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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gmcl19

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P. A. Kumar^a & V. G. K. M. Pisipati^a

^a Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences, Nagarjuna University, Nagarjunanagar, 522 510, India Published online: 27 Oct 2006.

To cite this article: P. A. Kumar & V. G. K. M. Pisipati (2001) Design and Synthesis of a Novel Wing Shaped Achiral Antiferroelectric Liquid Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 147-160, DOI: <u>10.1080/10587250108025291</u>

To link to this article: http://dx.doi.org/10.1080/10587250108025291

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Design and Synthesis of a Novel Wing Shaped Achiral Antiferroelectric Liquid Crystal

P. A. KUMAR and V. G.K. M. PISIPATI^{*}

Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences, Nagarjuna University, Nagarjunanagar 522 510 India

A novel wing shaped achiral antiferroelectric liquid crystalline compound, 1,3-phenylene bis-[phenylene-1-biphenyldicarboxylato)-3-(4-*n*-tetradecyloxybenzoyl)biphenyl dicarboxylate] (abbreviated as PBPBTB), having 1,3-phenylene [4-biphenyldicarboxylate-(4-*n*-tetradecyloxy benzoate)] units as wings, has been synthesized while its liquid crystalline behaviour is characterized by thermal microscopy (TM), differential scanning calorimetry (DSC), spontaneous polarization (P_s) and response times (τ) studies. The preliminary investigations on the ferroelectric properties of the present material show the presence of an antiferroelectric phase.

Keywords: PBPBTB; synthesis; achiral; AFLC; Ps

INTRODUCTION

Since the discovery of ferroelectricity in achiral polyphilicmolecules by Tournilhac *et al*^[1], a great deal of attention has been focussed on the synthesis of achiral ferroelectric liquid crystal (FLC) compounds possessing C_{2v} symmetry. Due to this recent trend of inducing chirality in liquid crystals which is largely

^{*} Corresponding author.

being associated with the shape of the molecular structure, many research groups^[2-4] are now actively engaged in the isolation of achiral FLC materials. Nevertheless, in such achiral FLC molecules, the alignment of the bent molecules in the smectic layers (either synclinic or anticlinic) is rather a crucial factor for deciding the class of ordering. Recently, many research groups^[2-6] have adopted such assumptions to account their experimental observations with various possible molecular arrangements.

Based on recent views ^[2-6] relating to the intra- and interlayer molecular interactions and with our previous experience ^[7-10] on ferro- and antiferroelectric materials, for the first time in the class of achiral molecules we made a successful attempt to design and synthesize a first ever antiferroelectric compound of its kind (Fig. 1) which exhibits antiferroelectric ordering. The molecular skeleton of



FIGURE 1 Molecular structure of PBPBTB

PBPBTB has been designed in such a way that: the combination of a central core which comprises of 1,3-phenylene bis(biphenyldicarboxylate) with two lateral wings of 1,3-phenylene [4- biphenyldicarboxylate-(4-n-tetradecyloxy benzoate)] units *via* ester linkage. In this communication, we discuss the synthetic details along with the preliminary studies on the ferroelectric behaviour.

EXPERIMENTAL

Materials and methods

The ingredients, 1,3-dihydroxybenzene and 4,4'biphenyldicarboxyllic acid are supplied by Sigma Chemical Company, USA. The solvents used in the present study are of Merck grade and are used as such without further purification.

Optical observations are made with Hertel & Reuss polarizing microscope while the temperature is monitored and controlled with an accuracy of \pm 0.01 K by an Instec milli Kelvin temperature controller interfaced to a computer. DSC thermograms are recorded on a DSC-7 Perkin Elmer with a scan rate of 5 °C/minute. Spontaneous polarization in PBPBTB molecule, filled in a polyimide buffed cell with a 10 micron spacer (Display Tech., USA), is measured by field reversal method^[11] applying a field of

12.5 volts per micron at a frequency of 8 Hz and the resulting polarizing current profiles are recorded using 500 MHz digital storage oscilloscope (Hewlett Packard - 54610B). Response times are measured from the polarizing current profiles by calculating the full width at half height^[11]. While measuring the spontaneous polarization, simultaneous phase identification along with the switching behaviour is also observed through the polarizing microscope.

The synthetic route for the preparation of PBPBTB along with the reaction conditions are illustrated in Scheme 1 while a detailed synthetic procedure including various intermediates is presented as follows:

p-tetradecyloxyphenol (1) was prepared by dissolving 1,4dihydroxybenzene (2.75 g, 25.0 mmol), 1-bromotetradecane (3.46 mL, 12.5 mmol) and potassium hydroxide (0.78 g, 15.0 mmol) in 20 ml of dimethylformamide solution. The contents were then stirred under reflux for ~ 4h at 75 °C. The volume of the reaction mixture was reduced to ~ 5 mL under reduced pressure and then extracted with 40 ml of diethylether. The etherial layer was dried over anhydrous sodium sulphate for 12 h. The crude product 1, obtained as an 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 get an yield of 5.6 g (72.2 %). *l*,4-dichlorobiphenyl dicarboxylic acid (2) was synthesized by mixing together 1,4-biphenyldicarboxyllic acid (4.25 g, 25.0 mmol) and SOCl₂ (3.0 ml, 40.0 mmol) in 40 ml of dichloromethane under nitrogen atmosphere and kept the reaction mixture under reflux with continuous stirring at 75 $^{\circ}$ C for 8 h. After the evolution of SO₂ gas was ceased, the volume of the resulting solution was reduced by vacuum distillation to get an yellow solid product which was suction filtered, washed several times with cold methanol and recrystallised from hot benzene solution. The yield obtained was 2.6 g (44.0 %).





Scheme 1 Synthetic route for PBPBTB

l-chlorocarbonyl-4-(p-n-tetradecyloxyphenyl) biphenyl carboxylate (3) was obtained by mixing dichloromethane solution (40 ml) containing 1 (7.65 mL, 25.0 mmol) and 2 (3.48 g, 12.5 mmol) and magnetically stirred at ambient temperature for 2 h. 0.5 ml (3.6 mmol) of triethylamine was then added to the reaction mixture drop wise and refluxed at 60 $^{\circ}$ 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 was then extracted with petroleum ether and dried over Na₂SO₄ for 6h. The white crude product obtained on removing the excess ether, followed by repeated washings with cold methanol, was recrystallized from hot benzene.

1-(3-hydroxyphenyl)-4-(p-n-tetradecyloxyphenyl) biphenyl dicarboxylate (4) was prepared following the procedure as described in the above step: by dissolving 3 (6.85 g, 12.5 mmol) and 1,3-dihydroxy benzene (0.66 g, 6.0 mmol) in 40 ml of absolute dichloromethane and to it added 0.5 ml (3.6 mmol) of triethylamine with constant stirring at room temperature. The product separated as a white solid on cooling the reaction mixture to room temperature was purified by recrystallization from hot benzene.

1-chloro-biphenyldicarboxylic acid (5) was obtained by stirring together 1,4-biphenyldicarboxyllic acid (6.05 g, 25.0 mmol) and SOCl₂ (1.48 ml, 12.5 mmol) in 40 ml of dichloromethane under nitrogen atmosphere and kept the reaction mixture under reflux with continuous stirring at 75^oC for 8 h. After the evolution of SO₂ gas was ceased, the volume of the resulting solution was reduced by vacuum distillation to get an yellow solid product which was suction filtered, washed several times with cold methanol and recrystallized from hot benzene solution.

1,3-bis-(4,4'-biphenyldicarboxylato)-benzene (6) was synthesized by dissolving 1,3-dihydoxy benzene (2.75 g/25.0 mmol) [4] and 5 (13.0 g/50.0 mmol) in 40 ml of dry dichloromethane and stirred at ambient temperature for 4 h. To the resultant reaction mixture 0.4 ml (4.3 mmol) of PCl₃ was added drop wise and refluxed the reaction mixture at 75 $^{\circ}$ C with constant stirring for 22 h. After cooling to room temperature, the reaction solution was poured into ~ 100 ml of cold water. The product separated, as yellow solid was suction filtered, washed twice with cold ethanol, extracted with petroleum ether and dried over Na_2SO_4 for 8h. The crude product was purified by passing through a silica gel column using a mixture of petroleum ether: acetone (5 : 1 v/v) as eluent. The product was recrystallized from hot benzene solution.

1,3-bis-(4,4'-dichlorobiphenyldicarboxylato)-benzene (7) was synthesized by stirring together 6 (3.07 g, 5.5 mmol) and SOCl₂ (1.48 ml, 12.5 mmol) in 40 ml of dichloromethane under nitrogen atmosphere and kept the reaction mixture under reflux with continuous stirring at 75 °C for 8 h. After the evolution of SO₂ gas was ceased, the volume of the resulting solution was reduced by vacuum distillation to get an yellow solid product which was suction filtered, washed several times with cold methanol and recrystallized from hot benzene solution.

1,3-bis-[(4,4'-biphenyldicarboxyllic-1(3-hydroxyphenyl)-4-(pn-tetradecyloxyphenyl) biphenyl dicarboxylate] benzene (8) was prepared by mixing together absolute dichloromethane solutions (30 ml) of 7 (1.19 g/2.0 mmol) and 4 (2.48 g/4.0 mmol) stirred at ambient temperature for 4 h under nitrogen atmosphere. To the reaction mixture added 0.5 ml (3.6 mmol) of triethylamine with constant stirring at room temperature. The product separated as a white solid on cooling the reaction mixture to room temperature was purified by recrystallization from hot benzene to get 58.8 % yield.

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1H NMR data (δ , ppm in CDCl₃): 0.9 (t, 6H, (CH₂) _n-CH₃); 1.2 - 1.7 (d, 56H, (CH₂) _n-CH₃); 4.02 (d, 4H, -OCH₂-); biphenyl ring: 6.8 - 7.0 (m, 16H); terminal phenyl ring: 7.2 - 7.4 (m, 4H, C₂H-, C₆H-); 7.5 - 7.6 (m, 4H, C₃H-, C₅H-); central core phenyl ring: 8.1 (m, 6H, C₂H-, C₄H-); 8.3 (m, 3H, C₃H-); 8.6 (m, 3H, C₃H-)

RESULTS AND DISCUSSION

Thermal studies (TM and DSC)

The phase variants and their transition temperatures are determined by comparing the characteristic textures of traditional liquid crystals^[12] while the identification of antiferroelectric phase is confirmed by spontaneous polarization studies.

On cooling the isotropic melt, the compound exhibits yellow focal conic fans of Sm-A like texture at 148 °C which is designated as S₁. On further cooling, concentric striations are developed over the focal conic fans with the simultaneous colour change from yellow to green at 131.8 °C indicating the onset of S₂ phase which is similar to Sm-C* phase of chiral molecules. It is interesting to notice that a distinct colour change (green to red) over the entire region of arced focal conic texture at 126.1 °C implies the existence of ferro- to antiferroelectric (S₂ - S₃) transition. Further decrease of temperature to 100.4 °C, resulted in the formation of broken focal conic fans of Sm-F like texture and is assigned as S_4 . The phase transition temperatures observed through the thermal microscope are found to be in good agreement with the DSC thermograms. The corresponding thermal ranges of these observed phases are further confirmed by the characteristic individual profiles of the polarizing current peaks (Fig. 2).

Ferroelectric behavior

The preliminary measurements on spontaneous polarization and response times are carried out simultaneously using a 10μ polyimide buffed cell. From the individual profiles of the polarizing current peaks, ferro- and antiferroelectric orderings are clearly identified. The polarizing current peaks at different temperatures are analyzed to obtain the magnitude of spontaneous polarization. Figure 2 illustrates polarizing current profiles in ferro- and antiferroelectric phases while the temperature variation of spontaneous polarization is shown in figure 3. The saturated value of spontaneous polarization attained in the antiferroelectric phase at 124.2 °C (110 nC/cm²) is nearly five fold in magnitude when compared to the value obtained in S₂ phase (~20 nC/cm²). This increasing trend of spontaneous polarization of dipolar interactions in the adjacent molecular layers.



FIGURE 2 Polarizing current profiles in different phases: (A) onset of S₂ phase at 131.8 °C, (B) phase transition from S₂ to S₃ at 128.8 °C, (C) S₃ phase at 127.2 °C and (D) S₄ phase at 120 °C.

The magnitude of microsecond response times in different phases is simultaneously measured with the spontaneous polarization studies. Figure 3 illustrates the temperature variation of response times for the present compound. As expected, the temperature profile of response times is similar to that of spontaneous polarization in the entire antiferro, ferroelectric thermal ranges. In the ferroelectric phase the magnitude of τ increases with decreasing temperature and attains a value of ~ 200 µs in the antiferroelectric phase.



FIGURE 3 Temperature variation of spontaneous polarization and response times in different phases

SUMMARY

The preliminary studies of TM, DSC and spontaneous polarization reveal that PBPBTB compound exhibits the following enantiotropic liquid crystalline phases with the corresponding transition temperatures in degree centigrade while the well resolved enthalpy values (J/g) are given in parentheses.

Iso. $\frac{148.0}{(4.22)}$ S₁ $\frac{131.8}{(0.01)}$ S₂ $\frac{126.1}{(0.25)}$ S₃ $\frac{100.4}{(0.10)}$ S₄ $\frac{65.3}{(20.21)}$ Cryst.

The origin of antiferroelectric ordering in the PBPBTB molecule can be substantiated by the presence of conjugation, which is maintained throughout the present molecule. The existence of this condition has a pronounced influence on the appearance of antiferroelectric ordering through the dipolar interactions (ester moieties) between the adjacent layers which intern enhances the inherent stabilization of the antiferroelectric phase. The resultant pairing of the transverse dipoles in the neighbouring layers is supposed to be the origin of antiferroelectric ordering^[13]. Further, our previous studies^[8] on antiferroelectric materials reveal that the presence of the biphenyl rings as spacer units, which facilitates the extension of conjugation, may also promote the occurrence and stabilization of antiferroelectric ordering. However, it is not reasonable to rule out the significant role of long alkyl end chains which may also favour the appearance of antiferroelectric ordering^[5].

Further detailed investigations on other physical properties of this material are now in progress

Acknowledgements

The authors are thankful to the Council of Scientific and Industrial Research (CSIR), University Grants Commission (UGC) and Department of Science and Technology (DST), New Delhi, India for financial support.

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