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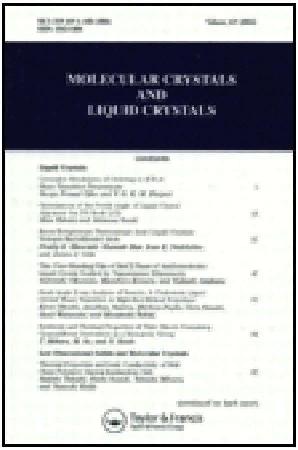

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Diastereomer Liquid Crystalline CF_3 Molecules: Conformational Probe for (Anti)Ferroelectricity and Spontaneous Resolution of the Racemates

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Version of record first published: 24 Sep 2006

To cite this article: Koichi Mikami, Tomoko Yajima, Jun Kojima, Masahiro Terada, Susumu Kawauchi, Hiroko Shirasaki, Kenji Okuyama, Yoshiichi Suzuki, Ichiro Kobayashi, Yoichi Takanishi & Hideo Takezoe (2000): Diastereomer Liquid Crystalline CF_3 Molecules: Conformational Probe for (Anti)Ferroelectricity and Spontaneous

Resolution of the Racemates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 346:1, 41-49

To link to this article: http://dx.doi.org/10.1080/10587250008023864

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Mol. Cryst. Liq. Cryst., 2000, Vol. 346, pp. 41-49
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Diastereomeric α- or β-CF_3 liquid crystalline molecules (LCs) with *double stereogenic centers* are reported as conformational probes for the bent (L-shape) conformation of antiferroelectric LCs. The diastereomeric LCs show their intriguing features that the racemic composition for both diastereomers self-assemble into the enantiomeric domain spontaneously to exhibit the electrooptic switching.

Keywords: antiferroelectricity; ferroelectricity; conformation; spontaneous resolution; MHPOBC analogues; TFMHPOBC analogues

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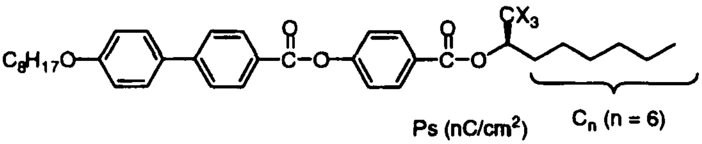
INTRODUCTION

A number of molecules that show a ferroelectric (F) phase or an anti-ferroelectric (AF) phase such as α-methyl-substituted MHPOBC and the α-trifluoromethyl analogue, TFMHPOBC with greater spontaneous polarization (Ps), have been prepared [1] and their physical properties have been investigated because of potential application in electrooptic devices for liquid-crystalline displays (LCDs).



			Ps (nC/cm^2)
X=H	AFLC/FLC	MHPOBC	87
X=F	AFLC	TFMHPOBC	148

An attempt to correlate the molecular structure of the AFLC molecules to the appearance of the AF (SmCA*) phase has been carried out. However, only a limited type of AFLC molecules have been reported thus far, containing a chiral alkyl terminus with a ***single stereogenic center*** such as MHPOBC and TFMHPOBC, wherein the odd-even effect is often observed; The AFLC SmCA* phase appears in the molecules with an even numbered (n) alkyl chain. The FLC SmC* phase appears in molecules with an odd n.

EXPERIMENTAL

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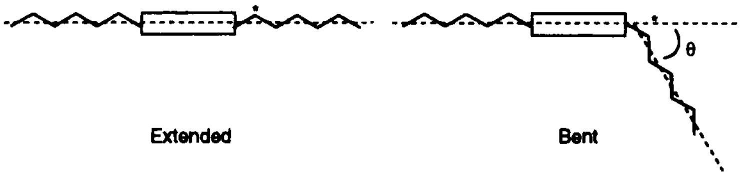
The LC material was sandwiched between glass plates to prepare a 2.7 μm-thick homogeneously aligned cell by rubbing. Optical transmittance *vs*, applied triangular wave electric field at an indicated temperature. The electric response was measured by applying a 1 Hz triangular wave electric field to the cell under the crossed polarizers so that one of the uniform domains becomes dark.

RESULTS AND DISCUSSION

Conformational Probe for Antiferro-Electricity

For AFLCs, either a bent or extended conformer is proposed on the chiral alkyl terminus. The extended conformer is necessarily proposed for a main chain polyester LC[2]. By contrast, X-ray crystallographic studies showed the bent conformations of (TF)MHPOBC in its crystalline phase[3]. However, it is very difficult to determine the SmCA* structure by X-ray diffraction (XRD), because of the liquid-like order rather than the crystalline order in smectic layers.



In order to investigate the relationship between the conformation and AF properties, we designed diastereomeric molecules with *double stereogenic centers*, β-Me-substituted TFMHPOBC analogues with odd and even numbered (5 and 6) chiral alkyl chains (n)[4]. The diastereomeric β-Me-TFMHPOBC analogues were

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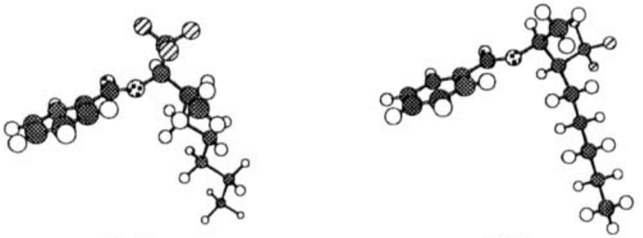
synthesized highly diastereo- and enantioselectively by the chiral titanium complex-catalyzed fluoral-ene reaction with ethylidenecycloalkanes[5]. We thus proposed the bent (L-shape) conformation as the key for AFLCs [6].

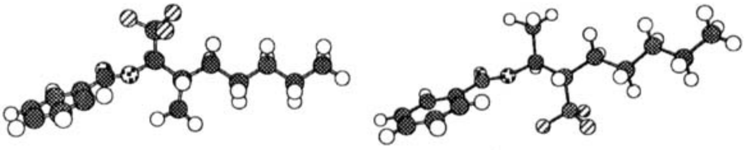
On the basis of our paradigm of bent conformation for AFLC molecules, we further designed the (*S**,*S**)-diastereomer of β-CF_3-MHPOBC analogues (Figure 1). Indeed, (*S*,*S*)-diastereomer of the $PhCO_2CH(CH_3)CH(CF_3)C_5H_{11}$ is preferentially localized in the bent conformation by *ab initio* (RHF/6-31G*) calculations; (*S*,*S*)-

(*R*α, *S*β)-β-Me-TFMHPOBC analogue (*S*α,*S*β)-β-CF_3-MHPOBC analogue



Bent
−0.62 kcal/mol

Bent
−1.96 kcal/mol



Extended
0.0 kcal/mol

Extended
0.0 kcal/mol

FIGURE 1 *Ab-initio* calculations (Ar = Ph).

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$PhCO_2CH(CH_3)CH(CF_3)C_5H_{11}$ is more stabilized up to 1.96 kcal/mol than the extended conformation.

As expected, (*S*,*S*)-diastereomers have a much wider SmCA* temperature range (0 ~ 101 °C) than the (*R*,*S*)-diastereomer of β-CH_3-TFMHPOBC analogues (72 ~ 103 °C) (Figure 2). Thus, the SmCA* phase is more stabilized by the bent-favored (*S*,*S*)-diastereomers of β-CF_3-MHPOBC analogues. These results further strengthen our bent paradigm for AFLCs.

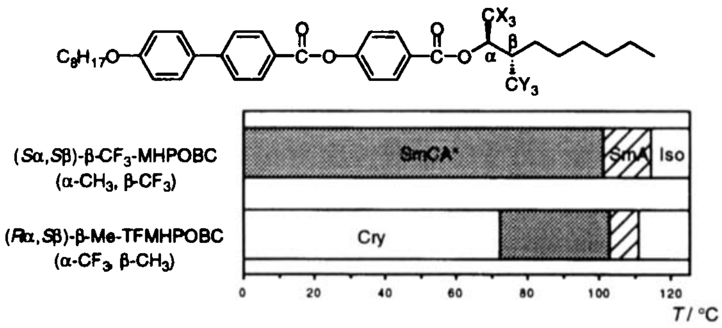

FIGURE 2 Phase transition temperatures.

Spontaneous Resolution of the Racemates

The phase sequences and transition temperatures for β-CF_3-MHPOBC and β-CH_3-TFMHPOBC analogues are taken with varying enantiomeric excesses for the (*R*,*S*)- and (*S*,*S*)-diastereomers. Usually, the direct transition from SmA to SmCA* takes place in high % ee and SmC* is injected between SmA and SmCA* in the racemic region of AFLC molecules with ***single stereogenic center*** such as (TF)MHPOBC. However, we found a direct transition from SmA to a yet unknown (SmX) phase in the racemic composition for either (*R**,*S**)- or (*S**,*S**)-diastereomers (Figure 3)[7].

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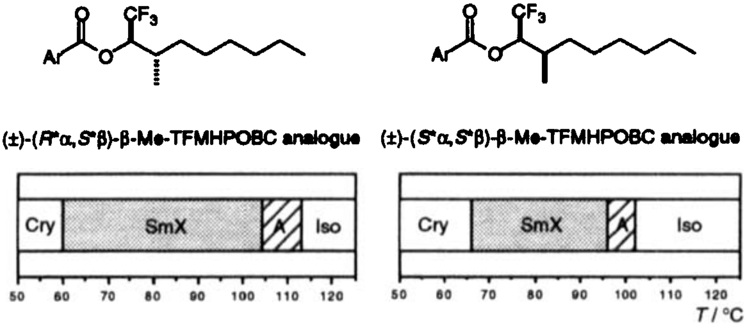

FIGURE 3 Phase transition temp. of (±)-(*R**,*S**)- and (±)-(*S**,*S**)-β-Me-TFMHPOBCs.

Of interest is the spontaneous resolution of the racemic LC molecules into the enantiomeric domains. This can be observed by the electrooptic response of racemic LC-diastereomers. The racemic diastereomers shows an unprecedented shape of hysteresis for either diastereomers (Figure 4).

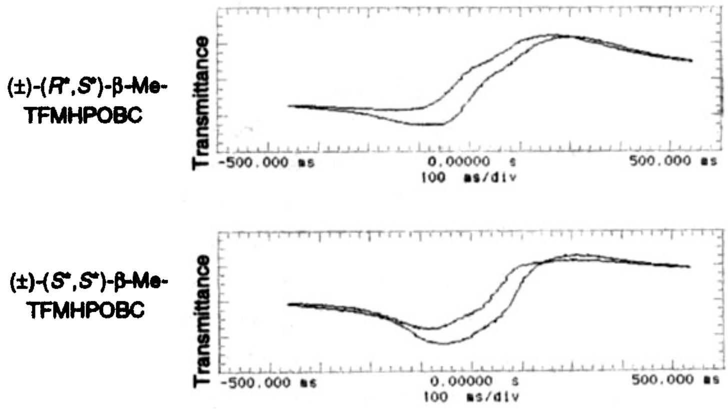

FIGURE 4 Electrooptic switching (at 80 °C) of (±)-β-Me-TFMHPOBC.

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Pasteur's first observation of crystalline salt of "acide racemique" (Na NH_4 tartrate·$4H_2O$) in two enantiomorphos forms not only uncovered existence of enantiomeric molecules, but stimulated the development of modern structural theory and molecular asymmetry in nature. Ever since, chemists have been fascinated to find out that racemic molecules are spontaneously resolved to give a conglomerate[8] in a distinct phase from static crystalline state. However, only few example of chiral symmetry breaking from racemic molecules has so far been reported, for example, in Langmuir monolayer films by atomic force microscopy (AFM)[9]. A similar two-dimentional (2-D) conglomerate has been observed on a crystalline graphite surface by scanning tunneling microscopy (STM)[10]. Quite recently, formation of macroscopic chiral domains rather than spontaneous resolution was reported in a fluid smectic phase of achiral molecules[11]. We have herein reported spontaneous chiral resolution of racemic CF_3-containing diastereomeric LCs with great Ps into three-dimentional (3-D) conglomerate in fluid liquid crystalline phase. The racemic composition of MHPOBC or TFMHPOBC with ***single stereogenic center*** did not so effectively show such significant electrooptic response (Figure 5). The more conformationally rigid diastereomeric TFMHPOBC analogues self-assemble into the enantiomeric domains spontaneously to exhibit the electrooptic response more effectively than the single stereogenic molecules such as TFMHPOBC or MHPOBC. The ease of spontaneous resolution is in the order; the double stereogenic β-Me-TFMHPOBC >> single stereogenic TFMHPOBC ≥ MHPOBC. These results indicate the first example of spontaneous chiral resolution in dynamic liquid crystalline state rather than in static crystalline state of Pasteur's famous system[12].

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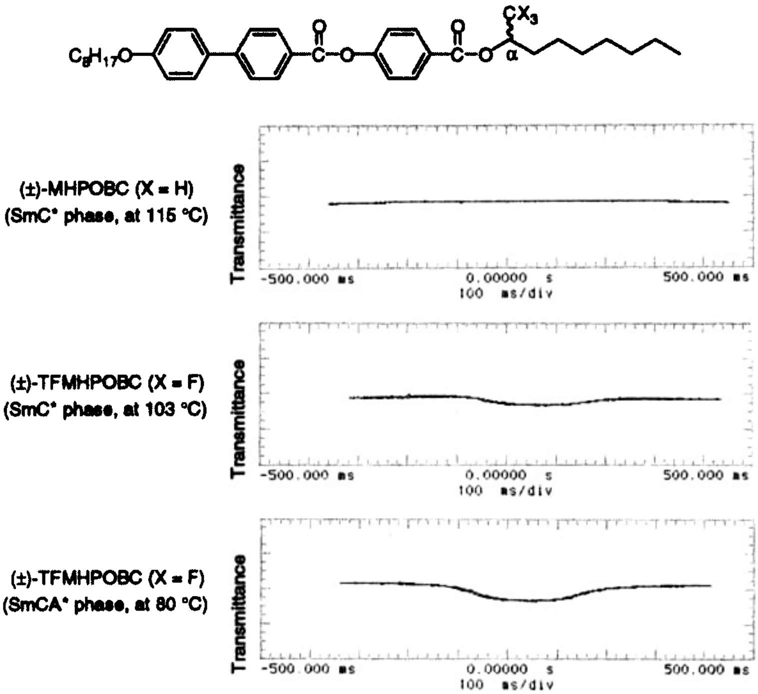

FIGURE 5 Electrooptic switching of (±)-TFMHPOBC (X = F) and (±)-MHPOBC (X = H).

CONCLUSIONS

We have thus reported the diastereomeric α- or β-CF_3 liquid crystalline molecules (LCs) with ***double stereogenic centers*** as conformational probes for the bent (L-shape) conformation of AFLCs. Furthermore, the racemic composition for both diastereomers self-assemble into the enantiomeric domain to exhibit the opto-electric switching. This is the first example of the spontaneous resolution of racemic liquid crstalline molecules in smectic phases.

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