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Synthesis of a novel antiferroelectric liquid crystal with high P_s

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An antiferroelectric liquid crystal material, (*S*)-4-[4-(dodecyloxycarbonylphenoxy)-2-chloropropionyl] phenyl 4-{4-[2-chloro-3-(4-benzamidoacetyloxyphenyl)propionyloxy] benzoyloxy}-benzoate (DCPCPB), has been designed and synthesized by using L-tyrosine as a chiral source. Preliminary investigations of the ferroelectric properties of the present material show a high magnitude of spontaneous polarization (190 nC cm^{-2}) and response times (135 μs) in the antiferroelectric SmC_A^* phase. The possible molecular contributions towards the appearance of the antiferroelectric phase are summarized.

1. Introduction

Owing to their technical importance in memory devices, tristable antiferroelectric liquid crystal (AFLC) materials have attracted much attention in recent years. Since the discovery [1] of the first ever AFLC compound MHPOBC, the quest for these interesting materials has become an important activity among material chemists. Despite the fact that spontaneous polarization is one of the important parameters of these antiferroelectric materials, recently many groups have developed new AFLC materials exhibiting a high magnitude of spontaneous polarization [2]. In search of materials with high spontaneous polarization we have made a successful attempt to isolate an AFLC molecule. The molecular skeleton (figure 1) has been designed in such a way that (a) two asymmetric centres are incorporated along the long molecular axis using L-tyrosine as a chiral source, (b) highly electronegative chlorine atoms are introduced at the chiral carbons by nucleophilic substitution with the retention of asymmetric configuration [3] and (c) the number of transverse dipoles and phenyl rings are increased along the long molecular axis. In continuation of our previous efforts [4, 5] to generate ferroelectric materials with high P_s, this communication deals with a novel route of synthesis and also summarizes some important physical parameters which make the present compound most suitable for future application demands.

2. Experimental

2.1. *Synthesis*

The two chiral centres introduced in the present compound were derived from a chiral ingredient, (*S*)-2-amino-3-(4-hydroxyphenyl)propionic acid (L-tyrosine), available commercially (CDH, India) in high enantiomeric purity. The synthetic route for the preparation of DCPCPB, along with reaction conditions, is illustrated in the scheme while a detailed synthetic procedure including various intermediates is presented below.

All intermediate and final products were purified by passing through a silica gel column using appropriate eluent mixtures and their identities confirmed by PMR spectral analysis (Jeol FX-90Q multinuclear spectrometer). DCPCPB is highly stable at room temperature and also showed a high degree of thermal stability when subjected to repeated thermal scans for DSC, P_s and response time measurements.

2.1.1. *(S)-2-Chloro-3-(4-hydroxyphenyl)propionic acid (**1**)*

This compound was prepared by dissolving (*S*)-2-amino-3-(4-hydroxyphenyl)propionic acid (5.43 g, 30.0 mmol) in

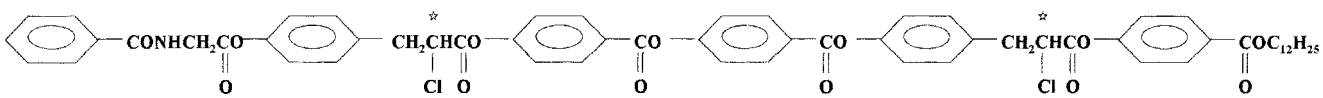

Figure 1. Molecular structure of DCPCPB.

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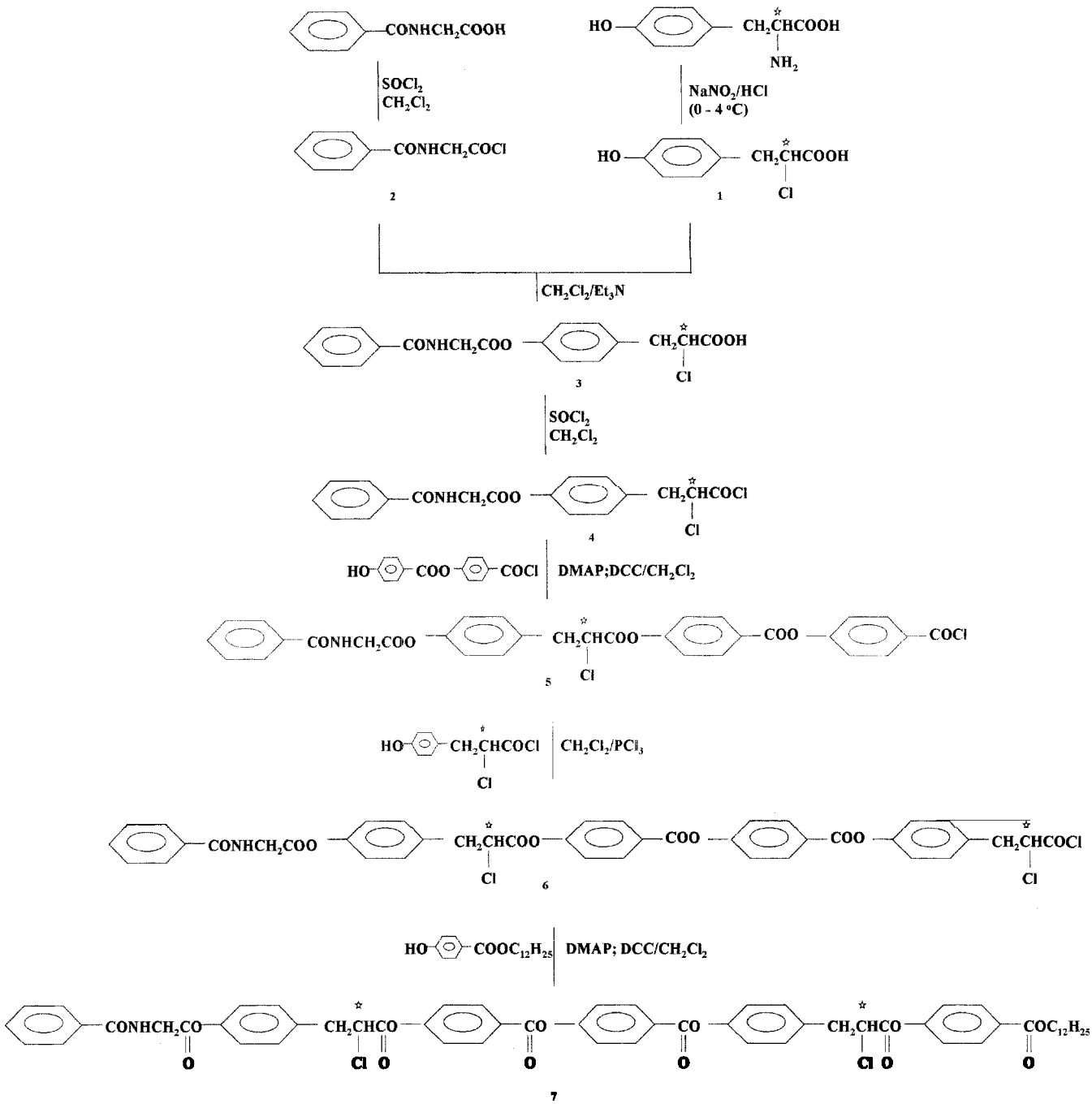

Scheme. Synthetic route for DCPCPB.

20 ml of 6.0N HCl at 0°C. Freshly pulverized sodium nitrite (2.72 g, 32.0 mmol) was added to the solution in small portions with vigorous stirring while maintaining the reaction temperature between 0 and 5°C. The reaction mixture was stirred for 14–16 h and then extracted with 40 ml of diethylether. The ether layer was dried over anhydrous sodium sulphate for 12 h. The crude product **1**, obtained as a yellow product on removing the excess solvent by distillation under reduced pressure, was washed repeatedly with cold EtOH and finally recrystallized from hot dichloromethane to give a yield of 3.2 g (53.2%).

2.1.2. *Benzamidoacetyl chloride (**2**)*

This was synthesized by mixing together 2-benzamidoacetic acid (4.48 g, 25.0 mmol) and $SOCl_2$ (3.0 ml, 40.0 mmol) in 40 ml of dry benzene under nitrogen atmosphere and heating the mixture under reflux with

continuous stirring at 75°C for 8 h. After the evolution of SO_2 gas ended, the volume of the resulting solution was reduced by vacuum distillation to give a yellow solid product which was suction filtered, washed several times with cold methanol and recrystallized from hot benzene solution. The yield obtained was 2.6 g (52.6%).

2.1.3. *(S)-2-Chloro-3-(4-benzamidoacetyloxyphenyl)-propionic acid (**3**)*

A dichloromethane solution (40 ml) containing **2** (3.95 g, 20.0 mmol) and **1** (5.0 g, 25.0 mmol) was magnetically stirred at ambient temperature for 2 h. Triethylamine (0.5 ml, 3.6 mmol) was then added dropwise and the reaction mixture was heated under reflux at 60°C with constant stirring for 10–12 h. The resultant solution, after cooling to room temperature, was poured into a beaker containing ~50 ml of cold water. The product separated as a white solid which was then extracted with petroleum ether and dried over Na_2SO_4 for 6 h. The white crude product obtained on removing the excess ether, followed by repeated washings with cold methanol, was recrystallized from hot benzene to give a yield of 2.81 g (69.82%).

2.1.4. *(S)-2-Chloro-3-(4-benzamidoacetyloxyphenyl)-propionyl chloride (**4**)*

This was prepared by dissolving **3** (5.84 g, 16.2 mmol) in 40 ml of absolute dichloromethane and adding 2.5 ml (21.2 mmol) of $SOCl_2$ with constant stirring at room temperature. The reaction mixture was heated to 60°C till the evolution of SO_2 ceased. The product separated as a white solid on cooling the reaction mixture to room temperature, and was purified by passing through a silica gel column using an eluent mixture of ether and acetone (4:2 v/v) to give a yield of 4.22 g (68.84%).

2.1.5. *(S)-4-{4-[2-Chloro-3-(4-benzamidoacetyloxyphenyl)-propionyloxy]benzoyloxy}benzoyl chloride (**5**)*

This compound was obtained by stirring together dry dichloromethane solutions (40 ml) of **4** (1.52 g, 4.0 mmol) and 4-[4-(hydroxy)benzoyloxy] benzoyl chloride (1.24 g, 4.0 mmol) [4] in equimolar ratio for 6 h at room temperature under nitrogen. To the resultant reaction mixture, 0.38 g (3.1 mmol) of 4-dimethylaminopyridine (DMAP) and 0.82 g (4.0 mmol) of *N,N′*-dicyclohexylcarbodiimide (DCC) were added dropwise with constant stirring. The mixture was then heated at reflux for 15–18 h at 75°C. The volume of the resultant yellow solution was reduced by vacuum distillation to give an oily product. This was extracted twice with diethylether and the ether layer dried over anhydrous Na_2SO_4 for 12 h. The crude product obtained on slow evaporation of ether was washed repeatedly with cold acetonitrile and was finally recrystallized from hot benzene solution to give a yield of 1.37 g (54.5%).

2.1.6. *(S)-4-(2-Chloro-2-chlorocarbonylethyl)phenyl 4-{4-[2-chloro-3-(4-benzamidoacetyloxyphenyl)-propionyloxy]benzoyloxy}benzoate (**6**)*

This was synthesized by dissolving equimolar quantities of (*S*)-2-chloro-3-(4-hydroxy)phenylpropionyl chloride (0.86 g, 4.0 mmol) [4] and **5** (2.42 g, 4.0 mmol) in 30 ml of dry dichloromethane and stirring at ambient temperature for 4 h under nitrogen. To the resultant reaction mixture 0.4 ml (4.3 mmol) of PCl_3 was added dropwise and the mixture heated under reflux at 75°C with constant stirring for 22 h. After cooling to room temperature, the reaction solution was poured into ~100 ml of cold water. The yellow solid product was suction filtered, washed twice with cold ethanol, extracted with petroleum ether and dried over Na_2SO_4 for 8 h. The crude product was purified by passing through a silica gel column using a mixture of petroleum ether and acetone (5:1 v/v) as eluent. The product was recrystallized from hot benzene solution with a yield of 1.74 g (55.4%).

2.1.7. *(S)-4-[4-(Dodecyloxycarbonylphenoxy)-2-chloropropionyl]phenyl 4-{4-[2-chloro-3-(4-benzamidoacetyloxyphenyl)propionyloxy]benzoyloxy}-benzoate (**7**)*

This was prepared by mixing together absolute dichloromethane solutions (30 ml) of **6** and dodecyl 4-hydroxybenzoate [4] in equimolar ratio and stirring at ambient temperature for 4 h under nitrogen. The reaction mixture was then heated under reflux with DMAP (6.0 mmol) and DCC (8.5 mmol) at 75°C with constant stirring for 20–22 h. After extracting with diethylether and evaporating the solvent, the desired product was obtained as a yellow solid. It was then washed twice with cold ethanol and passed through a silica gel column using petroleum ether and acetone (4:2 v/v) as eluent. The product was recrystallized from hot benzene solution to give a yield of 2.10 g, clearing point 147.2°C. ^{1}H NMR (δ ppm in $CDCl_3$) 10.83 (b, 1H, –NH–); 4.17 (d, 2H, –CH$_2$–CO–) 4.35 (d, 4H, –CH$_2$–CH(Cl)–); 3.21 (t, 2H, –CH(Cl)–); 2.82–3.34 (m, 20H, –(CH$_2$)$_{10}$–CH$_3$); 3.66 (t, 2H, OCH$_2$–); 6.81–8.12 (m, 25H, Ph); 1.16 (t, 3H, –(CH$_2$)$_{10}$–CH$_3$).

2.2. *Characterization*

The phase variants and their transition temperatures were determined [6] from characteristic textural observations under a polarizing microscope (Hertel-Reuss Super pan-II) equipped with a PC-monitored hot stage. The phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with DSC thermograms (Perkin-Elmer DSC-7).

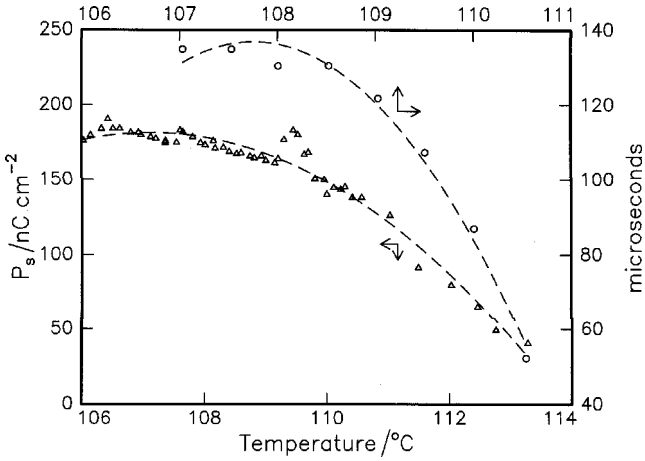

Figure 2. Temperature variation of spontaneous polarization (nC cm^{-2}) and response times (μs) of DCPCPB.

The phase sequence and transition temperatures (°C) of the present compound can be represented as:

Iso (147.1) SmA (113.1) SmC^*_α (111) SmC* (110.5)

SmC^*_γ (110) SmC^*_A (106.2) I* (69.6) Cr

The spontaneous polarization and switching times were measured in a 10 μm polyimide buffed cell (Display Tech, USA) by the field reversal method with a modified integrator part [7]. The magnitude of these two parameters was found to increase with decreasing temperature, attaining a saturated value in the SmC^*_A phase (figure 2). The present compound showed a high magnitude of P_s (190 nC cm^{-2}) and response time (135 μs) at 107°C in the antiferroelectric phase (figure 2). These high values in the SmC^*_A phase may be attributed to the strong dipolar and electrostatic interactions between each molecule in adjacent layers.

3. Discussion

A number of factors influencing the origin and stabilization of antiferroelectric ordering may be listed.

(a) Conjugation plays an important role in the appearance of antiferroelectric ordering, by means of dipolar interactions between adjacent layers, which in turn enhances the inherent stabilization of the antiferroelectric phase. The resultant pairing of the transverse dipoles in neighbouring layers is supposed to be the origin of the antiferroelectricity [8].

(b) The presence of two highly polar asymmetric carbon atoms in the molecule will favour the appearance of the antiferroelectric SmC^*_A phase. Further, the role of these two asymmetric configurations can best be interpreted [9] in terms of an elongated delocalized electron cloud between the two asymmetric carbon atoms which is achieved through conjugation. Moreover, our systematic studies [4] on the analogous series of FLC compounds with a single chiral centre suggest the non-existence of an antiferroelectric SmC^*_A phase.

(c) Extended conjugation along the long molecular axis by the incorporation of phenyl rings as spacer units may further enhance the stabilization of antiferroelectric ordering [2].

Further detailed investigations on other physical parameters of this compound are in progress.

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