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A novel ferroelectric liquid crystal having a trifluoromethyl group at the chiral centre

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A novel ferroelectric liquid crystal (FLC), 4-(1,1,1-trifluoro-2-octyl)phenyl 4′-nonyloxybiphenyl-4-carboxylate has been synthesized using optically active 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoic acid. Although the FLC seemed to satisfy an empirical rule for a large spontaneous polarization (P_s) value, the observed maximum P_s value, *c.* 100 nC cm^{-2}, was not as large as expected. However a relatively short response time of 68 μs at 50°C was observed.

1. Introduction

Recently many ferroelectric liquid crystals (FLCs) have been synthesized for application in flat panel display devices [1, 2]. In order to obtain good FLC materials, the relationship between the molecular structure and such physical properties as the response time, the rotational viscosity, the tilt angle and the phase sequence, has been investigated, although it is very complicated. For display devices, the response time of a liquid crystal is a dominant factor. The response time (τ) is represented by a following equation (1):

$$\tau = \frac{\eta}{P_s \, E}. \tag{1}$$

Here, η is the rotational viscosity, P_s is the spontaneous polarization and E is the applied electric field. Therefore, it is important to obtain FLC materials having a low rotational viscosity and a large spontaneous polarization value. It has been generally accepted that the faster the switching speed, the greater the variety of application of the material.

The relationship between the molecular structures and the spontaneous polarization has been empirically clarified [3, 4]. The magnitude of spontaneous polarization in liquid crystals has been concerned with the size and orientation of the dipole at the chiral centre, with the spatial configuration of the chiral centre, and with the position of the chiral centre of the molecule. The stronger the dipole at a given chiral centre, the larger its lateral component relative to the molecular long axis, and hence the greater the spontaneous polarization. Thus many FLC molecules showing a large P_s value have a strong polar group, for example, fluoro [5–9], trifluoromethyl [10–13], cyano [14, 15] and carbonyl groups. The closer the chiral centre to core, the less the freedom of its movement due to steric hindrance with the rigid core. In addition to the FLC molecules having the polar group close to the core, many compounds having a γ- or a δ-lactone structure [16–21], an oxazolidinone structure [22], a cyclopropane structure [4, 23] and a trifluoromethylated pyranose structure [24] have also been synthesized. These FLC compounds tend to exhibit a large P_s value.

The relationship between the chiral structure and the physical properties is interesting although it is very complicated. Recently the new liquid crystalline phases, for example, the twist grain boundary (TGB) phase [25] and the antiferroelectric liquid crystal (AFLC) phase [26], have been studied. These interesting phases should be correlated to the chiral structure in the liquid crystalline molecule.

In this paper, we report a ferroelectric liquid crystal with a trifluoromethyl group at the chiral centre, and discuss the relationship between the molecular structure and the physical properties.

2. Synthesis

Synthesis and optical resolution of the intermediates, 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoic acid (**1***), the alcohol derivative (**2***) and its tosylate (**3***) have been previously reported [27]. The liquid crystal was prepared by the following route (see scheme).

1,1,1-Trifluoro-2-(4-methoxyphenyl)octane (**4***) was obtained by the coupling reaction of lithium dibutylcuprate (I) with the tosylate (**3***) [28]. Demethylation of **4*** with hydrobromic acid afforded 1,1,1-trifluoro-

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2-(4-hydroxyphenyl)octane (**5***). The liquid crystal **6*** was prepared by the esterification of **5*** with 4′-nonyloxybiphenyl-4-carboxylic acid.

3. Analysis

The liquid crystalline phases were observed with a polarizing microscope (Nikon Optiphot 2-POL) equipped with a heating stage (Mettler FP-82HT) and a thermal control unit (Mettler FP-90). The phase transition temperatures and enthalpies were determined with a DSC (MAC Science, DSC-3100). The electro-optical properties were observed with a polarizing microscope equipped with a photo multiplier (Hamamatu R2228) and an oscilloscope (Phillips PM-3350). The cell gap was 1·4 μm, which was determined by the capacitance measurements.

4. Results and discussion

The phase transition temperatures and some physical properties of **6*** are summarized in tables 1 and 2.

4.1. *Phase behaviour*

The liquid crystal showed only a smectic A (SmA) phase on heating, while on cooling the SmA and chiral smectic C (SmC*) phases were observed. The phase transition temperature between the isotropic liquid and SmA phase was about 83°C, and the enthalpy of transition was about 4·7 J g^{-1}. These phase transitions were reproducible. However, whereas on cooling the reproducible values were observed, on heating the phase transition from the crystalline to the SmA phase was unstable. Since the crystallization enthalpy was smaller than the melting enthalpy, this crystallization was not sufficient, namely this crystalline phase was a metastable state.

Using for examples, **7*** [11] and **8*** [29, 30], shown in figure 1, the relationship between the chiral structure and the phase sequence is discussed.

The FLC **7*** exhibits a stable liquid crystalline phase whose temperature range is wider than that of **6***, and possesses an enantiotropic SmC* phase. Therefore the liquid crystalline phase, especially the SmC* phase of **6***, is probably labilized by a trifluoromethyl moiety close to the core. As a trifluoromethyl group is a relatively bulky group, the terminal alkyl chain of **6*** can be considerably bent in a direction perpendicular to the molecular long axis.

The liquid crystal **8*** derived from 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoic acid (**1***) showed an antiferroelectric liquid crystalline phase. Although **6*** and **8*** have the same chiral structure, they show different phase transition behaviour. Therefore it is clear that not only the chiral structure, but also other factors, namely the core structure, the terminal chain and the linkage structure, influence the liquid crystalline behaviour. Goodby has reported the relationship between the chirality and the helical phases [31, 32]. As the degree of chirality of a molecule is related to the physical properties of the mesophases, the degree of chirality of **6*** is probably lower than that of **8***.

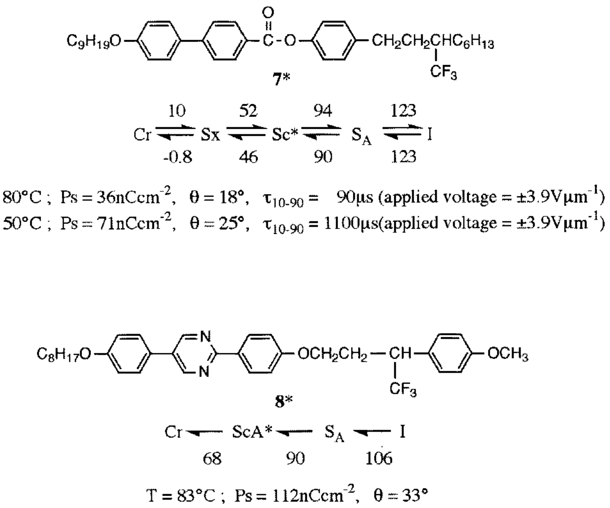


Figure 1. Physical properties of **7*** and **8***.

4.2. *Spontaneous polarization*

The temperature dependence of the P_s value of **6*** is shown in figure 2. The P_s value gradually increases from the T_c point on cooling step, suggesting that the phase transition from SmA to SmC* phase was probably second order. The maximum P_s value of **6*** was about 100 nC cm^{-2}. This P_s value was still relatively large,

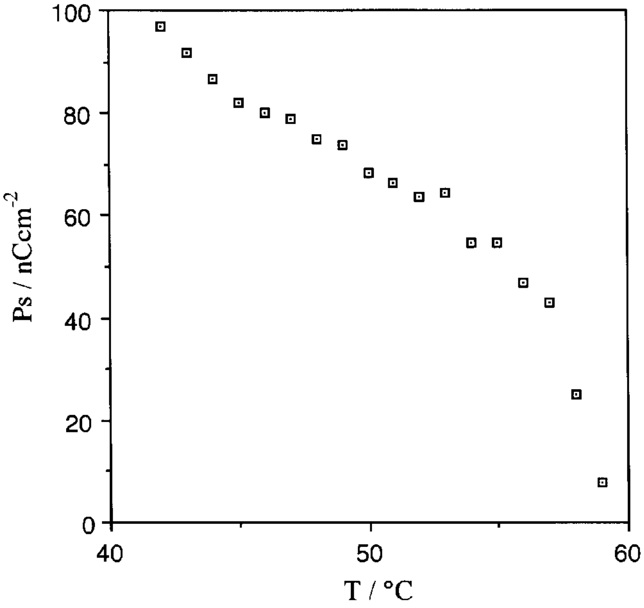


Figure 2. The relationship between temperature and P_s values of **6***.

however, at 50°C, and both **6*** and **7*** showed nearly equal P_s values of about 70 nC cm^{-2}. As the trifluoromethyl moiety of **6*** should be fixed more than that of **7***, it was expected that the P_s value of **6*** would be larger than that of **7***. However both FLCs showed nearly equal P_s values. It is known that the spontaneous polarization is primarily controlled by the chiral moiety of the liquid crystalline molecule, which is generally decoupled from the core [2]. Nevertheless, the coupling of the chiral moiety and the dipole from the core is important, and the effects of groups or substituents having a large dipole moment have been studied [33–35]. The core of **6*** contains a carbonyl group having a large dipole moment, so that the coupling of the trifluoromethyl group and the carbonyl moiety should be considered. As the distance between the trifluoromethyl group and the carbonyl moiety of **6*** is shorter than that of **7***, their coupling in **6*** can be considered stronger. However, it can be assumed that the direction of the trifluoromethyl group and the carbonyl moiety of **6*** does not contribute effectively to the P_s value as was expected. An X-ray diffraction study should be useful to clarify the chiral structure and the direction of the trifluoromethyl moiety.

4.3. *Tilt angle*

The temperature dependence of the tilt angle of **6*** is shown in figure 3. The tilt angle of **6*** also gradually increased from the T_c point. This means that the phase transition from SmA to SmC* is second order. From the DSC measurement the enthalpy of this transition was 0·6 J g^{-1}, which is a small value. This enthalpy value also indicates that the phase transition from SmA to SmC* is second order.

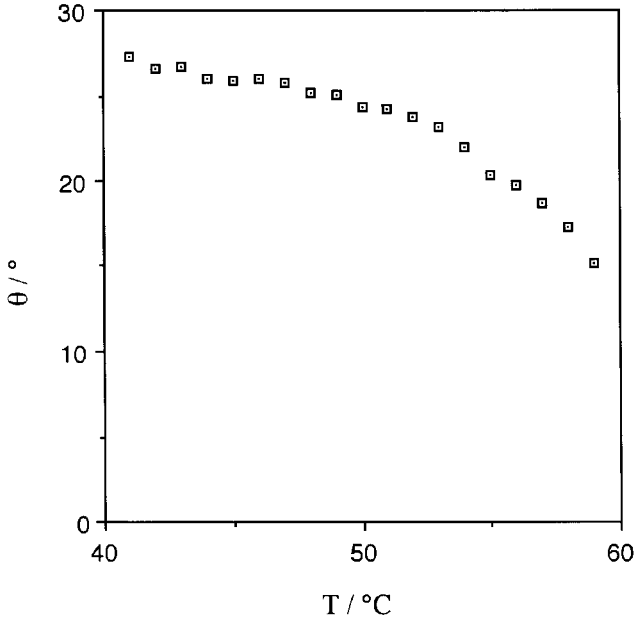
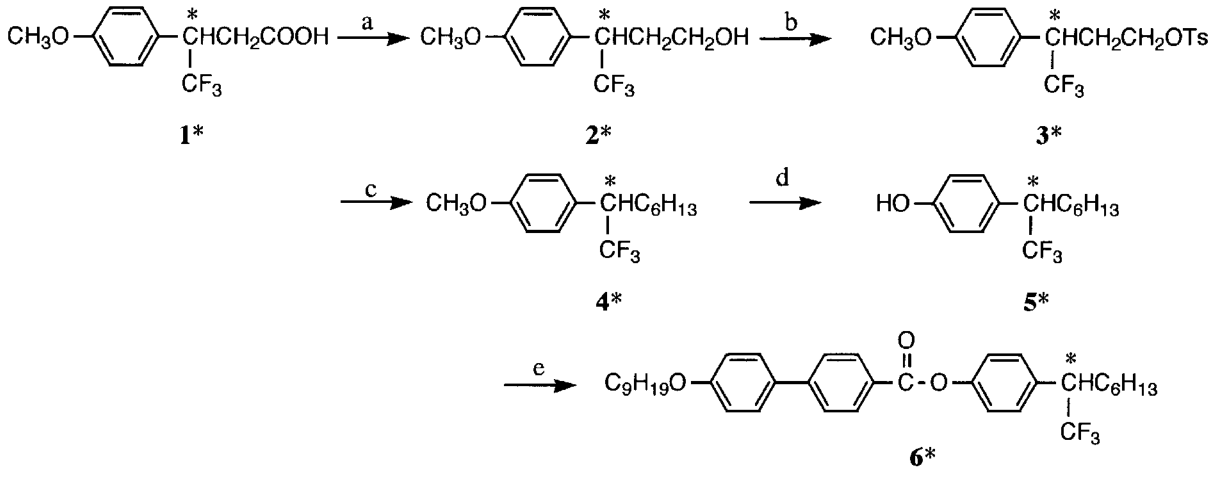


Figure 3. The relationship between temperature and tilt angle of **6***.

The maximum tilt angle of **6*** was about 27°, which is a relatively large value. At 50°C, the tilt angle of **6*** was 24°, and that of **7*** was 25°. It is difficult to compare each tilt angle because of a different temperature range for each SmC* phase.

4.4. *Response time*

The temperature dependence of the response time of **6*** is shown in figure 4. An approximately linear relationship exists between the temperature and the response time. At 50°C, **6*** showed a relatively fast switching,



a) $LiAlH_4$, THF b) TsCl, DABCO, CH_2Cl_2 c) *n*-Bu_2CuLi, ether d) HBr, AcOH e) core, DCC, DMAP, CH_2Cl_2

Scheme. The synthesis of the new ferroelectric liquid crystal.

Table 1. Phase transition temperatures (T/°C) and enthalpies (in square brackets [ΔH/J g^{-1}]) of compound **6*** recorded at a cooling rate of 5°C min^{-1}.

	Cr		SmC*		SmA		I
1st heating	●	64 [57]	—		●	83[4·9]	●
Cooling	●	40 [33]	●	59[0·6]	●	82[4·6]	●
2nd heating	●	66–69[45]	—		●	83[4·6]	●
3rd heating	●	66–69[45]	—		●	83[4·7]	●

Table 2. Physical properties of **6*** on cooling.

T/°C	P_s/nC cm^{-2} [a]	θ/°	τ_{10-90}/µs [b]
55	55	20	52
50	68	24	68
45	82	26	100

[a] The magnitude of P_s was measured by the triangular wave method.

[b] The change of transmittance (from 10 to 90 per cent) of light was observed when a square wave of ±5 V µm^{-1} was applied.

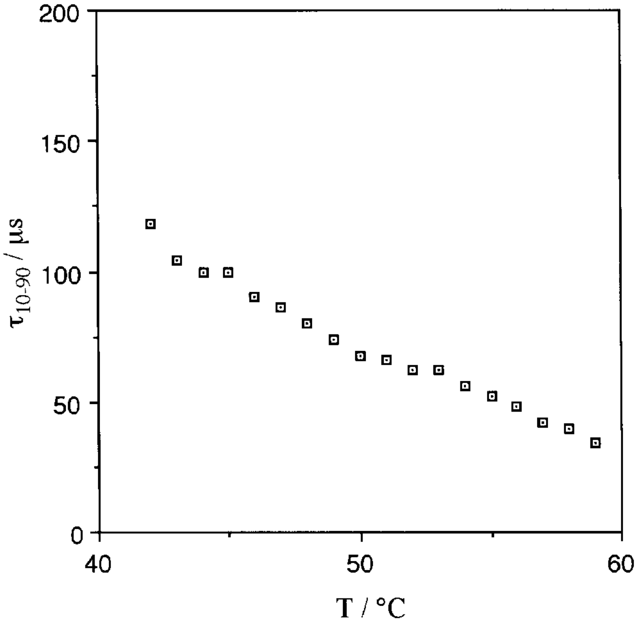


Figure 4. The relationship between temperature and response time ($\tau_{10\text{-}90}$) of **6*** (applied voltage = ±5 V µm^{-1}).

τ_{10-90} = 68 µs (P_s = 68 nC cm^{-2}). The FLC **7*** also showed a relatively fast switching at high temperature, while at 50°C the response time was long, τ_{10-90} = 1100 µs (P_s = 71 nC cm^{-2}). This result suggests that the rotational viscosity of **7*** rapidly increases with lowering of the temperature, while that of **6*** gradually increases.

5. Conclusions

A new ferroelectric liquid crystal (**6***) was synthesized using optically active 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoic acid. The new FLC showed a normal phase sequence on cooling, namely I 82 SmA 59 SmC* 40 Cr, and its maximum P_s value was *c.* 100 nC cm^{-2}, and its maximum tilt angle was about 27°. The response time of **6*** was relatively short (τ_{10-90} = 68 µs) at 50°C.

6. Experimental

All compounds were identified by ^{1}H NMR (Jeol FX-90Q), IR (Perkin–Elmer FT1640) and MS (Jeol DX-303). Their specific rotations, i.e. $[\alpha]_D$ was determined by a Jasco DIP-360. The chemical purities of the products were measured by gas chromatography or a high performance liquid chromatography.

6.1. *4,4,4-Trifluoro-3-(4-methoxyphenyl)butanoic acid (**1***), 4,4,4-trifluoro-3-(4-methoxyphenyl)butanol (**2***) and 4,4,4-trifluoro-3-(4-methoxyphenyl)butyltosylate (**3***)*

The syntheses of **1***, **2*** and **3*** have been previously reported [27]. **1***: $[\alpha]_D^{26} = -45{\cdot}7°$ (*c.* 1·56, 99 per cent EtOH). The optical purity was over 99%ee. **2***: $[\alpha]_D^{27} = -58{\cdot}8°$ (*c.* 1·16, $CHCl_3$). **3***: $[\alpha]_D^{27} = -46{\cdot}5°$ (*c.* 1·25, $CHCl_3$).

6.2. *1,1,1-Trifluoro-2-(4-methoxyphenyl)octane (**4***)*

Under nitrogen, after cooling to −20°C, a 1·62 M *n*-butyllithium hexane solution (2·6 ml, 4·2 mmol) was slowly added to a suspension of copper (I) iodide (0·407 g, 2·14 mmol) and dry ether (3 ml), and the mixture stirred for 10 min at −20°C. An ether solution of (-)-4,4,4-trifluoro-3-(4-methoxyphenyl)butyltosylate (0·276 g, 0·711 mmol) was added to the mixture, and the mixture stirred for 2 h at −20°C. A saturated aqueous ammonium chloride solution was added; the resulting mixture was filtered and the phases separated. The organic phase was washed twice with saturated aqueous sodium chloride, and dried over sodium sulphate. Removal of the solvent and purification by preparative TLC yielded 0·161 g (0·588 mmol, 82·6 per cent) of **4*** as a colourless liquid. IR (neat): 1614, 1516, 1466, 1304, 1252, 1180, 1159, 1127, 1100, 1038, 828 cm^{-1}. MS m/z = 274 [M$^+$], 205 [M-(CF_3)], 189 [M-(C_6H_{13})]. ^{1}H NMR (90 MHz, $CDCl_3$): δ 0·8 (t, 3 H, CH_3), 1·0–2·0 (m, 10 H, CH_2), 2·9–3·4 (m, 1 H, $CHCF_3$), 3·8 (s, 3 H, OCH_3), 6·9 (d, 2 H, Ar), 7·2 (d, 2 H, Ar). $[\alpha]_{\mathrm{D}}^{27} = -43{\cdot}0^\circ$ (*c.* 1·23, $CHCl_3$).

6.3. *1,1,1-Trifluoro-2-(4-hydroxyphenyl)octane* (5*)

(-)-1,1,1-Trifluoro-2-(4-methoxyphenyl)octane (0·161 g, 0·588 mmol) dissolved in 4·3 ml of acetic acid, and 47 per cent hydrobromic acid (0·86 ml) were mixed and heated at reflux for 10 h. After cooling to room temperature, water and ether were added and the phases separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate and dried over sodium sulphate. Removal of the solvent and purification by preparative TLC yielded 0·151 g (0·581 mmol, 98·8 per cent) of 5* as a colourless liquid. IR (neat): 1614, 1517, 1455, 1255, 1159, 1127, 1101, 828 cm^{-1}. MS $m/z = 260$ $[M^+]$, 191 $[M\text{-}(CF_3)]$, 175 $[M\text{-}(C_6H_{13})]$. ^1H NMR (90 MHz, $CDCl_3$): δ 0·8 (t, 3 H, CH_3), 1·0–2·0 (m, 10 H, CH_2), 2·9–3·4 (m, 1 H, $CHCF_3$), 5·0 (s, 1 H, OH), 6·8 (d, 2 H, Ar), 7·1 (d, 2 H, Ar). $[\alpha]_{\mathrm{D}}^{27} = -39{\cdot}4^\circ$ (*c.* 0·991, $CHCl_3$).

6.4. *4-(1,1,1-Trifluoro-2-octyl)phenyl 4′-nonyloxybiphenyl-4-carboxylate* (6*)

Under nitrogen, 4-*N*,*N*-dimethylaminopyridine (0·065 g, 0·53 mmol) was added to a mixture of (-)-1,1,1-trifluoro-2-(4-hydroxyphenyl)octane (0·138 g, 0·531 mmol) and 4′-nonyloxybiphenyl-4-carboxylic acid (0·188 g, 0·531 mmol) and dry dichloromethane (7 ml), and stirred for 30 min at room temperature. A dry dichloromethane solution (2·6 ml) of dicyclohexylcarbodiimide (0·115 g, 0·588 mmol) was added, and the reaction mixture was stirred for 14 h at room temperature. Ether was added; the resulting mixture was filtered, the filtrate washed with a saturated aqueous sodium chloride and then dried over sodium sulphate. Removal of the solvent and purification by preparative TLC yielded 0·238 g (0·408 mmol, 77·0 per cent) of 6* as a white solid. IR (KBr): 1736, 1626, 1606, 1578, 1509, 1263, 1209, 1189, 1171, 1128, 1101, 1074, 828, 767 cm^{-1}. MS $m/z = 582$ $[M^+]$. ^1H NMR (90 MHz, $CDCl_3$): δ 0·7–1·0 (m, 6 H, CH_3), 1·0–2·1 (m, 24 H, CH_2), 3·0–3·4 (m, 1 H, $CHCF_3$), 4·0 (s, 2 H, OCH_2), 7·0 (d, 2 H, Ar), 7·2–7·4 (m, 4 H, Ar), 7·7–7·8 (m, 4 H, Ar), 8·3 (d, 2 H, Ar). $[\alpha]_{\mathrm{D}}^{27} = -23{\cdot}8^\circ$ (*c.* 0·525, $CHCl_3$).

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