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

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(Received June 3, 1996)

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_α,S_β)-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_α,S_β)-diastereomers. We refer to the phenomena as diastereotropic ones.

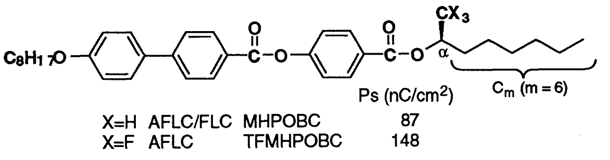
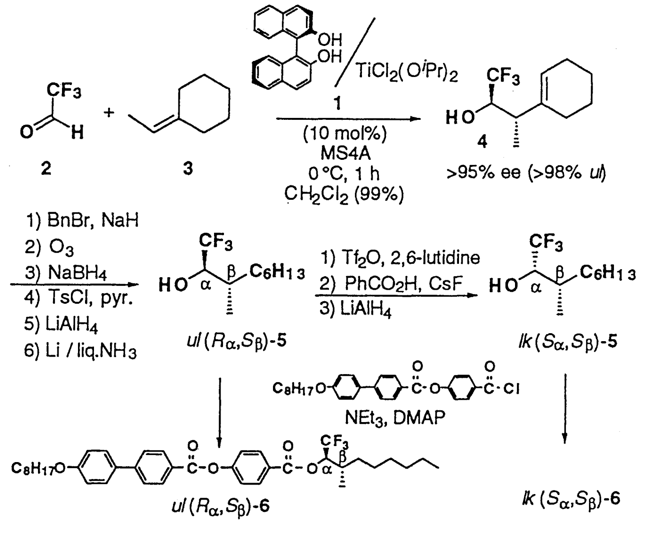


Figure 1.



Scheme 1.

Diastereomeric LC molecules are synthesized diastereo- and enantioselectively through the chiral titanium complex-catalyzed carbonyl-ene reaction[6] of fluoral (**2**) with ethylidenecycloalkanes (**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 procedure[7] outlined in Scheme 1. Product ratios were determined by capillary GLC analysis (PEG 20M, 25m). The enantiomeric purity of the product was determined by ^{1}H 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_α,S_β)-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_α,S_β)-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 fluoride[9] in DMF at room temperature afforded stereochemically pure *lk* (S_α,S_β)-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 varing 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-hysterisis. By contrast, *lk*-

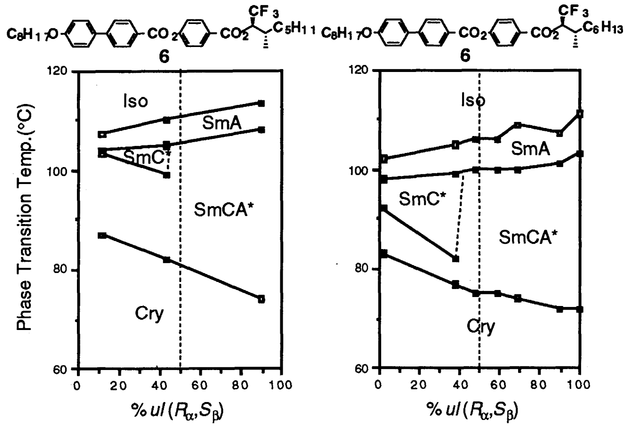


Figure 2.

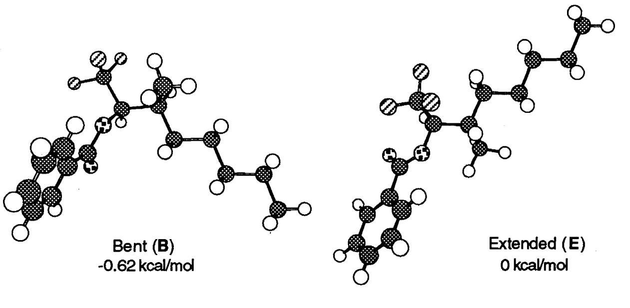


Figure 3.

diastereomers (**6**) exhibited single-loop-hysterisis, 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*-$PhCO_2CH(CF_3)CH(CH_3)C_5H_{11}$ (Figure 3).[12]

We are grateful to Professors Atsuo Fukuda, Hideo Takezoe, Tomoya Kitazume, and Tamejiro Hiyama of Tokyo Institute of Technology for their encouragement and useful discussions.

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