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New ferroelectric liquid crystals having a trifluoromethyl group at the asymmetric centre and a three-ring heterocyclic core

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New ferroelectric liquid crystals with a trifluoromethyl group at the asymmetric centre and a three-ring heterocyclic core have been synthesized. These compounds possessed a large spontaneous polarization and exhibited a S_C^* phase over a wide temperature range. Their properties were largely affected by the structure of the spacer group and the core part.

1. Introduction

In general, ferroelectric liquid crystals inevitably have a two- or three-ring aromatic core in their molecular structures. For example, 4,4′-substituted biphenyls and 2-(4-substituted phenyl)-5-alkylpyrimidines are used practically as the smectic liquid crystal materials. There have also been several reports concerning FLC materials with a three-ring heterocyclic core which showed a large spontaneous polarization [1].

We have recently reported ferroelectric liquid crystal materials with a fluorinated asymmetric centre, for example, a fluorine or a trifluoromethyl group at the asymmetric centre [2–4]. These materials were found to possess a large spontaneous polarization and a fast response due to the C–F bond having a large dipole moment.

In this paper, we report some new ferroelectric liquid crystal materials having a trifluoromethyl group at the asymmetric centre and a three-ring heterocyclic core as shown in figure 1, and describe their physical properties.

2. Experimental

2.1. *Preparation of the optically active component*

Optically active 3-trifluoromethylalkanoic acids **1**, shown in the scheme (*a*), were prepared by a method reported previously [3]. Optically active 3-butoxy-4,4,4-trifluorobutanoic acid **2** was synthesized for the first time as shown in the scheme (*b*). Ethyl trifluoroacetoacetate was hydrogenated using sodium borohydride and the hydroxyl group alkylated using butyl bromide over silver oxide [5]. The subsequent hydrolysis gave racemic **2** in a total yield of 47·6 per cent. Optically active **2** was prepared by the diastereoisomeric salt formation method using optically active *p*-tolylethylamine (TEA) as resolving agent. The specific rotations of (−)-**2** were

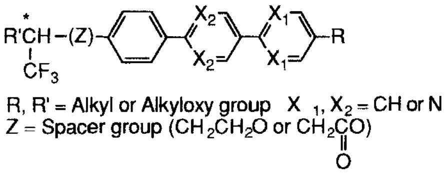

Figure 1. General structure of FLCs.

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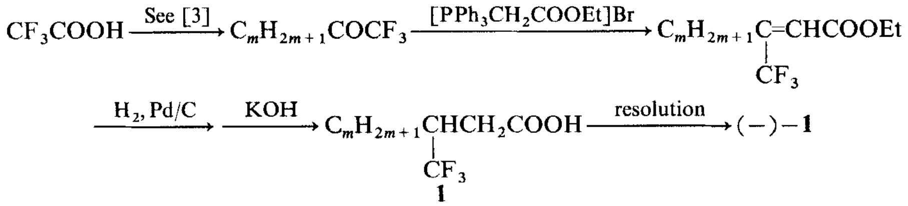
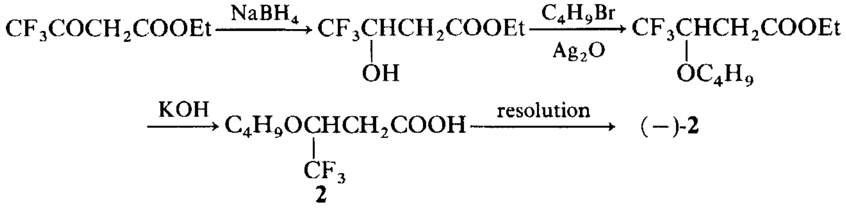


$$CF_3COOH \xrightarrow{\text{See [3]}} C_mH_{2m+1}COCF_3 \xrightarrow{[PPh_3CH_2COOEt]Br} C_mH_{2m+1}\underset{\displaystyle CF_3}{\underset{|}{C}}{=}CHCOOEt$$
$$\xrightarrow{H_2,\,Pd/C} \xrightarrow{KOH} C_mH_{2m+1}\underset{\underset{\displaystyle \mathbf{1}}{\displaystyle CF_3}}{\underset{|}{C}}HCH_2COOH \xrightarrow{\text{resolution}} (-)-\mathbf{1}$$

(*a*) Synthetic route to (−)-3-trifluoromethylalkanoic acids.



$$CF_3COCH_2COOEt \xrightarrow{NaBH_4} CF_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2COOEt \xrightarrow[Ag_2O]{C_4H_9Br} CF_3\underset{\displaystyle OC_4H_9}{\underset{|}{C}}HCH_2COOEt$$
$$\xrightarrow{KOH} C_4H_9O\underset{\underset{\displaystyle \mathbf{2}}{\displaystyle CF_3}}{\underset{|}{C}}HCH_2COOH \xrightarrow{\text{resolution}} (-)\text{-}\mathbf{2}$$

(*b*) Synthetic route to (−)-3-butoxy-4,4,4-trifluorobutanoic acid.

23·2°($[\alpha]_D$) and 41·8° ($[\alpha]_{435}$) respectively. The optical purity was assessed by HPLC analysis and (−)-**2** was shown to be of 98 per cent enantiomeric excess.

2.1.1. (±)-*3-Butoxy-4,4,4-trifluorobutanoic acid* **2**

To a mixture of 1·89 g (50·0 mmol) of sodium borohydride and 25 ml of distilled water was added dropwise 18·4 g (100 mmol) of ethyl trifluoroacetoacetate while stirring under a nitrogen atmosphere. The mixture was stirred at room temperature for 19 h, and then 6 M hydrochloric acid was added dropwise. The product was extracted into ether and the extract dried over anhydrous magnesium sulphate. Ethyl 3-hydroxy-4,4,4-trifluorobutanoate was purified by distillation under reduced pressure; bp 122–130°C/93 mm Hg. The yield was 12·5 g (67·2 mmol).

To a mixture of 15·2 g (81·7 mmol) of purified ethyl 3-hydroxy-4,4,4-trifluorobutanoate, 100 ml of dimethylformamide and 27·6 g (201 mmol) of butyl bromide was added 46·7 g (201 mmol) of silver oxide. This mixture was heated at 60°C and stirred for 89 h. The precipitate was filtered off and extracted with ether. After the ether had been removed, a mixture of 60 ml of methanol and 22·9 g (407 mmol) of potassium hydroxide was added to the residue, and the whole was heated under reflux for 16 h with stirring. The mixture was acidified with 6 M hydrochloric acid and the product extracted into ether and dried over anhydrous magnesium sulphate. Distillation under reduced pressure gave 3-butoxy-4,4,4-trifluorobutanoic acid. The yield was 12·4 g (57·9 mmol) 47·6 per cent, bp 110–127°C/20 mmHg.

Spectral data: IR (neat) 2963, 1721, 1281, 1170, 1134, 649 cm^{-1}. ^{1}H NMR (400 MHz in $CDCl_3$) δ 10·5 (s, 1 H), 4·13 (m, 1 H), 3·73 (m, 2 H), 2·71 (dd, 2 H, J = 1·4 Hz, 6·4 Hz), 1·56 (m, 2 H), 1·35 (m, 2 H), 0·90 ppm (dt, 3H, J = 1·6 Hz, 7·4 Hz). ^{19}F NMR (376 MHz in $CDCl_3$) δ −68·9 ppm (d, J = 6·0 Hz). ^{13}C NMR (50 MHz in $CDCl_3$) δ 176·0, 124·7 (*q*, J = 283·7 Hz), 74·4 (*q*, J = 30·7 Hz), 73·2, 34·8, 31·7, 18·8, 13·4 ppm.

2.1.2. *Optical resolution of* **2**

Into a solution of racemic 3-butoxy-4,4,4-trifluorobutanoic acid 12·4 g (57·9 mmol) in 58 ml of hexane was added 7·83 g (57·9 mmol) of (+)-1-(*p*-tolyl)ethylamine (TEA); the mixture was then stirred for a while at room temperature. The resulting insoluble diastereoisomeric salt was filtered off and recrystallized from a mixture of 43 ml of hexane and 0·5 ml of propan-2-ol. To the purified salt was added 1 M sodium hydroxide solution, so liberating the TEA. After the amine had been extracted using ether, 3-butoxy-4,4,4-trifluorobutanoic acid was liberated from the water layer by acidifying with 2 M hydrochloric acid. The liberated acid was extracted into ether, and **2** was purified by distillation under reduced pressure; bp 110–122°C/26 mm Hg. The yield was 1·90 g (8·88 mmol) 31·0 per cent based on half the amount of racemic **2**. Specific rotation:

(+)-TEA(−)-**2** salt	$[\alpha]_D + 7{\cdot}0°$	$[\alpha]_{435} + 18{\cdot}7°$(*c*. 3·0, $CHCl_3$).
(−)-**2**	$[\alpha]_D - 23{\cdot}2°$	$[\alpha]_{435} - 41{\cdot}8°$(*c*. 1·0, $CHCl_3$).

2.1.3. *Determination of optical purity of* (−)-**2**

(−)-3-Butoxy-4,4,4-trifluorobutanoic acid **2** was condensed with optically active 1-(1-naphthyl)ethylamine using dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine (DMAP). The diastereoisomeric amide was analysed by high pressure liquid chromatography (HPLC) using a silica gel column (Gaskuro Kogyo Inertsil, silica gel column 4·6 × 250 mm) and the areas of the two peaks corresponding to the diastereoisomers were calculated. The optical purity was determined by use of the following equation where S1 and S2 are these areas.

Enantiomeric excess (per cent) = (S1 − S2)/(S1 + S2) × 100.

2.2. *Preparation of ferroelectric liquid crystals*

Two types of core part were used as shown in figure 2. One of the three aromatic rings was 2,5-substituted pyrimidine. The spacer group connected between the core and the optically active part was $-CH_2CH_2O-$ or $-CH_2COO-$.

All final products were synthesized by routine chemical methods and purified by column chromatography on silica gel, using a mixture of hexane/ethyl acetate as the eluent, followed by recrystallization from a mixture of hexane/ethanol. The chemical structures of all the materials were confirmed by a combination of nuclear magnetic resonance (Bruker AM-400, AC-200 FT-NMR) and infrared spectroscopy (Perkin–Elmer FT-1600 FT-IR).

2.3. *Measurement of physical properties*

Phase assignments and corresponding transition temperatures for the compounds **1** ~ **10** were determined by a combination of differential scanning calorimetry (Seiko I&E DSC20) at a scanning rate of 1 ~ 2°C min^{-1} and polarized optical microscopy (Olympus POS, Nikon Optiphoto-POL) in conjunction with a heating stage (Mettler FP 82 HT with a FP 90 central processor).

Spontaneous polarizations were measured by the triangular-wave method of Miyasato *et al.* [6]. Response times were measured by the field reversal method of Skarp *et al.* [7]. The frequency and the amplitude were 20 Hz and ± 36 V, respectively.

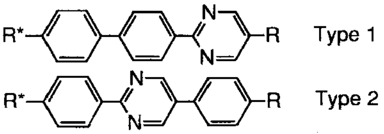


Figure 2. Structures of three-ring heterocyclic cores.

These measurements were carried out using cells of 18 μm thickness constructed from indium/tin oxide (ITO) coated glass plate. The inner surfaces of the cells were coated with rubbed polyimide in order to achieve a homogeneous planar alignment. On the other hand, optical tilt angles were measured using thinner cells of thickness 1·3 μm constructed similarly.

3. Results and discussion

3.1. *Phase behaviour of the ferroelectric liquid crystal materials*

Phase sequences and the transition temperatures are collected in table 1. Identification of liquid crystalline phases was achieved principally by polarized optical microscopy. Some compounds showed the higher order smectic phase (S_X), but mostly the materials exhibited the phase sequence crystal–smectic C*–smectic A–isotropic liquid over a wide temperature range. Especially, compounds **1–8** showed S_C^* phases over temperature ranges of more than 60 degrees on cooling cycles. The stabilities of the liquid crystal phases of **1** and **2** were similar, while the temperature ranges of the S_C^* liquid crystalline phases on cooling were in sharp contrast. Compound **2** has a higher order orthogonal phase (S_X) below the S_C^* phase. Compounds **1**, **2** and **9** having the dimethyleneoxy group as spacer ($Z = CH_2CH_2O$) were found to show liquid crystalline phases over wider temperature ranges compared with other compounds having the methylenecarbonyloxy group ($Z = CH_2COO$). Furthermore, the stability of the S_C^* phase varied with the length of the terminal alkyl chain in the case of compounds **6**, **7** and **8** which have the same spacer group and the same core structure. The shorter terminal alkyl chain restricted the S_A phase and expanded the S_C^* phase. Surprisingly, compound **10** had no S_C^* phase and **9** only showed this phase over the temperature range from 98–108°C. The oxygen atom next to the asymmetric centre appears to restrict the appearance of the S_C^* phase.

3.2. *Spontaneous polarization, response time and tilt angle*

Spontaneous polarization values are summarized in table 2. The materials **1–8** possess large polarization values which varied with the position of the heterocyclic part (compare **1** to **2**, **4** to **6**, and **5** to **7**) and the type of spacer group (compare **1** and **2** to the others). In any given case, the value of the polarization was larger with the type 2 heterocyclic core (see figure 2). The nitrogen atom having a lone pair causes an increase in the electron density around the asymmetric centre and results in a large polarization value. Additionally, differences in the twist angles of the planes of the three aromatic rings between the two types of core are concerned with the polarization value. Our results are fundamentally opposed to those of the early studies by Inoue *et al.* [8]. They have reported FLC materials which are three-ring heterocyclic compounds including two chiral groups. In their report, it has been shown that the compounds with the type 1 core with nitrogen atoms at the outlying positions from the asymmetric centre possess larger spontaneous polarization values and tilt angles than the type 2 compounds. On the other hand, the material **9** was found to possess a small polarization despite the oxygen atom situated beside the asymmetric centre. It seems that this position for the oxygen atom abates the lateral dipole.

Response time for the materials are also collected in table 2. All the measurements were carried out with an electric field of 4 V μm^{-1}. In all cases, fast switching was observed due to the large polarization, and the temperature dependence was comparably large. However, the response times we measured were *polarization reversal*

Table 1. Phase sequences and transition temperatures of the FLCs $\mathrm{S_x}$, $\mathrm{S_{x_1}}$, $\mathrm{S_{x_2}}$ are the higher order smectic phases.

Compound	*R′*	(X_1, X_2)	*Z*	*R*	Phase transition temperature/°C
1	C_6H_{13}	N, CH	CH_2CH_2O	OC_8H_{17}	$\mathrm{C}\ \underset{49}{\overset{69\cdot5}{\rightleftarrows}}\ \mathrm{S_{X_1}}\ \xrightarrow{103}\ \mathrm{S_C^*}\ \underset{111}{\overset{111}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{143}{\overset{144\cdot5}{\rightleftarrows}}\ \mathrm{I}$ $\mathrm{S_C^*}\ \xrightarrow{101}\ \mathrm{S_{X_2}}\ \xrightarrow{86}\ \mathrm{S_{X_1}}$
2	C_6H_{13}	CH, N	CH_2CH_2O	OC_8H_{17}	$\mathrm{C}\ \underset{44\cdot5}{\overset{62}{\rightleftarrows}}\ \mathrm{S_C^*}\ \underset{111}{\overset{111}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{145}{\overset{146}{\rightleftarrows}}\ \mathrm{I}$
3	C_6H_{13}	CH, N	CH_2COO	C_8H_{17}	$\mathrm{C}\ \underset{69}{\overset{89}{\rightleftarrows}}\ \mathrm{S_C^*}\ \underset{102}{\overset{103\cdot5}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{130}{\overset{132}{\rightleftarrows}}\ \mathrm{I}$
4	C_8H_{17}	N, CH	CH_2COO	OC_8H_{17}	$\mathrm{C}\ \underset{77\cdot4}{\overset{89\cdot3}{\rightleftarrows}}\ \mathrm{S_C^*}\ \underset{115}{\overset{115\cdot4}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{143}{\overset{144}{\rightleftarrows}}\ \mathrm{I}$
5	C_6H_{13}	N, CH	CH_2COO	OC_8H_{17}	$\mathrm{C}\ \underset{83\cdot3}{\overset{94}{\rightleftarrows}}\ \mathrm{S_C^*}\ \underset{132}{\overset{133}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{154}{\overset{153}{\rightleftarrows}}\ \mathrm{I}$
6	C_8H_{17}	CH, N	CH_2COO	OC_8H_{17}	$\mathrm{C}\ \underset{75\cdot5}{\overset{97}{\rightleftarrows}}\ \mathrm{S_C^*}\ \underset{110\cdot4}{\overset{111\cdot4}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{141}{\overset{142\cdot5}{\rightleftarrows}}\ \mathrm{I}$
7	C_6H_{13}	CH, N	CH_2COO	OC_8H_{17}	$\mathrm{C}\ \underset{74}{\overset{95}{\rightleftarrows}}\ \mathrm{S_C^*}\ \underset{124}{\overset{125}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{151}{\overset{151}{\rightleftarrows}}\ \mathrm{I}$
8	C_4H_9	CH, N	CH_2COO	OC_8H_{17}	$\mathrm{C}\ \xrightarrow{95}\ \mathrm{S_C^*}\ \underset{140}{\overset{140}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{164}{\overset{164}{\rightleftarrows}}\ \mathrm{I}$ $\mathrm{S_C^*}\ \xrightarrow{69\cdot5}\ \mathrm{S_X}\ \xrightarrow{45}\ \mathrm{C}$
9	C_4H_9O	CH, N	CH_2CH_2O	OC_8H_{17}	$\mathrm{C}\ \underset{<\mathrm{r.t.}}{\overset{61}{\rightleftarrows}}\ \mathrm{S_X}\ \underset{95}{\overset{98}{\rightleftarrows}}\ \mathrm{S_C^*}\ \underset{106}{\overset{108}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{153}{\overset{153}{\rightleftarrows}}\ \mathrm{I}$
10	C_4H_9O	CH, N	CH_2COO	OC_8H_{17}	$\mathrm{C}\ \underset{64}{\overset{77}{\rightleftarrows}}\ \mathrm{S_X}\ \underset{104}{\overset{105}{\rightleftarrows}}\ \mathrm{S_A}\ \underset{161}{\overset{161}{\rightleftarrows}}\ \mathrm{I}$

Table 2. Physical properties of the FLCs at the temperature T_c–$T=30$°C; data for **1** were measured at T_c–$T=10$°C and for **9** at T_c–$T=4$°C.

Compound	Ps/nC cm^{-2}	τ/μs	θ/°
1	54·4	12·9	13·0
2	127	42·8	33·0
3	220	26·8	30·5
4	182	36·0	NA
5	132	26·9	24·0
6	199·1	41·2	NA
7	172·1	48·0	31·5
8	187·1	16·7	30·0
9	34	59	NA

times obtained by measuring the time from the field reversal to the peak-top of the polarization current. Consequently, the larger polarization causes the larger surface interaction, and arrests uniform switching, with delay in the optical response.

Optical tilt angles of the materials are collected in table 2. Most of the materials give large tilt angles of more than 30 degrees and this causes large spontaneous polarization values. As described in a previous paper, 4-substituted phenyl-4-alkoxybiphenyl-4′-carboxylate type FLC materials, which have the same optically active part, possessed polarization values of approximately 60 nCcm^{-2} with tilt angles of 30 degrees. Thus the trifluoromethyl group at the asymmetric centre, together with the three-ring heterocyclic cores, is beneficial for the generation of large polarization FLC materials.

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