

Diastereotropic Phenomena for the Appearance of SmCA* Phase in α -Trifluoromethyl- β -methyl-substituted Liquid Crystalline Molecules

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Anti-ferroelectric (SmCA*) and ferroelectric (SmC*) phases of α -trifluoromethyl- β -methyl-substituted liquid crystalline (LC) molecules, synthesized highly diastereo- and enantioselectively through our chiral titanium complex-catalyzed fluoral-ene reaction, were determined by thermal analysis and electro-optic measurements. Phase transitions were thus found to be critically dependent on the diastereomeric excess (diastereotropic) for *ul* ($R_{\alpha}S_{\beta}$)-diastereomers of the LC molecules.

Recently, anti-ferroelectric (AF)¹ liquid-crystalline (LC) molecules have been studied intensively both experimentally and theoretically because of their potential application in electro-optic devices.² A number of molecules showing an AF (SmCA*) phase have been synthesized and an attempt to correlate the molecular structure of the AFLC molecules to the appearance of the SmCA* phase has been carried out.³ However, only a limited types of AFLC molecules have been reported (Figure 1), containing a chiral alkyl terminus with a single stereogenic center such as methyl-substituted aryl ester (MHPOBC)^{3a} and the trifluoromethyl analogue (TFMHPOBC)^{3b} with greater spontaneous polarization (Ps). In order to investigate the relationship between molecular asymmetry and AFLC properties, we designed diastereomeric molecules with double stereogenic centers.⁴ α -trifluoromethyl- β -methyl-substituted aryl esters with even and odd numbered (6 and 7) chiral alkyl chains (m). Herein, we report the synthesis of these molecules through diastereo- and enantioselective catalysis of the fluoral-ene reaction. Furthermore, we discuss the remarkable phenomena that the transition temperature and the phase sequence depend critically on the diastereomeric excess (% de) of the *ul*⁵ ($R_{\alpha}S_{\beta}$)-diastereomers. We refer to the phenomena as diastereotropic ones.

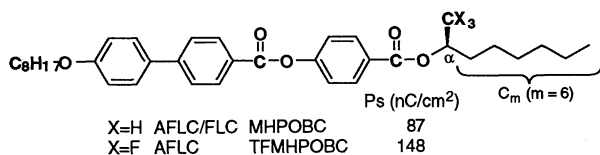
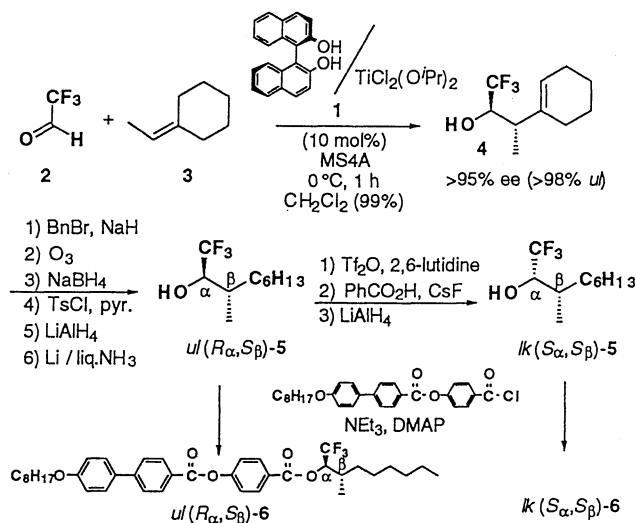


Figure 1.

Diastereomeric LC molecules are synthesized diastereo- and enantioselectively through the chiral titanium complex-catalyzed carbonyl-ene reaction⁶ of fluoral (2) with ethylenecycloalkanes (3), which we have previously reported to be an efficient route to highly diastereo- and enantioselective synthesis of α -trifluoromethyl- β -methyl-substituted carbinols (4).⁷ Fluoral-ene reactions were carried out using a (*R*)-binaphthol-derived chiral titanium catalyst ((*R*)-1)⁸ according to a previously reported procedure⁷ outlined in Scheme 1. Product ratios were determined



Scheme 1.

by capillary GLC analysis (PEG 20M, 25m). The enantiomeric purity of the product was determined by ¹H NMR (300 MHz) spectral analysis of the (*S*)- and (*R*)-MTPA ester derivatives of the products. The absolute stereochemistry of the product was determined by the Mosher method. Thus, the *ul* ($R_{\alpha}S_{\beta}$)-alcohols (4) were obtained in almost quantitative yield in more than 95% ee and 95% de. Protection of the alcohol, ozonolysis, reduction, and de-protection sequence lead to the *ul* ($R_{\alpha}S_{\beta}$)-diastereomer (5) of the chiral portion in LC molecules in essentially stereo-pure form (>95% ee, >95% de). Inversion of stereochemistry of the α -hydroxy group through the triflate derivative with benzoic acid and cesium fluoride⁹ in DMF at room temperature afforded stereochemically pure *lk* ($S_{\alpha}S_{\beta}$)-diastereomer (5) (>95% ee, >95% de). Standard esterification of *ul*- and *lk*-5 afforded the diastereomeric LC molecules, *ul*- and *lk*-6, respectively.

The phase transition temperatures of 6 were determined in varying the ratio of the diastereomeric mixture of the *ul*- and *lk*-diastereomers (Figure 2).¹⁰ These diastereomeric LC molecules show a direct transition from SmA to SmCA* in the region of high % de for *ul*-diastereomer, while SmC* is injected in the *lk*-diastereomer region. Although we attempted to observe the electric-field-induced SmCA*-SmC* phase transition, the phase transition from SmCA* to SmC* phase did not occur for *ul*-6. Furthermore, *ul*-diastereomers have a wider SmCA* temperature range of more than 10 degrees than *lk*-diastereomers. Thus, the SmCA* phase tends to be stabilized in *ul*-diastereomers. Furthermore, the electro-optic response of *ul*-diastereomers (6) showed AF double-loop-hysteresis. By contrast, *lk*-

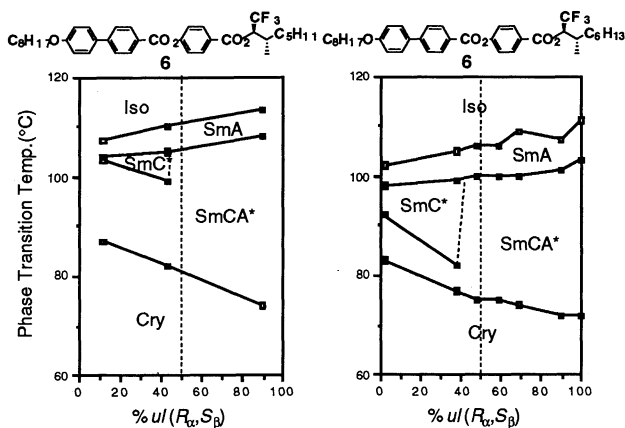


Figure 2.

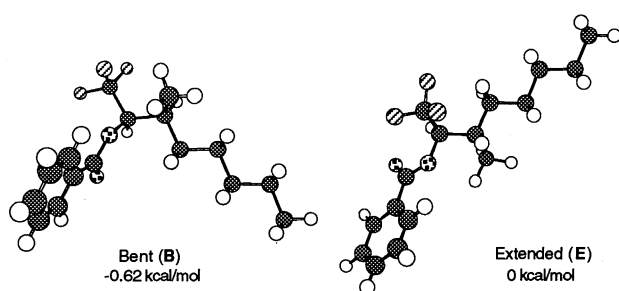


Figure 3.

diastereomers (**6**) exhibited single-loop-hysteresis, which is characteristic to FLC. These results suggest that the anti-ferroelectric property of *ul*-diastereomers is due to the bent conformation (**B**),¹¹ preferentially localized by *ab initio* (RHF/6-31G*) calculations on *ul*-PhCO₂CH(CF₃)CH(CH₃)C₅H₁₁ (Figure 3).¹²

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