Synthesis of Antiferroelectric Liquid Crystal Material Containing Three Asymmetric Carbons

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Z. Naturforsch. **57a**, 807 – 811 (2002); received June 25, 2002

A novel antiferroelectric liquid crystal compound, (S)-4-(2-chloro-3-(4-(2chloro)propyloxyl) phenylpropionato-4′-(2-methyl)butyloxy-biph enylcarboxylate (CCPMBB), comprising of three asymmetric centres, has been synthesized using L-tyrosine as one of the chiral ingredients. The thermal and phase behaviour is studied by thermal microscopy (TM) and differential scanning calorimetry (DSC). The ferroelectric studies imply the existence of antiferroelectric phase and a wide thermal span of SM-C* phase. A comparative discussion is made towards the influence of the number of asymmetric centres (more than two in the present case) on the ferroelectric behaviour with its structural analogues.

Keywords: CCPMBB; AFLC; Spontaneous Polarization; Smectic-C_A^*.

Introduction

Due to their technical significance 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 aspect among the material chemists. Despite the fact that spontaneous polarization (P_S) is one of the important parameters of these materials, many novel AFLC materials with high spontaneous polarization were developed in recent years [2 – 6]. In continuation of our earlier efforts [7 – 16] to generate ferroelectric materials with high P_S, this communication deals with a novel route of synthesis and characterization in terms of magnitude of spontaneous polarization. In the pursuit of AFLCs with a high ferroelectric thermal range we were successful in synthesizing a novel AFLC material, CCPMBB (Fig. 1). Its molecular skeleton is designed in such a way that **(a)** three asymmetric centres are incorporated along the long molecular axis using L-tyrosine, (S)-2-chloropropionic acid and (S)-2-methylbutanol as optical by active ingredients, **(b)** highly electronegative chlorine atoms are introduced at the α-carbon of L-tyrosine by nucleophilic substitution with the retention of asymmetric configuration [17, 18], and **(c)** the number of transverse dipoles and phenyl rings are increased along the long molecular axis.

Experimental

Materials and Methods

The three chiral ingredients *viz.* (S)-2-amino-3-(4-hydroxy)phenyl propionic acid (L-tyrosine) (CDH, India), (S)-2-chloro-propionic acid (Sigma-Aldrich Company, USA) and (S)-2-methylbutanol (Frinton Laboratory, USA) used are available commercially in high enantiomeric purity. All the solvents used in the present work are of E. Merck grade and are used as such without any further purification. The optical

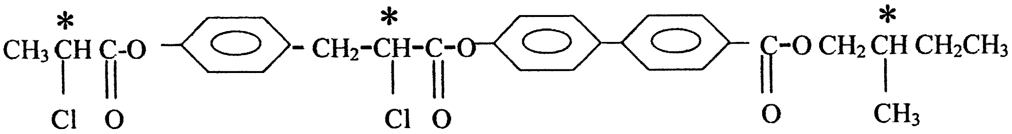

Fig. 1. Molecular structures of CCPMBB.

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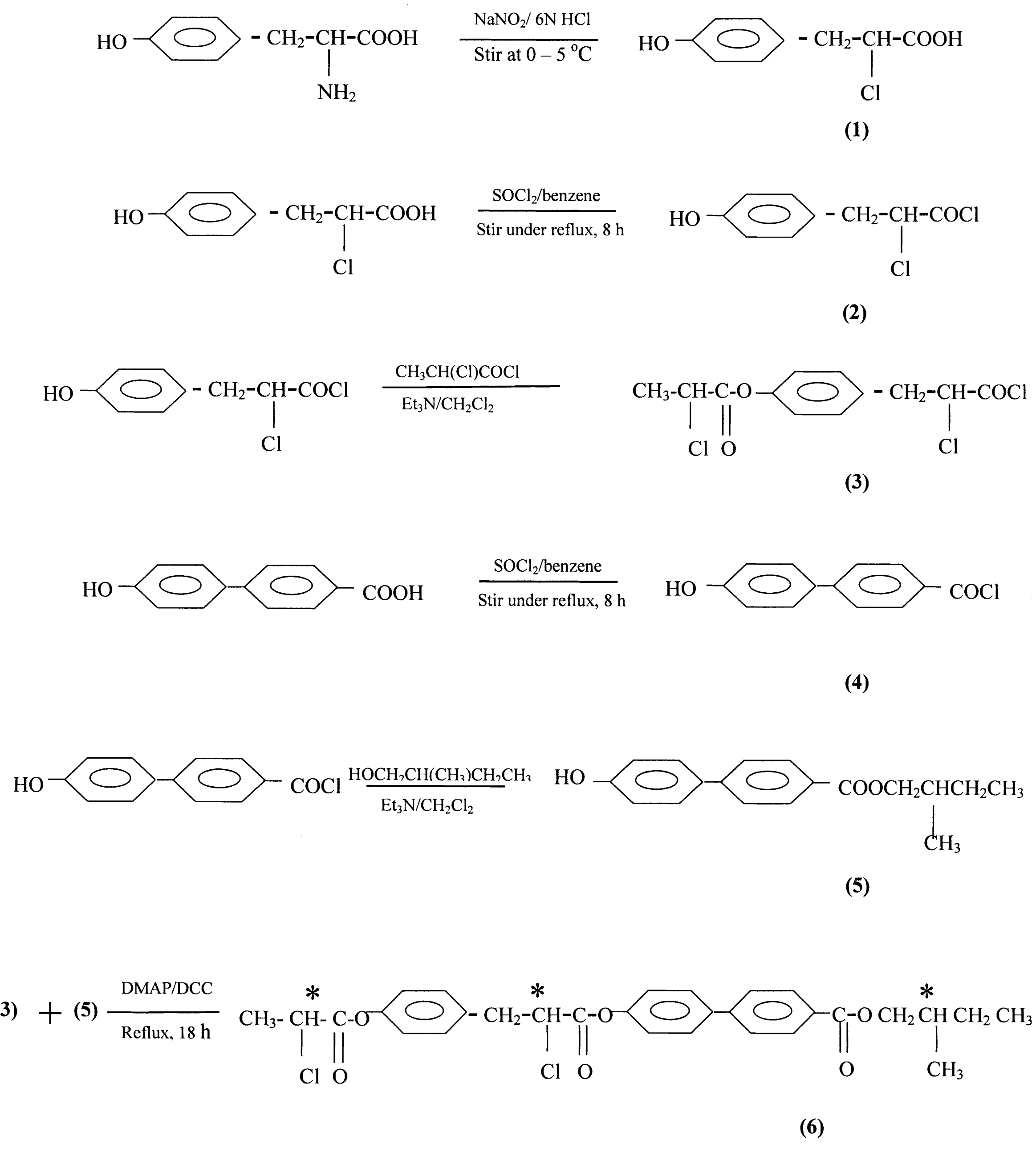

Scheme 1. Synthetic route for CCPMBB.

textural observations were carried out by a thermal microscopy (Olympus BX 50) equipped with an optical display (DP-10). Differential Scanning thermograms were recorded on a Perkin-Elmer DSC-7. Spontaneous polarization was measured on a Automated Property Tester (APT III) equipped with an Instec Temperature Controller (Display Tech., USA).

The synthetic route for the preparation of CCPMBB along with the reaction conditions is illustrated in Scheme 1 while a detailed synthetic procedure including various intermediates is presented in the following.

(S)-2-chloro-3-(4-hydroxy)phenyl propionic acid **(1)** is prepared by dissolving (S)-2-amino-3-(4-hydroxy)phenyl propionic acid (5.43 g, 30.0 mmol) in 20 cm^3 of 6 N HCl, the solution is brought to 0 °C. Freshly pulverized sodium nitrite (2.72 g, 32.0 mmol) is added to the solution in small portions with vigorous stirring while maintaining the reaction temperature between 0 and 5 °C. The reaction mixture is stirred for 14 – 16 h and then extracted with 40 cm^3 of diethylether. The etherial layer is dried over anhydrous sodium sulphate for 12 h. The crude product obtained as a yellow product on removing the excess solvent by distillation under reduced pressure is washed repeatedly with cold EtOH and finally recrystallized from hot dichloromethane to get 53.2% yield.

(S)-1,2-dichloro-3-(4-hydroxy)phenyl propionic acid **(2)** is synthesized by mixing **1** (25.0 mmol) with $SOCl_2$ (40.0 mmol) in 40 cm^3 of dry benzene under nitrogen atmosphere, and the mixture is kept under reflux with continuous stirring at 75 °C for 8 h. After the evolution of SO_2 gas has ceased, the volume of the resulting solution is reduced by vacuum distillation to get a yellow product which is suction filtered, washed several times with cold methanol and recrystallized from hot benzene solution to get a yield of 53.1%.

(S)-1,2-dichloro-3-(4-(2-chloro)propionato)phenyl propionic acid **(3)**: A dichloromethane solution (40 cm^3) containing **2** (20.0 mmol) and (S)-1,2-dichloro-propionic acid [9] (25.0 mmol) is magnetically stirred at room temperature for 2 h. Triethylamine (4.0 mmol) is then drop wise added to the reaction mixture, which is refluxed at 60 °C with constant stirring for 10 – 12 h. After cooling to room temperature, the resultant solution is poured into a beaker containing ~50 cm^3 of cold water. The product, separated as a yellow solid, is 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, is recrystallized from hot benzene to get 33.7% yield.

p-hydroxy-biphenylcarboxylic chloride **(4)** is synthesized by mixing 4-hydroxy-biphenylcarboxylic acid (25.0 mmol) with $SOCl_2$ (40.0 mmol) in 40 cm^3 of dry benzene under nitrogen atmosphere, and the reaction mixture is kept under reflux with constant stirring at 75 °C for 8 h. After the evolution of SO_2 gas has ceased, the volume of the resulting solution is reduced by vacuum distillation to get a yellow solid product which is suction filtered, washed several times with cold methanol and recrystallized from hot benzene solution to get a yield of 48.6%.

(S)-4-hydroxy-(2-methyl)butyloxy-biphenylcarboxylate **(5)** is prepared by refluxing together **4** (25 mmol) and (S)-2-methylbutanol (27 mmol) in 40 cm^3 of dichloromethane solution for ~4 h. Triethylamine (4.0 mmol) is then drop wise added to the reaction mixture and refluxed at 60 °C with constant stirring for 10 – 12 h. After cooling to room temperature, the resultant solution is poured into a beaker containing ~50 cm^3 of cold water. The product, separated as a white solid, is 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, is recrystallized from hot benzene to get 41.2% yield.

The final desired product, CCPMBB **(6)** is obtained by stirring together dry dichloromethane solution (40 $cm^{3)}$ of **3** (6.0 mmol) and **5** (6.0 mmol) at room temperature under inert atmosphere. 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) are added drop wise under constant stirring. The mixture is then refluxed for 15 – 18 h at 75 °C. The volume of the resultant yellow solution is reduced by vacuum distillation to get an oily product. This oily residue is then extracted twice with diethylether, and the etherial layer is dried over anhydrous Na_2SO_4 for 12 h. The crude product obtained on slow evaporation of ether is washed repeatedly with cold acteonitrile solution, and is finally recrystallized from hot benzene solution to get a yield of 34.8%.

The final product and all intermediate products are purified by passing through silica gel columns using appropriate eluent mixtures, and their structures are confirmed by IR and NMR spectral analyses. CPCDBD is highly stable at room temperature and also showed a high degree of thermal stability when subjected to repeat thermal scans for differential scanning calorimetry and spontaneous polarization measurement.

Results and Discussion

The phases and transition temperatures of CCPMBB are determined [19] from characteristic textural observations under a polarizing thermal microscope (Olympus BX 50) equipped with an optical display (DP-10) at a scan rate of 0.1 °C per minute. On cooling the isotropic melt, CCPMBB exhibits focal conic fans (smectic-A), concentric striations across focal conic fans (smectic-C*), distinct colour change from red to green (smectic-C_A^*), and broken focal conic fans (smectic-F*). The phase transition temperatures observed through thermal microscopy are found to agree reasonably with DSC data (Perkin-Elmer DSC-7). The phase sequence and transition temperatures (°C) of the present compound are:

Iso (124) Sm-A (106) Sm-C* (95) Sm-C_A^* (78) SM-F* (51) Cryst.

The spontaneous polarization was measured in a 10 microns polyimide buffed cell (Display Tech., USA) by the field reversal method with a modified integrator part. Polarizing current peaks at different temperatures are analyzed to obtain the magnitude of spontaneous polarization. From the individual profiles of the polarizing current peaks, different modifications, namely C* and C_A^* phases were clearly identified. Figure 2 illustrates such polarizing current profiles recorded in antiferroelectric C_A^* phase. It is worth to recall the phase assignment in the case of a reported [8] AFLC material, (S)-2-chloro-3-(4-benzamidoacetophenyl)-1-[4′-(2-chloro-3-benzoatophenyl-1-(*p*-decycloxybenzoly)-propionato)]-benzoatopropionate, where a similar trend in the current profiles is observed.

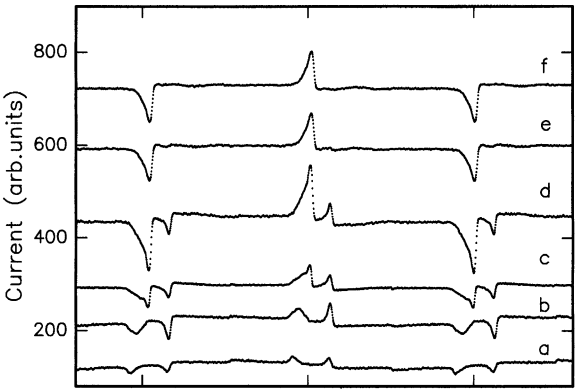

Fig. 2. Polarizing current profiles: manifestation (a – d) and stabilization (e – f) of smectic-C_A^* phase.

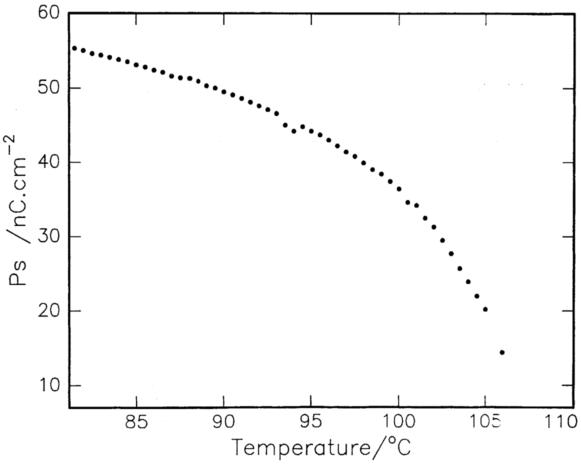

Fig. 3. Temperature variation of spontaneous polarization.

The temperature variation of the spontaneous polarization is represented in Figure 3. The magnitude of spontaneous polarization is found to increase with decreasing temperature and to attain a saturated value in the Sm-C_A^* phase. The present compound shows a relatively high P_S (~55 nC · cm^{-2}) at 81.5 °C with a wide thermal span of antiferroelectric phase. This high value in the Sm-C_A^* phase may be attributed to the strong dipolar and electrostatic interactions between molecules in the adjacent layers [2, 21].

Impact of Asymmetric Carbons on Antiferroelectric Ordering

In order to understand the influence of asymmetric carbons on the ferroelectric behaviour and the related phenomena, a comparative study was made with the analogous FLC material. (S)-4-(2-chloro-3-(4-*n*-dodecyloxy)phenylpropionato)-4′-(2-methyl)-butyloxy-biphenylcarboxylate (CDPMBB) [20] containing two asymmetric carbons as shown in Figure 4.

A comparative study reveals that incorporation of an asymmetric configuration at both terminal ends of CCPMBB (Fig. 1) maintains the antiferroelectric ordering. This clearly suggests the significance of the advent of this third asymmetric centre in ascertaining the ferroelectric ordering. Interestingly,

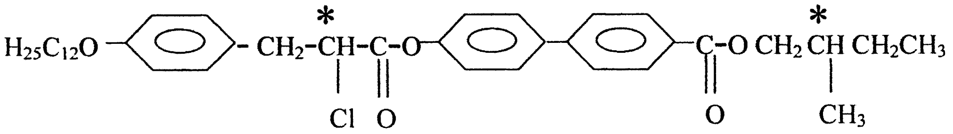

Fig. 4. Molecular structure of CDPMBB.

the overall magnitudes of spontaneous polarization (saturated value ∼ 55 nC · cm^{-2}) and their thermal spans (∼ 30 °C) are almost unaffected in both compounds. Further, it is notified that the liquid crystallinity is enhanced (∼ 6 °C) in the present material.

The possible molecular contributions towards the appearance of antiferroelectric ordering are summarized as follows:

1. Dipolar interactions between the adjacent layers play an important role in the appearance of antiferroelectric ordering which intern enhances the inherent stabilization of the antiferroelectric phase [2]. The resultant pairing of the transverse dipoles in neighbouring layers leads to antiferroelectricity [21].
2. The presence of highly polar asymmetric carbons in the molecule favours the appearance of antiferroelectric Sm-C_A^* phase. The role of these asymmetric configurations (more than two) can best be interpreted [8] in terms of elongated delocalized electron clouds between the asymmetric carbons. Moreover, our systematic studies [22] on the analogous series of FLC compounds with a single chiral center suggest the non-existence of antiferroelectric Sm-C_A^* phase.
3. The presence of the biphenyl moiety as spacer unit, resulting in the elongated conjugation along the long molecular axis, may further enhance the stabilization of antiferroelectric ordering.

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

Acknowledgement

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

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