A chiral electrooptic response in a racemic liquid crystal

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Over recent years, little attention has been paid to the electrooptic properties of racemic modifications of smectic liquid crystals, however, in this communication we report on a chiral response of a racemic modification to an applied electrical field while in its synclinic smectic C phase.

In a seminal review of 1977, Meyer demonstrated when the symmetry of the 'synclinic' smectic C liquid crystal phase is reduced from C_{2h} to C_2, *via* the incorporation of stereogenic centres into the structures of the constituent rod-like molecules of the mesophase, extrinsic ferroelectric properties can arise.[1] Ferroelectric behaviour was experimentally found the year before in the now classical material DOBMBC.[2] The discovery of ferroelectricity in liquid crystals led directly to the invention of a wide variety of electrooptic devices for use as light valves, gates and displays.[3] In recent years surface stabilised bistable devices (SSFLCDs) have been commercialised in reflective mode microdisplays for use in the eyepieces of digital cameras and camcorders,[4] and monostable and 'V-shaped' switching mode devices have been utilised in prototype fast-switching displays (sub-millisecond) operating with grey-scale.[5]

Conversely, in 1972 McMillan[6] theorised that various forms of the synclinic smectic C phase could be ferroelectric in the absence of molecular chirality, however, such behaviour has never been observed in practice. More recently, a similar theoretical model for ferroelectricity in non-chiral materials was proposed by Tredgold for molecules with kinked molecular shapes associated with ester or imine linking groups.[7] For these structures he postulated that the dipoles associated with such linkages become spontaneously aligned to give a ferroelectric phase without the need for chirality.

However, like McMillan, Tredgold's theoretical models have never been realised under experimental conditions. However, in recent years banana-like liquid crystals have been shown to exhibit ferroelectricity in domains, without the presence of molecular chirality.[8]

In the following we focus our attention on one particular material, compound **11**, based on the classical material MHPOBC.[9] We took the generic structure of the MHPOBC family of materials, and modified it such that the non-branched aliphatic chain was substituted with a terminal carbocyclic ring – cyclohexane being selected because of its non-polarity, steric bulk and compatibility with aliphatic chains. In this case we expected that the bulky nature of the terminal group would cause disruption of the packing of the tails of the molecules at the layer interfaces, thereby possibly weakening the inter-layer interactions, and allowing us control over properties such as mesophase formation and tilt angle.

Although we prepared examples of material **11** in its enantiomeric *R*- and *S*-forms, we specifically focus in this article on its *racemic* modification and describe its synthesis, chemical analysis and physical properties.

In order to ensure that the racemic form (*ee* of zero) of **11** was obtained we decided to start its synthesis with the reduction of 2-octanone, **1**, with sodium borohydride, see Scheme 1 below. The synthesised 2-octanol, **2**, was first subjected to analysis using NMR and chiral GC, and then used immediately in subsequent transformations, thereby reducing any possibility that it could be contaminated or subjected to microbial attack. Chiral GC was found to separate the enantiomers to give symmetrical peaks, however, these could not be resolved to the baseline.

Phenol **6** was prepared by standard methods starting from 4-hydroxybenzoic acid, **3**. The hydroxy group was first protected as the carbonate to give **4**, this intermediate was esterified with the racemic form of 2-octanol in the presence of diisopropyl azodicarboxylate (DIAD), triphenylphosphine and THF to give **5**. Compound **5** was deprotected using a mixture of ammonia and ethanol to generate the phenol **6**. The optical purity of the phenol was determined using chiral GC analysis before it was used further. In this case the phenol was able to be resolved to the baseline, and within the limits of experimental error the enaniomeric excess was found to be zero.

4′-(11-Hydroxyundecyloxy)biphenyl-4-carboxylic acid, **9**, was prepared starting from 4-cyano-4′-hydroxybiphenyl, **7**, which was first alkylated with 11-bromoundecan-1-ol in the presence of potassium carbonate in butanone to give **8**, followed by base hydrolysis of the nitrile to give **9**.

Acid **9** and phenol **6** were esterified in the presence of 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride (EDAC) and 4-(dimethylamino)pyridine to give **10**. Under these conditions **10** is formed without any self-esterification of **9**. The last step in the pathway was the esterification, under the same conditions, for **10** with cyclohexylacetic acid to give the racemic modification **11**.

The chemical and structural analyses of the racemic modification of 4-(1-methylheptyloxycarbonyl)phenyl 4′-[11-(2-cyclohexylacetoxy)undecyloxy]biphenyl-4-carboxylate, **11**, gave the following results:

Transition temperatures: K 58.4 SmC 77.1 SmA 83.0 °C Iso Liq

Enthalpies of transition: 73.6, 0.4, 2.84 J g^{-1}

^{1}H NMR ($CDCl_3$) δ: 0.86–1.01 (5H, m), 1.20–1.40 (24H, m), 1.47 (2H, quint), 1.53–1.87 (14H, m), 2.17 (2H, d), 4.02 (2H, t), 4.05 (2H, t), 5.16 (1H, sext), 7.00 (2H, d), 7.31 (2H, d), 7.60 (2H, d), 7.70 (2H, d), 8.13 (2H, d), 8.23 (2H, d) ppm.

IR (KBr) ν_{max}: 1262, 1601, 1720, 1738, 2848, 2922 cm^{-1}.

EA: Calc.: C, 76.18; H, 8.70. Found: C, 76.31; H, 8.97%).

OR: $[\alpha]_D^{23} = 0.00°$; 0.0025 g ml^{-1} in $CHCl_3$.

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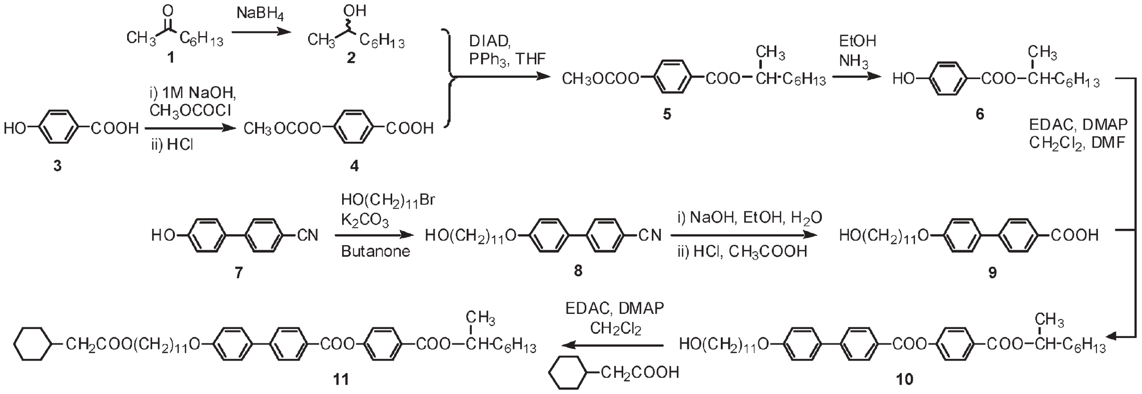

Scheme 1

Initial mesophase classification was achieved using polarized-light optical microscopy (POM). Fig. 1 shows the homeotropic and focal-conic forms of the smectic A phase (a) and the Schlieren and broken focal-conic textures of the smectic C phase of racemate (b). The Schlieren texture is typical of an achiral smectic C phase, which shows no colour change upon rotation of the analyzer indicating that the phase has no helical structure.

X-Ray diffraction studies on aligned and unaligned specimens of the racemic modification were performed as a function of temperature. In all cases the X-ray patterns obtained were for layered phases with disorganized arrangements of their constituent molecules. For example, the results obtained for the wide angle region showed broad diffuse peaks related to the lateral positional order between the molecules. In the narrower angle region, strong reflections were seen which were related to the correlations between the layers. For all of the mesophases the layers were found to be uncorrelated with diffuse packing of the molecules. The layer spacings were, however, at higher *q* values in the tilted smectic C phase, than in the smectic A phase.

The layer spacing as a function of temperature is shown in Fig. 2. The smectic A layer spacing was found to be approximately 42 Å. As the temperature is lowered further the transition to the smectic C phase is marked by a rapid decrease in the layer spacing over a temperature range of approximately 5 °C, upon which the layer spacing becomes temperature independent. This behavior is typical of a smectic C phase formed from a smectic A phase *via* a second-order phase transition, with the layer spacing falling and eventually levelling off with the reduced temperature.

A schematic of the type of cell construction used for electrical field investigations of tilted smectic liquid crystals is shown in Fig. 3. The molecules are arranged in layers, where the layers are perpendicular to the surfaces of the cell. For chiral materials, when the associated spontaneous polarization couples to the DC field two switched states are obtained, one with the polarization pointing up, the other with it pointing down. Switching occurs as shown by the movement of the molecules about a cone of degenerate energy. Thus for a positive DC bias one state is formed, and for a negative bias the other state is obtained. For a racemate an equivalent mixture of switched states would be expected to be obtained, provided that enantioselective separation occurs. Approximately 50% transmission under crossed polars thus would be expected.

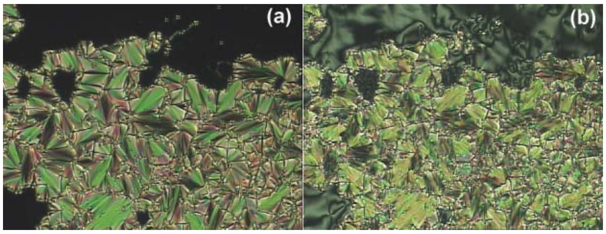

Fig. 1 (a) The homeotropic and focal-conic textures of the SmA phase, and (b) the Schlieren and broken focal-conic textures of the SmC phase of racemate **11**.

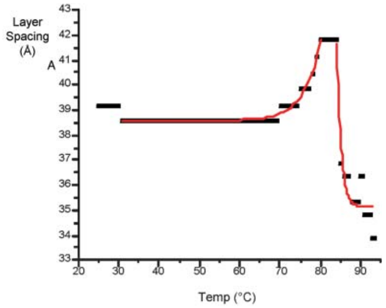

Fig. 2 The layer spacing (Å) for **11** as a function of temperature (°C).

Thus, electrical field studies were performed on the racemate using a variety of wave forms and ITO coated cells of different alignment agents (polyimide, nylon *etc.*), orientations of the buffing directions, (parallel- and anti-parallel rubbed) and cell spacings (1.5 and 5 μm). Remarkably, switching behaviour typical of ferroelectricity, rather than those associated with dielectric or flexoelectric effects, was observed for the achiral synclinic smectic C phase of the racemate.

The racemate was found to be relatively sensitive to the nature and quality of the aligning agent and the origins of the cells, with the best results being obtained in cells obtained from the University of Chalmers (Sweden). For the bright extreme switched state, 95% transmission was obtained relative to the transmission through an empty cell (*i.e.* to act as a baseline for the contrast ratio). For the fully switched dark state transmission was close to that for an empty cell observed between crossed polars. Similar results were obtained in thin cells (1.5 μm) and thick cells (5 μm) alike, see Fig. 4. In this figure the switched states are shown upon reversal of the DC field. The bright state corresponds to an

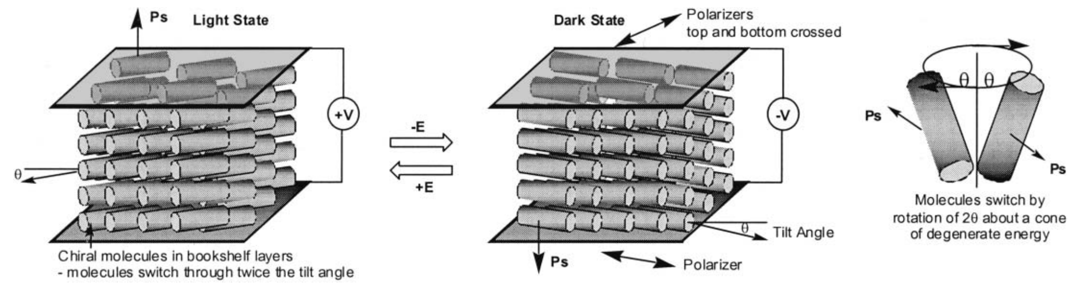

Fig. 3 A schematic representation of the two switched states for a ferroelectric liquid crystal in a device constructed of ITO coated glass surfaces coated with suitable homogeneous aligning agent. The spontaneous polarization, which is associated with molecular chirality, couples to the DC field.

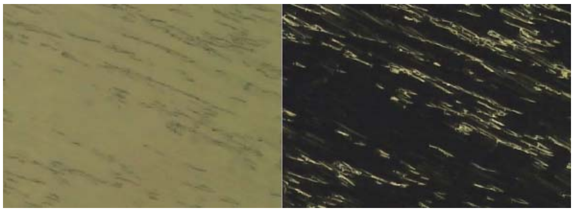

Fig. 4 The switched states for the racemic material **11** in a cell with a 1.5 μm spacing and parallel rubbed polyimide alignment coatings. Left side >90% transmission, right side less than 5% transmission.

approximate value of 95% transmission, and the dark state less than 5% transmission. However, the value of the "*induced spontaneous polarization*" was found to be zero, but the sign was determined to be positive ("*Ps*+").[10] In addition, in thicker cells the switching profiles gave V-shaped optical/transmission and electrical responses. As a result, this gives us the possibility of creating devices with gray-scale operation, and without the need for chiral materials which are often expensive to produce.[11]

Comparison of the results obtained for the determination of the spontaneous polarization for the racemate with those obtained for the enantiomers, shows that the enantiomers typically reached maximum values of approximately 80–100 nC cm^{-2} at reduced temperatures of 50° from the Curie point, see Fig. 5(a). The slight differences between the *R*- and *S*-enantiomers arises from slight differences in optical purity. This result confirms that the racemate is indeed racemic as no polarization could be determined, and the behaviour of each enantiomer is typical of a conventional ferroelectric liquid crystal. Interestingly the switched tilt angle of the racemate (23°) was considerably lower than the values found for either of the enantiomers (36°), see Fig. 5(b).

These results appear to be quite remarkable in that we have an apparent chiral response to an electric field applied to a racemic modification. Such a response may be due to amplification by the liquid crystalline media. This outcome suggests that either our conventional understanding of ferroelectric behaviour in chiral smectic C* phases requires modifying, and there is a greater dependency on flexoelectric and dielectric effects, or that parity at the macroscopic level has been broken in liquid crystals in a way that we as yet do not understand. Similar observations, and comments, have also been made in the study of absolute asymmetric synthesis.[12]

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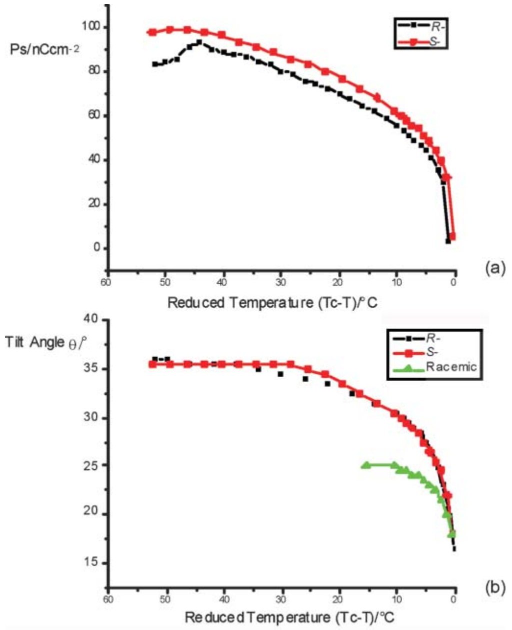

Fig. 5 (a) The polarization (nC cm^{-2}) and (b) the tilt angle (°) of the *R*-, *S*- and racemic forms of **11**, as a function of the reduced temperature.

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