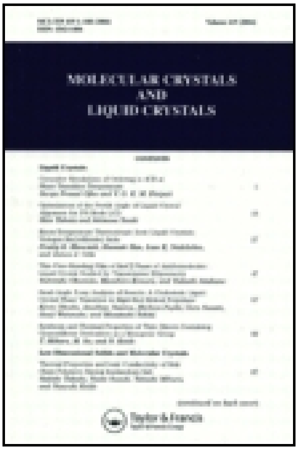

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Chiral Textures Formed by Achiral p-Substituted Biphenylcarboxylic and Benzoic Acids

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Chiral Textures Formed by Achiral p-Substituted Biphenylcarboxylic and Benzoic Acids

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We have observed by means of polarizing light microscopy a novel spontaneous chiral textures with helix axis in the cell plane deep in the smectic phase of achiral p-octyl- and p-octyloxybiphenylcarboxylic acids and close to the nematic-smectic transition of p-octyloxybenzoic acid. The chiral domains appeared in the mesophase, mostly on cooling. The character and the size of the domains depended on the temperature rate. The domains were stable in a large temperature range. The appearance of chiral domains followed a thermal stress. The presence of the spontaneous chiral structures is here explained by a mechanism involving the hydrogen bonding among monomeric molecules, providing as a consequence the presence of both achiral dimeric- and chiral oligomeric molecules in the mesophase.

Keywords: liquid crystals; chirality; textures; hydrogen bonding

INTRODUCTION

The study of mesogenic materials formed by achiral molecules, which nevertheless can exhibit domains with spontaneous twist deformation, is now calling the attention of many researchers[1]. Earlier we discovered a spontaneous chiral ordering in thermotropic nematic liquid crystals forming intermolecular hydrogen bonds, namely *trans*-4-hexylcyclohexane-carboxylic acid, by achiral moleculs[2]. The observed spontaneous chiral structure is similar to the common cholesteric one, with helix axis normal to the cell plates. The explanation of the macroscopic texture was given in terms of molecular structure, based on the ability of the carboxylic acids to organize through hydrogen bonds not only dimers, but also trimers and oligomers. This packaging is induced by the formation of open dimers in a short temperature range just below the clearing point, due to thermodynamical reasons. After interaction between one open dimer and one monomer, or between two open dimers it is possible to have trimer or tetramer and so on. These oligomers can have a spiral structure as in the case of biological cells where the achiral molecules are forming chiral polimeric chains via hydrogen bonding[3]. It is enough to have a trimer in order to provide microscopic chirality either right or left handed[2]. The chiral structures can play the role of a chiral dopant.

It was also discovered the presence of macroscopic chiral structures in lyotropic liquid crysals, based on achiral molecules[4].

With the purpose to find a spontaneous chiral ordering, we investigated biphenylcarboxylic[5] and benzoic acids with p-alkyl- or p-alkyloxy-substituents, which also are characterized by achiral molecules. It is necessary to mention, that a spontaneous twisted domains induced by the surface in the nematic phase of alkyloxybenzoic acids were found by authors[6] and discussed later by the presence of cybotactic clusters, responsible of the chiral symmetry[7].

EXPERIMENT

The cells used were of common sandwich type, with a gap of 2 μm. The inner surfaces of the cell glass plates were simply cleaned. No any particular chemical treatment of the glass plates was used to build up the cells.

The sample was mounted in a Mettler hot stage and the temperature was controlled within 0.1°C accuracy. The optical investigation was carried out using a Leitz polarizing microscope. A JVC color CCD camera was used for the observation recording: the digital image acquisition from the camera was done by a color video digitizer, driven by a computer.

The investigated acids (and their phase sequences) are the following:

p-octyloxybezoic acid[8] K 98 Sm_C 105 N 140 I (°C)
p-octyloxybiphenylcarboxylic acid[9] K183 Sm_C 255 N 264.5 I (°C)
p-octylbiphenylcarboxylic acid[10] K147 Sm_C 243 N 255 I (°C)

RESULTS AND DISCUSSION

The chiral textures appeared mostly on cooling and not every time. It was necessary to have a special regime of cooling rate. The cooling was from isotropic phase with the speed 10°C/min to a definite temperature (specific for each substance); after this few degrees with the speed 1°C/min till the appearance of the chiral textures, which are stable in a large temperature range. We would like to underline that, if the rate of cooling is very fast or very slow, it is impossible to observe the chiral textures in biphenylcarboxylic acids.

For p-octylbiphenylcarboxylic acid the speedy cooling (10°C/min) was from isotropic phase to 236.8°C, after this with the speed 1°C/min to 232.4°C. At this temperature domains with smectic C* texture appeared (Fig. 1). They were stable to 218°C.

FIGURE 1 The chiral texture of p-octylbiphenylcarboxylic acid. See Color Plate III at the back of this issue.

For p-octyloxybiphenylcarboxylic acid the speedy cooling (10°C/min) was from isotropic phase to 247.7°C, after this with the speed 1°C/min to 245.7°C. At this temperature domains with smectic C* texture appeared (Fig. 2). They were stable to 236.1°C. At this temperature some of them disappeared. The remainders were present to 220.4°C.

For p-octyloxybenzoic acid the speedy cooling (10°C/min) was from isotropic phase to 107.3°C. By means of a slow scan (0.5°C/min) around the smectic C- nematic transition (105°C), a typical transition texture (scroll texture) can be revealed[11]. As soon as the texture appeared, we immediately stopped the cooling, just below the transition point. After this appeared the texture, resembling the striped domains in the cholesteric materials[12] (Fig. 3).

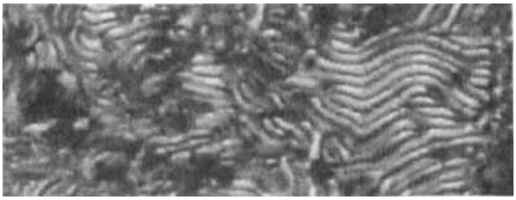

FIGURE 2 The chiral texture of p-octyloxybiphenylcarboxylic acid. See Color Plate IV at the back of this issue.

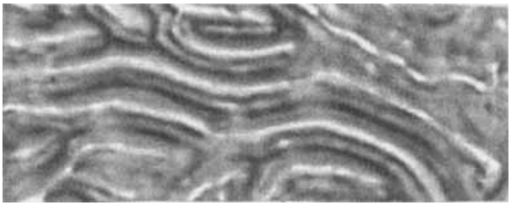

FIGURE 3 Large periodic structure with in-plane period in the smectic C phase of p-octyloxybenzoic acid
See Color Plate V at the back of this issue.

These domains were present in the smectic phase on cooling from the nematic phase: on heating from the smectic to the nematic phase they were not evident but only the scroll texture appeared. Lowering the temperature of half a degree, the striped domains disappeared and the presence of a bidimensional periodic texture was observed (Fig. 4), similar to the one observed by Johnson and Saupe[13] in smectic C phase of 4-n-pentyloxybenzylidene-4'-n-heptylaniline and of 4-n-pentylphenyl-4'-n-octylthiobenzoate. These domains remain for 4 - 5 degrees on cooling from the transition temperature. Figure 4 clearly shows the presence of such bidimensional periodic structure with a periodicity in the cell plane: the double period is evident.

FIGURE 4 Johnson-Saupe textures obtained by cooling the cell after the nematic-smectic transition.
See Color Plate VI at the back of this issue.

The shorter period length of the texture in Fig. 4 is about 3 - 4 μm. The presence of the double period, with one periodicity that is the double of the other, was predicted by the theory[13]. The same Johnson-Saupe stripes were found by authors[14] in the smectic phase of p-nonyloxybenzoic acid by rapid cooling from nematic phase with elastic distortions. According to our opinion this double layered periodicity is consistent with the hypothesis of the arising of spontaneous twisted structures.

The striped domains which appear near the transition temperature (see Fig. 3), are completely different from the Johnson-Saupe texture: they never reveals a double layered periodicity and the stripe pitch is definitely larger (20 μm as compared with 4 μm).

In order to compare the observed textures with the one of a cholesteric we prepared a mixture of 5CB and 1% of the chiral dopant HDN-1. The texture obtained is shown on Fig. 5.

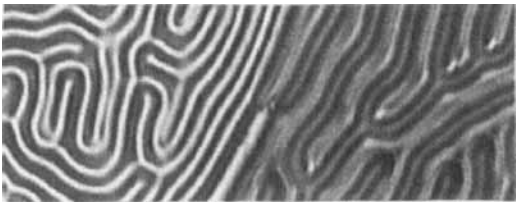

FIGURE 5 The cholesteric texture of 5-CB with 1% of chiral dopant. See Color Plate VII at the back of this issue.

In the case of *trans*-4-hexylcyclohexanecarboxylic acid the appearance of chiral textures just below the clearing point (96°C) was described by us as due to the formation of oligomers[2]. The presence of oligomers in the smectic phase of this acid was shown by the method of IR-spectroscopy[15]. So, our suggestion can be valid both for p-octyloxybenzoic acid and for p-substituted biphenylcarboxylic acids. Moreover the stability of the chiral domains in the smectic phase of p-substituted biphenylcarboxylic acids far from the clearing point (near 20°C below) could be also due to the strong stacking interactions of aromatic rings, which is providing the stability of twisted packaging.

CONCLUSION

We have shown that spontaneous chiral domains appear in smectic phase of p-octyl, p-octyloxybiphenylcarboxylic acids and p-octyloxybenzoic acid on cooling. Their appearance strictly depends on the regime of cooling and requests a thermal stress. The interpretation of the effect is given, as well as for *trans*-4-hexylcyclohexanecarboxylic acid, in terms of the formation of helix-like oligomeric structures, build up from open dimers by means of intermolecular hydrogen bonds. In the case of molecules containing aromatic rings, it is necessary to take into consideration also the influence of stacking interactions.

ACKNOLEDGEMENTS
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