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Xiaotun Yang; Kazuki Abe; Ryuji Kato; Shinichi Yano; Takashi Kato; Kazutoshi Miyazawa; Hiroyuki Takeuchi

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Mesomorphic phase transitions and electro-optical properties of benzyl fluoroalkyl ether derivatives

XIAOTUN YANG, KAZUKI ABE, RYUJI KATO, SHINICHI YANO*
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido,
Gifu 501-11, Japan

TAKASHI KATO, KAZUTOSHI MIYAZAWA and HIROYUKI TAKEUCHI
Speciality Chemical Research Center, Chisso Petrochemical Corporation,
Goikaigan 5-1, Ichihara, Chiba 290, Japan

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Three series of liquid crystalline (LC) compounds containing benzyl fluoroalkyl ether groups (BFE), 4-*n*-propylbicyclohexylbenzyl fluoroalkyl ethers (3-C2BFE-*X*, *X*: fluoroalkyl group), 4-*n*-alkylcyclohexylbenzyl fluoroalkyl ethers (*m*-C1BFE-*X*, *m*: carbon no. of *n*-alkyl group) and 4-*n*-alkoxyphenylbenzyl fluoroalkyl ethers (*m*O-BBFE-*X*), were newly synthesized for several fluoroalkyl groups (*X*) such as *n*-fluoroalkyl, branched fluoroalkyl, and 2-perfluoropropoxy-2,3,3,3-tetrafluoropropyl. The mesomorphic phase transitions and electro-optical properties were investigated for BFE. 3-C2BFE-*X* and *m*O-BBFE-*X* have SmB phases, and SmA and/or E phases, respectively, while *m*-C1BFE-*X* showed no mesophases. The occurrence and thermal stability of the LC phases are related to the chemical structures of the rigid core part and the terminal groups. The electro-optical properties were investigated for 15 wt% of BFE in host ZLI-1132. It was found that the BFE compounds have a good solubility of more than 15 wt% in ZLI-1132 and can be used as a component for lowering the refractive anisotropy of the host ZLI-1132 solvent.

1. Introduction

New functional liquid crystalline (LC) compounds have been sought and developed with the advance of LC science and display devices. Fluorinated LC compounds have been notable as a new class of LC materials, especially since the discovery of fluorophenyl compounds such as 1,2-difluoro-4-[*trans*-4-(*trans*-4-alkoxycyclohexyl)-cyclohexyl]benzene having excellent electro-optical properties, particularly excellent voltage holding ratios (*Vh*) [1–5]. Among the many fluorinated LC compounds, those containing fluorinated terminal groups are certainly one of the attractive targets for obtaining useful LC compounds: much research has been devoted to LC compounds bearing fluoroalkyl, fluoroalkoxy and fluoroalkoxycarbonyl terminal groups [6–12], and moreover, chiral fluoroalkyl groups which sometimes generate ferroelectricity [13, 14]. Some LC compounds having $-CF_3$ and $-OCF_3$ terminal groups have been reported to have a large dipole moment along the molecular long axis and to give some good electro-optical properties [15–17]. The development of new fluorinated LC compounds is certainly an important way to find new phenomena and/or a LC material with good electro-optical properties; this encourages us to investigate many kinds of fluorinated LC compounds.

It has been reported that several benzyl *n*-alkyl ether derivatives show good electro-optical properties, and especially a low viscosity which results from the $-CH_2-O-CH_2-$ ether moiety in the terminal group [18]. On the other hand, from the characteristic nature of fluorine, fluoroalkyl terminal groups are expected to generate low birefringence, low viscosity and good thermal stability. It is therefore worthwhile to investigate LC compounds containing the benzyl fluoroalkyl ether group. In a previous communication [19], we preliminarily noted that a few benzyl fluoroalkyl ether compounds can act as one component lowering the anisotropy of the refractive index of ZLI-1132 acting as nematic solvent.

In this work we synthesize three new kinds of benzyl fluoroalkyl ether derivatives (BFE): 4-*n*-propylbicyclohexylbenzyl fluoroalkyl ethers (3-C2BFE-*X*), 4-*n*-alkylcyclohexylbenzyl fluoroalkyl ethers (*m*-C1BFE-*X*) and 4-*n*-alkoxyphenylbenzyl fluoroalkyl ethers (*m*O-BBFE-*X*) whose chemical structures are shown in table 1; we investigate the mesomorphic phase transitions in detail,

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*Author for correspondence; e-mail: yano@apchem.gifu-u.ac.jp

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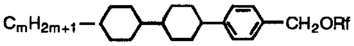
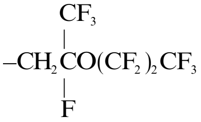
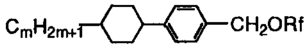
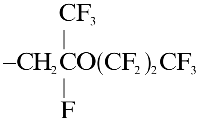
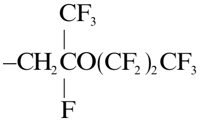
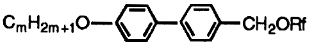
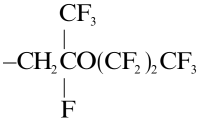
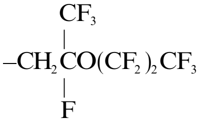
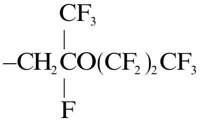
Table 1. Phase transition temperatures and their enthalpy changes for the benzyl fluoroalkyl/alkoxy ethers. The figures for the phase transitions indicate transition temperatures in °C (enthalpy changes in kJ mol^{-1}); ● : enantiotropic phase transition; ▲ and [ ]: monotropic phase transition.

Compound	*m*	*Rf*	Cr		E		SmB	SmA		I
m-C2BFE-X										
3-C2BFE-PF	3	 $-CH_2\overset{CF_3}{\underset{F}{C}}O(CF_2)_2CF_3$	●	146.2 (10.2)			▲		[144.5] [(8.2)]	●
3-C2BFE-F1F	3	$-CH_2CF_3$	●	32.1 (23.7)			●		167.4 (10.1)	●
3-C2BFE-F2F	3	$-CH_2CF_2CF_3$	●	36.5 (22.4)			●		160.6 (8.4)	●
3-C2BFE-F2H	3	$-CH_2(CF_2)_2H$	●	32.6 (28.2)			●		147.5 (8.8)	●
m-C1BFE-X										
3-C1BFE-PF	3	 $-CH_2\overset{CF_3}{\underset{F}{C}}O(CF_2)_2CF_3$	●	− 69.8 (1.4)						●
5-C1BFE-PF	5	 $-CH_2\overset{CF_3}{\underset{F}{C}}O(CF_2)_2CF_3$	●	− 21.5 (5.7)						●
3-C1BFE-F1F	3	$-CH_2CF_3$	●	6.8 (29.2)						●
3-C1BFE-F2F	3	$-CH_2CF_2CF_3$	●	4.5 (27.7)						●
mO-BBFE-X										
3O-BBFE-PF	3	 $-CH_2\overset{CF_3}{\underset{F}{C}}O(CF_2)_2CF_3$	●	50.9 (4.7)				●	78.0 (5.1)	●
5O-BBFE-PF	5	 $-CH_2\overset{CF_3}{\underset{F}{C}}O(CF_2)_2CF_3$	●	62.2 (6.1)				▲	[62.2] [(6.4)]	●
8O-BBFE-PF	8	 $-CH_2\overset{CF_3}{\underset{F}{C}}O(CF_2)_2CF_3$	●	53.1 (39.4)				▲	[51.4] [(5.6)]	●
3O-BBFE-F2F	3	$-CH_2CF_2CF_3$	●	70.4 (17.3)	●	76.2 (5.1)		●	93.6 (8.4)	●
3O-BBFE-F2H	3	$-CH_2(CF_2)_2H$	●	44.7 (16.1)	●				61.6 (11.5)	●
3O-BBFE-F4H	3	$-CH_2(CF_2)_4H$	●	76.1 (7)[a]				●	78.6 (7)[a]	●
3O-BBFE-F6H	3	$-CH_2(CF_2)_6H$	●	59.8 (10.7)	●	87.4 (6.1)		●	96.0 (9.4)	●
3O-BBFE-F8H	3	$-CH_2(CF_2)_8H$	●	108.0 (24.7)				●	111.8 (12.0)	●
3O-BBFE-DFE	3	$-CH_2CH_2(CF_2)_2CF(CF_3)_2$	●	87.7 (6.7)				●	109.2 (12.4)	●

[a] These data are not exact, because the DSC peaks for the Cr–E and E–I phase transitions overlap.

and moreover, study the electro-optical properties of these compounds in ZLI-1132 as solvent. It is found that all the fluoroalkyl compounds decrease the refractive anisotropy of ZLI-1132 nematic solvent. The mesogenicity is discussed from the standpoint of the structures of the fluoroalkyl terminal groups and rigid core parts.

2. Experimental

The compounds 3-C2BFE-*X*, *m*-C1BFE-*X* and *m*O-BBFE-*X* were synthesized by nucleophilic substitution on the corresponding benzyl chloride using the sodium salt of a fluoroalkanol. The reaction scheme is shown in figure 1, and as an example the synthetic procedure for 3-C2BFE-F2F is described below.

4-*n*-propylbicyclohexylbenzoic acid (**I**) was kindly supplied by the Chisso Petroleum Co., and 4-*n*-propylbicyclohexylbenzoic acid ethyl ester (**II**) was prepared by boiling a mixture of **I** (8.22 g, 0.03 mol), dry ethanol (30 ml) and conc. H_2SO_4 for 45 h; the crude product was recrystallized from ethanol (yield: 60%).

Compound **II** (6.4 g, 0.018 mol) dissolved in THF (20 ml) was added dropwise to $LiAlH_4$ (1.9 g, 0.05 mol) and THF (20 ml), and the mixture was heated at reflux for 18 h. The cooled reaction mixture was treated with ethyl acetate and then with 3 M HCl. The crude compound was obtained by extracting into ethyl acetate and the extract washed with water. Evaporation and recrystallization from distilled ethanol gave a white powder of 4-*n*-propylbicyclohexylbenzyl alcohol (**III**) (yield: 66%).

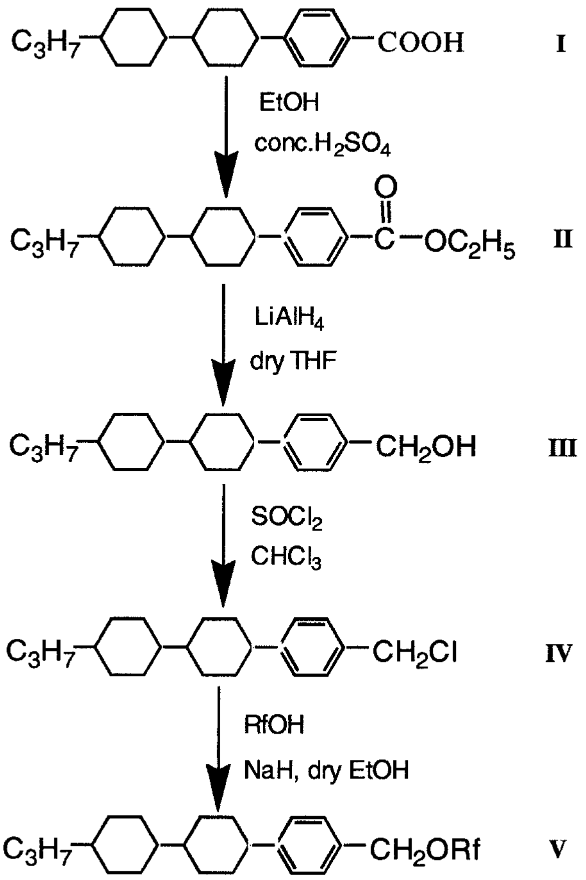


Figure 1. Reaction scheme.

Thionyl chloride (1 ml) was added to compound **III** (3.1 g, 0.012 mol) in $CHCl_3$ (30 ml) and the mixture was stirred at room temperature for 2 h. The crude product obtained after evaporation was recrystallized from hexane to yield 4-*n*-propylbicyclohexylbenzyl chloride (**IV**) as a white powder (yield: 93%).

2,2,3,3-Tetrafluoropropanol (2.9 g, 0.022 mol) was added to NaH (0.43 g, 0.018 mol) in dry ethanol (20 ml) and the mixture was stirred for 1 h. 3-C2BFE-F2H was obtained by adding compound **IV** (3.1 g, 0.011 mol) to the mixture and then heating under reflux for 16 h. The product was extracted into ethyl ether, washed with water and evaporated to dryness. The crude product was separated by column chromatography (silica gel, benzene/hexane 1/1) and further purified by recrystallizations from hexane, giving a white powder (yield: 70%).

3-C2BFE-F2H was judged to be pure by ^1H NMR and ^{19}F NMR spectroscopy (JEOL FT-NMR 400 MHz) and elemental analysis. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, CH_3, $J = 7.31$), 1.75 (2H, m, CH_2, $J = 10.98$), 3.81 (2H, t, CH_2, $J = 12.56$), 4.59 (2H, s, CH_2), 7.20 (2H, d, Ph–H, $J = 8.54$), 7.23 (2H, d, Ph–H, $J = 8.30$). ^{19}F NMR (400 MHz, $CDCl_3$): δ 79.91, 95.15, 95.30, 110.00 (JEOL FT-NMR 400 MHz). Elemental analysis: calc., C 70.09, H 8.41; found, C 70.06, H 8.51%.

Phase transition temperatures and their enthalpy changes were measured using a differential scanning calorimeter (Seiko Denshi Co. Type DSC-210, SSC-5000 system) at a scanning rate of 5 K min^{-1} and under a dry nitrogen flow of 30 ml min^{-1}. Indium and tin were used as the enthalpy standards. The textures of the mesophase were observed using a Nikon OPTIPHOT-POL polarizing microscope equipped with a Mettler FP-82 hot stage.

The wide angle X-ray diffraction measurements were made with a Rigaku, Rinto 2000 diffractometer with a home-made cell using 1.5406 Å Cu K_α radiation (scan rate 4.0° min^{-1}, scan range $2\theta = 2°$–$30°$). The temperature of the sample was monitored by an alumel–chromel thermocouple.

The electro-optical properties were measured for 15 wt % of *m*-C1BFE-*X*, *m*O-BBFE-*X* or 3-C2BFE-*X* in ZLI-1132. The refractive anisotropy (Δn) was measured by an ATAGO 4T & 2T Abbé refractometer at 25°C; the dielectric anisotropy ($\Delta \varepsilon$) was obtained by a Hewlett Packard 4284A LCR meter at 25°C and the viscosity (η) was recorded by a Tokimec ELD-R rotational viscometer.

3. Mesomorphic phase transitions

Figure 2 shows DSC curves for several of the fluoroalkyl benzyl ethers, and the phase transition parameters obtained from DSC on 2nd heating cycles are listed in table 1, where the type of mesophase was determined from the polarized microscopic observations and X-ray diffraction data as described later. For 3-C2BFE-F2F, figure 2 (*a*), two peaks are observed near 36.5 and 160.6°C on 1st heating; these are caused by melting from the crystalline (Cr) to the smectic B (SmB) phase and clearing from SmB to the isotropic liquid (I), respectively. On 1st cooling, the I–SmB transition occurs near 158.7°C and the SmB–Cr transition near − 8.0°C. The appearance of an enantiotropic SmB phase, similar to that of 3-C2BFE-F2F, was also seen in other 3-C2BFE-*X* compounds. However, for 3-C2BFE-F1F and 3-C2BFE-F2H, the reversal of the Cr–SmB phase transition is not seen on 1st cooling as shown in figure 2 (*b*) for 3-C2BFE-F2H, indicating the existence of a glassy SmB state at low temperatures. On the 2nd heating, the glassy SmB state changes into a Cr state and then a Cr–SmB and the SmB–I phase transitions take place successively. For 3-C2BFE-F2H, the Cr–SmB transition temperature on the 2nd heating is about 32.6°C, much lower than that on 1st heating, probably inplying a difference in the packing structure of the crystals obtained from hexane solution and those from the SmB glass. The phase transition behaviour for 3-C2BFE-PF is interesting, figure 2 (*c*). On 1st heating, an endothermic peak due to the melting of Cr to the I phase is seen near 146.2°C. On cooling from the I phase, the SmB phase appears monotropically near 144.5°C ($T_{\text{Cr-SmB}} < 146.2$°C), but no exothermic peak corresponding to crystallization appears on the 1st cooling, indicating again the existence of a glassy SmB state at low temperature. On 2nd heating, the DSC curve shows no exothermic peak from glassy SmB to Cr phase or any endothermic peak from Cr to SmB phase, giving only an endothermic peak from SmB to the I phase near 146°C (nearly equal to $T_{\text{Cr-I}}$ on the 1st heating). This result suggests the existence of glassy SmB ⇔ SmB phase transition; DSC, dielectric and adiabatic heat capacity studies are progressing in our laboratories to obtain convincing evidence for this glassy SmB ⇔ SmB phase transition.

DSC curves for 3-C1BFE-PF are shown in figure 2 (*d*). The curves show an exothermic peak near − 75.1°C and a broad feature near − 90.6°C on 1st cooling, corresponding to a crystallization temperature and a glass

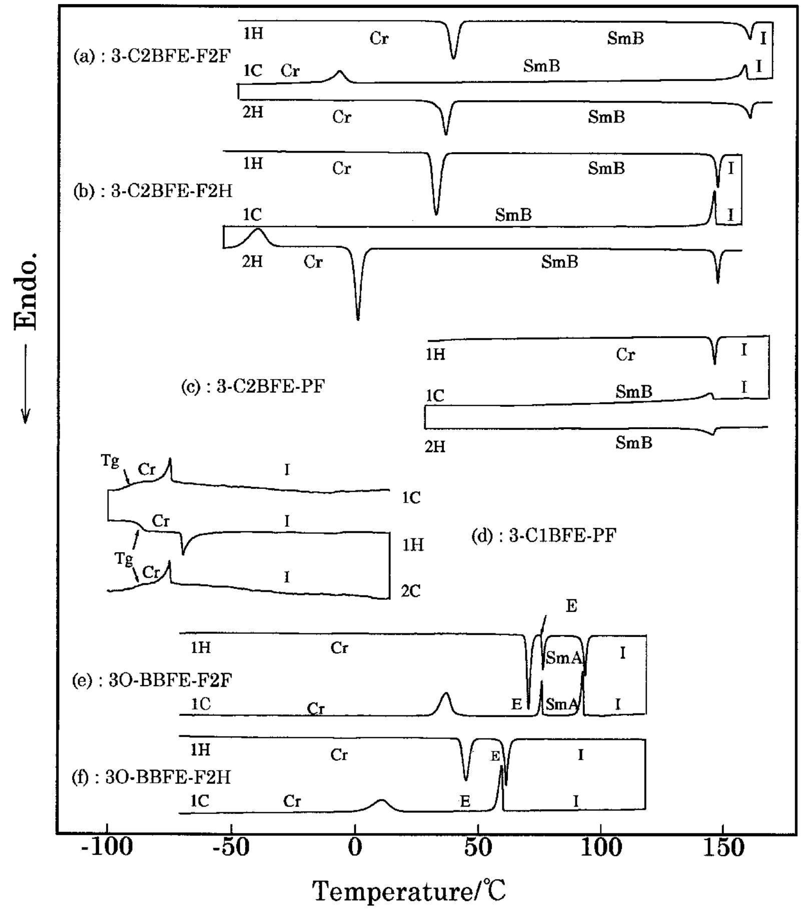


Figure 2. DSC thermograms of several typical fluoroalkyl benzyl ethers (BFE).

transition temperature (T_g), respectively; on 1st heating, the broad feature near – 90.6°C and an endothermic peak near – 69.8°C occur. 3-C1BFE-PF is of course in the I state at room temperature. These phase transition behaviour are also seen for all the other *m*-C1BFE-PF compounds (table 1). Therefore the *m*-C1BFE-PF compounds used here show no mesophase.

Figures 2(*e*) and 2(*f*) give the DSC curves for 3O-BBFE-F2F and 3O-BBFE-F2H, respectively. In 3O-BBFE-F2F, a crystal E and a SmA phase are shown in the ranges 70.4–76.2°C, and 76.2–93.6°C, respectively, on 1st heating; 3O-BBFE-F6H also shows the E and SmA phases in the ranges 59.8–87.4°C, and 87.4–96.0°C, respectively (table 1). On the other hand, 3O-BBFE-F2H gives only the E phase between 44.7 and 61.6°C and 3O-BBFE-F8H has only the SmA phase between 108.0 and 111.8°C. As seen in table 1, the other *m*O-BBFE-*X* compounds show only a SmA phase, but the SmA phase is monotropic in 5O-BBFE-PF and 8O-BBFE-PF.

Polarized microscopic observations and X-ray diffraction measurements were made to determine the types of mesophase. In 3-C2BFE-F2H, a typical mosaic texture with the doubly refracting lancets and pseudo-isotropic regions of a SmB phase were observed on cooling from the I phase. This texture was assigned as SmB [20] and was also observed for the LC phases on cooling for the other 3-C2BFE-*X* compounds. Figure 3 shows the X-ray diffraction pattern for 3-C2BFE-F2F at 60°C. The pattern shows two peaks near 18.24° and 7.7° of scattering angle (2θ), respectively, which correspond to 4.87 and 11.37°Å spacings (d), respectively. From references [21, 22], this pattern may be characteristic of SmB state. In the SmB phase, the rod-shaped molecules are packed in a layered structure, and with a hexagonal close packing inside the layer. The [2 0 0] and [1 0 0] reflections are superposed due to the hexagonal symmetry, leading to one diffraction peak [22]. The peak at $2\theta = 7.77°$ ($d = 11.37$ Å) is considered to be the secondary reflection from the layer structure, because the molecular length is estimated using PM3 (Parametric Method) as 23.00 Å in the fully extended conformation.

Polarized microscopic observations were made on cooling from the I phase for the 3O-BBFE-*X* compounds, using crossed polarizers. For example, in 3O-BBFE-F2F, on cooling, the SmA fan texture was observed over a lower temperature range below 93°C, and tie lines (or arcs appeared on the SmA fans from 75°C, from which this phase may be assigned as a crystal E phase [23]. The phases for the other 3O-BBFE-*X* compounds were also identified as SmA or E phases by microscopy as described above. Figure 4 shows the X-ray diffraction pattern for 3-BBFE-F2H at 60°C as an example. The pattern shows five sharp peaks at 8.670°, 19.670°, 21.750°, 22.083°, 27.290° of 2θ. Table 2 lists the reflection indices and cell parameters with those calculated by assuming a crystal E packing structure, where the lattice parameter is $a = 8.17$ Å, $b = 5.41$ Å, $c = 20.38$ Å, and the molecular length is estimated as about 19.89 Å in a fully extended conformation, again using the PM3 method. The observed spacings (d) are very consistent with those calculated, and hence the phase at 60°C was identified as the E phase by both polarized microscopy and X-ray

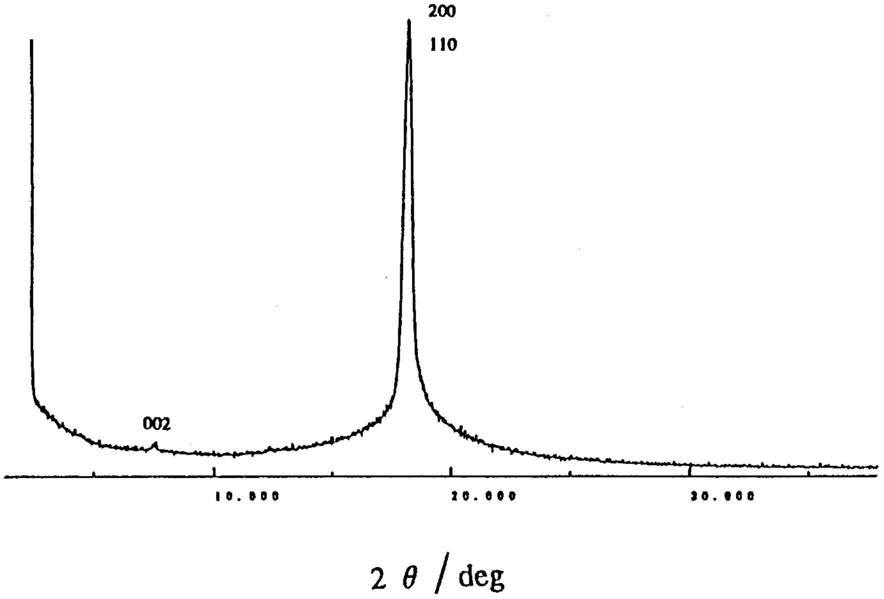


Figure 3. The wide angle X-ray diffraction pattern for 3-C2BFE-F2F at 60°C (SmB).

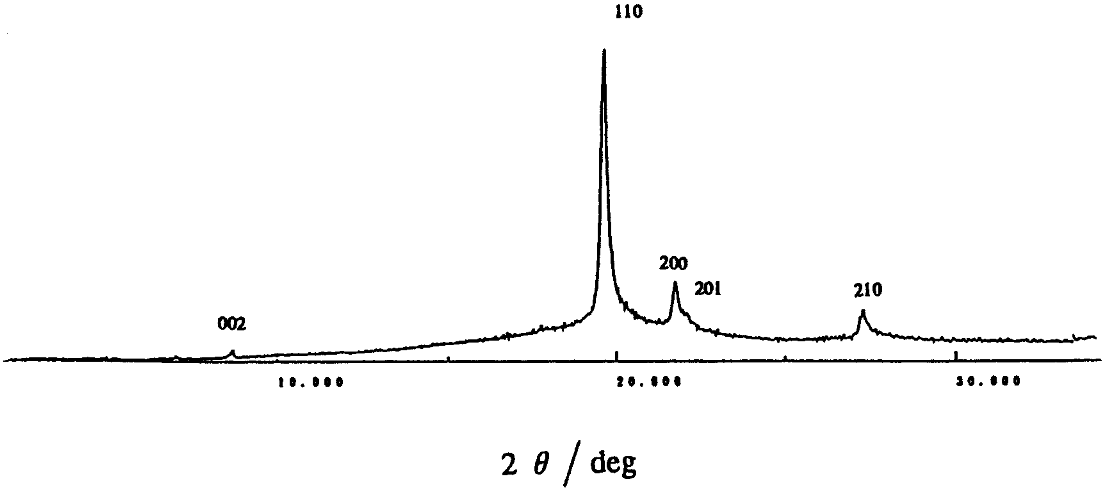


Figure 4. The wide-angle X-ray diffraction pattern for 3O-BBFE-F2H at 60°C (crystal E).

Table 2. Reflection indices and cell parameters of the unit cells in the E phase of 3O-BBFE-F2H (60°C). $a = 8.17$ Å, $b = 5.41$ Å, $c = 20.38$ Å, $V = 900.79$ Å.

2θ/°	d-spacing/Å		Indices ($h\ k\ l$)
	Observed	Calculated	
8.670	10.1905	10.1905	(0 0 2)
19.670	4.5095	4.5095	(1 1 0)
21.750	4.0828	4.0828	(2 0 0)
22.083	4.0204	4.0033	(2 0 1)
27.290	3.2652	3.2587	(2 1 0)

diffraction. Consequently, it was concluded that the BFE compounds used here undergo the mesomorphic phase transitions given in table 1.

We find that the mesogenicity faithfully reflects the chemical structures for the following reasons. (1) The mesogenicity appears to be governed by the rigidity, length and perhaps the polar nature of the rigid core part. The 3-C2BFE-*X* compounds having bicyclohexylphenyl groups as the rigid core part show the SmB phase, but the 3-C1BFE-*X* compounds having only a cyclohexylphenyl group have no mesophase and very low melting points, while the 3O-BBFE-*X* compounds having biphenyl groups generate SmA and/or E phases. (2) In series *m*O-BBFE-PF, as the terminal *n*-alkoxy group becomes longer, the clearing point is lowered, which has been found for many LC compounds, while in 3O-BBFE-F$_m$H having terminal $-CH_2-O-CH_2-(CF_2)m$H, the clearing point increases with increasing fluoroalkyl length. The enhancement of the thermal stability on increasing the fluoroalkyl length may be explained by the rigidity of the fluoroalkyl chains. (3) Branching of the fluoroalkyl terminal group clearly lowers the clearing temperature (the thermal stability). (4) The terminal fluoroalkyl groups having ω-CF$_2$H are lower in clearing temperature than those having ω-CF$_3$.

4. Electro-optical properties

Electro-optical properties were measured for eight nematic solutions of ZLI-1132 nematic solvent with BFE compounds at room temperature; the data are listed in table 3, where all the BFE compounds used had a solubility of more than 15 wt % in ZLI-1132, the solutions showing a nematic phase. As seen in table 3, the nematic–isotropic transition temperature (T_{NI}) is almost unchanged by 3-C2BFE-F1F, –F2F and –F2H, but is lowered by 15–24°C with the addition of *m*-C1BFE-PF and *m*O-BBFE-PF having branched fluoroalkyl terminal groups, associated with the low melting points shown in table 1. The dielectric anisotropy ($\Delta\varepsilon$) values are somewhat decreased ($\leqq 2$) by the branched fluoroalkyl additives, but the η values are not increased too much. It is noted that all the BFE compounds lower the refractive anisotropy (Δn) in ZLI-1132; for example from 1.37 of ZLI-1132 to 1.16 of the 3-C1BFE-PF mixture. From these results, we judge that the BFE compounds can be used as a component for decreasing birefringence in nematics for LC display devices.

5. Summary

In this work, we have synthesized a new class of liquid crystalline benzyl fluoroalkyl ethers (BFE) and investigated their mesomorphic transitions and electro-optical properties. The mesogenicity reflects the chemical structure: 3-C2BFE-*X*, having a bicyclohexylphenyl group as the rigid core part, has a SmB phase with good thermal stability; *m* O-BBFE-*X*, having a biphenylyl group, show SmA and/or E phases; *m*-C1BFE-*X*, having a cyclohexyl

Table 3. Electro-optical data for 15 wt % of the benzyl fluoroalkyl ethers (BFE) in ZLI-1132 as nematic solvent. T_{NI} = phase transition temperature from nematic phase to isotropic phase (°C); $\Delta\varepsilon$ = dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constant parallel and perpendicular to the aligned molecule, respectively); Δn = refractive anisotropy ($\Delta n = n_o - n_e$, n_o and n_e are the ordinary and extraordinary refractive index, respectively); η = viscosity at 20°C.

Compound	T_{NI}	$\Delta\varepsilon$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	Δn	n_o	n_e	η
ZLI-1132	71.7	11.0	15.5	4.5	0.137	1.492	1.629	26.6
3-C1BFE-PF	47.8	8.9	13.6	4.7	0.116	1.484	1.600	29.4
5-C1BFE-PF	49.2	8.9	13.6	4.7	0.117	1.483	1.600	29.6
3-C2BFE-PF	67.7	9.9	14.5	4.6	0.125	1.484	1.609	—
3-C2BFE-F1F	74.2	10.0	14.5	4.5	0.129	1.490	1.619	27.2
3-C2BFE-F2F	70.7	9.9	14.5	4.6	0.127	1.488	1.615	28.5
3-C2BFE-F2H	70.1	10.0	14.7	4.7	0.127	1.490	1.617	30.7
3O-BBFE-PF	53.8	9.8	14.8	5.0	0.123	1.485	1.608	—
8O-BBFE-PF	57.0	9.9	14.7	4.8	0.126	1.485	1.611	33.7

phenyl group which is shorter by one cyclohexyl ring compared with 3-C2BFE-*X*, showed no mesophase. The terminal group also affected the mesogenicity significantly. As the length of terminal group is increased, the clearing point is higher in the case of the fluoroalkyl groups and lower with the *n*-alkyl/*n*-alkoxy groups. The clearing point (thermal stability) is sensitively affected by the chemical structure of the terminal group, for example whether it is branched, perfluoroalkyl, alkoxy or alkyl. These results appear to obey the relationships between chemical structure and mesogenicity which have been found for many compounds, but it should be noticed that each part in the molecule, such as the rigid core part and the terminal groups, plays a role in the mesogenicity, independently of the existence of the rather unique fluoroalkyl groups.

Another attractive point in the fluorinated compounds is their electro-optical properties for LC display devices as mentioned in §1. The electro-optical properties were studied for BFE compounds containing the benzyl fluoroalkyl ether group, using ZLI-1132 nematic solvent. We found that BFE compounds can be used as one component for lowering the refractive anisotropy of the host ZLI-1132. Synthetic and electro-optical studies of various LC compounds having benzyl fluoroalkyl ether and thioether groups are progressing in our laboratories and will be published in the near future.

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