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Liquid Crystals

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Effect of the naphthalene moiety on the mesogenic properties of ferroelectric liquid crystals containing diastereomeric propionic acids

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Two ferroelectric liquid crystals containing the naphthalene moiety were synthesized from 2(S)-[2(R)-methylhexyloxy] propionic acid and its (S,S)-diastereomer. Their mesogenic properties are compared with those of the analogous mesogens containing the biphenyl ring.

1. Introduction

The characteristic chevron structures of ferroelectric liquid crystals (FLCs) have been known for many years [1]. They are the cause of the so-called zigzag defects. Three types of new FLCs which give defect-free alignment were recently reported $\lceil 2-4 \rceil$. They all have one asymmetric carbon centre and two of them contain a naphthalene moiety bonding to a chiral molecule. In the course of our work on FLCs we have used the diastereomeric propionic acids 1 and 2 (see the figure) as chiral building blocks for the synthesis of FLCs. These chiral acids have two asymmetric carbon centres and are useful for the formation of SmC* phase. In order to study the stereochemical effect on liquid crystal properties, two FLCs, 3 and 4, containing the biphenyl ring bonding to 1 and 2, respectively, were previously synthesized and compared [5]. A large difference in the spontaneous polarization between 3 and 4 was observed. While the FLC 3 has a P_s value of 97 nC cm⁻², that of FLC 4 is 131 nC cm⁻². This difference is strongly related to their relative stereochemistry, which is changed from the (S,R)configuration for 3 to the (S,S)-configuration for 4. It is hard to explain such a difference by just considering the conformation change at the chiral molecular part of 3 and 4; the conformation change caused by the biphenyl ring bonding to the diastereomeric acids 1 and 2 seems to play a significant role for such a variation. A larger conformation modification would be expected when the biphenyl ring of 3 and 4 is substituted by the naphthyl ring, and it is important to know the effect on mesogenic properties induced by this modification. Two FLCs, 5 and 6, were synthesized for this study from the diastereomers 1 and 2 respectively. All structures are shown in the figure.

2. Results and discussion

The data for chemical shift, specific rotation, and liquid crystalline properties for compounds 5 and 6 are summarized in table 1. Spontaneous polarization values

	Chamical shift/norm (CDCL)		Phase transition/°C						
Compound	$-(CH_3)*CHO-C\underline{H}_2*CH(CH_3)-$	$[\alpha]_D^{28} (CHCl_3)/^{\circ}$	Cr		SmC*		SmA		Ι
5 6	3.36, 3.51 3.27, 3.63	-33 - 31	•	39 33	•	65 58	•	70 68	•

Table 1. Physical properties of compounds 5 and 6.

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Figure. Structures of compounds 1-6.

and tilt angles, measured at $T_c - T = 10^{\circ}$ C, are summarized in table 2. The corresponding values for 3 and 4 are included in table 2 for comparison, measured under the same conditions as those for 5 and 6. As in the case of 3 and 4, the configurations of the synthesized diastereomers 5 and 6 can be easily differentiated by the chemical shift of the methylene group situated between

Table 2.Spontaneous polarization and tilt angle for
compounds 3–6.

Compound	$\mathbf{P}_{s}/n\mathbf{C}\mathbf{cm}^{-2}$	$\theta/^{\circ}$	
5	78	13	
6	80	14	
3	97	6	
4	131	7	

the oxygen atom of the first asymmetric carbon centre and the second asymmetric carbon centre.

The phase sequence is changed from $Cr-SmC^*-N^*-I$ for 3 and 4 to $Cr-SmC^*-SmA-I$ for 5 and 6. The SmC* phase transition temperatures of 5 and 6 are c. 40°C lower than those of 3 and 4. The FLCs 5 and 6 still have wide SmC* phase ranges up to 26°C, although narrower than those of 3 and 4.

The spontaneous polarization data for 5 and 6, measured at $T_c - T = 10^{\circ}$ C, are significant. The values are much smaller than those of 3 and 4: 78 vs. 97 nC cm⁻² for 5 and 3, and 80 vs. 131 nC cm⁻² for 6 and 4. Interestingly, the spontaneous polarization difference between 5 and 6 is almost negligible, while it is very large between 3 and 4. This unexpected variation is apparently due to the conformation change when the biphenyl ring is replaced by the naphthyl ring. The change is so large that almost no difference in spontaneous polarization between 5 and 6 can be found. This can be understood from the situation in which the effective dipole moments of 5 and 6 are less perpendicular to the tilt plane, in comparison with those of 3 and 4. Although both the Boulder model and the zigzag configuration are successful in explaining the differences in spontaneous polarization of many diastereometic FLCs [6, 7], they do not give a convincing explanation for the FLCs 3-6.

This study shows that a more detailed and precise conformation analysis of FLC molecules is not only important, but necessary for a quantitative comparison of their ferroelectricities.

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