

A Novel Antiferroelectric Liquid Crystal with two Asymmetric Centres

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Z. Naturforsch. **57a**, 199–201 (2002); received February 14, 2002

An antiferroelectric liquid crystal material, (S)-4-(2-chloro-3-phenyl-1-(2-methylbutyloxy)carbamato-4'-n-dodecyloxy biphenylcarboxylate (CPCDBD), has been synthesized by using (S)-2-amino-3-(4-hydroxy)phenyl propionic acid (L-tyrosine) as one the optically active ingredients. Preliminary investigations on this material reveal high spontaneous polarization ($\sim 145 \text{ nC/cm}^2$) in the antiferroelectric Sm-C_A^{*} phase. Possible structural contributions towards the appearance of antiferroelectric ordering are discussed.

Key words: AFLC; CPCDBD; Spontaneous Polarization.

Despite their tri-stable switching state and high spontaneous polarization (P_S), a great deal of research has been directed towards antiferroelectric liquid crystal (AFLC) materials. The advent of this tri-stable switching behaviour is also of technical importance in memory devices. Since the discovery [1] of the first AFLC compound, MHPOBC, the quest for these interesting materials has increased among the material chemists. Recently many groups have developed new AFLC materials exhibiting high spontaneous polarization [2–6]. We have made a successful attempt to isolate an AFLC molecule: The molecular skeleton of CPCDBD (Fig. 1) is designed in such a way that: (a) two asymmetric centers are incorporated along the long molecular axis, using L-tyrosine and (S)-3-methyl-butanol as chiral ingredients, (b) the highly electronegative chlorine atom is introduced in the α -carbon of the amino acid by nucleophilic substitution with retention of the asymmetric configuration [7], and (c) the number of transverse dipoles and phenyl rings (biphenyl moiety) is increased along the long molecular axis. In continuation of our previous efforts [8–13] to isolate ferroelectric materials with high P_S , the present communication deals with preliminary investigations on CPCDBD.

The two chiral centers in CPCDBD, L-tyrosine and (S)-3-methyl-butanol, are available commercially in high enantiomeric purity (Sigma Chemical Company, USA). The preparation of CPCDBD is reported in [14]. All the intermediate products and the desired product are purified by passing through a silica gel column using appropriate eluent mixtures, and their structures are confirmed by IR and NMR spectral analyses. CPCDBD is highly stable at room temperature and also when subjected to repeated thermal scans for differential scanning calorimetry and spontaneous polarization measurement.

The phases of CPCDBD and transition temperatures were determined [15] from characteristic textural observations under a polarizing thermal microscope (Olympus BX 50) equipped with the optical display (DP-10) at a scan rate of 0.1°C per minute. On cooling the isotropic melt, CPCDBD exhibits focal conic fans (smectic-A), concentric striations across focal conic fans (smectic-C^{*}), a distinct colour change from red to green (smectic-C_A^{*}) [10], and broken focal conic fans (smectic-F^{*}). The phase transition temperatures observed through thermal microscopy agree reasonable with the DSC data (Perkin-Elmer DSC-7). The phases and their

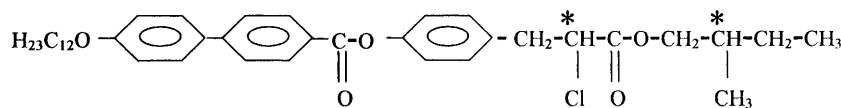


Fig. 1. Molecular structure of CPCDBD.

transition temperatures ($^{\circ}\text{C}$) are:

Iso (147.6) **Sm-A** (131.8)
Sm-C $_{\alpha}^*$ (131.2) **Sm-C *** (128.1) **Sm-C $_A^*$** (126.3)
Sm-F * (57.1) **Cryst.**

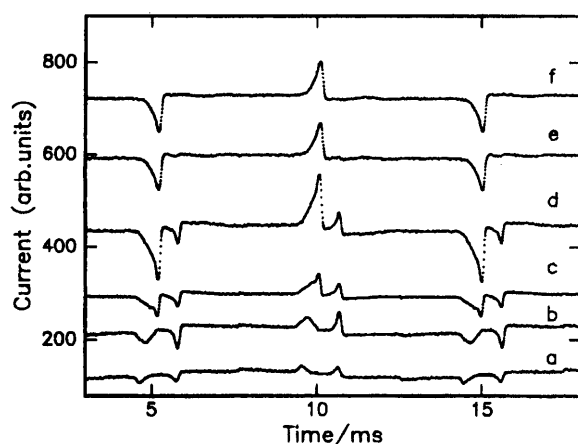


Fig. 2. Polarizing current profiles: (a) smectic- C_{α}^* phase at 131°C , (b-c) transition from smectic C_{α}^* to smectic- C^* at $129\text{--}128.5^{\circ}\text{C}$, (d) manifestation of smectic- C_A^* phase at 128°C , (e-f) stabilization of smectic- C_A^* phase.

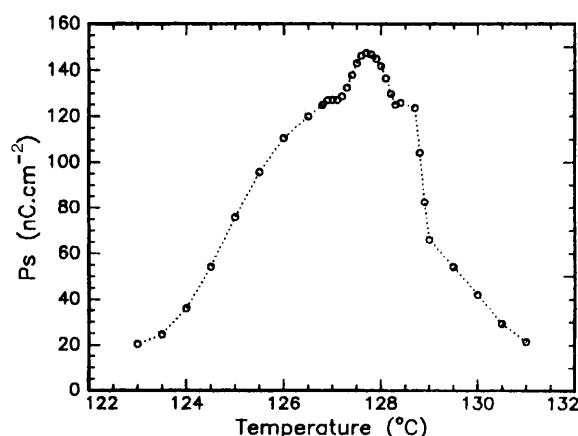


Fig. 3. Temperature variation of spontaneous polarization ($\text{nC} \cdot \text{cm}^{-2}$).

The spontaneous polarization and response times were measured in a 10 micron polyimide buffed cell (Display Tech, USA) by the field reversal method with a modified integrator part [16]. The polarizing current peaks at different temperatures were analyzed to obtain the magnitude of spontaneous polarization. From the profiles of the polarizing current peaks, the phases C_{α} ,

C^* , and C_A^* were clearly identified. Figure 2 (a-f) shows such polarizing current profiles of different chiral phases. It is worth to recall the phase assignment in the case of the reported [10] AFLC compound (S)-2-chloro-3-(4-benzamidoacetophenyl)-1-[4'-(2-chloro-3-benzoatophenyl)-1-(*p*-decyloxybenzoyl)-propionato)]-benzoatopropionate (CBCBDPBP), where a similar trend in the current profiles is observed.

The temperature variation of the spontaneous polarization is represented in Figure 3. The spontaneous polarization is found to increase with decreasing temperature and to attain a saturated value in the Sm- C_A^* phase (Fig. 3). The present compound shows a high P_s ($145 \text{ nC} \cdot \text{cm}^{-2}$) at 127°C in the antiferroelectric phase. This high value in the Sm- C_A^* phase may be attributed to the strong dipolar and electrostatic interactions between pairwise molecules in adjacent layers.

Structural Contributions to the Origin and Stabilization of Antiferroelectric Ordering

1. The conjugation across the long molecular axis leading to the dipolar interactions among the adjacent smectic layers enhances the inherent stabilization of the antiferroelectric ordering. The resultant pairing of the transverse dipoles in the neighbouring layers is supposed to be the origin of the antiferroelectricity [17].
2. The presence of two polar asymmetric carbons favours the appearance of the antiferroelectric Sm- C_A^* phase. The effective role of these asymmetric configurations can best be accounted for [10] by an elongated delocalized electron cloud between the two asymmetric carbons. Moreover, our systematic studies [8, 9] on tyrosine-based FLC compounds with a single chiral center suggest the non-existence of the antiferroelectric Sm- C_A^* phase.
3. The presence of biphenyl moieties as spacer units, resulting in elongated conjugation along the long molecular axis, may further enhance the stabilization of antiferroelectric ordering.

Detailed investigations, related to other physical parameters, *viz.* response times, viscosity, dielectric constant, tilt angle etc., are in progress.

Acknowledgement

The financial support rendered by the Council of Scientific and Industrial Research (Grant No: 13(7544-A)/Pool), New Delhi, India, is a gratefully acknowledged.

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