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## Liquid Crystals

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# New antiferroelectric liquid crystals with a trifluoromethyl group at the chiral centre

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New antiferroelectric liquid crystals (AFLCs) with a trifluoromethyl group at the chiral centre were synthesized using optically active 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acid. The new AFLCs showed the phase sequence on cooling: isotropic liquid (I)-smectic A ( $S_A$ ) phase-antiferroelectric (AF) phase-crystal (Cr). In the antiferroelectric phase, a d.c.-threshold, a double hysteresis loop, a small dielectric constant value and two sharp switching-current peaks were observed. These are the first examples that are AFLCs which do not have a carbonyl moiety in the molecule.

## 1. Introduction

Since the discovery of MHPOBC [1, 2], a number of antiferroelectric liquid crystals (AFLCs) have been synthesized and many investigations reported. All known AFLCs may be classified into two types, namely AFLC materials with a methyl group at the chiral centre and those with a trifluoromethyl group. Especially, many of the methyl type of AFLCs have been synthesized and their detailed properties investigated and reported [3, 4]. On the other hand, the trifluoromethyl type of AFLC has been synthesized and investigated for application in the AFLC display. The chiral frames of AFLCs have been reported to be  $-\text{COOCH}(\text{CH}_3)R$  [3],  $-\text{COCH}(\text{CH}_3)R$  [4],  $-\text{COOCH}(\text{C}_2\text{H}_5)R$  [5],  $-\text{COOCH}(\text{C}_3\text{H}_7)R$  [5],  $\text{COOCH}(\text{CF}_3)R$  [6-8], and so on. Recently, there appeared an interesting report that a non-chiral swallow-tailed liquid crystal material exhibited the antiferroelectric-like phase [9]. From a practical point of view, this meant the discovery of a non-chiral host liquid crystal for AFLC. On the other hand, liquid crystal materials exhibiting the smectic  $O^*$  phase, which was similar to smectic  $C_A^*$ , were reported [10, 11]. These liquid crystals materials have two chiral moieties and a highly symmetrical structure.

The basic frames of a number of AFLCs are similar to those of MHPOBC, having the  $-\text{COOCH}(\text{CH}_3)R$  structure as the chiral moiety. Especially, a carbonyl moiety seemed to be an essential part of the AFLC molecules, because the reported AFLCs always had this moiety in the molecules.

However, a carbonyl moiety is not always indispensable to an AFLC. The new AFLCs reported here show the antiferroelectric state without a carbonyl moiety in

the molecule. Moreover, the new AFLCs have a characteristic structure, in which the chiral frame lies between the two aromatic moieties. A liquid crystal material having a similar structure has been reported, and the relationship between the structure and the observed phase sequence was discussed [12, 13].

## 2. Experimental

The synthesis and properties of the new AFLCs as chiral dopants for FLCs have been previously reported [14, 15]. The liquid crystalline phases were observed with a polarizing microscope (Nikon Optiphot2-POL) equipped with a heating stage (Mettler FP-82HT) and a thermal control unit (Mettler FP-90). The phase transition temperatures were determined by DSC (Seiko I&E DSC-20 and Perkin-Elmer DSC7). The electro-optical properties were examined using a polarizing microscope equipped with a photomultiplier (Hamamatu R2228) and an oscilloscope (Philips PM-3350). The dielectric constants were measured using a LCR Hi Tester (Hioki 3520), in which the applied voltage was 1.0 V and the frequency was 1 kHz. The cell gap was *c.* 1.4  $\mu\text{m}$ , and was determined by the capacitance measurements.

## 3. Results and discussion

Among the chiral dopants for FLCs two compounds exhibited antiferroelectric properties. These compounds

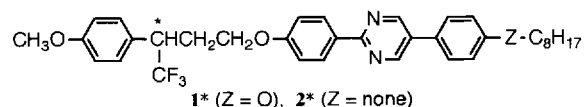


Figure 1. The structures of the new AFLCs.

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are shown in figure 1. The AFLC phase of 2-[4-[3-(4-methoxyphenyl)-4,4,4-trifluoro]butyloxy]phenyl-5-(4-octyloxyphenyl)pyrimidine (**1\***) was stable, while that of 2-[4-[3-(4-methoxyphenyl)-4,4,4-trifluoro]butyloxy]phenyl-5-(4-octylphenyl)pyrimidine (**2\***) was not stable. The phase transition temperatures and some physical properties are summarized in the table. On cooling, both compounds **1\*** and **2\*** exhibited the AFLC phase in the sequence I-S<sub>A</sub>-antiferroelectric phase-Cr. The mesophase textures of **1\*** are shown in figure 2. A typical focal-conic fan texture was observed for the smectic A phase, while a coloured striped pattern appeared for the antiferroelectric phase. The phase transition temperatures of **1\*** were higher than those of **2\***; generally phase transition temperatures of liquid crystal materials with an



(a)



(b)

Figure 2. Photomicrographs of the mesophases of **1\*** mounted between two glass slides. (a) smectic A phase,  $T = 100^\circ\text{C}$ . (b) antiferroelectric phase,  $T = 88^\circ\text{C}$ .

Table 1. Phase transition temperatures,  $P_s$  values and tilt angles.

Compound no.	Phase transition temperature/ $^\circ\text{C}^\ddagger$ (cooling)	$P_s/\text{nC cm}^{-2}$	$\theta/^\circ$
<b>1*</b>	Cr 68 AF 90 S <sub>A</sub> 106 I $^\ddagger$	112 $\ \ $	33 $\ \ $
<b>2*</b>	Cr 54 AF 58 S <sub>A</sub> 73 I $^\S$	154 $\ \ $	28 $\ \ $

$^\ddagger$  Cr indicates crystalline solid. AF indicates antiferroelectric phase. S<sub>A</sub> indicates smectic A phase. I indicates isotropic liquid.

$^\ddagger$  DSC measurement: cooling rate =  $1.5 \text{ K min}^{-1}$ .

$^\S$  DSC measurement: cooling rate =  $5.0 \text{ K min}^{-1}$ .

$\|\|$   $T = 83^\circ\text{C}$ .

$\|\|$   $T = 54^\circ\text{C}$ .

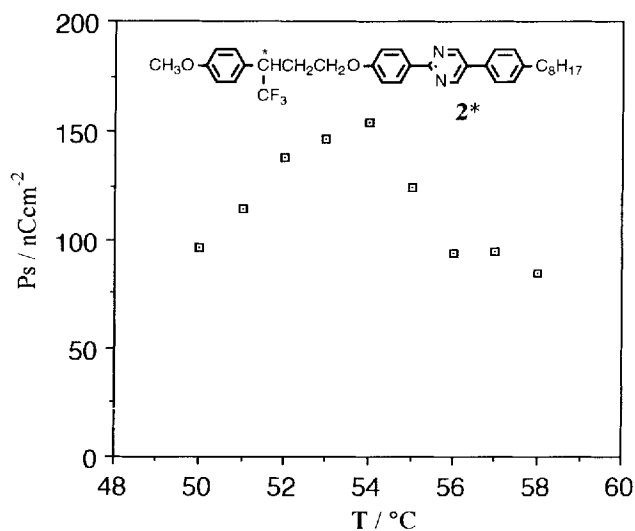
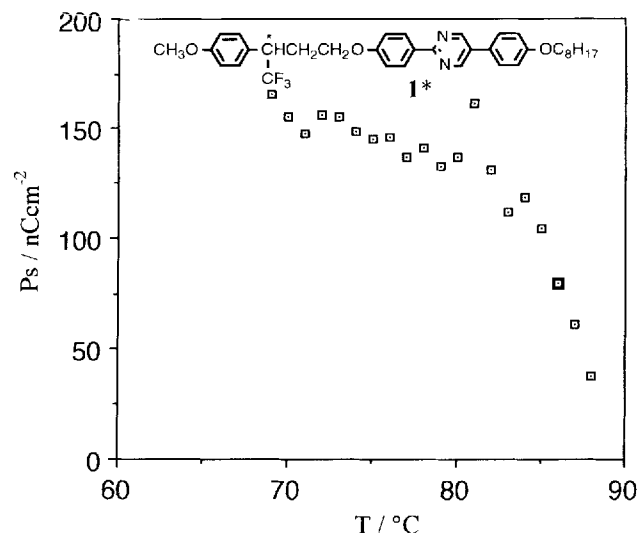


Figure 3. The relationship between temperature and the  $P_s$  value.

alkoxy terminated core are higher than for those with an alkyl terminated core [16]. Moreover the AFLC phase of the alkyl type **2\*** was not stable, and the temperature range of the phase was relatively narrow; moreover, on slow cooling (for example,  $-1.5 \text{ K min}^{-1}$ ), the AFLC phase disappeared.

The temperature dependencies of the  $P_s$  values are shown in figure 3. The maximum  $P_s$  values of both AFLCs were *c.*  $150 \text{ nC cm}^{-2}$ . These  $P_s$  values are nearly equal to that of TFMHPOBC [6]. As the AFLC phase of the alkyl type **2\*** is not stable, it was difficult to measure its physical properties.

The relationship between temperature and the tilt angle

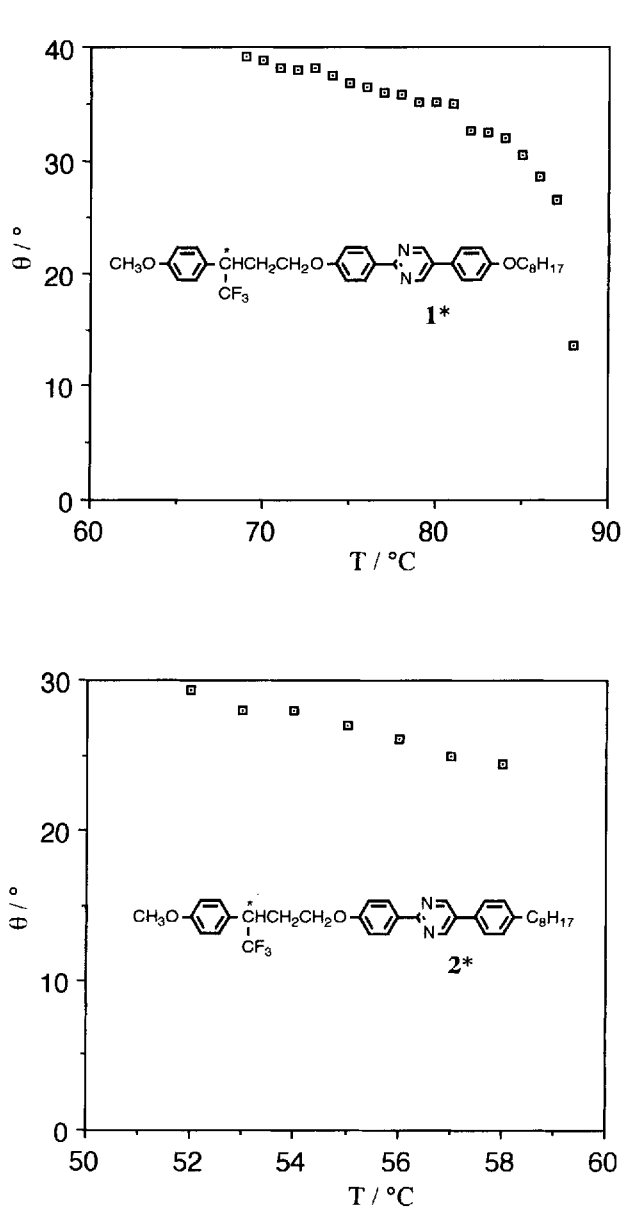


Figure 4. The relationship between temperature and the tilt angle.

are shown in figure 4. The tilt angle of the alkoxy type **1\*** was *c.* 40 degrees at  $70^\circ\text{C}$ , while the alkyl type **2\*** showed a tilt of *c.* 30 degrees. This is probably due to the narrow temperature range of the AFLC phase of the alkyl type **2\***.

Measurement of the dielectric constant is important for AFLC studies, because it gives useful information, for example about the mode of behaviour at the  $S_A$ -antiferroelectric phase transition [17–19]. The temperature dependencies of the real part of the dielectric constant ( $\epsilon'$ ) are shown in figure 5. The discontinuous change of  $\epsilon'$  at the transition point ( $T_c$ ) showed that the phase transition ( $S_A$ -antiferroelectric phase) of each

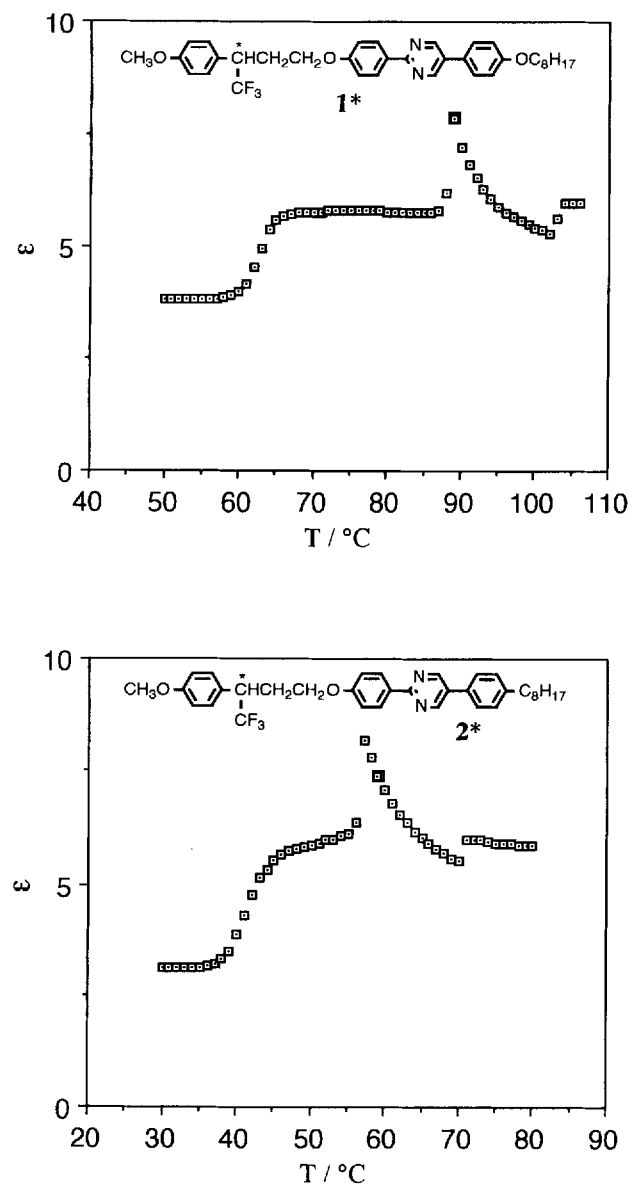


Figure 5. The relationship between temperature and the dielectric constant.  $f = 1 \text{ kHz}$ ,  $E = 1.0 \text{ V}$ , cooling rate =  $3 \text{ K min}^{-1}$ .

AFLC material was the first order. In the alkyl type **2\***, both the  $P_s$  value and the tilt angle were not zero at the  $T_c$  point. In the alkoxy type **1\***, however, the  $P_s$  value gradually increased from the  $T_c$  point, and the tilt angle, also. Therefore the phase transition ( $S_A$ -antiferroelectric phase) of **1\*** may be weakly first order. The decrease in  $\epsilon$  value for the alkoxy type **1\*** from 65 to 60°C marked the crystallization from the antiferroelectric phase. In the alkyl type **2\***, crystallization occurred at *c.* 45°C. The crystallization temperature of the liquid crystal in the cell and that in the DSC pan was different; this is probably due to a surface effect and the differences of the cooling rates in the dielectric constant and DSC measurements. As the alkyl type **2\*** material showed a particularly strong supercooling

effect, the difference in the crystallization temperatures was large.

Generally AFLCs exhibit some typical features, i.e. tristable switching, distinct threshold behaviour, two switching-current peaks and so on [20–22]. In the alkoxy type **1\***, the electrical and the optical response to a triangular wave are shown in figure 6. The typical two switching-current peaks of the alkoxy type **1\*** were also observed. This means that **1\*** has three states, namely the ferroelectric state, the antiferroelectric state and another ferroelectric state. In figure 5, the hysteresis loop of the alkoxy type **1\*** clearly showed a d.c.-threshold. In the alkyl type **2\***, the two switching-current peaks and the d.c.-threshold were also observed.

The structural formulae of the alkoxy type **1\*** and a similar FLC material are shown in figure 7 [23]. These molecules have the same core structure and in each, the trifluoromethyl group is at the chiral centre. The left side of the optically active moiety is the only different point. Therefore, in the AFLC this moiety, namely  $\text{CH}_3\text{OPh}$ -, probably plays an important role in the sense that the benzene ring fixes the dipole of the trifluoromethyl group. An alkyl chain is flexible, while a benzene ring is rigid, and bulky. Thus, the benzene ring strains the trifluoromethyl moiety, and this distorted molecule likes to show the antiferroelectric state.

Chirality is a very interesting subject in liquid crystals [24–26]. It is known that liquid crystal materials showing the antiferroelectric phase possess relatively high degrees of chirality. The alkoxy type **1\*** shows a large value of the specific rotation  $[[\alpha]_D^{23} = -131^\circ$  (*c.* 0.548,  $\text{CHCl}_3$ )], while the FLC material in figure 7 shows a small value of the specific rotation  $[[\alpha]_D^{29} = +4.5^\circ$  (*c.* 1.1,  $\text{CHCl}_3$ )]. Though a large value of the specific rotation does not always mean a high degree of chirality, this relationship between the value of the specific rotation and the antiferroelectricity of a liquid crystal is also an interesting point.

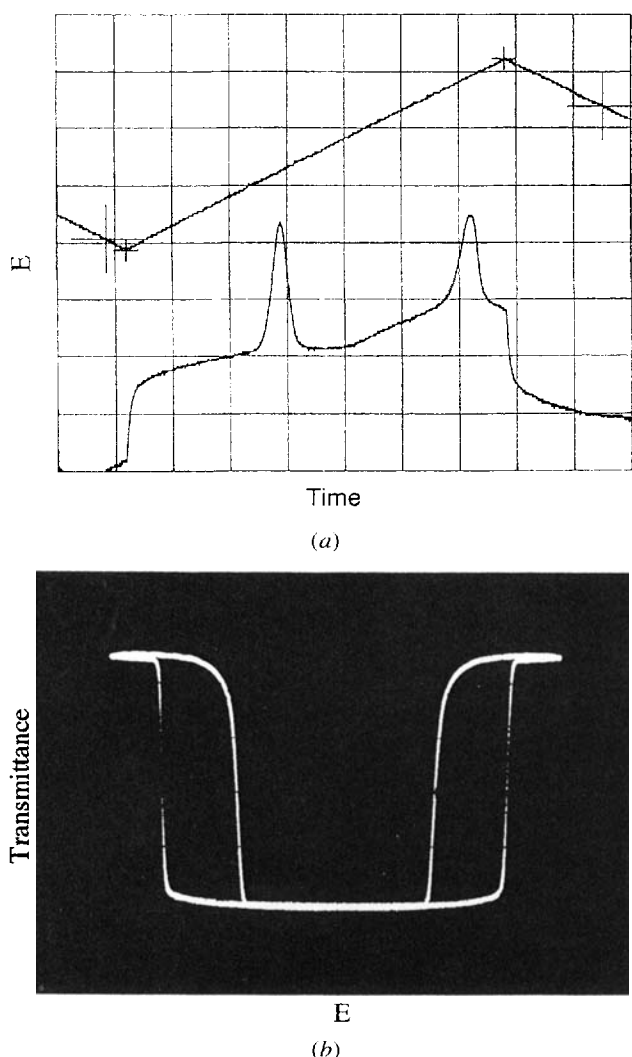


Figure 6. The electrical and the optical responses of **1\***. (a) The typical two switching-current peaks of **1\***.  $T = 81^\circ\text{C}$ ,  $f = 10\text{ Hz}$ ,  $E = \pm 60\text{ V } \mu\text{m}^{-1}$ . (b) The hysteresis loop of **1\***.  $T = 81^\circ\text{C}$ ,  $f = 1\text{ Hz}$ .

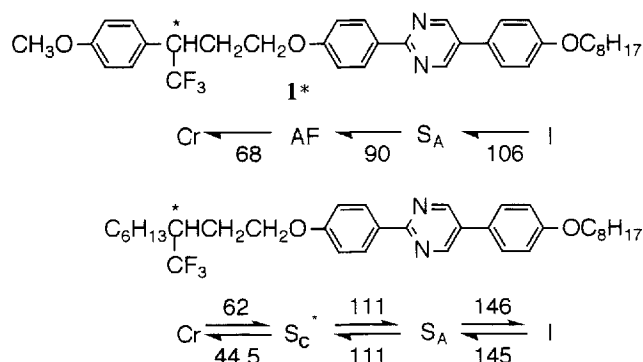


Figure 7. The structural formula of **1\*** and a FLC. Cr indicates crystalline solid. AF indicates antiferroelectric phase.  $S_A$  indicates smectic A phase. I indicates isotropic liquid.  $S_C^*$  indicates chiral smectic C phase.

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