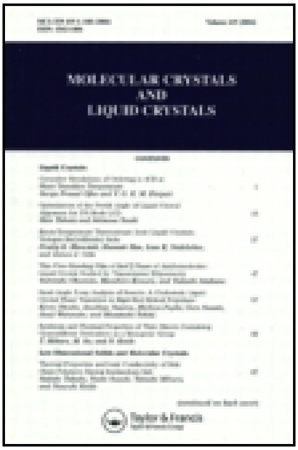

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Ichiro Kobayashi [a] , Shigeharu Hashimoto [a] , Yoshiichi Suzuki [a] , Tomoko Yajima [b] , Susumu Kawauchi [b] , Tatsuya Imase [b] , Masahiro Terada [b] & Koichi Mikami [b]

[a] Showa Shell Sekiyu K.K., Central Research Laboratory, Shimokawairi 123-1, Atsugi-shi, Kanagawa, 243-0206, Japan

[b] Department of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

To cite this article: Ichiro Kobayashi, Shigeharu Hashimoto, Yoshiichi Suzuki, Tomoko Yajima, Susumu Kawauchi, Tatsuya Imase, Masahiro Terada & Koichi Mikami (1999): Effects of Conformation of Diastereomer Liquid Crystals on the Preference of Antiferroelectricity, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 328:1, 131-137

To link to this article: http://dx.doi.org/10.1080/10587259908026053

*Mol. Cryst. Liq. Cryst.*, 1999, Vol. 328, pp. 131-137
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Printed in Malaysia

# Effects of Conformation of Diastereomer Liquid Crystals on the Preference of Antiferroelectricity

ICHIRO KOBAYASHI[a], SHIGEHARU HASHIMOTO[a],
YOSHIICHI SUZUKI[a], TOMOKO YAJIMA[b], SUSUMU KAWAUCHI[b],
TATSUYA IMASE[b], MASAHIRO TERADA[b] and KOICHI MIKAMI[b]

*[a]Showa Shell Sekiyu K.K., Central Research Laboratory, Shimokawairi 123–1, Atsugi-shi, Kanagawa 243–0206, Japan and [b]Department of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152–8552, Japan*

We have already synthesized a new type of antiferroelectric liquid crystals (AFLCs) with double stereogenic centers, β-methyl-substituted TFMHPOBC(4-(1-trifluoromethyl-heptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate) and its analogues, based on α-trifluoromethyl-β-methylcarbinol, and its conformational effects on the antiferroelectricity[1–5]. Now we report another new type of AFLC and ferroelectric liquid crystals (FLC) with double stereogenic centers bearing β-trifluoromethylcarbinol. which can be regarded as a β-trifluoromethyl-substituted MHPOBC(4-(methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate) analogue, and examined its properties such as the phase transition. From these results and *ab initio* calculations using Gaussian 94 program, we conclude that their conformations strongly affect their preference of antiferroelectricity and that the bend-like structure is more essential for the appearance of antiferroelectricity, than the extended-like one.

*Keywords:* antiferroelectricity; ferroelectricity; conformation; diastereomer; AFLC

## INTRODUCTION

Since the discovery of AFLCs, a lot of studies have been performed from the standpoints of not only scientific interests but also technological applications to electro-optic devices, and now AFLC display attracts much interest as one of the alternative of CRT display because of its wide view angle and short response time.

In terms of scientific interests, MHPOBC and TFMHPOBC have been regarded as two representatives of AFLCs. In order to clarify the characteristic properties of those compounds, dielectric measurements, electro-optic measurements, conoscopic observation, circular dichromism measurements, texture observation, X-ray diffraction analysis[6,7,8], infrared spectroscopy, Raman scattering measurements and adiabatic calorimetry measurement have been carried out. In spite of those experiments, it has not been clearly understood yet the relationship between molecular chirality and the antiferroelectric properties such as the phase transition and the spontaneous polarization in the chiral part of molecules.

In order to investigate the conformational arrangement of chiral alkyl termini requisite for AFLC properties, we designed and synthesized some diastereomer LC molecules with two stereogenic centers, α-trifluoromethyl-β-methyl aryl esters on the bases of the fluoral-ene reaction[9,10] and reported their diastereomeric and enantiomeric effects on the antiferroelectricity[1-5].

In order to make further investigation into the relationship between molecular chirality and the antiferroelectric properties, we designed and synthesized another new type of diastereomer LC molecules with two stereogenic centers bearing β-trifluoromethylcarbinol.

In this report, the relationship between conformational arrangement of LC molecules and the antiferroelectric properties such as the antiferroelectricity

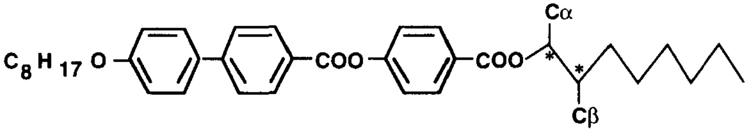
(SmCA$^*$) and the spontaneous polarization was discussed.

## PREPARATION OF LC MOLECULES 1-6

### Chemical Structure and Structural Formula of LC Molecules 1-6

The relationship between conformational arrangement and the antiferroelectric properties were investigated on diastereomer LC compounds 2 ($R_\alpha$,$S_\beta$) and LC 3 ($R_\alpha$,$R_\beta$), which are β-trifluoromethyl-substituted MHPOBC (MHPOBC-8-7) LCs, and LC 5 ($R_\alpha$,$R_\beta$) and LC 6 ($R_\alpha$,$S_\beta$), which are β-methyl-substituted TFMHPOBC (TFMHPOBC-8-7) LCs.

We also used LC compound 1 as a MHPOBC analogue (MHPOBC-8-7) and LC compound 4 as a TFMHPOBC analogue (TFMHPOBC-8-7) to compare the antiferroelectric properties of compounds 2,3 and 5,6, respectively. The chemical structures and structural formulae of chiral alkyl termini of LC compounds 1-6 are shown in Figure 1.



| LC molecule | Cα | Cβ | formula |
|---|---|---|---|
| 1 | $CH_3$ | H | $R_\alpha$ |
| 2 | $CH_3$ | $CF_3$ | $R_\alpha$,$S_\beta$ |
| 3 | $CH_3$ | $CF_3$ | $R_\alpha$,$R_\beta$ |
| 4 | $CF_3$ | H | $R_\alpha$ |
| 5 | $CF_3$ | $CH_3$ | $R_\alpha$,$R_\beta$ |
| 6 | $CF_3$ | $CH_3$ | $R_\alpha$,$S_\beta$ |

FIGURE 1 Chemical structure and structural formula of LC compounds 1-6

## RELATIONSHIP BETWEEN CONFORMATIONAL ARRANGEMENT OF LC MOLECULES 1-6 AND THEIR ANTIFERROELECTRIC PROPERTIES

### Relationship between conformation of LC molecule and its phase transition

Phase transition temperatures of 2 ($R_\alpha$,$S_\beta$), 3 ($R_\alpha$,$R_\beta$) and 1 (MHPOBC-8-7) are shown in Figure 2 along with those of 5 ($R_\alpha$,$R_\beta$), 6 ($R_\alpha$,$S_\beta$) and 4 (TFMHPOBC-8-7).

Phase transition temperatures were determined by the microscopic observations of the textures and the electro-optic response by using anti-parallel rubbing cell with a gap, about 2 μms and as an alignment film polyimide was used.

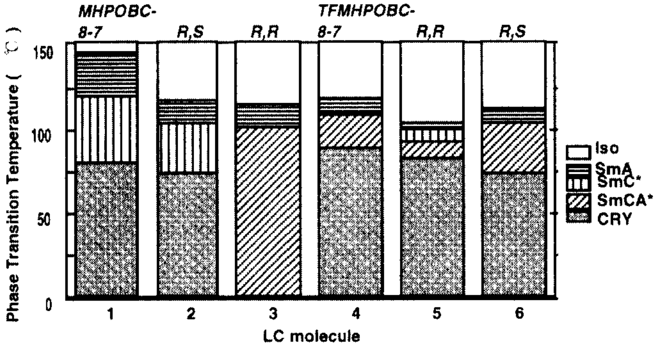


FIGURE 2 Phase transition temperatures of 1-6 on heating run.

1-3: β-Trifluoromethyl-substituted LCs (2,3) had lower transition temperatures than MHPOBC-8-7 (1) and only $R_\alpha$,$R_\beta$ (3) showed SmCA$^*$. 4-6: β-Methyl-substituted AFLCs (5,6) had also lower transition temperatures than TFMHPOBC-8-7 (4) and SmC$^*$ was injected only in $R_\alpha$,$R_\beta$ (5) and $R_\alpha$,$S_\beta$ (6) showed the widest temperature range of SmCA$^*$ phase.

These results suggest that both β-trifluoromethyl- and β-methyl-substitution of LCs with single stereogenic center could lower their transition temperatures. And their molecular structures strictly affected their appearance of SmCA$^*$, that is in β-trifluoromethyl-substituted LCs $R_\alpha,R_\beta$ was superior for the appearance of SmCA$^*$, but in β-methyl-substituted LCs $R_\alpha,S_\beta$ was superior for that.

Relationship between conformation of LC molecule and its spontaneous polarization

The magnitudes of spontaneous polarization of LC molecule 1-6 are shown in Figure 3. Their magnitudes were measured using Sawyer Tower circuits (100 Hz) for the cell described above.

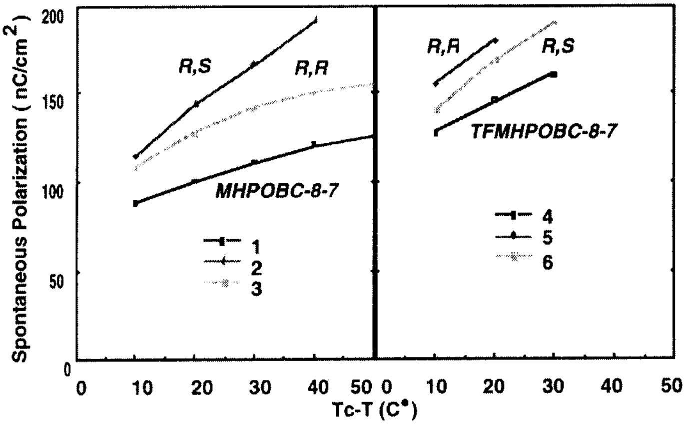


FIGURE 3 Magnitudes of spontaneous polarizations of LC 1-6.

For 1-3, β-trifluoromethyl-substituted LCs had higher magnitudes than MHPOBC-8-7 (1) and $R_\alpha,S_\beta$ (2) had the highest one among them. For 4-6, β-methyl-substituted AFLCs had also higher magnitudes than TFMHPOBC-8-7 (4) and $R_{\alpha}$,$R_{\beta}$ (5) had the highest one among them.

These results suggest that both β-trifluoromethyl- and β-methyl-substitution of LCs with single stereogenic center could rise their magnitudes of spontaneous polarization and their molecular structures could surely affect them.

## Relationship between conformation of LC molecules and their *Ab initio* calculations

*Ab initio* (RHF/6-31G*) calculations on chiral alkyl termini were carried out[5], and their results were described in Table 1.

TABLE 1 *Ab initio* calculations on chiral alkyl termini of 1-6

| LC molecule | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| bend -like (kcal/mol) | -0.84 | -0.34 | -1.96 | -1.15 | -0.24 | -0.62 |
| extended-like* (kcal/mol) | 0 | 0 | 0 | 0 | 0 | 0 |

*To clarify the energy difference between bend-like and extended-like structure, the energy of extended-like one was regarded as 0.

Among 1-3, $R_{\alpha}$,$R_{\beta}$ (3), which only showed SmCA$^*$, is the most likely to take bend-like conformation. In addition, among 4-6, $R_{\alpha}$,$R_{\beta}$ (5), which only appeared SmC$^*$, is the most preferable to take extended-like conformation.

These results supported that in both β-substitutions, bend-like structure could be superior to extended one for the appearance of SmCA$^*$.

## CONCLUSION

From above results, we concluded as follows;

1) Either of β-trifluoromethyl- or β-methyl-substitution of LCs with single stereogenic center could lower its phase transition temperature, and rise magnitude of spontaneous polarization.

2) Structural formula of chiral alkyl termini, that is $R_{\alpha},R_{\beta}$ or $R_{\alpha},S_{\beta}$, could greatly affect not only the appearance of $SmCA^{*}$ but also the magnitude of spontaneous polarization. This could be the conformational effects on the phase transition and spontaneous polarization.

3) In these diastereomer LCs, bend-like structure could be more essential for the preference of $SmCA^{*}$ than the extended-like one.

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