hysteresis loop shrinking into a thin line (Fig. 15c). It can be seen in Fig. 15c that the slope of the line is steep because a sharp change in transmission occurs between the two switched states. When the orientation of the cell was changed so the axis of the polarizer was set parallel to the smectic layer normal a V-shaped response was obtained (Fig. 15b). The shape of the curve remained unchanged for a relatively broad range of frequencies.

However, below a certain value the hysteresis loop reappeared. This effect can be explained in terms of the distribution of space charge in the surface-stabilised cell.<sup>19</sup> When an external field  $E_{\text{ext}}$  is applied to the liquid crystal cell the layer spontaneous polarization is aligned along the field direction, thereby generating opposite surface charges, which produce an electric field  $E_{\text{sur}}$ . Since  $E_{\text{sur}}$  is smaller than  $E_{\text{ext}}$ 



Fig. 14 The spontaneous polarization plotted as a function of the reduced temperature from the Curie point for compounds of structure F. Applied field: 20 Hz, 2 VPP.

positive and negative ions in the bulk move in opposite directions creating the ionic field  $E_{ion}$ , which opposes  $E_{ext}$ . If the frequency of the external field is high enough, the charges do not have time to move far away from each other and generate a substantial  $E_{ion}$  before the external field changes sign. Thus, a normal hysteresis response is produced as switching starts at point A and is completed at B (Fig. 16). When the frequency is low, the mobility of ions increases so that  $E_{ion}$  has a significantly high contribution and, thus a negative electric field exists when the external field is zero. Therefore, the switching actually starts at A' and finishes at B' (A" and B" on the solid curve). If |A"| > |B"| an abnormal hysteresis takes place, and when |A"| = |B"| a hysteresis-free V-shape response is produced.

As shown in Fig. 16, when the V-shaped curve is stabilised, complete extinction of light was observed at the tip of the V. The bottom line in Fig. 15b corresponds to zero transmission when no light passes through the cell. Thus, all the features of the switching described for the Tokyo mixture can be simulated in the ferroelectric smectic C\* phase. It should be noted that the voltage–transmission curves depicted in Fig. 15 were recorded at a temperature close to the smectic A\*–smectic C\* phase transition. At these temperatures if any type of randomisation of molecular tilt is induced by the surfaces at



Fig. 13 Two- and four-brush defects observed in the *schlieren* textures: a) compound C2,  $SmC_A^*$  phase, 54.2 °C; b) compound E2,  $SmC^*$  phase, 72.0 °C (×100).



Fig. 15 Voltage-transmission curves recorded for compound A2 at various fields, at a temperature of 105 °C (approximately 4 °C below the SmA\* to SmC\* phase transition). The relative level of transmission is shown along the *y*-axis.



Fig. 16 Schematic diagram explaining reappearance of hysteresis loop at low frequency of an external electric field.

the tip of the V, it cannot be a result of the competition between synclinic and anticlinic ordering as suggested by the random model. The antiferroelectric and intermediate subphases appear 40 °C below the temperature point where the V-shaped switching is observed, and therefore such sub-phases cannot affect the thermodynamic stability of the smectic C\* ordering.

However, the temperature still appears to be an important factor in the stabilisation of the intermediary switching state, as demonstrated for compound **B3**. A V-shaped curve was observed in the smectic C\* phase using the method described above for compound **A2**, but only at higher frequencies (see Fig. 17). At 90 °C, just a few degrees below the second-order smectic A\*–smectic C\* phase transition the dark state does not correspond to zero transmission. However, the transmittance level decreases with temperature and at 74 °C complete extinction is observed.

If one takes into account the polarization surface kink (PSK) model,<sup>4</sup> the temperature dependence of the transmission can be explained in terms of the high value of the spontaneous polarization at lower temperatures. According to the well-known result related to the Landau expansion for a second order phase transition<sup>20</sup> the spontaneous polarization as a

second order parameter undergoes gradual growth with the reduced temperature from the Curie point:

$$\theta = \left(\frac{\alpha}{\beta}\right)^{1/2} (T_{\rm C} - T)^{1/2}$$
$$P = \frac{1}{2} P_0 \sin 2\theta$$

where  $\alpha$  and  $\beta$  are the coefficients of the first two terms of the expansion.

The spontaneous polarization of the compound **B3** increases from approximately 76 nC cm<sup>-2</sup> at 90 °C to 101 nC cm<sup>-2</sup> at 74 °C. Such an increase in the value of the spontaneous polarization would seem to be enough to transform a twisted structure at zero field to a uniform polarization stabilised state which dominates the material between the two surfaces. As a result, the level of transmittance drops to zero. The PSK model may well describe the properties observed, however it should also be remembered that the materials possess a very short pitch of the helix in the SmC\* phase, and thus helielectric effects cannot be ruled out.

Attempts were also made to simulate V-shape curves of the voltage–transmittance function in the smectic C\* phases of siloxane materials **E4** and **E5**, see Fig. 18 for compound **E5**. These compounds exhibit first-order transitions from the isotropic liquid to the smectic C\* phase. The corresponding value of the tilt angle in the smectic C\* phase, which is just slightly less than  $45^{\circ}$ , does not change with temperature. The spontaneous polarization reaches 110 nC cm<sup>-2</sup> in the vicinity of the phase transition, and it monotonically increases with decreasing temperature to approximately 200 nC cm<sup>-2</sup>.

In this case, the V-shaped switching was not affected by temperature, and could be observed throughout the whole temperature range of the phase, with a small hysteresis being a function of the frequency of applied field. The V-shaped curve appears to be turned up side down as the plane of the incoming light was set parallel to the director in one of the ferroelectric states. When the molecules are in this state, light travels with a polarization direction parallel to the principal molecular axis,



Fig. 17 Voltage-transmission curves recorded for compound B3 at various electric fields.



Fig. 18 Compound E5. Photomicrographs show the appearance of the zero-field state (a) and the uniform ferroelectric state (b) during the switching in a 5  $\mu$ m cell, and relaxation to a bright state with no field applied (c).

so complete light modulation is achieved. As a result, the cell appears dark. For the second uniform state the molecules are switched along the smectic cone to the opposite tilt positions. The dark texture is observed again, as this time the polarization plane is perpendicular to the optic axis of the material. It can be seen in Fig. 18 that the light extinction is not complete for these states because the tilt angle is slightly less than  $45^{\circ}$ 

In the configuration described, the third zero-field state occurs when the molecules reach the central position on the smectic cone which is at  $45^{\circ}$  to the plane of incident light. The photomicrographs taken of compound **E5** (Fig. 18) show the difference in appearance of the uniform dark state and bright zero field state. The height of the transmission curve reaches almost the maximum value as shown in Fig. 18. When the electric field is switched off the material slowly relaxes to the bright ground state.

Similar electrooptic behaviour was observed for compound **E4**. It was found that even if the polarizers are set parallel to each other the transmission value does not reach a minimum level as indicated by the bottom line in Fig. 19b and remains at a rather high level. The absence of mirror symmetry between

the transmission curves recorded for parallel and crossed polarizers originates from the non-linear polarization eigenmodes. The results explicitly show that there is no uniformity achieved in the field-off state. Instead, a twisted structure seems to be a possibility for these compounds in the absence of an electric field, because the Mauguin condition is not fully satisfied as the incoming plane polarized light is not fully rotated by the twisted structure and emerges elliptically polarized.

Comparing the results obtained for compounds A2, B3, E4 and E5 shows that in the surface stabilised geometry there is competition between twisted and uniform, polarization stabilised states. Assuming that the spontaneous polarization plays an important role in stabilisation of the uniform state there seems to be a critical value for a particular material above which a twisted structure transforms into the uniform state. For example, such transformations occur for compound B3 only at low temperatures where the spontaneous polarization has a substantially high value. However they do not take place for compounds E4 and E5 despite the fact that the spontaneous polarizations are almost double those of compounds A2 and B3. A twisted structure dominates at all values



Fig. 19 Voltage-transmission curves recorded for compound E4 between crossed (a) and parallel (b) polarizers.

in the polarization-temperature function. Thus, the critical value of the spontaneous polarization is not universal, rather it is only one of a number of physical properties of a material that are important.

Any modification to the chemical structure which amplifies the intermolecular interactions at the same time will also reduce the chances of the uniform state being stabilized at zero field. In the case of compound **B3**, two fluorine atoms laterally attached to one phenyl fragment of the parent structure **A2** serve as additional sites for interactions between neighbouring molecules within a layer. Similarly, the siloxane chains of compound **E4** greatly affect the interlayer interactions. While the former can be overcome by a temperature driven increase in the spontaneous polarization, the latter remains fairly strong and can not be counteracted by the electrostatic torque even if the torque is induced by an exceptionally strong spontaneous polarization.

This hypothesis is supported by the results obtained for compound C2. The only difference in its chemical structure

from compound A2 is the terminal double bond attached to the non-chiral chain. The spontaneous polarization is also roughly the same, approximately 80 nC cm<sup>-2</sup>. The compound possesses a broad antiferroelectric phase, for which the electrooptical response was observed and compared to the results for the ferroelectric phase. In order to include surface effects in the discussion, the material was investigated when placed in two planar cells of different thickness (2 and 5  $\mu$ m).

It can be seen in Fig. 20 that complete extinction of light was achieved between crossed polarizers, however, between parallel polarizers the cell transmission reaches only a maximum and an almost symmetrical inversion of the 'V-shaped' response is observed. It is most likely that a uniform structure is fully realised here with the plane of polarization of the incoming light being parallel to the optical axis of the material in the zero field state.

At 44 °C in the antiferroelectric phase a double hysteresis loop was observed when the frequency was low enough for the material to relax into the antiferroelectric ground state. As



200 mHz, 1 VPP, 40° C

Fig. 20 Voltage-transmission curves for compound C2. Cell thickness is 5 µm unless stated otherwise.



Fig. 21 Photomicrographs taken for compound C2 while switching under the application of a low-frequency electric field.

shown in Fig. 20, the double hysteresis loop transforms into a typical ferroelectric hysteresis loop at high frequencies, an effect which has been described previously for antiferroelectric liquid crystals.<sup>21</sup> For the intermediate frequency range, where the antiferroelectric state appears transitory during switching, the optical response curve exhibits features of both ferroelectric 'W-shaped' switching and the double hysteresis loop of the antiferroelectric phase. By adjusting the frequency, the 'W-shaped' curve could be transformed into a 'V-shaped' line at which point the switching process clearly proceeds via four states. Surprisingly, the uniform state, which was formed at the tip of the 'V' in the ferroelectric phase is, however, still present in the antiferroelectric phase. As reflected by a voltagetransmission curve (Fig. 20), the molecular reorientation from the ferroelectric state occurs via the so-called uniform "structure", where complete extinction of light was observed and then relaxes back to the antiferroelectric ground state.

In fact it was found that for narrow cell gaps at least, the cell thickness does not affect either the width of the 'V-shape'<sup>22</sup> nor the general trends in the material's response to the electric field. In both cells a typical 'W-shaped' ferroelectric response was produced at 80 °C when a high frequency field was applied. This response was converted into a 'V-shaped' line at 240 mHz in a 2  $\mu$ m plate separation and at 2 Hz in a cell with a gap of 5  $\mu$ m.

Remarkably, the tip of the V-shaped switching curve still corresponds to zero field, thereby allowing the speculation that, at least during the dynamic switching process, the polarization stabilised uniform structure is thermodynamically more stable than the antiferroelectric state in surface-stabilised geometries. The differences in textural appearance of the antiferroelectric and uniform zero-field states are shown in Fig. 21.

# 4. Discussion

From the studies presented it is clear that V-shaped switching is not only dependent on the spontaneous polarization, but it is also dependent on the voltage, frequency, molecular design and the interactions of the molecules with the surfaces within the cells. With respect to molecular design, polar groups were incorporated into the cores of the molecules, which were expected to affect the in-plane correlations, and bulky terminal groups were incorporated in order to affect the out of plane correlations. If we consider a hysteresis loop for a standard ferroelectric material, as shown in Fig. 22, the points where the loop crosses the electric field axis, *i.e.* the coercive fields  $E_c$  and  $-E_c$ , are measures of the ease with which the material may be poled. Where the loop crosses the polarization axes, the remanent polarizations,  $P_r$  and  $-P_r$ , are measures of the degree of the retention of the poled ferroelectric structure at zero field, *i.e.* it provides information about the stability of the structure. For V-shaped switching, the loop is essentially collapsed, thus the coercive fields fall to zero and the structure of the mesophase becomes fairly fluid-like.

A similar situation applies for antiferroelectrics where the double hysteresis collapses and the threshold field,  $E_{\rm tr}$ , which induces switching between the zero field state and either of the switched states falls towards zero, as shown in Fig. 23. Thus V-shaped switching, whether associated with ferroelectric or antiferroelectric behaviour, requires the organisation of the molecules to be relatively weak. For example when the interlayer interactions are weak, as in the case of the bulky silyloxy materials, V-shaped switching is easily achieved, whereas where the interlayer interactions are stronger as in the case of the terminal alkenic materials antiferroelectricity becomes stabilised and V-shaped switching is unattainable.

The strength of the bulk ferroelectric ordering can be determined from the in- and out-of-plane correlation lengths of the molecules with respect to the layers. However, in surface stabilised devices the strength of the surface interaction and its penetration into the bulk also becomes important. The weaker the surface interactions the more likely it will be that V-shaped switching will occur.



Fig. 22 Hysteresis loop for a ferroelectric liquid crystal.



Fig. 23 Hysteresis loop for an antiferroelectric liquid crystal.

Overall decoupling of the layers and the incorporation of lateral groups which weaken the lateral interactions will destabilise the hysteresis loop and support a V-shaped response to applied electric fields.

#### 5. Conclusion

In conclusion for the results obtained on the various materials studied several observations and property–structure activities may be drawn:

1. The V-shape electrooptical response is a property of the material placed in the surface-stabilised geometry, and can be observed for switching in the ferroelectric smectic  $C^*$  phase.

2. At the tip of the V-shaped switching curve, the uniform polarization stabilised structure is likely to be formed according to the mechanism described by models of the polarization stabilised kink (PSK) and insulating layer structures.

3. The stability of the uniform state is greatly affected by the chemical structure of the material. Functional groups introduced onto the molecular core and chains may reduce the polarization effect thereby resulting in domination by the twisted state. In such cases, the V-shaped switching curve can still be observed, however, the transmission at the tip of the V does not become zero. An exception is the twisted structure formed by high tilt materials.

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