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Helix twist inversion in ferroelectric liquid crystals with one chiral centre

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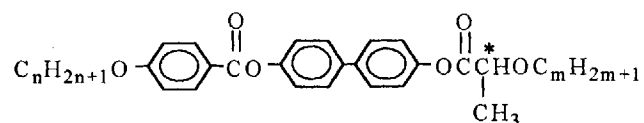
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The helix twist inversion in the chiral smectic C phase was studied for two new homologous series of lactic acid derivatives. The inversion phenomenon was attributed to a competition between spatial conformers leading to opposite helix handedness. The temperature of inversion was found to increase with increasing length of the chiral molecular tail. With all substances studied, high values of the spontaneous polarization P_s were found which did not reach saturation on cooling, in spite of a saturated tilt angle θ_s .

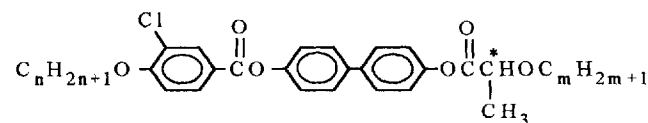
1. Introduction

Chiral liquid crystals have attracted considerable interest in recent years as they exhibit a great variety of spatially modulated phases. It is well known that chirality influences the properties of the smectic C* phase leading to the helioelectricity of this phase. However, it is possible that ferroelectric properties exist when the helix unwinds either by surface interactions in the surface stabilized geometry [1] or spontaneously by a molecular mechanism [2]. Spontaneous helix unwinding was frequently reported in the cholesteric phase, especially with materials having two chiral centres in the molecules [2]. On the other hand only a few cases are known for the S_C^{*} phase so far [3, 4].

In this communication we describe the spontaneous helix unwinding and the inversion of helix handedness for two series of lactic acid derivatives



1



2

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Besides the data describing the helix inversion, we give the basic characteristics of the materials studied, namely the phase sequences and the spontaneous polarization and tilt angle values.

2. Synthesis

The synthesis route and purification of the series of substances **1** have been described in [5].

The mesogenic part of series **2** has been prepared from ethyl 3-chloro-4-hydroxybenzoate by alkylation, for example, 1-bromo-octane (where $n = 8$), followed by hydrolysis and esterification with biphenol by a similar method to that described in [5].

The (S)-(-)-2-pentyloxypropionic acid was obtained by alkylation of (S)-(-)-ethyl lactate with 1-iodopentane in the presence of Ag₂O, followed by hydrolysis of the ester group. Esterification of 2-pentyloxypropionic acid by the above mesogenic part using dicyclohexylcarbodiimide as a condensation agent yielded the final product. The product was purified by column chromatography in a similar way to that described [5].

The NMR spectra were consistent with the molecular structure. Moreover, they show that for the compounds of both homologous series **1** and **2**, the two hydrogen atoms (H_α , H_β) located at the carbon atom neighbouring the ether oxygen are not equivalent, suggesting strongly hindered rotation around the C*-O bond due to spatial interaction with the methyl group on the asymmetric carbon. The proton multiplet signals of the CH₂H_β-O-C* group are $\delta = 3.5$ and 3.6 ppm. The lack of environmental equiva-

lence of the two hydrogen atoms breaks the symmetry of this centre in the molecule, but this centre cannot be essential for the ferroelectric or helical properties.

3. Experimental results

3.1. Mesomorphic properties

The sequences of phases have been determined from texture observations made on both planar and homeotropic samples (smectic layers perpendicular and parallel to the sample plane, respectively). With some homologues the phase transitions have been checked by DSC.

The data are collected in the table for substances of series **1** denoted as Hn/m and for those of series **2** denoted as Cl_n/m , where n and m are the lengths of the aliphatic chains. In most of the compounds studied the S_C^* phase persists down to about 40°C, when recrystallization takes place. Several substances of the Hn/m homologous series exhibit an additional low temperature phase. In this phase, ferroelectric switching is not observed, and X-ray measurements show that the phase is an orthogonal highly ordered smectic or a crystalline phase.

All phase transitions studied seem to be first order and characterized by a phase coexistence region, except for the $S_A-S_C^*$ transition which is second or weakly first order.

3.2. The helical properties in the S_C^* phase

In the planar geometry, the dechiralization lines appear on cooling just below the upper transition temperature (T_c) to the S_C^* phase, showing the occurrence of the helical structure [6, 7]. On cooling a few degrees below T_c , the lines gradually disappear. There is a temperature interval of about 30 K where the lines do not exist. At still lower temperatures, the lines can be again generated by a low a.c. electric field. When the field is switched off, the lines are not completely stable, and may again disappear, and anyhow, they do not exhibit a regular pattern throughout the whole sample.

The temperature dependence of the helical pitch was established by the diffraction of laser light (630 nm) using planar cells. The pitch was found to be practically thickness independent for cells more than 25 μm thick. The temperature variation of the helical pitch for the material H6/10 obtained with 25 and 350 μm thick cells is shown in figure 1. The pitch increases when cooling from the temperature T_c of the $S_A-S_C^*$ phase transition. At a temperature a few degrees below T_c , the diffraction picture disappears due to the disappearance of the dechiralization lines. In the temperature range where a non-regular pattern of dechiralization lines appears under the applied a.c. field, the diffraction picture was not clear enough for a precise evaluation of the helix pitch.

It can be inferred from the results of the diffraction experiment that the helix becomes unwound in a certain

temperature range in the S_C^* phase and that the helix pitch continuously increases when approaching this temperature region from both sides. In that region the structure is still not spatially homogeneous, but exhibits a twist through the sample thickness, the same as in normal planar samples [7]. This twist manifests itself as a rotation of polarized light by $2\theta_s$, where θ_s is the tilt angle.

In order to determine the helix handedness, we have studied the optical rotatory power using freely suspended films. In this geometry, the optical axis is perpendicular to the film surface. The results for H6/10 are given in the inset of figure 1. One can see a continuous change in the rotatory power with temperature and a jump-like change in its sign. This behaviour gives evidence for the helix sense at the temperature T_i , which was defined as the centre of the temperature range of about 8 K in which no optical rotation was detected and a schlieren texture appeared. If

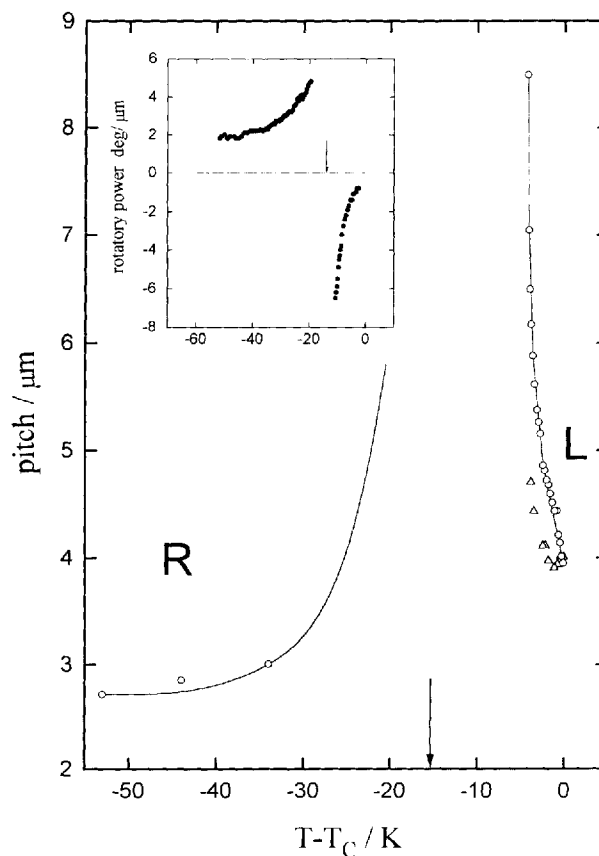


Figure 1. Pitch of the helix in the smectic C^* phase in H6/10 measured by light diffraction (630 nm). Circles and triangles are results obtained with 350 and 25 μm thick cells, respectively. R and L stand for left and right helix, respectively; the lines connecting the experimental points serve only as guides for the eyes. The inset shows the optical rotatory power. The arrows indicate the helix twist inversion temperature.

Table 1. Phase transition temperatures ($^{\circ}\text{C}$) for the homologous series H n/m and Cl n/m , T_i ($^{\circ}\text{C}$) is the helix twist inversion temperature, P_s (nC cm^{-2}) is the spontaneous polarization in the S_C^* phase at a temperature 10 K below the transition. (●), The phase exists, (—), the phase does not exist.

n/m	S_C^*	S_A	N^*	BP	I	T_i	P_s				
H6/12	●	131.5	●	139.5	●	142.0	●	143.0	●	122.0	68.0
H6/10	●	134.0	●	140.0	●	140.5	●	141.0	●	115.0	70.0
H6/9	●	131.0	●	135.0	●	143.5	●	144.0	●	106.0	73.0
H6/8	●	132.0	—	●	148.0	●	149.0	●	●	102.0	81.0
H6/7	●	134.0	—	●	155.0	—	●	●	●	85.0	73.0
H6/5	●	137.0	—	●	161.5	●	161.8	●	●	68.0	102.0
H10/10	●	137.0	—	—	—	—	●	●	●	100.0	68.0
H10/8	●	137.5	—	●	138.5	●	140.0	●	●	88.0	77.0
H9/9	●	137.3	—	●	140.0	●	140.2	●	●	100.0	69.0
H8/8	●	141.0	—	●	147.5	●	148.0	●	●	85.0	68.0
Cl8/5	●	124.0	—	●	124.3	●	124.5	●	●	88.0	187.0
Cl8/7	●	120.2	—	—	—	—	●	●	●	106.0	154.0
Cl8/9	●	123.5	—	—	—	—	●	●	●	—	120.0
Cl10/5	●	122.2	—	●	123.0	—	—	●	●	86.0	121.0
Cl10/9	●	129.0	—	—	—	—	—	●	●	—	96.0
Cl12/5	●	116.9	—	—	—	—	—	●	●	85.0	124.0

the thicker films were cooled to the vicinity of T_i a striped texture was observed [8].

Using the same convention as in [4], one can deduce that at temperatures above T_i , the helix is left-handed, and below T_i it is right-handed. This is true for all the substances studied in which the helix inversion was detected (see the table). The temperature T_i increases in the homologous series with the number of carbon atoms in the chiral chain m , as presented in figure 2.

Substances Cl8/9 and Cl10/9 do not exhibit the helix inversion (see the table). With these substances, a continuous decrease in the right-handed helix pitch length has been found on cooling. This behaviour corresponds to a hypothetical T_i extrapolated into the isotropic phase.

3.3. Spontaneous polarization and tilt angle

In the ferroelectric S_C^* phases, the temperature dependence of the spontaneous polarization (P_s) and the tilt angle (θ_s) of the molecules from the smectic layer normal were determined. The values of P_s were evaluated from the $P(E)$ hysteresis loop detected during P_s switching in an a.c. electric field E of frequency 60 Hz. The θ_s values were calculated from the difference between extinction positions of a planar sample between crossed polarizers and under opposite d.c. fields high enough to unwind the helical structure. The coercive electric field E_c was determined from the hysteresis loop as a field corresponding to $P_s = 0$. An almost linear increase of E_c with increasing applied field was detected, in spite of a well-saturated value of P_s (see figure 3). The behaviour was confirmed not to be related to surface treatment of the cell glasses. For all compounds studied, the sign P_s was

determined as positive, according to the convention used in [4].

The temperature behaviours of P_s for compounds H6/10 and Cl8/5 are shown in figures 4(a) and (b),

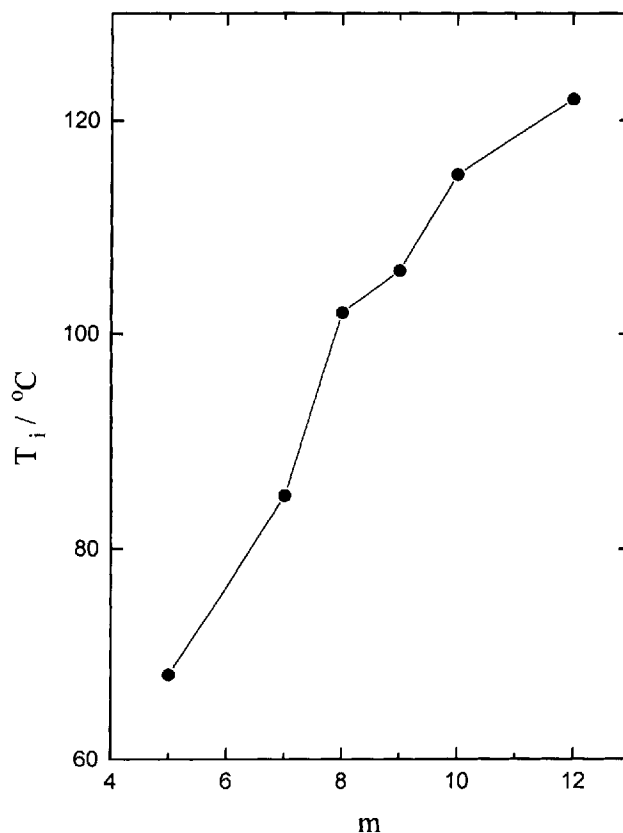


Figure 2. Helix twist inversion temperature T_i in the homologous series H6/ m .

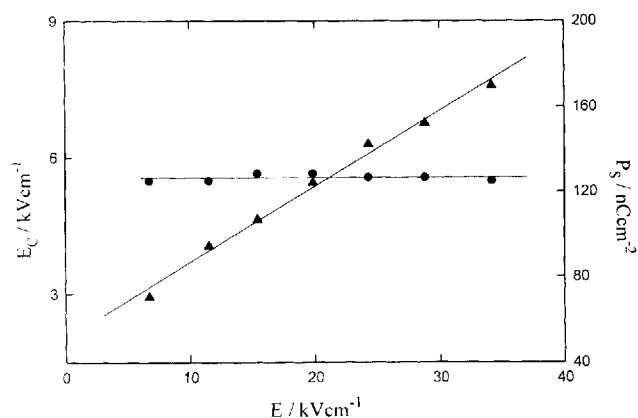


Figure 3. Coercive field E_c (triangles) and spontaneous polarization P_s (circles) versus applied electric field for Cl8/5 at 116°C.

respectively. In all chloro-substituted derivatives, the spontaneous polarization was found to be almost twice as high as for the unsubstituted materials. With substances having a $S_A-S_C^*$ phase transition, both P_s and θ_s increase continuously from zero when the temperature decreases from T_c (see figure 4 (a)). This behaviour is a manifestation of the second order phase transition. The jump in P_s and θ_s at T_c , which is typical for a first order transition was found with substances exhibiting either $I-S_C^*$ or $N^*-S_C^*$ phase transitions (see figure 4 (b)).

In none of the compounds studied was the helix sense inversion accompanied by any anomaly in the trends of P_s or θ_s with temperature (see figures 4 (a) and (b)). However, for all the materials, there was no saturation in the value of P_s which continuously increased on cooling. Similar

behaviour was previously reported also for methyl substituted lactic acid derivatives [5]. On the other hand, in all the materials studied the θ_s reaches its saturated value within an interval of 35 to 40 degrees, that is at a temperature about 40 K below the phase transition on cooling into the S_C^* phase.

4. Discussion

The helical twist sense and the sign of the spontaneous polarization depend [4], respectively, on the location of the bulky group and on the direction of the lateral dipole moment at the chiral centre, in relation to the mesogenic core. For a certain spatial rotational conformer these quantities could be determined for a given absolute configuration (*R* or *S*) of chiral centre and its distance from the mesogenic core (parity of the atoms) [4, 9]. In the case of non-rigid molecules, more than one rotational conformational species can appear in the system, and their twist senses and dipole moment directions can be opposite. The competition between conformational species has been considered previously as being responsible for the helix twist inversion phenomenon [4].

In the case of the lactic acid derivatives **1** and **2**, a similar mechanism can be considered. Using the molecular modelling package HyperChem 3, one can determine the energy of conformers created through rotation around the C-C* bond (see figure 5). The conformers A, B and C corresponding to the energy minima are shown in figure 6(a). Species A and C have the 'bulky' group, methyl or oxygen, respectively, pointing towards opposite sides of the molecule (see figure 6(a)). Since formation of the helix is driven by steric factors, conformers A and C

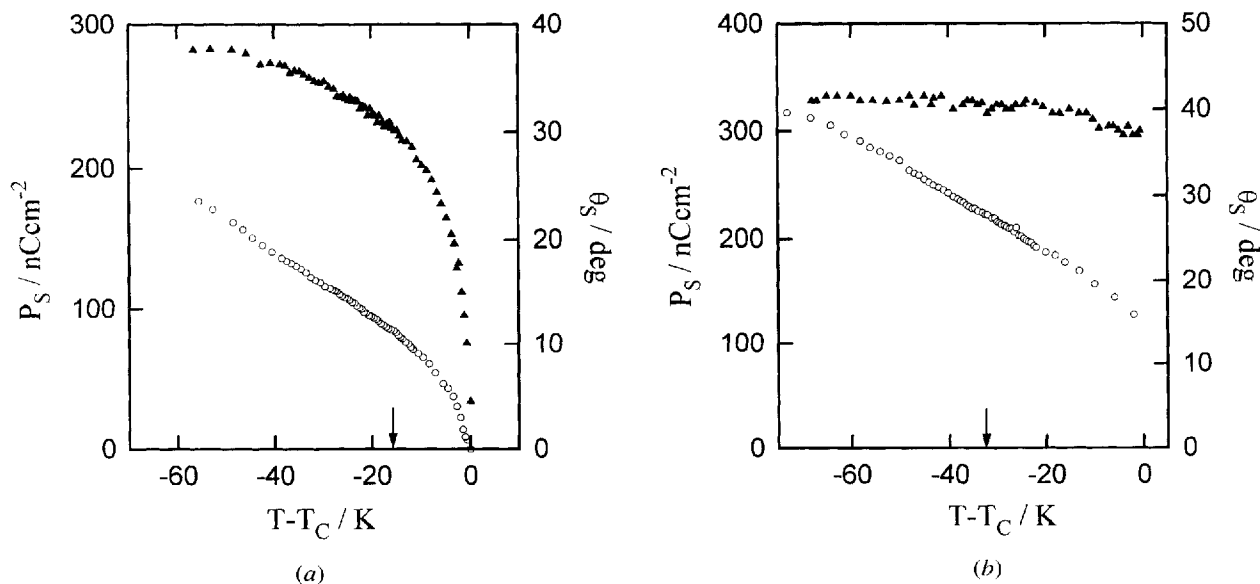


Figure 4. Spontaneous polarization P_s (circles) and apparent tilt angle θ_s (triangles) versus temperature for (a) H6/10 and (b) Cl8/5. Arrows indicate the helix twist inversion temperatures.

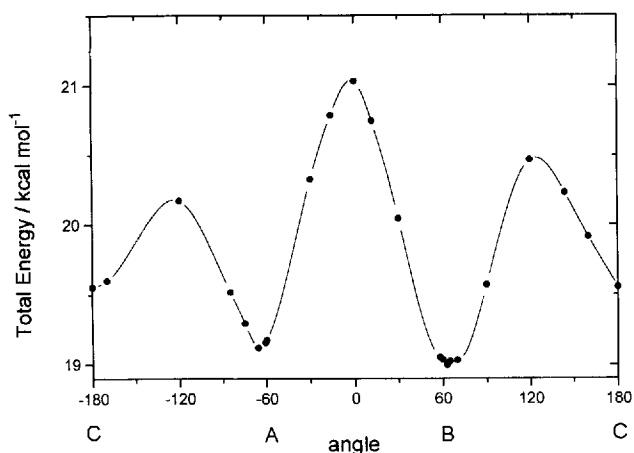


Figure 5. The total free energy obtained for H 1/6 as a function of the rotation angle around the C-C* bond. The torsion angle CH₃-C*-O-C was fixed at 60 deg. Note that conformers A, B, and C have almost the same energy.

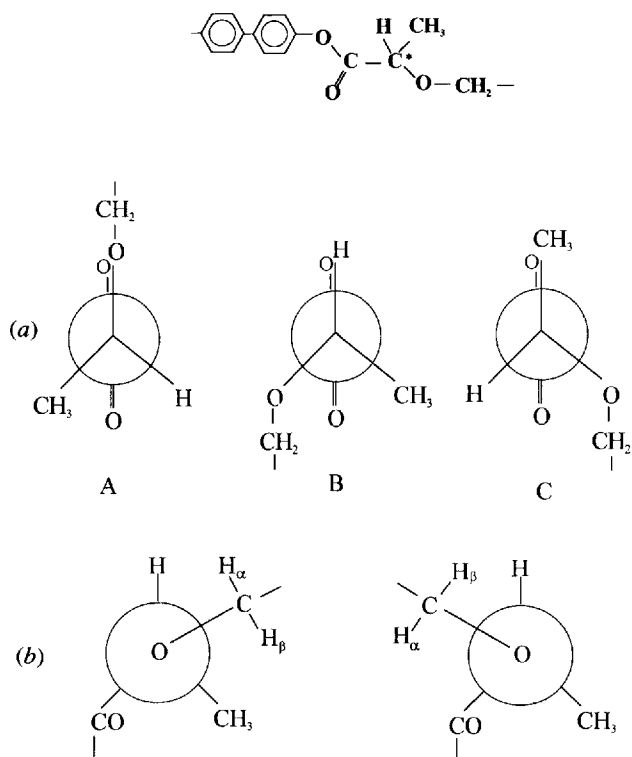


Figure 6. Fragment of the molecule and the Newman projections of the structures of spatial conformers (*S*-enantiomer) created by rotation around (a) C-C* bond and (b) C*-O bond.

might lead to opposite helix handedness. In species *B*, the oxygen and methyl substituents are positioned on opposite sides of the molecular long axis (see figure 6 (a)). Thus, in the first approximation, it might be expected that the steric effects of these two off-axis substituents will compensate

more or less for one another. If the relative population of each conformer is affected by temperature change, the competition between conformers A and C can lead to the helix twist inversion.

On the other hand, as the energies of conformers A, B and C are rather similar (see figure 5), their population will be only slightly temperature dependent. In that situation, conformers produced by hindered rotation about the C*-O bond might become important. The existence of this steric hindrance has been established in the NMR spectra as a non-equivalence of the two hydrogen atoms of the methylene group adjacent to the ether oxygen. There exist two low energy conformers in relation to the C*-O bond (see figure 6 (b)), with diverse directions of the aliphatic chains with respect to the molecular axis. These conformers can affect the 'twisting ability' of the oxygen atom bound to the chiral carbon for the *B* conformer, while the methylene group remains unaffected (see figure 6 (a)). In this way, when the concentration of the conformers for the C*-O bond is changed with temperature, a balance of the action of both oxygen and methylene substituents can cause the helix inversion at a certain temperature.

This interpretation is also supported by the observed strong dependence of the helix twist inversion temperature on the length of the terminal chain attached to the chiral part of the molecule. The energy barrier for rotation around the C*-O bond would increase with increasing length of the alkyl chain; thus, for higher homologues we can expect a higher twist inversion temperature, as indeed has been found experimentally.

The comparison between P_s values of compounds 1 and 2 shows the chloro-substitution increases significantly the spontaneous polarization. We suppose that this increase of P_s is caused mainly by a closer arrangement of mesogenic cores, which could take place due to a density decrease of π -electrons on the phenyl rings, which are drained by the chlorine. A closer packing distance of the mesogenic cores would result in an increase in mass density of the chloro substituted compounds, and might also cause more hindered rotation of the molecules around their long axes. One should also take into account the dipole connected with the C-Cl bond, which influences the total lateral molecular dipole. However, its orientation relative to the dipole of the chiral part of the molecule is not fixed, and therefore its contribution to P_s could be eliminated.

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