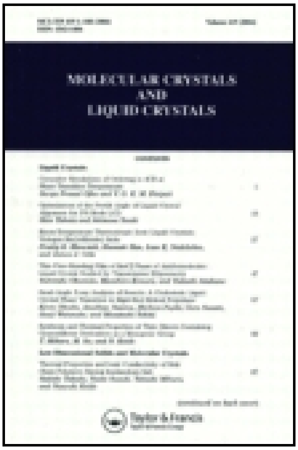

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Design and Synthesis of Linear and Bow Shaped Ferroelectric Liquid Crystal Isomers Derived From L-Tyrosine

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Design and Synthesis of Linear and Bow Shaped Ferroelectric Liquid Crystal Isomers Derived From L-Tyrosine

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A novel series comprising of two distinct ferroelectric liquid crystalline structural isomers, viz., (S)-1,4-diphenylene bis(2-chloro-3-(4-dodecyloxyphenyl)- propionate) (DCDP-1) and (S)-1,3-diphenylene bis(2-chloro-3-(4-hydroxyphenyl)- propionate) (DCDP-2), have been synthesized and characterized by thermal microscopy (TM), differential scanning calorimetry (DSC), spontaneous polarisation (P_S) and response times (τ). The preliminary studies on thermal and ferroelectric properties reveal that the isomers show altogether a different trend of thermal and phase behaviour. The thermal analyses (TM and DSC) suggest the existence of different phase variants. Further, the ferroelectric studies infer a different chiral behavior among DCDP-1 and DCDP-2 compounds wherein DCDP-2 showed a wide ferroelectric thermal range with high magnitudes of P_S (three fold) and response times (two fold).

Keywords: DCDP-1; DCDP-2; ferroelectric liquid crystal; spontaneous polarisation

INTRODUCTION

Chirality of the molecules and their tilted association into a smectic layer, reducing the overall symmetry of the mesogen molecules, are essential for a conventional linear ferroelectric liquid crystal (FLC)[1]. Moreover, the impact of the chirality on phase behaviour and macroscopic structure can be envisaged either by substituting a electronegative atom at asymmetric carbon or by increasing the additional transverse dipoles along the long molecular axis. On the other hand, the recent trend of obtaining ferroelectricity is ascribed to the polar C_{2v} symme-

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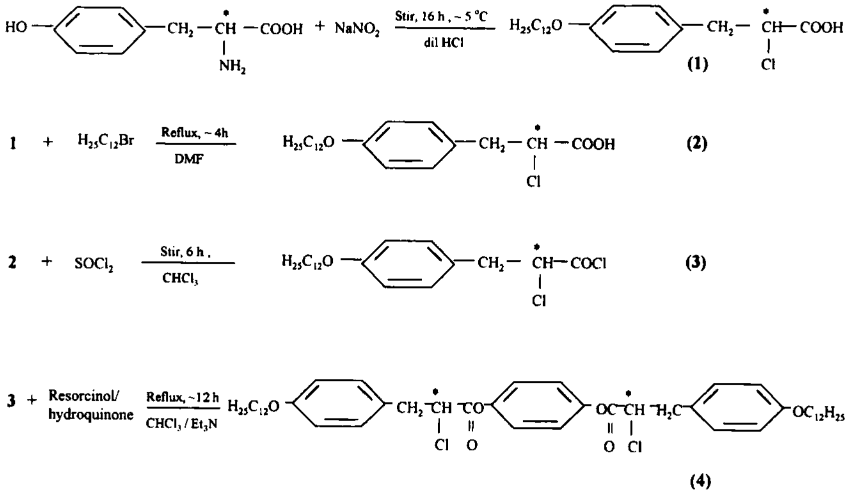
* Corresponding Author.

try which is obtained from the efficient packing of bow (banana) shaped molecules in to a smectic layer[2]. However, the mesomorphic nature of these achiral molecules is not fully addressed owing to their new unidentified phases and their related textural morphology[3–6]. Further, the advent of molecular symmetry on the ferroelectric properties is also realized by the microsecond response times and high magnitude of spontaneous polarization. In fact, no attempt has been made to correlate the linear and bow FLC molecules in the direction of their comparative ferroelectric properties due to their structural dissimilarities. A proper correlation between the ferroelectric properties of such compounds with respect to their molecular structure (linear and bow) is possible only when the molecules possess a structural isomerism. Furthermore, if one of the isomers exhibit different mesomorphic properties that can be attributed, without ambiguity, to the symmetry of the molecule. In view of such a significant role of this structural isomerism, an attempt has been made, for the first time, to design a chiral mesogen having same empirical formula with different molecular symmetries. Nevertheless, this structural anomaly also facilitates to elucidate the role of asymmetric carbons on bent molecules possessing C_{2v} symmetry and vice-versa.

In continuation of our earlier work on chiral and achiral liquid crystalline compounds[7- 10], the present communication deals with the synthesis of two distinct ferroelectric structural isomers, viz., (S)-1,4-diphenylene bis(2-chloro-3-(4-dodecyloxyphenyl)-propionate) (DCDP-1) and (S)-1,3-diphenylene bis(2-chloro-3-(4-hydroxyphenyl)-propionate) (DCDP-2) and also we report the results pertaining to the preliminary investigations on their thermal and ferroelectric properties. The molecular skeleton of the present ferroelectric mesogens has been designed in such a way that: (a) two electronegative chlorine atoms are introduced at asymmetric carbons with the retention of asymmetric configuration in both the isomers and (b) the desired molecular shape is achieved by the esterification of central phenyl moieties at 1,3- and 1,4- positions.

EXPERIMENTAL

Optical textural observations were made with Olympus DX 50 polarizing microscope equipped with DP10 CCD display while the temperature was monitored and controlled by an Instec milli Kelvin temperature controller with an accuracy of ± 0.01 K. DSC thermograms were recorded on a DSC-7 Perklin Elmer, with a scan rate of 5°C/min in the cooling run. Spontaneous polarisation along with the switching behaviour was measured in a polyimide buffed 10μ spacer cell



SCHEME 1 Synthetic route for DCDP-1 and DCDP-2

(Device Tech., USA) by field reversal method[11]. The PMR spectra were run on a Bruker (400 MHz) multinuclear spectrometer.

The asymmetric centers introduced in the present isomers were derived from a chiral ingredient, (S)-2-amino-3-(4-hydroxy)phenyl propionic acid (L-tyrosine), available commercially (CDH, India) in high enatiomeric purity. The synthetic route for the preparation of DCDP-1 and DCDP-2 along with the reaction conditions are illustrated in scheme-1 while a detailed synthetic procedure including various intermediates is presented as follows:

(S)-2-chloro-3-(4-hydroxy)phenyl propionic acid (1)

Was prepared by dissolving (S)-2-amino-3-(4-hydroxy)phenyl propionic acid (5.43 g, 30.0 mmol) in 20 cm^3 of 6.0 N HCl and the solution was brought to 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 cm^3 of diethylether. The etherial layer was dried over anhydrous sodium sulphate for 12 h. The crude product **1**, obtained as an yellow solid 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 3.2 g (53.2 %).

(S)-2-chloro-3-(4-dodecyloxy)phenyl propionic acid (2)

Was prepared by mixing together 4.01 g, 20.0 mmol of **1** (20 ml of DMF) and a 20 cm^3 of DMF solution containing KOH (1.23 g, 22.0 mmol)) and 1-bromododecane (4.95 cm^3, 20 mmol). The resulting reaction mixture, stirred under reflux, yielded an yellow precipitate (as KBr) which was suction filtered and washed repeatedly with the solvent medium. The yellow resulting solution was extracted with diethyl ether and dried over sodium sulphate for ~12 h. The yellow oil product of **2** with 43.4% yield (3.2 g) was obtained by removing the excess ether by distillation under reduced pressure.

The esterification of α-chloro acids with 1,3- and 1,4-dihydroxy benzenes was made via acid chloride in $CHCl_3/Et_3N$ with the retention of asymmetric configuration, as reported by Sierra et. al.[12].

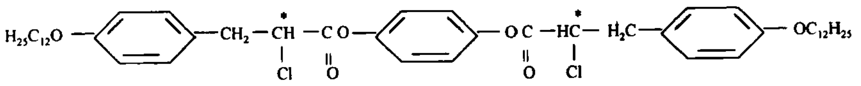
(S)-2-chloro-3-(4-dodecyloxy)phenyl propionyl chloride (3)

Was prepared by dissolving **2** (4.42 g, 12.0 mmol) in 25 $cm^3$of absolute dichloromethane and to it added 1.8 cm^3 (16.0 mmol) of $SOCl_2$ with constant stirring at room temperature. The reaction mixture was heated to 60°C till the evolution of SO_2 was ceased. The product, separated as a white solid on cooling the reaction mixture to room temperature, was purified by passing through a silica gel column using an eluent mixture of ether and acetone (4 : 2 v/v) to get an yield of 2.6 g (56.01 %).

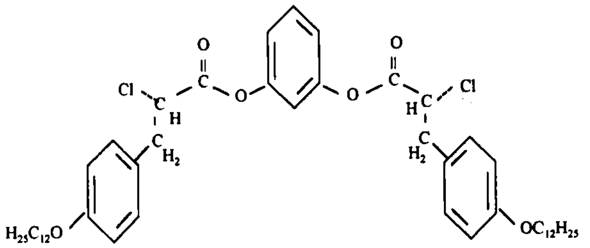
1,3- and 1,4-diphenylene bis(2-chloro-3-(4-dodecyloxy) phenyl propionate) (4)

Were obtained by stirring the dichloromethane solution (40 cm^3) containing **3** (5.80 g, 15.0 mmol) and appropriate substituted benzenes (0.82 g, 7.5 mmol) at ambient temperature for 2 h. To this reaction mixture, 0.5 cm^3 (3.6 mmol) of triethylamine was then added dropwise and refluxed 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 cm^3 of cold water. The product, separated as a white solid, was then extracted with petroleum ether and dried over Na_2SO_4 for 6h. The white crude product obtained on removing the excess ether, followed by repeated washings with cold methanol, was recrystallized from hot benzene to get an yield of 5.3 g (41.6 %).

The formation of these compounds were confirmed by recording PMR spectra in $CDCl_3$ solution at room temperature. The PMR spectra show all the signals at



DCDP-1



DCDP-2

FIGURE 1 Molecular structures of DCDP-1 and DCDP-2

the expected order of their multiplicities. An additional signal at δ, 8.60 corresponding to the $C_2\underline{H}$- proton of central ring moiety in DCDP-2 compound confirms the esterification of -OH groups of central 1,3-dihydroxybenzene. The PMR data along with their assignments are given as follows:

^1H NMR of DCDP-1 (δ, ppm in $CDCl_3$), 1.16 (t, 3H, $-(CH_2)_n-C\underline{H}_3$); 1.28 – 1.62 (m, 20H, $-(C\underline{H}_2)_n-CH_3$); 1.92 (d, 2H, $C\underline{H}_2-CH(Cl)-$); 4.02 (d, 2H, $-OC\underline{H}_2-$); 4.14 (t, 1H, $CH_2-C\underline{H}(Cl)-$); phenyl protons: central core- 8.07 (d, 2H, $C_2\underline{H}$-, $C_6\underline{H}$-); 8.32 (d, 2H, $C_3\underline{H}$-, $C_5\underline{H}$-); terminal rings- 6.91 (d, 2H, $C_{2'}\underline{H}$-, $C_{6'}\underline{H}$-); 7.48 (d, 2H, $C_{3'}H$-, $C_{5'}H$-)

^1H NMR of DCDP-2 (δ, ppm in $CDCl_3$); 1.16 (t, 3H, $-(CH_2)_n-C\underline{H}_3$); 1.27 – 1.64 (m, 20H, $-(C\underline{H}_2)_n-CH_3$); 2.62 (d, 2H, $C\underline{H}_2-CH(Cl)-$); 4.04 (d, 2H, $-OC\underline{H}_2-$); 4.14 (t, 1H, $CH_2-C\underline{H}(Cl)-$); phenyl protons: central core- 8.60 (s, 1H, $C_2\underline{H}$-); 8.11 (d, 2H, $C_4\underline{H}$-, $C_6\underline{H}$-); 8.04 (d, 1H, $C_5\underline{H}$-); terminal rings- 6.94 (d, 2H, $C_{2'}H$-, $C_{6'}H$-); 7.51 (d, 2H, $C_{3'}\underline{H}$-, $C_{5'}\underline{H}$-)

All the intermediate products including the desired product were purified by passing through a silica gel column using appropriate eluent mixtures and confirmed by PMR spectral analysis. DCDP compounds are 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 times measurements.

RESULTS AND DISCUSSION

The phase variants and their transition temperatures were determined[13] from the characteristic textural observations using polarizing microscope. On cooling the isotropic liquid, the DCDP-1 compound exhibited threaded nematic texture in chiral nematic (N^*) phase, yellow coloured focal conic fan texture in smectic-A phase, appearance of concentric striations across these fans in smectic-C^* phase, broken focal conic texture in smectic-$F^*$and smooth multi coloured mosaic texture in smectic-G phase. However, the textural observations of DCDP-2 molecule imply a threaded nematic (N^*), schlieren marble smectic-C^*, broken focal conic smectic-F^* and smooth mosaic smectic-G phases.

The phase transition temperatures observed through the thermal microscope were found to be in reasonable agreement with the DSC data obtained from the thermograms (Fig. 2).

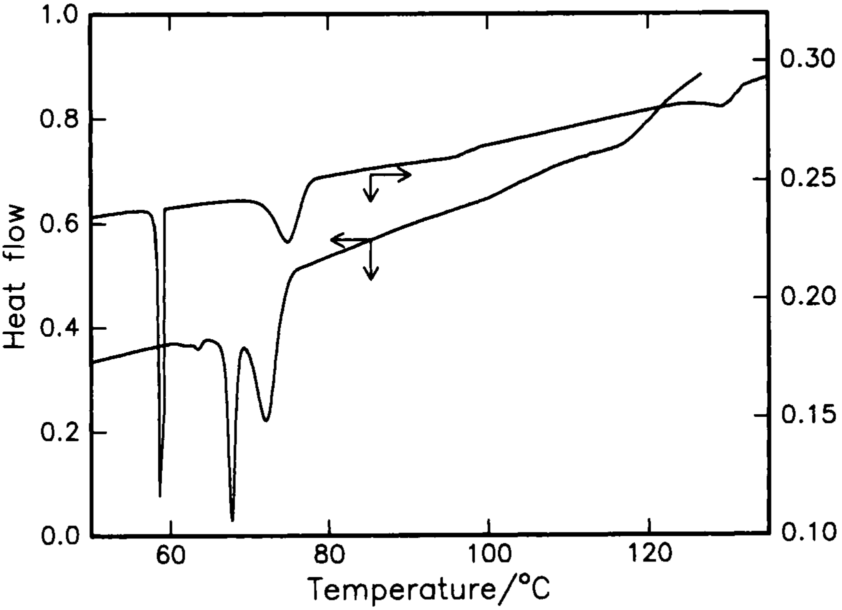


FIGURE 2 DSC thermograms of DCDP-1 and DCDP-2

The phase sequence variant and the transition temperatures (in degrees centigrade) of the present isomers are represented below with the corresponding enthalpy values (in J/g) in parentheses.

DCDP-1:

$$\mathrm{Iso}\frac{129.2}{(7.2)}\mathrm{N}^*\frac{94.9}{(4.0)}\mathrm{SmA}\frac{77.3}{(-)}\mathrm{SmC}^*\frac{74.9}{(14.9)}\mathrm{SmF}^*\frac{66.6}{(-)}\mathrm{SmG}\frac{58.9}{(75.6)}\mathrm{K}$$

DCDP-2:

$$\mathrm{Iso}\frac{116.9}{(8.6)}\mathrm{N}^*\frac{103.1}{(1.5)}\mathrm{SmC}^*\frac{99.8}{(8.7)}\mathrm{SmF}^*\frac{96.2}{(-)}\mathrm{SmG}\frac{72.2}{(22.2)}\mathrm{K}$$

The temperature variation of the spontaneous polarization and response times of DCDP-1 and DCDP-2 compounds are illustrated in figure 3 and 4, respectively.

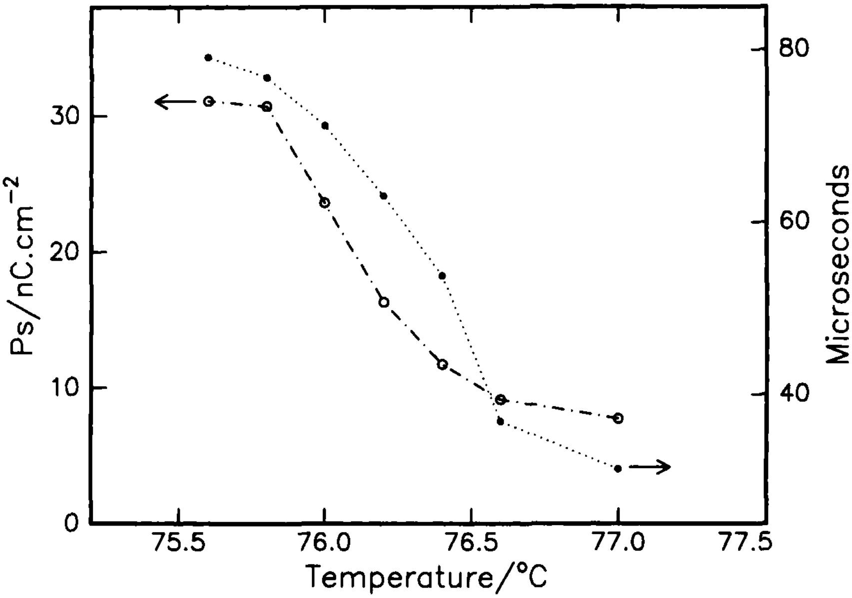


FIGURE 3 Temperature variation of spontaneous polarization and response times of DCDP-1

Polarizing current profiles at different temperatures were analyzed to obtain the magnitude of spontaneous polarization. In the DCDP-1 mesogen, the onset of smectic C* was observed at 77.1 °C with the magnitude of spontaneous polarization of 9 nC/cm^2. The magnitude of the spontaneous polarization increased with decreasing temperature and attained a saturated value of 32 nC/cm^2 at 75.7°C. On further decrease of temperature, the value of spontaneous polarization starts to decrease indicating the onset of subsequent smectic F* phase. In the entire thermal span of smectic C*, the proportional increase of spontaneous polariza-

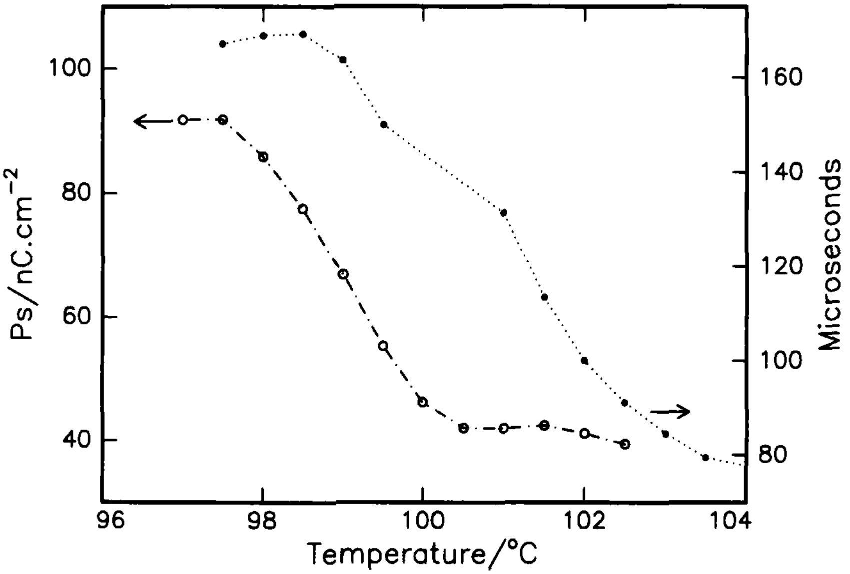


FIGURE 4 Temperature variation of spontaneous polarization and response times of DCDP-2

tion with temperature indicates the stabilization of this phase. On the other hand, DCDP-2 molecule showed a similar trend of temperature variation, but a three fold increase in the magnitude of P_S (~ 95 nC/cm^2 at 98°C) in smectic C* phase.

A linear variation of response times with decreasing temperature was obtained for the DCDP-1 compound with a saturated value of 80 μ seconds at 75.7°C. The response times falls sharply with the onset of smectic F* phase. In the case of DCDP-2 compound, the magnitude of response times increases with decreasing temperature and attains a saturated value of 170 μ seconds at 99 °C. Further decrease of temperature leads to a steep fall of the response times indicating the onset of smectic F* phase.

CONCLUSIONS

The preliminary studies on thermal and ferroelectric properties reveal that the isomers show altogether a different trend of thermal and phase behaviour. The thermal analyses (TM and DSC) suggest the existence of different phase variants viz., N* – SmA, SmA – SmC* (DCDP-1) and N* – SmC* (DCDP-2). Further, the ferroelectric studies infer a different chiral behavior among DCDP-1 and

DCDP-2 compounds wherein DCDP-2 showed a wide ferroelectric thermal range with high magnitudes of P_S(three fold) and response times (two fold). Moreover, the trend in the magnitudes of response times and P_S clearly illustrates a relatively high viscous nature of the smectic C^* phase of DCDP-2. This can be reasonably substantiated on account of the inducement of C_{2V} symmetry in a linear molecule which certainly has a pronounced influence on the dipolar orientations in the adjacent smectic layers. Nevertheless, the presence of two highly electronegative chlorine atoms at both the asymmetric centers in the bent molecule play a crucial role on the enhancement of the magnitude of spontaneous polarization. Further detailed investigations on the ferroelectric and diellectric studies of the present isomers are in progress.

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