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Diastereomer Effects on Antiferroelectricity and Ferroelectricity of the Newly Synthesized Liquid Crystals

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DIASTEREOMER EFFECTS ON ANTIFERROELECTRICITY AND FERROELECTRICITY OF THE NEWLY SYNTHESIZED LIQUID CRYSTALS.

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ABSTRACTS Using the novel-model liquid crystals (LC) having two stereogenic centers in the molecule (CF_3 and CH_3), which were synthesized by the chiral titanium complex-catalyzed carbonyl-ene reaction with fluoral, the relationship between the appearance of antiferroelectricity and conformational arrangement were examined. From the results of our investigation, we concluded that the relative stereochemistry of the diastereomeric chiral portion should give strong effect on the preference and the thermotropic stability of SmCA* phase.

INTRODUCTION

The antiferroelectric liquid crystals (AFLC) have recently attracted much interest as one of the electro-optic devices[1], because of their unique characteristics such as tristable switching, sharp DC threshold and double-hysteresis. In spite of some examination[2], it has not been clearly understood yet the relationship between molecular chirality and the appearance of antiferroelectricity. Furthermore only a few kinds of AFLC molecules have been reported bearing a chiral alkyl terminus with *one stereogenic center* such as MHPOBC and TFMHPOBC, wherein odd-even effect was observed.

In order to investigate the conformational arrangement of chiral alkyl termini requisite for AFLC properties, we designed and synthesized diastereomeric molecules with *two stereogenic centers*, α-trifluoromethyl-β-methyl aryl esters with odd and even number (5, 6 and 7) of the chiral alkyl chain on the bases of the fluoral-ene reaction. The chiral titanium complex-catalyzed carbonyl-ene reaction with fluoral serve as an efficient route to the diastereoselective and enantioselective synthesis of CF_3-substituted compounds[3].

In this report, the relationship between conformational arrangement of the novel-model LC molecule and the preference and the thermotropic stability of $SmCA^*$ phase was discussed.

PREPARATION OF NOVEL-MODEL DIASTEREOMERIC LC MOLECULES

Preparation of LC molecules (1)

Novel-model diastereomeric LC molecules 1 were prepared on the basis of the carbonyl-ene reaction of fluoral with vinylsulfides as shown in figure 1.

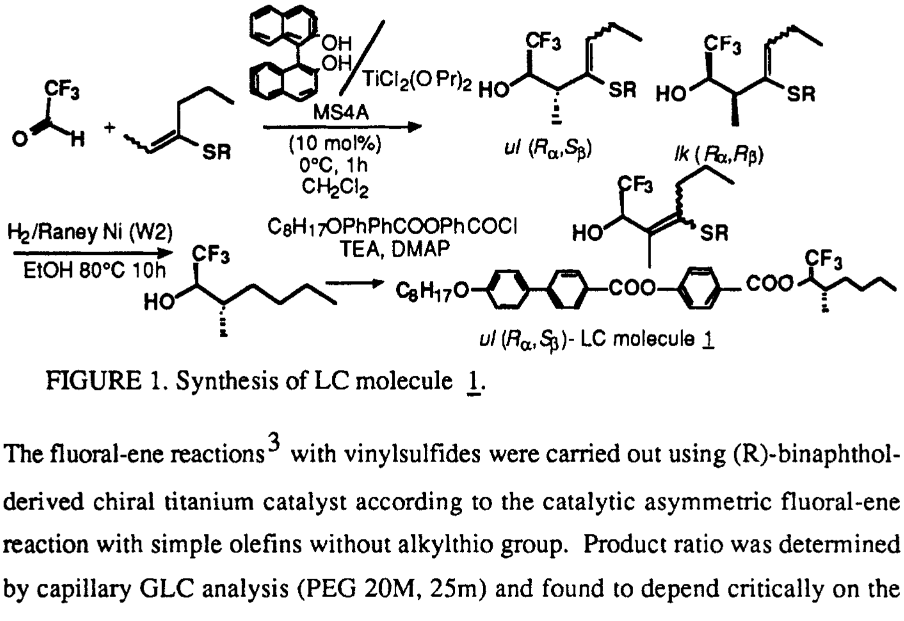

FIGURE 1. Synthesis of LC molecule 1.

The fluoral-ene reactions[3] with vinylsulfides were carried out using (R)-binaphthol-derived chiral titanium catalyst according to the catalytic asymmetric fluoral-ene reaction with simple olefins without alkylthio group. Product ratio was determined by capillary GLC analysis (PEG 20M, 25m) and found to depend critically on the geometry and alkylthio substituent in the vinylsulfides. The enantiomeric purity of the product was determined by ^{1}HNMR (300 MHz) spectral analysis of the (S)-(-)- and (R)-(+)-MTPA ester derivatives of the preceding product. The absolute stereochemistry of the product was determined by the Mosher method. Thus, the *ul*-tert-butylsulfide provided mainly (62.9%) the *ul* (R_α,S_β)-diastereomer[4] (93% e.e.)

along with 25.5% of *lk* (R_α,R_β)-diastereomer[4] and 11.6% of allylic alcohol. Surprisingly, phenylsulfide provided mainly (56.1%) the allylic alcohol (86% e.e.) along with 30.3% of *lk* (R_α,R_β)-diastereomer (92% e.e.). Medium pressure liquid chromatography gave the *ul*-tert-butylsulfide and *lk*-phenylsulfide along with allylic alcohol, respectively. Reductive desulfurization of the *ul*-tert-butylsulfide with the Raney nickel gave the *ul*-diastereomer in 76% diastereomer purity (R,S : S,R = 81.5 : 18.5). In a similar manner, *lk*-diastereomer was obtained from *lk*-phenylsulfide in 65% diastereomer purity (R,R : S,S = 74.0 : 26.0). After several ordinary esterifications of *ul*-diastereomer and *lk*-diastereomer, *ul* (R_α,S_β)-diastereomer 1 and *lk* (R_α,R_β)-diastereomer 1 were prepared, respectively.

Preparation of LC molecules (2) and (3)

Diastereomeric LC molecules 2 and 3 were prepared through chiral titanium complex-catalyzed carbonyl-ene reaction[3] of fluoral with ethylidenecycloalkanes.

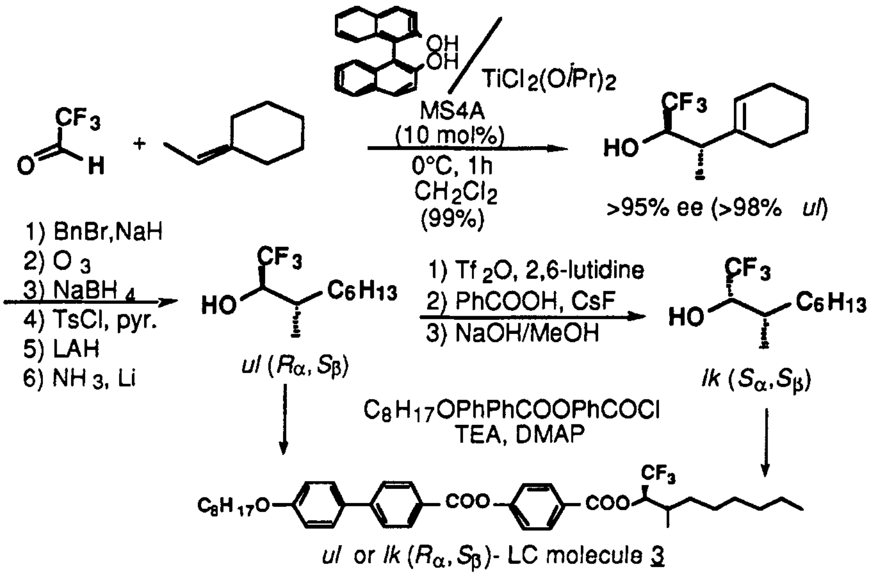

FIGURE 2. Synthesis of LC molecule 3.

The *ul* (R_α,S_β)-alcohols were obtained in almost quantitative yield in more than 95% e.e. and 95% d.e.. A sequence of the protection of the alcohol, ozonolysis, reduction, and de-protection leads to the *ul* (R_α,S_β)-diastereomer of the chiral portion in LC molecules in essentially stereo-pure form (>95% e.e., >95% d.e.). After several usual esterifications of *ul*-diastereomers and *lk*-diastereomers, *ul* (R_α,S_β)-diastereomers 2,3 and *lk* (R_α,R_β)-diastereomers 2,3 were prepared, respectively (Figure 2).

RELATIONSHIP BETWEEN PHASE TRANSITION AND CONFORMATIONAL ARRANGEMENT OF NOVEL-MODEL LC MOLECULES (1), (2), (3)

Relationship between phase transition and conformation of LC molecules (1)

Phase transition temperatures of *ul* (R_α,S_β)- and *lk* (R_α,R_β)-diastereomer of molecule 1 in the heating process are shown in Table 1. Microscopic observation of their textures was carried out by using anti-parallel rubbing cell whose gap was about 2 μm and polyimide was used as alignment films. The texture of *ul*-diastereomer of 1 was like typical of SmCA*, although that of *lk*-diastereomer of 1 was not like SmCA* but was similar to well-known SmC*. Consequently, the difference of conformational arrangement could give strong effect on the preference of SmCA*, preferently in *ul*-diastereomer rather than in *lk*-diastereomer.

TABLE I Phase transition temperatures of *ul*- and *lk*-diastereomer 1.

	Cry		SmCA*		SmC*		SmA		Iso
ul - diastereomer 1 (R_α,S_β)		71	•	—	•	114	•	119	
lk - diastereomer 1 (R_α,R_β)		—	•	74	•	111	•	116	

Relationship between phase transition and conformation of LC molecules (2) and (3)

Phase transition temperatures of LC molecule 2 and 3 were taken for various proportions of diastereomeric mixtures of the *ul* (R_α,R_β)- and *lk* (R_α,R_β)-diastereomers (Figure 3)[5]. Both diastereomeric LC molecules 2 and 3 showed the direct phase transition from SmA to SmCA* in the region of high % for *ul*-diastereomer. By contrast, SmC* was inserted between SmA and SmCA* in the region of low % for *ul*-diastereomer, that is, in the *lk*-diastereomer rich region. In both LC molecules 2 and 3, SmC* could disappear in the region of about 50 % for *ul*-diastereomer. It is clear that the temperature range of SmCA* of *ul*-diastereomer is wider than that of *lk*-diastereomer and these results suggest that the SmCA* should be more thermotropically stable in *ul*-diastereomer rather than in *lk*-diastereomer.

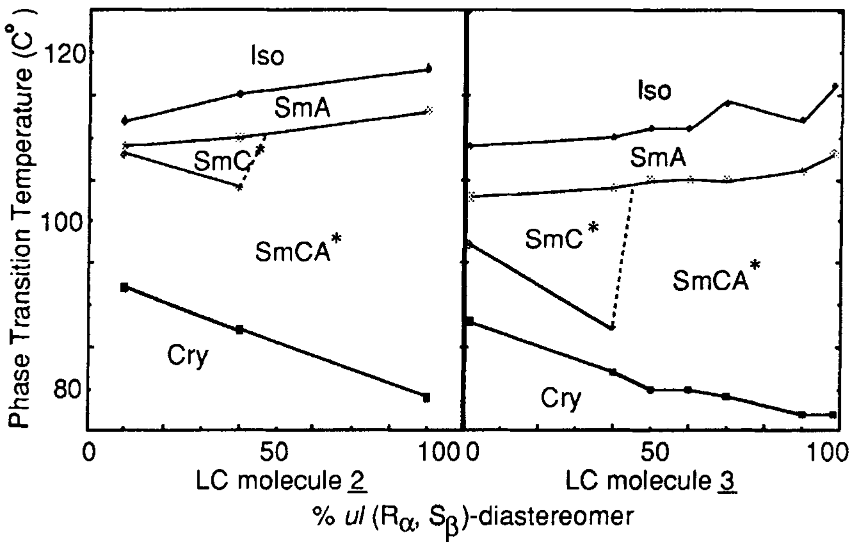

FIGURE 3 Phase transition temperatures of various proportions of diastereomer mixtures of *ul*- and *lk*-diastereomer of LC molecules 2 and 3.

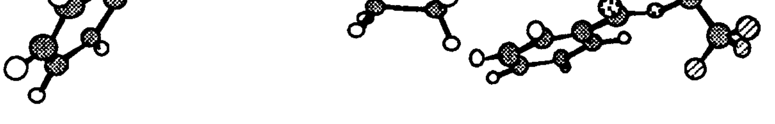

FIGURE 4 Conformational arrangement of bend-like conformer (A) and extended-like one (B) in *ul*-diastereomers of LC molecule 3.

Ab initio (RHF/6-31G*) calculations on *ul*-$PhCO_2CH(CF_3)CH(CH_3)C_4H_{19}$

was carried out using Gaussian 94 program (Gaussian 94, Gaussian, Inc., Pittsburgh PA. 1995.). There is obvious conformational preference of bend-like conformer (A) to extended-like one (B) in *ul*-diastereomers (Figure 4).

According to these results, conformational difference between *ul*- and *lk*-diastereomer of these novel-model LC molecules gives apparently strong influence on the thermotropic stability of SmCA* phase, and for the appearance of antiferroelectricity, the bend-like structure could be superior to the extended-like one.

CONCLUSION

From some examination with a series of novel-model LC molecules 1, 2 and 3, which were synthesized by the chiral titanium complex-catalyzed carbonyl-ene reaction with fluoral serves, we concluded as follows;

1) Conformational difference between *ul*- and *lk*-diastereomer does not affect on their magnitude of spontaneous polarization but do influence on the preference and the thermotropic stability of SmCA* phase.

2) For the appearance of SmCA*, the bend-like structure could be more essential than the extended-like one .

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4. *ul* and *lk* are abbreviations of unlike (R,S or S,R) and like (R,R or S,S).
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5. Their magnitude of spontaneous polarization were almost equal.