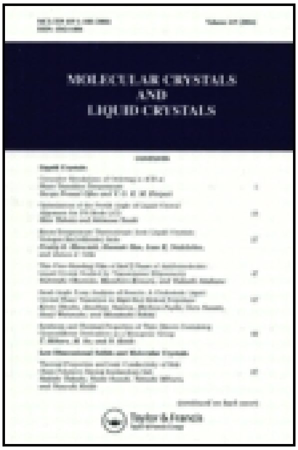

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Version of record first published: 24 Sep 2006

To cite this article: Yoshiichi Suzuki, Shunichi Koide, Yoshihiko Aihara, Ichiro Kawamura, Hitoshi Suenaga & Tomoya Kitazume (2000): Effect of Molecular Polarity and Conjugated System on Antiferroelectricity in AFLC's, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 351:1, 351-360

To link to this article: http://dx.doi.org/10.1080/10587250008023285

Mol. Cryst. and Liq. Cryst., 2000, Vol. 351, pp. 351-360
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Effect of Molecular Polarity and Conjugated System on Antiferroelectricity in AFLC's

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Series of pyrimidine and pyridine analogous compounds have been developed in order to interpret the relationship between stability of antiferroelectricity and the conjugation along the long axis of the molecule. On the appearance of antiferroelectricity, the longitudinal polarization of whole molecules promotes to stabilize the antiferroelectricity.

Keywords: antiferroelectricity; Molecular Polarity; Conjugated System

1. INTRODUCTION

Antiferroelectric Liquid Crystals (AFLC's) typically reported as TFMHPOBC[1] have already demonstrated their potential for exploring several new phenomena as well as for applying electro-optic devices for LCD's. AFLC materials show quite specific properties such as a tristable switching , sharp DC threshold. and double loop hysteresis. Hence extensive studies to interpret the appearance of antiferroelectricity have led to understand the correlation between the molecular structure of the

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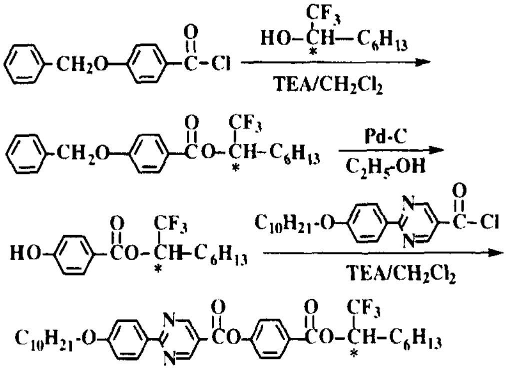
AFLC molecules and the appearance of SmCA* phase[2]. However, the relationship between molecular structure and physical properties, especially stability of antiferroelectricity has not been fully understood yet.

In this study, well designed liquid crystal materials having pyridine and pyrimidine core structure have been synthesized by using fluorine containing chiral synthons with a CF_3 group directly linked to the chiral center. The relationship between phase range and transition temperature of antiferroelectric phase and the conjugation along the long axis of the molecule was investigated by considering molecular polarity.

2. EXPERIMENT

A series of TFMHPDPPmC analogues were synthesized as described below (see SCHEME 1). 4-hydroxybenzoic acid was used as the starting materials. 1-(trifluoromethyl)heptyl 4-hydroxybenzoic acid was obtained by the reaction of 4-benzyloxybenzoic acid chloride and (R)-(+)-1-trifluoromethylheptanol, followed by the deprotection using Pd-carbon catalyst in ethanol. Series of compounds were synthesized by the esterification of (R)-(+)-1-(trifluoromethyl) heptyl 4-hydroxybenzoate



Scheme-1 The synthesis of compounds:
4'-(1-trifluoromethylheptyloxy)phenyl-4-yl
4'-decyloxypyrimidinylphenyl-4-carboxylate

and 4-decyloxy-pyrimidinyl phenyl -4'- carboxylic acid chlorides with triethylamine in CH_2Cl_2. Other series of analogues were also obtained in analogy with the synthetic route of series of TFMHPDPPmC analogues. Texture and phase transition temperature were determined using a polarizing optical microscope in conjunction with a Mettler FP80HT hot stage at a rate of 1.0 °C /min and RIGAKU TAS-200 differential scanning calorimeter. To evaluate the electrooptical properties, homogeneously aligned cells of 2-μm thickness were prepared by rubbing thin polyimide films coated on the substrate plates.

The spontaneous polarization was measured by the triangular wave voltage method. The threshold voltage V_{AF-F} and the critical frequency defined as the transition frequency from antiferroelectric phase to ferroelectric one were obtained from Voltage-Transmission curve commonly measured by applying a triangular wave voltage; the crossed polarizers were set for parallel or perpendicular to the smectic layer direction.

3. RESULTS AND DISCUSSION

Series of TFMHPDPmPC analogues

Series of TFMHPDPmPC analogues exhibited the phase sequence of Iso-SmA-SmCA*. Fluorine-substitution in the core reduced the thermal stability and lowered the temperature range of SmCA* phase as shown in FIGURE 1. 3-fluoro-substitution in benzoate ring was more dominant in the 2-fluoro-substitution over the wide temperature range of SmCA* phase.

Series of TFMHPDPPmC analogues

In series of TFMHPDPPmC analogues where only the position of the two nitrogen of the pyrimidine units is changed, the temperature range of SmCA* phase became very narrow and phase sequence changed from Iso-SmA-SmCA* to SmCA* by means of the fluoro-substitution as shown in FIGURE 2.

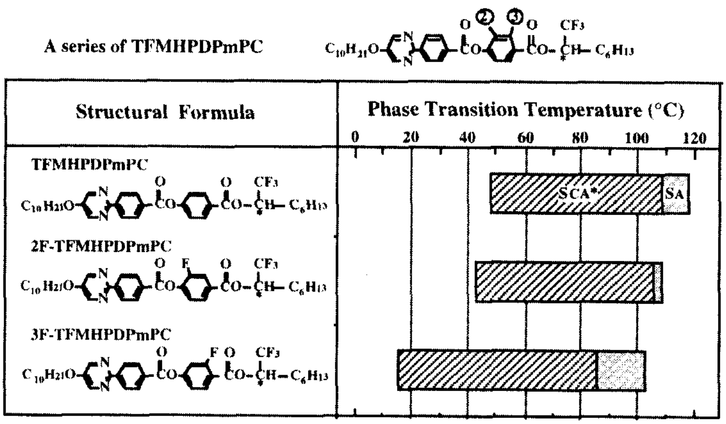


FIGURE 1 Phase Sequence and Transition Temperature in a series of TFMHPDPmPC Pyrimidine analogues.

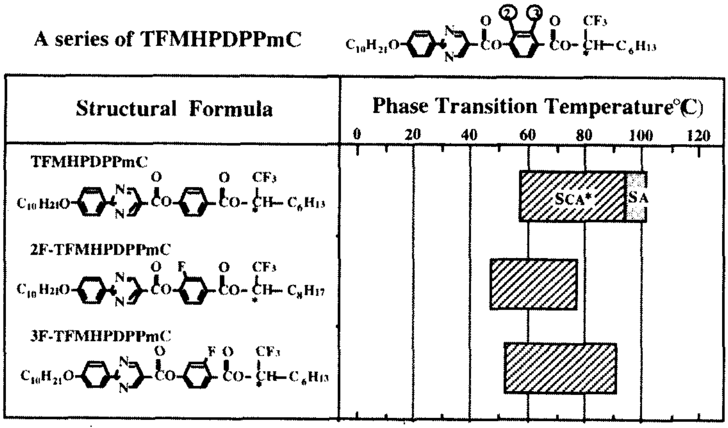


FIGURE 2 Phase Sequence and Transition Temperature in a series of TFMHPDPPmC Pyrimidine analogues.

Thus, fluorine-substitution in the core structure resulted in the lower thermal stability of SmCA* phase and the position of nitrogen in pyrimidine ring in the core structure was supposed as an important factor to appear SmCA* phase.

Series of TFMHPOPm2FPC analogues

Fluoro-substitution in the phenyl directly connected with pyrimidine ring loweded the thermal stability of the liquid-crystalline phase compared with TFMHPDPmPC as indicated in FIGURE 3. Furthermore, in case of substitution of hydrogen by fluorine in the phenyl of benzoate, the temperature range of SmCA* in 2F-TFMHPOPm2FPC became very narrow about 7 °C in comparison with corresponding 3F-substituent. Therefore, 3-fluoro-substituent in TFMHPOPm2FPC predominated over 2-fluoro-substituent as a result of enhancing the molecular polarity of AFLC's.

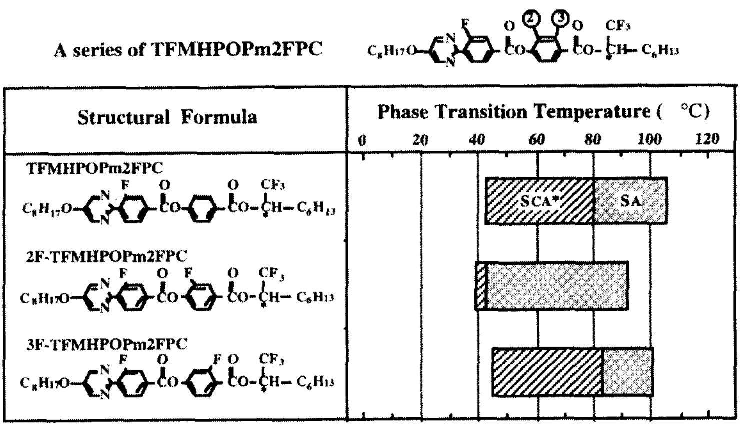


FIGURE 3 Phase Sequence and Transition Temperature in a series of TFMHPOPm2FPC Pyrimidine analogues.

Series of TFMHPDPPrC analogues

Introduction of pyridine ring in the core structure was no effect on liquid crystalline properties intensively in comparison with a series of TFMHPDPPmC analogues as shown in FIGURE 4.

It was considered that the effect of the excluded volume based on pyridine ring on the stability of antiferroelectric SmCA* phase would affect less than that of pyrimidine ring. The substituent effect of fluorine in the core structure occurred in a similar manner as describe the previous section.

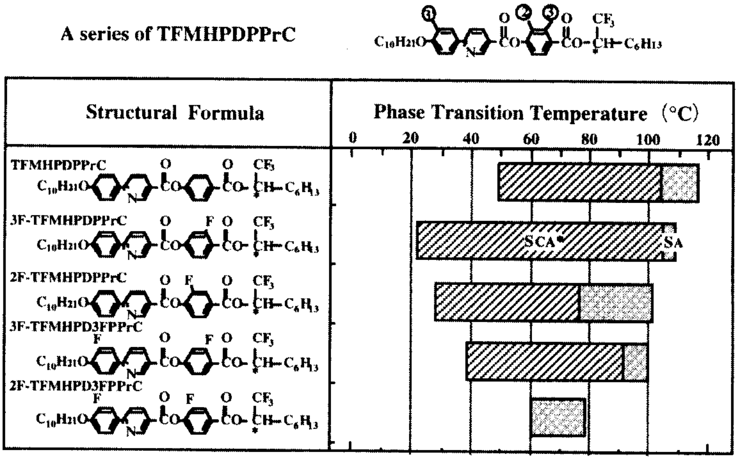


FIGURE 4 Phase Sequence and Transition Temperature in a series of TFMHPDPPrC Pyridine analogues.

The relationship between threshold voltage and spontaneous polarization

We had already proposed that the magnitude of spontaneous polarization (Ps), closely related to the polarization of chiral part, was one of the significant factors for the appearance of the antiferroelectricity[3]. Also, some of the important interactions among intersmectic layers has been reported; a pairing model[4] based on the transverse pairing of the dipole moments located in the chiral alkyl and Px model[5]: spontaneous polarization exist in the vicinity of layer boundary parallel to the tilt plane.

Based on those concepts, the contribution of Ps, which indicated the longitudinal polarization of AFLC molecule, to stabilizing the antiferroelectricity was investigated. The spontaneous polarization was plotted against threshold voltage V_{AF-F} as shown in FIGURE 5.

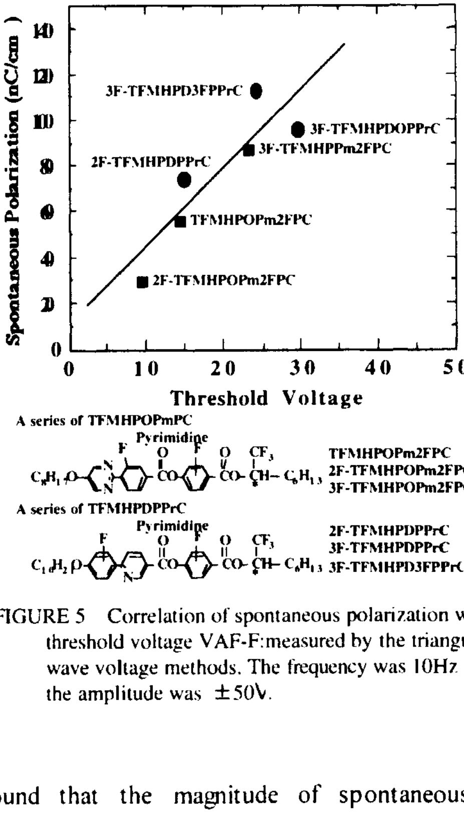


FIGURE 5 Correlation of spontaneous polarization with threshold voltage VAF-F:measured by the triangular wave voltage methods. The frequency was 10Hz and the amplitude was ±50V.

It was found that the magnitude of spontaneous polarization proportionally correlated threshold voltage V_{AF-F}. Furthermore SmCA* phase was rather stabilized in 3- or 2,3-fluoro-substituent than in 2-fluoro-substituent because of the fact the higher voltage indicates more stable SmCA* phase. This fact implies that incorporation of the fluorine into the core controlled the longitudinal polarization of the AFLC molecule and that fluoro-substitution functioned to intensify the molecular polarization along the long axis of the AFLC molecule, which resulted in producing the more stable antiferroelectric SmCA* phase.

Critical frequency and threshold voltage

In the switching process of the field-induced antiferroelectric -ferroelectric phase transition, the critical frequency and $V_{AF\text{-}F}$ were presumed to be proportional to the stability of the SmCA* phase; i.e. the higher critical frequency and larger $V_{AF\text{-}F}$ the AFLC has, the more stable SmCA* phase appeared. In FIGURE 6, the critical frequency was plotted against $V_{AF\text{-}F}$ in order to investigate the stability of the SmCA* phase. The critical frequency showed proportional co- relation with the threshold voltage $V_{AF\text{-}F}$, that is, the critical frequency increased in the order of 3- or 3,3-fluoro-substituent and 2-fluoro- substituent. The fluorine substitution in the core part such as 3-fluoro substituent, enhanced the polarization of the long axis of the molecule, which results in the strong stabilization of

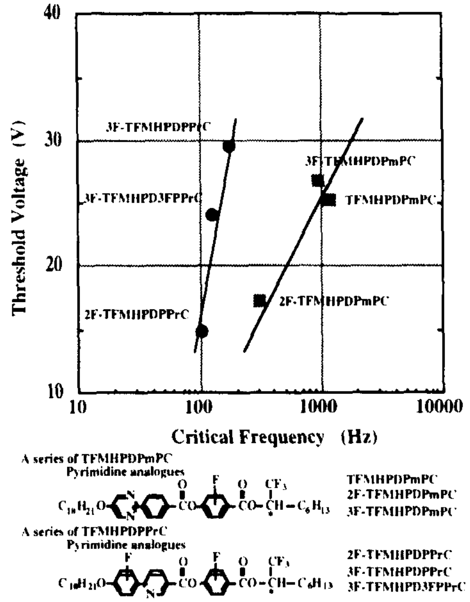


Figure 6 Correlation of critical frequency with threshold voltage VAF-F:measured by the triangular wave voltage methods. The frequency was 10Hz and the amplitude was ±50V.

antiferroelectric SmCA* phase based on the increase in the critical frequency. To the contrary, 2-substituent depressed the longitudinal polarization which results in suppressing the stability of the SmCA* phase.

4. CONCLUSIONS

In the series of each pyrimidine and pyridine analogues, the molecular design by introducing the fluorine into the core part was performed in order to investigate the factor of stabilizing antiferroelectric SmCA* phase. Each pyrimidine and pyridine core structure which had the dipole moment of nitrogen was appropriate to form the antiferroelectric molecular ordering in the case of enhancing the molecular polarity. Moreover, fluorine substitution to phenyl ring stabilized antiferroelectricity in the case of the molecular polarity was intensified by the dipole moment of C-F bonding.

In summary, we proposed the longitudinal polarization of whole molecule, based on the conjugation between chiral part and core structure along the long axis of the molecule, promoted to the antiferroelectric stability (see FIGURE 7).

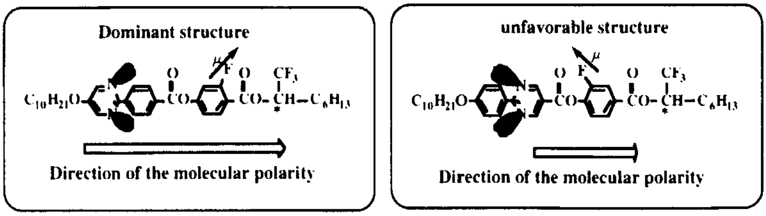


FIGURE 7 Tentative representation of the the longitudinal polarization in AFLC's having pyrimidine core structure.

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